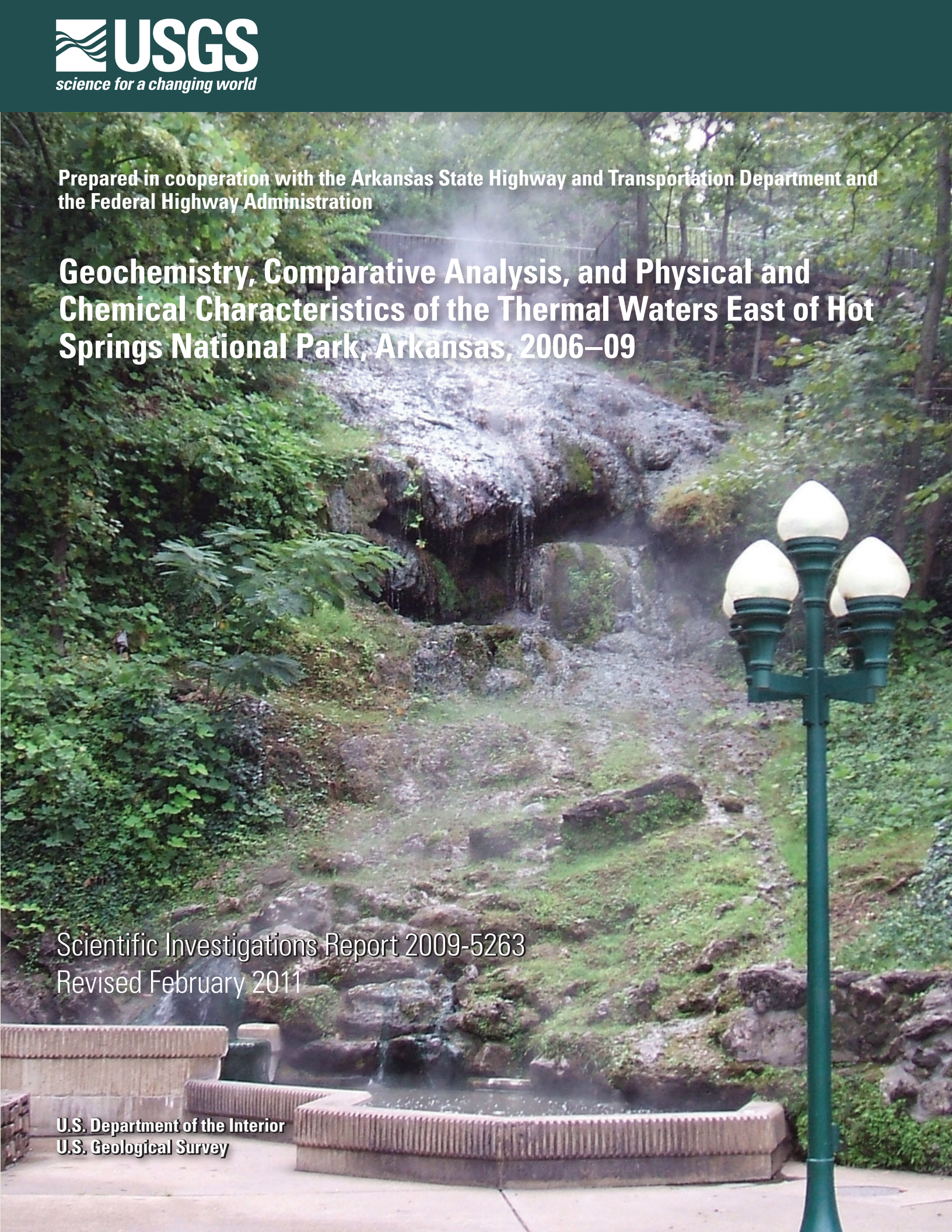


Prepared in cooperation with the Arkansas State Highway and Transportation Department and the Federal Highway Administration

# Geochemistry, Comparative Analysis, and Physical and Chemical Characteristics of the Thermal Waters East of Hot Springs National Park, Arkansas, 2006–09

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**Cover photograph.** Display Springs in Hot Springs National Park, Arkansas. Photograph by Ralf Montanus, U.S. Geological Survey.

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**U.S. Geological Survey**  
Marcia K. McNutt, Director

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# Geochemistry, Comparative Analysis, and Physical and Chemical Characteristics of the Thermal Waters East of Hot Springs National Park, Arkansas, 2006–09

By Timothy M. Kresse and Phillip D. Hays

## Abstract

A study was conducted by the U.S Geological Survey in cooperation with the Arkansas State Highway and Transportation Department to characterize the source and hydrogeologic conditions responsible for thermal water in a domestic well 5.5 miles east of Hot Springs National Park, Hot Springs, Arkansas, and to determine the degree of hydraulic connectivity between the thermal water in the well and the hot springs in Hot Springs National Park. The water temperature in the well, which was completed in the Stanley Shale, measured 33.9 degrees Celsius, March 1, 2006, and dropped to 21.7 degrees Celsius after 2 hours of pumping—still more than 4 degrees above typical local groundwater temperature. A second domestic well located 3 miles from the hot springs in Hot Springs National Park was discovered to have a thermal water component during a reconnaissance of the area. This second well was completed in the Bigfork Chert and field measurement of well water revealed a maximum temperature of 26.6 degrees Celsius. Mean temperature for shallow groundwater in the area is approximately 17 degrees Celsius. The occurrence of thermal water in these wells raised questions and concerns with regard to the timing for the appearance of the thermal water, which appeared to coincide with construction (including blasting activities) of the Highway 270 bypass-Highway 70 interchange. These concerns were heightened by the planned extension of the Highway 270 bypass to the north—a corridor that takes the highway across a section of the eroded anticlinal complex responsible for recharge to the hot springs of Hot Springs National Park.

Concerns regarding the possible effects of blasting associated with highway construction near the first thermal well necessitated a technical review on the effects of blasting on shallow groundwater systems. Results from available studies suggested that propagation of new fractures near blasting sites is of limited extent. Vibrations from blasting can result in rock collapse for uncased wells completed in highly fractured rock. However, the propagation of newly formed large fractures that potentially could damage well structures or result in pirat-

ing of water from production wells appears to be of limited possibility based on review of relevant studies.

Characteristics of hydraulic conductivity, storage, and fracture porosity were interpreted from flow rates observed in individual wells completed in the Bigfork Chert and Stanley Shale; from hydrographs produced from continuous measurements of water levels in wells completed in the Arkansas Novaculite, the Bigfork Chert, and Stanley Shale; and from a potentiometric-surface map constructed using water levels in wells throughout the study area. Data gathered from these three separate exercises showed that fracture porosity is much greater in the Bigfork Chert relative to that in the Stanley Shale, shallow groundwater flows from elevated recharge areas with exposures of Bigfork Chert along and into streams within the valleys formed on exposures of the Stanley Shale, and there was no evidence of interbasin transfer of groundwater within the shallow flow system.

Fifteen shallow wells and two cold-water springs were sampled from the various exposed formations in the study area to characterize the water quality and geochemistry for the shallow groundwater system and for comparison to the geochemistry of the hot springs in Hot Springs National Park. For the quartz formations (novaculite, chert, and sandstone formations), total dissolved solids concentrations were very low with a median concentration of 23 milligrams per liter, whereas the median concentration for groundwater from the shale formations was 184 milligrams per liter. Ten hot springs in Hot Springs National Park were sampled for the study. Several chemical constituents for the hot springs, including pH, total dissolved solids, major cations and anions, and trace metals, show similarity with the shale formations in exhibiting elevated concentrations, though mean and median concentrations for most constituents were lower in the hot springs compared to water from the shale formations. The chemistry of the hot springs in Hot Springs National Park is likely a result of rock/water interaction in the shale formations in the deeper sections of the hot springs flow path; the initially, low ionic strength waters, originating as shallow recharge through quartz formations, move through the upper section of the flow path into deeper sections of the flow path and are modified

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by passage through shale formations present at depth. Mixing curves for lithium, manganese, and strontium concentrations, which were greatest in the shale formations, indicate that the hot springs represent an approximate 40-percent contribution of water from the shale formations and a 60-percent contribution of water from the quartz formations.

Characterization of strontium geochemistry and analysis of strontium isotopic signatures were conducted by comparing geochemical analyses from the hot springs in Hot Springs National Park, shallow groundwater samples in the study area from the quartz and shale formations, and samples from two western hot springs 30 to 50 miles west of Hot Springs in Montgomery County. Mixing model analysis indicated that the strontium geochemistry of the hot springs results from an approximately 35-percent contribution from the shales and a 65-percent contribution from the quartz formations, similar to that found from trace-metal analysis curves. The geochemistry results of the newly discovered thermal water sites at the two domestic wells were not similar to the geochemistry results for the hot springs in Hot Springs National Park with respect to strontium chemistry, but rather resemble that of the groundwater of the local outcropping formations. The very different isotopic and geochemical signatures observed for the thermal water from the two domestic wells as compared with the Hot Springs National Park springs do not provide evidence of any direct hydraulic connection with the hot springs in Hot Springs National Park.

The occurrence of thermal water throughout the Ouachita Mountains tends to be found in similar geologic settings; along the nose of plunging anticlines and closely aligned with mapped thrust faults. The shallow flow systems have been identified as being confined within the regional surface watershed boundaries. The deep flow systems for thermal water are likely a result of the local hydrologic and geologic framework and represent an analog to the geologic framework model for propagation of groundwater to the hot springs in Hot Springs National Park, rather than being systems in direct communication with the Hot Springs National Park thermal system. Thermal-water sites across the Ouachita Mountains appear to represent discrete systems that are associated with a specific set of hydrologic and geologic conditions, which occur at numerous locations across the region, and are viewed as analogs to the hot spring flow system in Hot Springs National Park rather than connected components of the same hydraulic system. Concerns related to pirating of water from the hot springs in Hot Springs National Park because of blasting near the thermal well sites were not supported by the data gathered for this study.

## Introduction

A study by the U.S Geological Survey (USGS) in cooperation with the Arkansas State Highway and Transportation Department was conducted to characterize the source and

hydrogeologic conditions responsible for the occurrence of thermal water east of Hot Springs National Park (HSNP), Hot Springs, Arkansas, and to determine the degree of hydraulic connectivity between the thermal water in the well and the hot springs in HSNP. The well (Bratton site) is approximately 5.5 miles east of the hot springs in HSNP. In addition to the distance, the well is separated from HSNP by two anticline complexes, at least two major thrust faults, and one surface watershed. On March 1, 2006, the well owner contacted HSNP personnel regarding the appearance of warm water in a well on his property. The well had supplied water to the residence for 15 years until a municipal system began supplying water in 2002 and was used intermittently thereafter, without previously yielding any noticeably warm water. A visit to the site by HSNP personnel on March 1, 2006, documented a temperature of 33.9°C for water flowing from a hose outside of the house (Steve Rudd, Hot Springs National Park, oral commun.), and the owner reported this phenomena had not been experienced during past use of the well. On March 13, 2006, USGS personnel visited the site and pumped the well while monitoring water temperature. The beginning temperature was measured at 30.5°C and never dropped below 21.7°C after 2 hours of pumping. Mean temperature for shallow (less than 400 ft) groundwater in the area is approximately 17°C, and the occurrence of thermal water in the well raised questions and concerns with regard to the timing for the appearance of the thermal water. For the purposes of this study, “thermal water” is defined as groundwater having a temperature substantially exceeding that of normal shallow groundwater adjusted for seasonal variability; the maximum temperature of the hot springs in HSNP—based on silica geothermometry—was 66.6°C (Bell and Hays, 2007).

Of interest to HSNP personnel was that the discovery of the thermal water in the well appeared to coincide with the construction and associated blasting of the State Highway 270 East bypass, which terminated less than 1 mile from the residence at the intersection with State Highway 70 West and was completed in the spring of 2006. HSNP personnel raised concerns over the continuation of the bypass north of State Highway 70 West, which would be routed east of HSNP through the previously defined recharge area for the hot springs (Bedinger and others, 1979) to eventually intersect with State Highway 7 South (fig.1).

The discovery of thermal water outside of HSNP implied that the geologic formations constituting the geothermal system in HSNP—the highly fractured Hot Springs Sandstone Member of the Stanley Shale, the Big Fork Chert, and the Arkansas Novaculite—are capable of supporting geothermal activity east of HSNP, and that the two spatially separated systems might be hydraulically connected. The existence of the thermal system east of HSNP and observed hydrologic behavior highlighted the potential vulnerability of the thermal system resource in HSNP to changes resulting from human activities. Land-use changes in the area of HSNP include continuing urban and suburban development and expansion of infrastructure; this expansion includes building and extension

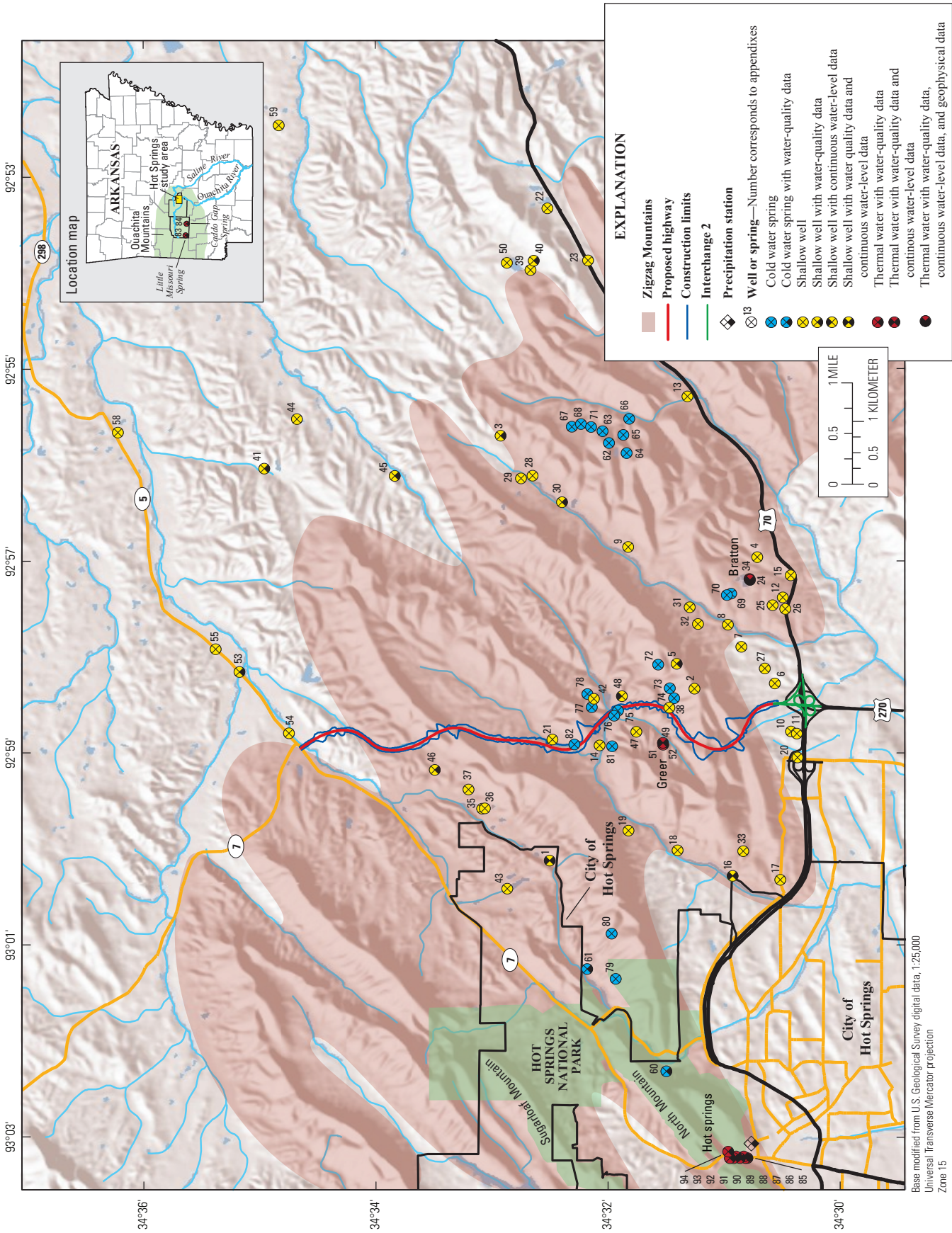


Figure 1. Location of study area.

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of major roadways. Such activities are of particular interest to the National Park Service and other entities interested in protecting the hot springs.

Personnel with the HSNP initially were concerned with potential new fracture connections to the hot springs as a result of blasting. If no fracture connections were identified, the area still proved of interest as a useful analog and natural model to assist in understanding the effect of human activities in the area of recharge for the hot springs. For example, if the hydrologic system at the residence with thermal water had been altered by blasting activities, especially as related to development of new flow paths, this discovery would aid in understanding potential effects of similar activities on the shallow and deep flow components of the HSNP hot springs thermal system.

The HSNP, the Arkansas State Highway and Transportation Department (AHTD), the USGS, and stakeholders including other State and Federal agencies identified the need for a study to characterize the newly discovered thermal water. The study by the USGS, in cooperation with the AHTD, began in January 2007, and new highway construction was suspended until the study was completed. The main components of the study are to: (1) perform a groundwater temperature reconnaissance, documenting the existence and distribution of thermal waters outside of HSNP; (2) conduct borehole geophysical surveys of thermal wells; (3) conduct discrete-zone geochemical sampling of the thermal well and other additional sites; (4) assess the degree of hydraulic connection between the geothermal system of the hot springs in HSNP and the thermal well through continuous water-level monitoring at sites near both locations; (5) assess the degree of hydraulic connection between the HSNP waters and the thermal well through geochemical characterization of groundwater from suspected recharge areas for both systems; and (6) construct a potentiometric-surface map defining local flow directions and boundaries in the surficial aquifer underlying potential recharge areas. All data for the study were collected during 2006 through 2009.

### Purpose and Scope

The purpose of this report is to describe the geochemistry, physical, and chemical characteristics of thermal waters and to perform a comparative analysis and evaluate the degree of hydraulic connectivity, if any, of thermal waters outside of HSNP to the hot springs in HSNP. This report presents field and water-quality data and an interpretation based on the data for the occurrence, source, and distribution of thermal water outside of HSNP.

Included in the report is a description and comparison of the geochemistry of shallow groundwater from cold springs and wells, thermal water from springs and wells outside of HSNP, and water from the hot springs in HSNP. Although the report focuses on groundwater in the study area, two thermal springs were identified outside of the study area located about

30 and 50 miles west of the city of Hot Springs. The geochemistry of these springs was characterized and compared to groundwater in the study area. Because there was some initial concern related to potential effects of blasting associated with highway construction in the study area, a literature review was made of the effects of blasting on shallow groundwater.

### Description of Study Area

The study area is located in west-central Arkansas, east of and including the HSNP in the city of Hot Springs, Arkansas (fig. 1). The study area is approximately 70 mi<sup>2</sup> and generally is bounded to the north by State Highways 5 and 7 and to the south by State Highway 70. The western extent of the study area generally coincides with and includes the hot springs in HSNP located in the city of Hot Springs, and the eastern extent of the study is approximately 8 miles east of HSNP.

The study area is in the eastern part of the Ouachita Mountains and is characterized by a series of steep ridges and valleys. The land surface ranges from an altitude of greater than 1,050 ft above National Geodetic Vertical Datum of 1929 (NGVD29) on the ridge tops to less than 450 ft NGVD29 in the valleys with an average slope of 0.35 ft/ft. The southern part of the study area is in the Ouachita River Basin, and the northern part is in the Saline River Basin. Except for the hot springs in HSNP, most well and spring sites inventoried and sampled for this study were located in the sparsely populated, densely forested rural area east of the city of Hot Springs.

### Overview of Hydrogeologic Setting

A basic knowledge of the geology and hydrology of the study area is important in understanding the occurrence and distribution of the various sources of thermal water inside and outside the area of the hot springs in HSNP. The ridge and valley terrain that defines the topography of the area in and near Hot Springs is part of the Zigzag Mountains, which extend northeast and southwest from Hot Springs over a total length of approximately 22 miles and a width of up to 7 miles northwest of Hot Springs (Arndt and Stroud, 1953). The Zigzag Mountains comprise rocks ranging in age from Ordovician to Mississippian (table 1). These strata are intensely folded, the folds are closely compressed, and all folds are overturned to the south. As a result, the dips off of fold axes are to the north (Purdue, 1910). Fold axes in the study area strike generally to the northeast, and major faults are essentially parallel to the trends of the axes of folds and thus are longitudinal faults (fig. 2). Because the system of fractures lies along east-west trending lines, wells of equal water-yielding capacity typically lie east or west of each other, and yields of wells north or south of each other generally are unrelated (Halberg and others, 1968). Because the topographic basins generally are defined by the folded strata in the study area, resulting in synclinal and anticlinal basins, and shallow groundwater yields and flow directions reflect the structural geology, orientation, and

**Table 1.** Generalized section of sedimentary rocks in the vicinity of the hot springs.

[o, outcrops in the vicinity of Hot Springs National Park; modified after Bedinger and others, 1979]

System	Formation	Maximum thickness in Hot Springs area (feet)
Mississippian	Stanley Shale (o)	8,500
	Hot Springs Sandstone (o)	150
	Arkansas Novaculite (o)	650
Devonian		
Silurian	Missouri Mountain Shale, (o) Blaylock Sandstone, and Polk Creek Shale, undifferentiated	195
Ordovician	Bigfork Chert (o)	700
	Womble Shale	1,500

hydraulic connection of the major east-west trending faults, early researchers speculated that shallow groundwater basins within the Zigzag Mountains likely had little interbasin flow of groundwater (Halberg and others, 1968).

The primary porosity of most rocks in the study area is negligible, and the occurrence and distribution of secondary porosity, such as joints, fractures, and separation along bedding planes, controls hydrologic behavior and water availability; hence, the amount of water available from the rocks is a function of the amount of fracture density and distribution (Halberg and others, 1968). A review of domestic wells in the study area revealed that shallow wells are to be found completed in all of the formations, but that yields are considerably lower in shale units than in novaculite and chert rocks. The brittle nature and extreme fracturing of the chert and novaculite rocks in the area lead to enhanced secondary porosity, and realization of this fact led early researchers to identify the Bigfork Chert as the most important aquifer throughout the area in terms of yield (Purdue, 1910; Purdue and Miser, 1923; Albin, 1965; Halberg and others, 1968; Bedinger and others, 1979). The broad exposure and distribution of the Bigfork Chert in the area of the hot springs combined with its hydrologic importance resulted in most researchers identifying the formation, potentially in combination with the Arkansas Novaculite, as the primary recharge formation for the hot springs flow system (Purdue, 1910; Bedinger and others, 1979).

## Nature and Origin of the Hot Springs in Hot Springs National Park

Because this report characterizes the occurrence of thermal water outside of HSNP and assesses any hydraulic relations with the hot springs in HSNP, better understanding of the hot springs flow path, particularly including the source of heat, is critical for defining potential hydraulic connections and the potential for a similar hydrogeologic origin where there is no physical hydraulic connection. The origin, chemistry, and therapeutic value of hot springs in HSNP have been of interest to researchers from the early 1800s to the present. References to the hot springs, general chemistry of the springs, and the surrounding geology were made in early reports by Owen (1860), Glasgow (1860), Branner (1892), Haywood (1902) and Weed (1902). Purdue (1910) was one of the first researchers to systematically address the origin of the hot springs. Based on the intervening structure of the compressed folds, their lateral overlapping, and the large degree of fracturing in the Ouachita Mountains, Purdue (1910) concluded that the recharge area must be in the near vicinity of the springs, and, based on the topography, stratigraphy, and structure, that the recharge area must be located on the overturned, anticline valley between Sugarloaf and North Mountains (fig. 1) with the Bigfork Chert as the dominant recharging formation. The Bigfork Chert was identified as the most likely formation through which recharge occurs based on the considerable thickness and outcrop extent, the intensely fractured nature of the rock, and the thin layers that define the unit. Purdue (1910) attributed the location of the springs to the southwestern plunge of the Hot Springs anticline (fig. 2) and to resulting fracturing and faulting in the process of folding, although no major faults were identified in his report.

The most comprehensive study of the origin of the hot springs was conducted by Bedinger and others (1979). The radioactivity and chemical composition of the hot springs was compared to that of cold-water springs; tritium and carbon-14 isotopes were analyzed to age date the hot springs; and a mathematical model was used to test the various conceptual models of the hot springs flow system. Bedinger and others (1979) demonstrated a similarity between chemistry of the hot springs and cold-water springs and wells in the vicinity of the hot springs. The main difference was in the elevated silica concentrations of the hot springs, which were used to estimate the temperature at depth based on the increased solubility of silica with increasing water temperature (Fournier, 1981). Bedinger and others (1979) estimated that the maximum temperature at depth was no more than a few degrees higher than the temperature of the emerging springs.

Bell and Hays (2007) calculated the maximum temperature at depth of 66.6°C; the mean temperature of the emerging hot springs is approximately 62°C. Hot springs temperatures vary from spring to spring and vary with time for individual springs because of changing cold-water input and to seasonal surface temperature variation. The maximum temperature attained by different thermal flow systems in the area likely



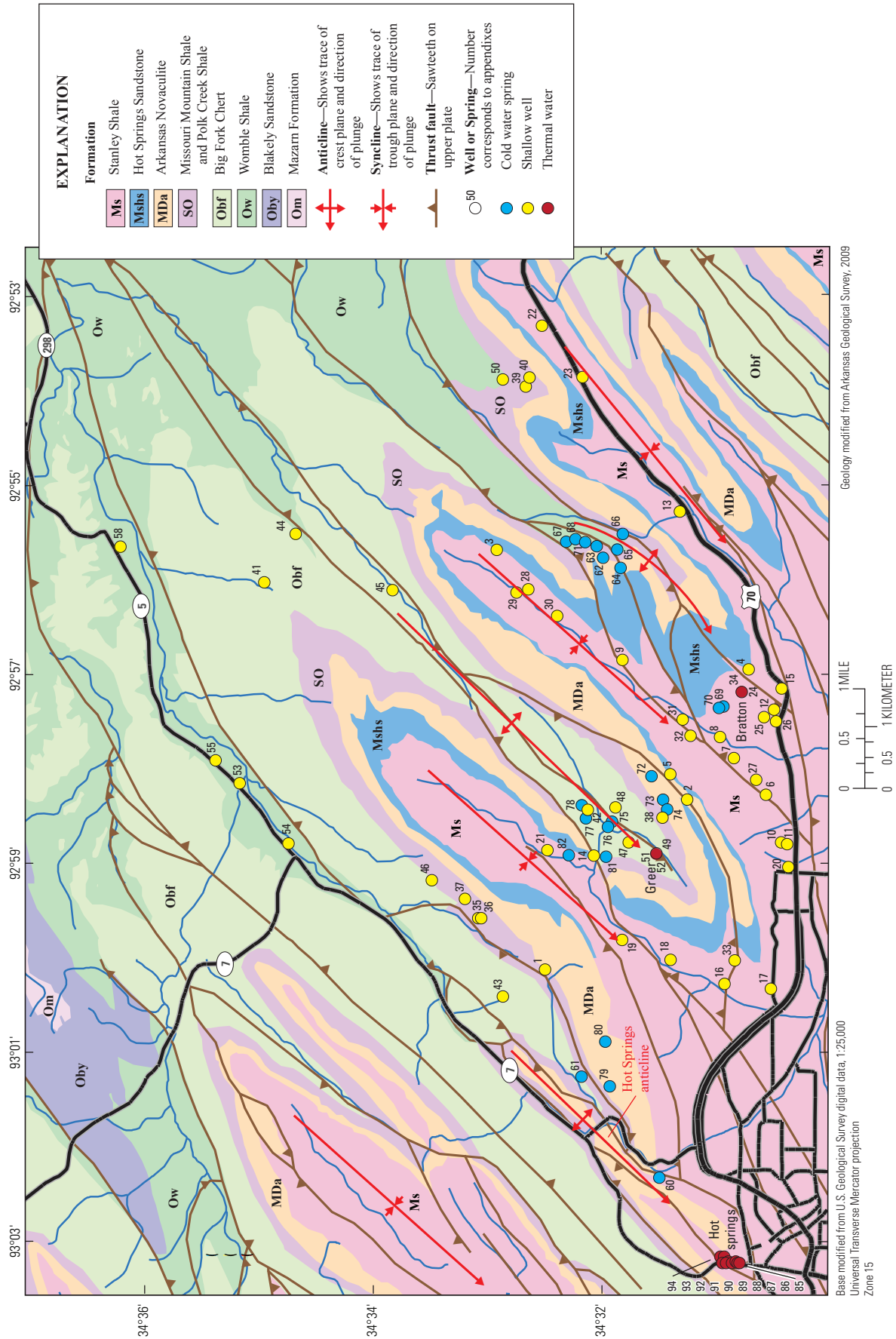


Figure 2. Geology of study area.

varies based on maximum depths of flow and local variation in geothermal gradient; temperature in these springs also can be expected to vary because of cold-water input, as is the case for the springs in HSNP. Tritium and carbon-14 isotope analyses indicated a mixture of a small volume of young water less than 20 years in age and a preponderance of water approximately 4,400 years old. The mathematical model, together with the geochemical data, flow measurements, and regional geologic structure, supported a concept of local, meteoric origin by recharge through the Bigfork Chert and Arkansas Novaculite. The water was theorized to be heated at depths of 5,000 to 8,000 ft through the normal geothermal gradient (thought to be between 0.006°C/ft to 0.009°C/ft; Bedinger and others, 1979), and fault conduits provided the avenue for rapid transport to the surface. This model remains the most widely accepted by the scientific community for the origin of the hot springs. For reference, past authors have posited upwelling of juvenile water (Arndt and Stroud, 1953), the existence of an underlying magmatic body (Weed, 1902), or reaction of minerals, such as sulfides (Bergfelder, 1976) to explain the heat.

Bell and Hays (2007) conducted a comprehensive geochemical and water-quality study and quantified the hot springs' local, cold-water component. Yeatts (2006) investigated the recharge area for the shallow, cold-water component of the hot springs, and performed groundwater tracer tests to calculate recharge areas. Yeatts (2006) showed a traveltime of 1 to 3 weeks from various dye-release points to the hot springs. Continuous temperature monitoring data (Bell and Hays, 2007; Yeatts, 2006) showed that recharge from rainfall generally caused downward spikes in water temperature for many of the springs, providing direct evidence that cooler, shallow groundwater was mixing with the thermal water of the springs. Yeatts (2006) calculated the recharge area for the cold-water component of flow to be approximately 0.1 to 0.2 mi<sup>2</sup>. Bell and Hays (2007) collected geochemical data on the hot springs and showed statistically significant differences for silica, total dissolved solids (TDS), strontium, sulfate, and barium for analyses of hot springs during base-flow and stormflow events. Using silica in a binary mixing model, it was demonstrated that contribution of cold-water recharge to hot springs during base-flow conditions varied from 0 to 16 percent, and the contributions during stormflow conditions varied from 21 to 31 percent.

## Methods

The following sections describe methods used for collection and analysis of water-quality samples; collection of field data including water level, pH, temperature, dissolved oxygen, and specific conductance; collection of borehole geophysical data from selected wells; collection of continuous water-level and temperature data at selected sites in the study area; and collection of precipitation data. All data were collected by USGS personnel from March 2006 through June 2009.

## Water-Quality Sampling and Analysis

A general reconnaissance of wells and springs in the study area was conducted during numerous trips between October 2006 and March 2007. The reconnaissance included spring and well location and georeferencing, collection of water-level data (where accessible), and field measurement of specific conductance, temperature, and pH of the water. Water samples were collected at 27 sites, including 15 wells, 10 hot springs in HSNP, and 2 cold-water springs in September 2007 and analyzed for major cations and anions, trace metals, and isotopes at selected sites, including carbon-14 and tritium abundance, and strontium, carbon, oxygen, and hydrogen stable isotopes. An additional 28 well and spring sites were sampled in April 2008 for strontium isotope analysis only. Samples for major cations, anions, and trace metals were analyzed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, following procedures described in Fishman (1993) and Garbarino (1999). Complete analyses are found in appendix 1. Concentrations preceded by a “<” symbol in appendix 1 denote that the concentration was less than the laboratory reporting level; one-half of the laboratory reporting level concentration was used for statistical purposes. For instance, the laboratory reporting level for iron is less than 6.0 µg/L, and 3.0 µg/L was the value used to calculate mean concentrations for iron. Estimated concentrations for some constituents are noted by an “E” in front of the concentration. Concentrations are marked as estimated for cases in which the concentration is between the long-term method detection limit and the laboratory reporting level (Childress and others, 1999). Because there is a 95 percent confidence level that only 1 percent of concentrations above the long-term method detection limit are false positives, estimated concentrations were used as listed for statistical purposes in this report. Two thermal springs, Little Missouri and Caddo Gap Springs, listed in Bryan (1922) and located in western Arkansas, were additionally sampled in June 2008 for comparison to the well and spring data from the study area; samples were submitted to the Arkansas Department of Environmental Quality (ADEQ) Water Quality Laboratory for analysis of major ions and samples for strontium analysis were submitted to the USGS NWQL. Field measurements including water temperature, pH, dissolved oxygen, and specific conductance were collected at reconnaissance and water-quality sampling sites following procedures described in Wilde (2008).

Analysis of samples for determination of isotopic composition was performed at various laboratories. Oxygen and hydrogen stable isotope (oxygen-18/oxygen-16, <sup>18</sup>O/<sup>16</sup>O, and deuterium/protium, <sup>2</sup>H/H) analyses were performed at the USGS Reston Stable Isotope Laboratory in Reston, Virginia, by isotope-ratio mass spectrometry (Revesz and Coplen, 2008a, 2008b). Tritium (<sup>3</sup>H) and strontium isotope (strontium-87/strontium-86, <sup>87</sup>Sr/<sup>86</sup>Sr) analyses were performed by the USGS Water Resources Radiogenic Isotope Laboratory in Menlo Park, California; tritium analysis was performed by use of electrolytic enrichment and liquid scintillation (Thatcher

and others, 1977; Ostlund and Werner, 1962), and strontium analysis was performed by mass spectrometry (Bullen and others, 1996). Carbon stable isotope (carbon-13/carbon-12,  $^{13}\text{C}/^{12}\text{C}$ ) composition and carbon-14 analyses were performed at the Environmental Isotope Laboratory on the campus of University of Waterloo, Waterloo, Ontario, Canada, by accelerator mass spectrometry (Drimmie and others, 1990; Stuiver and Polach, 1977). Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element. For oxygen, the ratio is  $^{18}\text{O}/^{16}\text{O}$ . The relative abundance of the oxygen isotopes can be expressed as a deviation from a standard quantity using delta ( $\delta$ ) notation and symbolized as  $\delta^{18}\text{O}$ ; values are expressed in per mil (‰):

$$\delta^{18}\text{O}_x = (R_x - R_{std}) / R_{std} \times 1000 \text{‰} \quad (1)$$

where

$\delta^{18}\text{O}_x$  is the  $\delta$  value of a sample  $x$ ,  
 $R_x$  is the  $^{18}\text{O}/^{16}\text{O}$  ratio of that sample, and  
 $R_{std}$  is the  $^{18}\text{O}/^{16}\text{O}$  ratio of the standard.

A positive value of  $\delta^{18}\text{O}$  represents water with more  $^{18}\text{O}$  relative to  $^{16}\text{O}$  than the standard water, Vienna Standard Mean Ocean Water (VSMOW). A zero value of  $\delta^{18}\text{O}$  represents water that has the same ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  as VSMOW. A negative value of  $\delta^{18}\text{O}$  represents water with less  $^{18}\text{O}$  relative to  $^{16}\text{O}$  than VSMOW. Similar notation is used to express the concentrations of the stable isotopes of hydrogen (deuterium/protium,  $\delta^2\text{H}$ ) also referenced to VSMOW, carbon ( $^{13}\text{C}/^{12}\text{C}$ ) referenced to the Pee Dee Belemnite (PDB), and sulfur isotopes ( $^{34}\text{S}/^{32}\text{S}$ ) referenced to the Canyon Diablo Troilite.

Strontium is a divalent, reactive metal that behaves similarly to calcium in chemical interactions and substitutes for calcium in many minerals. Like  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  is a trace component of most groundwaters. Strontium has four naturally occurring isotopes:  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$ . Strontium isotopes are reported as absolute  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, typically to a four- to six-decimal notation (Kendall and McDonnell, 1998). Variability in strontium isotope ratios in rocks is caused by radiogenic formation of  $^{87}\text{Sr}$  at the expense of parent rubidium. Strontium isotope ratios show great variability through much of geologic time, particularly for the Phanerozoic, due to relative contributions of strontium to the ocean from terrestrial weathering and hydrothermal influx from the mid-ocean ridges. Rock-water interaction imparts this strontium isotope variability as a signature to aquifers. Strontium isotopic ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) have proven to be a useful tracer for groundwater movement (Clark and Fritz, 1997; Kendall and McDonnell, 1998). Aquifer-framework minerals often have distinctive strontium content and specific strontium isotopic signatures that can be picked up by water, enabling identification of recharge sources, transport pathways, and mixing.

Protocols for instrument calibration (Wilde, 2008) and equipment cleaning (Wilde and others, 1998) were followed to maintain proper quality assurance and quality control (QA/QC) of water-quality data associated with all sampling events.

Four replicate samples and one blank sample were submitted with the September 2007 sampling event. A stainless-steel, positive-displacement pump with Teflon rotors (gears) was used to purge and sample wells (including constructed monitoring wells) that lacked dedicated pumps. An equipment blank was collected using inorganic-free water passed through the pump prior to field use for the September 2007 sampling event. All results from the QA/QC sample data indicated that cleaning procedures were adequate in preventing cross contamination of samples and that the laboratory results were reproducible. Results for QA/QC samples are available at the USGS National Water Information System webpage (<http://waterdata.usgs.gov/nwis>) and can be obtained through the USGS Arkansas Water Science Center in Little Rock, Arkansas.

## Collection and Analysis of Field Data

Continuous monitoring of water-level and temperature was conducted at 1-hour intervals for five wells (well 1, 16, 24, 48, and 52) located in the study area. Two of the wells were equipped with real-time monitoring capability; data were transmitted by satellite on an hourly basis. The other three wells were equipped with data loggers and the data were downloaded monthly. Data were subsequently checked for accuracy, corrected where necessary, and stored in the USGS National Water Information System. Water levels were measured manually on a monthly basis and compared to transducer levels to check for cable stretch and instrument drift; any discrepancies were entered into the calculation for the corrected data to account for the variation. Precipitation data were collected by using a tipping-bucket rain gage at a USGS gaging station (07358280) in Hot Springs, Arkansas. The data were collected at 15-minute intervals, and daily totals were calculated from these data for comparison to water-level data at selected well sites in the study area.

A potentiometric-surface map was constructed using water levels from 53 shallow (less than 400 ft) wells and 24 cold-water springs located in the study area. Water levels were measured in the wells using an electric tape, which was calibrated to one-hundredth of a foot. Water levels were subtracted from surface altitudes at each site, which were extracted from topographic maps with a default accuracy of plus or minus 10 ft for each well altitude. Potentiometric-contour lines were manually contoured within a geographical information system using 50-ft contour intervals. Abundant control points in the southwestern part of the study area reflected strong topographic control, and topographic contours were followed for estimated depth to water to extend contour intervals at locations with a lower density of control points.

Borehole geophysical logging was conducted on one existing well (well 24) and one newly installed monitoring well (well 34) in the study area to characterize the geology, fracture zones, relative fracture yields, fluid temperature, and other elements of site hydrogeology. All logging was

conducted by staff of the USGS Arkansas Water Science Center. Geophysical logs included natural gamma radiation, spontaneous potential, fluid resistivity, long and short normal resistivity, lateral resistivity, specific conductance, temperature, single-point resistance, caliper data, induction data, acoustic televiewer data (Keys, 1997), and electromagnetic flowmeter data (Century Geophysical Corporation, 2006).

Three monitoring wells were constructed from June 27-29, 2007, at two sites for the purpose of isolating zones of thermal water contribution noted in domestic wells at each site. A 4-inch monitoring well (Bratton 2) completed with polyvinyl chloride (PVC) casing and screen was drilled within 20 ft of the domestic well at the Bratton site to a depth of 165 ft; a 20-ft screen was installed across the thermal zone. Groundwater with elevated temperature (maximum temperature of 26.6°C) additionally was discovered in a second domestic well, the Greer site, on June 26, 2007, during the original reconnaissance of existing wells and springs (fig. 1). Two monitoring wells (Greer2, Greer3), one 4-inch and one 2-inch, were installed at this site at depths of 120 ft and 155 ft. Conventional rotary drilling methods were employed, and the wells were developed until clear water appeared and field measurements (pH, temperature, dissolved oxygen, and specific conductance) stabilized.

## Effects of Blasting on Shallow Groundwater

Concerns regarding the possible effects of blasting associated with highway construction near the newly discovered thermal well (Bratton site) necessitated a literature review on the effects of blasting on shallow groundwater systems. Although the effects of blasting on surface structures, including buildings, have been well documented in the literature (Duvall and Fogelson, 1962; Siskind and others, 1980), few studies have been performed that document the effects of blasting on the hydrology and water quality of shallow aquifer systems, including physical effects on production wells completed in these aquifers.

One of the first investigations into the effects of blasting on groundwater supplies was in the coal production region of the Appalachian Range physiographic province (Robertson and others, 1980). One part of the investigation focused on researching 36 case histories of complaints from homeowners reporting problems with their domestic wells. The complaints ranged from turbidity issues to perceived reduction in yield. Of the 36 case histories of complaints, 24 of these sites were investigated with no clear evidence that any of the well problems were related to blasting; however, evaluating existing wells with little or no knowledge of construction details, preblasting water-quality, preblasting specific yields, and other information makes a preconstruction/postconstruction comparison and comprehensive evaluation of blasting effects inconclusive. As such, results from the investigations prompted the

researchers to conduct a separate study using project-specific, newly constructed wells with monitoring conducted before and after blasting in the vicinity of each well. Four wells were drilled for that project, enabling collection of project-specific water-quality data, aquifer data, well specific capacity, and other information gathered before and after advancement of blasting and excavation associated with mining activities. Ground vibrations and water levels were monitored continuously. As mining and pit development approached within approximately 300 ft of the wells, a drop in static water level occurred in three of the four wells, followed by a substantial improvement in well performance as measured by specific capacity. At the fourth site, there were no recorded changes in the water levels. The timing of the changes recorded in the three wells indicated the changes were not the direct result of blasting. The period of change, the length of time involved, and the location of active mining at the time of the occurrence indicated that the lowering of the static water levels resulted from increased storage space in the aquifers as the result of fractures becoming more open because of downslope excavation and resulting lateral stress relief associated with the mining activities. Subsequent filling of excavations resulted in lowering yields in the wells back to previous production values.

Fracturing of rock commonly is used to improve permeability for enhanced recovery of hydrocarbons and at groundwater-remediation sites for improving recovery efficiency of contaminated water and hydraulic control of groundwater-flow directions. Lane and others (1996) used various geophysical techniques to characterize a fractured bedrock aquifer and a blast-fractured contaminant recovery trench. Borehole geophysical methods applied included video, acoustic televiewer, heat-pulse flowmeter under nonpumping and low-rate pumping conditions, natural gamma, electromagnetic induction, fluid temperature and conductivity, caliper, deviation, and borehole radar. An azimuthal square-array, direct-current resistivity surface geophysical technique also was used. Aquifer testing was performed before and after blasting. Characterization was conducted before and after blasting of a trench used for recovery of a petroleum plume in low-permeability fractured bedrock. Information from six observation wells near the trench, borehole and surface geophysical methods, and aquifer tests indicated that the blasting created an intensely fractured zone about 10-ft wide and 85-ft deep, along the 165-ft length of the recovery trench. An increase in porosity and transmissivity near the trench resulted from apparent hydraulic cleaning that occurred when water was ejected out of the observation wells within 30 ft of the trench during the blast (water was ejected 40 ft to 50 ft into the air during blasting). Estimated aquifer transmissivity after the blast in wells within 30 ft of the trench was an order of magnitude higher than before the blast; however, no new blast-induced fractures or increases in fracture apertures in the observation wells were identified on the video or televiewer logs and none of the calcite-filled fractures appeared to be opened by the blast. As such, fractures developed during the blasting did not extend

to observation wells, which were within 30 ft of the blast-fractured trench.

A key observation of Lane and others (1996) was that the relatively high-energy blasting approach—designed specifically to fracture the aquifer and increase hydraulic connectivity—did not result in observable fracture propagation any large distance from the blasting locus. Begor and others (1989) similarly reported on an artificially produced fracture zone for hydraulic control of a contaminant plume. The blast-induced fracture zone was 325-ft long and 7-ft wide and was created to provide enhanced fracture connectivity for intercepting a contaminated groundwater plume. Extensive fracturing was extended several feet radially from each shot hole with hairline cracks extending as far as 10 to 15 ft from blasting locations.

Much of the damage created away from blasts is associated with the travel of wave fronts at the ground surface, and studies have shown much lower vibration at depths in observation wells; these observations are consistent with large-scale seismic events in that most of the damage caused during earthquakes is a result of surface waves. Ground vibrations normally are measured with seismographs and are reported in feet per second. The point during a measuring event where the velocity is at a maximum is termed the peak particle velocity. Robertson and others (1980) noted that vibrations near the bottom of wells were considerably attenuated at depths of 140 to 160 ft. Daniel B. Stephens and Associates (2002) studied effects on yield and water quality in domestic wells at five coal-mining sites in Pennsylvania (at least two wells at each site). This study, similar to Robertson and others (1980), also observed very little change in water quality and other factors; the minor changes in water quality noted for the study were related to household well use and sensor drift. There were no changes in well yield over the period of measurement for the study; however, distances of the study wells from blasting sites ranged from 1,293 to 5,140 ft and averaged 2,607 ft. Daniel B. Stephens and Associates (2002) also placed transducers to measure peak particle velocities near the surface (0.42 ft) and at depth (from 1.1 to 20 ft) at the sites and showed that peak particle velocities decreased with depth. The average decrease in velocity was 0.0015 inches per second per foot below the ground surface. Golder and Associates (2004) reviewed numerous studies for a report on potential effects from extension of a quarry in Canada and stated that fracture development from blasting was usually limited to the equivalent distance of about 20 times the blast borehole diameter (typically 0.25 ft), except for minor microfracturing beyond this distance. Golder and Associates (2004) postulated that a ground-vibration limit of 2.0 inches per second is adequate to protect wells from any damage.

Although additional studies are needed to fully characterize the effects of blasting on the hydrogeology of shallow aquifer systems, results from available studies indicate that propagation of new fractures near blasting sites is of limited extent. Safe levels of ground vibration from blasting range from a peak particle velocity of 0.5 to 2.0 in/sec for residential

structures (Siskind and others, 1980), and this range in vibrations appears to be safe for protection of groundwater wells ranging from 300-5,100 ft from blasting sites based on a review of pertinent studies. Vibrations from blasting can result in rock collapse for uncased wells completed in highly fractured rock. However, the propagation of newly formed large fractures that potentially could damage well structures or result in pirating of water from production wells appears to be of limited possibility based on review of relevant studies.

## Hydrogeology of the Shallow Aquifer System

The hydrogeology of the shallow groundwater-flow system in the study area was defined by constructing a potentiometric-surface map to evaluate flow directions and reviewing hydrologic data from continuously monitored wells to evaluate the hydrologic response of wells completed in different formations to regional rain events. A potentiometric-surface map was developed from water levels measured in 53 wells and 25 springs within the study area. Well depths were obtained for 35 of the wells cataloged during the reconnaissance. Of these 35 wells with known well depths, 29 (83 percent) were less than or equal to 200 ft in depth and all of the 35 wells were less than 400 ft in depth. Because wells produce mainly from fractures in the study area, and fractures tend to be increasingly smaller in aperture and frequency at greater depths, aquifer yields below depths greater than approximately 400 ft typically are insufficient to supply user needs. Potentiometric contours of the shallow groundwater system (fig. 3) present a subdued reflection of topography, which indicates a high degree of topographic control on shallow groundwater flow in the area. Hydraulic behavior of this shallow aquifer also is strongly controlled by local geology. Steep and topographically rugged ridges in the area are defined and supported by the resistant Arkansas Novaculite and Bigfork Chert with gentle sloping valleys formed on the Stanley Shale. Recharge areas for infiltrating rainwater are located in the topographically higher areas of exposures of Bigfork Chert and Arkansas Novaculite, and the valleys serve as groundwater-discharge areas. Discharge occurs naturally as base flow in streams draining the study area and through numerous springs. Springs can be found throughout the region in topographically higher areas and in the valleys. Most springs were located in the Bigfork Chert and Arkansas Novaculite formations, although springs were present in all formations exposed in the study area (fig. 2).

Potentiometric-surface gradients are steeper in the valleys and less steep near the top of the ridges (fig. 3). The high storage and high permeability of the Bigfork Chert and Arkansas Novaculite allow rapid conveyance of recharging water from rain events through these rocks and distribute this water throughout the numerous fractures; thus maintaining lower gradients. The lower fracture density and resulting

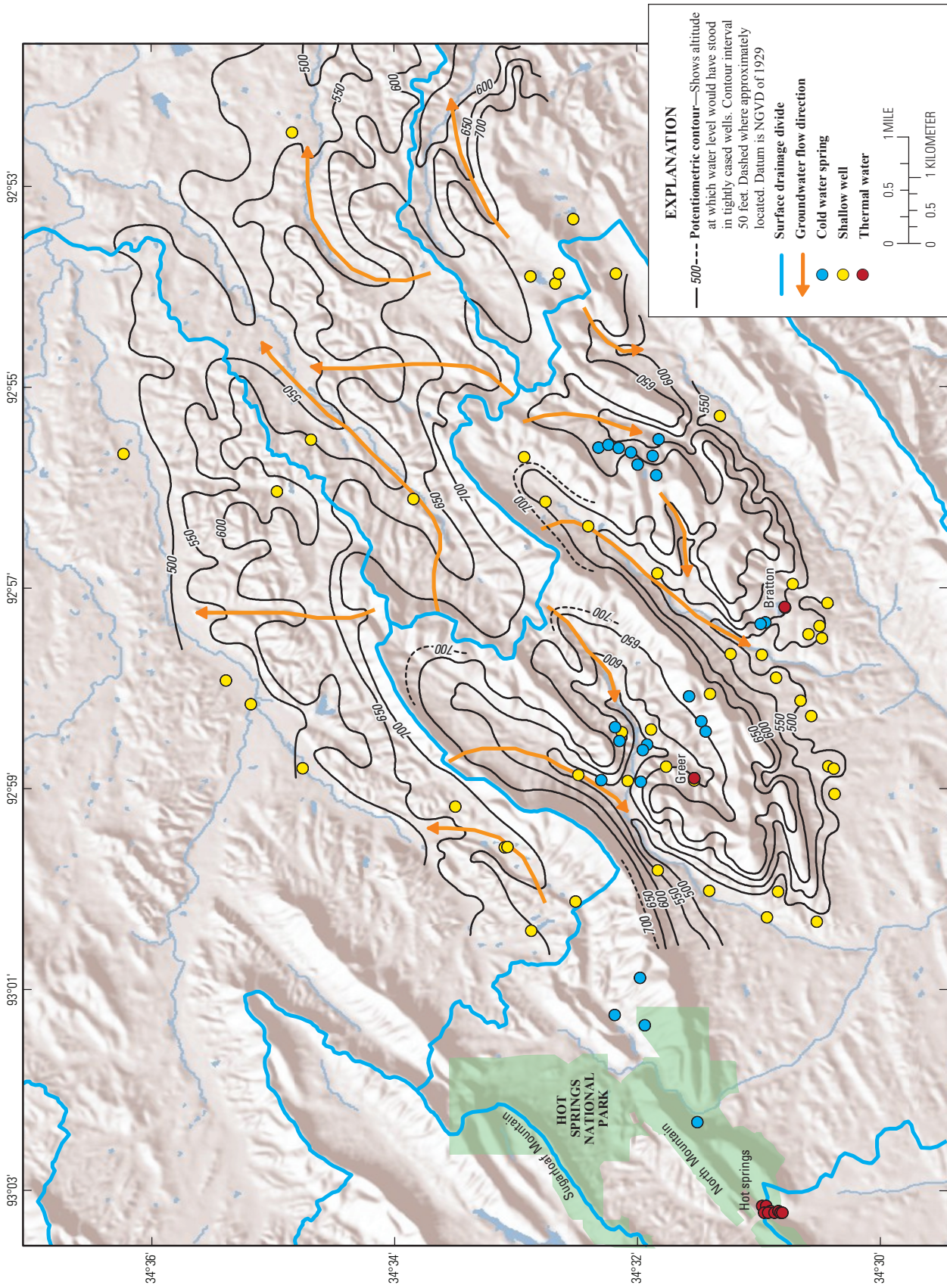


Figure 3. Potentiometric surface of shallow groundwater in study area, 2006–07.

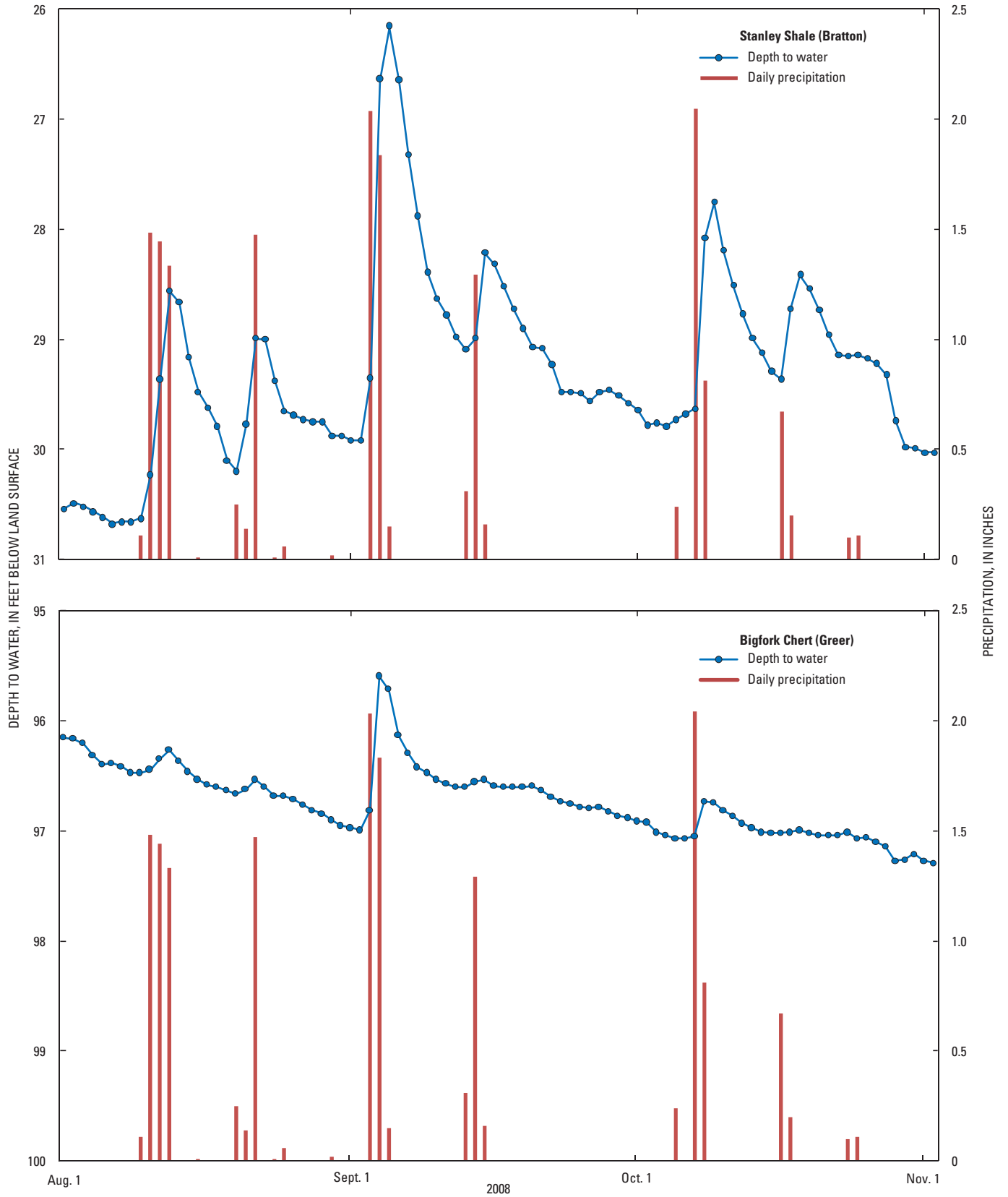
lower permeability, porosity, and storage in the shale formations, including the Stanley Shale, result in a highly uneven distribution of recharged water, a rapid filling of fractures, and a correspondingly greater increase in water levels and flow gradients with rain events. The mean depth to water in 25 wells completed in the Stanley Shale was 16 ft below land surface, as compared to mean depth to water of 75 ft in 11 wells completed in the Bigfork Chert (fig. 2). The greater depth to water in wells completed in the Bigfork Chert also fits regional models, which show that deep unsaturated zones exist in recharge areas between the water table and the land surface; whereas, the water table is found close to or at the land surface in discharge areas (Fetter, 1988). Nine of the 25 water levels measured in wells completed in the Stanley Shale were less than 10 ft below land surface at the time of measurement. Four flowing artesian wells were identified during the early field reconnaissance, and seven of the wells measured during the reconnaissance had water levels less than 5 ft below the land surface at the time of measurement.

Aquifer properties, including porosity and storage, within the various formations were investigated by the continuous monitoring and evaluation of water-level responses to regional precipitation events for selected wells in the study area. Hydrographs for two wells were examined, including a well completed in the Stanley Shale and one completed in the Bigfork Chert, representing water-level changes within these two lithologies in the study area. The relation between continuously recorded water levels for a 3-month period (August through October 2008) in a well completed in the Stanley Shale (Bratton site) and a well completed in the Bigfork Chert (Greer site) are shown in figure 4. Five major rain events (one or more days) greater than 1 inch for each day occurred during the 3-month period. The first rain event occurred from August 10-12, 2008, and resulted in an approximate 2-ft increase in the water level in the Stanley Shale well (Bratton site) but an increase of only 0.2 ft in the Bigfork Chert well (Greer site). The next 1-inch rain event on August 21, 2008, resulted in a water-level increase of 1.2 ft in the Stanley Shale well but an increase of only 0.1 ft in the Bigfork Chert well. Responses for four of the five major rain events during this period resulted in increases in the Bigfork Chert well of less than 0.3 ft, though increases for these four events in the Stanley Shale ranged from 1.2 to 2.0 ft. The only substantial increase in the Bigfork Chert well was for the third rain event (two consecutive days of 2.0 inches and 1.8 inches of rain, respectively), which resulted in a water-level increase of 1.4-ft increase in the Bigfork Chert well compared to an increase of 3.7 ft in the Stanley Shale well. Similar responses were noted for all rain events in both wells with water levels rising substantially less in the Bigfork Chert well than in the Stanley Shale well for the entire period of measurement (September 2007 through May 2009). Following the steep increases in water level after major rain events, water levels were observed to drop sharply in the Stanley Shale well; whereas, decreases occurring over a longer period of time were typical of the Bigfork Chert well.

Comparisons of the net response of these two wells over a time period of more than 1.5 years revealed seasonal responses in water level and provided information on the storage characteristics for each formation (fig. 5). From December 2007 through May 2008, water levels in the Stanley Shale well responded strongly for individual rain events, but dropped to a relative average base level that was approximately 31 ft below land surface from September 2007 through December 2007. This base level increased slightly by 1 ft to approximately 30 ft below land surface during the wet season from February 2008 through April 2008; however, the rapid post rain event water-level decreases continued. Water levels dropped to the original average base level of approximately 31 ft below land surface from May 2008 through August 2008 and began to rise in September 2008 to the slightly higher base level of 30 ft. The hydrograph from the Greer well, completed in the Bigfork Chert, showed a very different response from the hydrograph from the Bratton well, completed in the Stanley Shale, for the same period of measurement. Water levels slowly rose more than 7.8 ft in the Bigfork Chert well from December 2007 through April 2008 with only subtle inflections as a result of individual rain events during this period. In late May 2008, water levels in the Bigfork Chert well began to decrease, and this trend continued into December 2008 when water levels began to increase. Winter and early spring are wet seasons for Arkansas and much of the annual aquifer recharge typically occurs during this period; whereas, the summer to early fall seasons are times of lower rainfall, marked by falling water levels for aquifers throughout Arkansas.

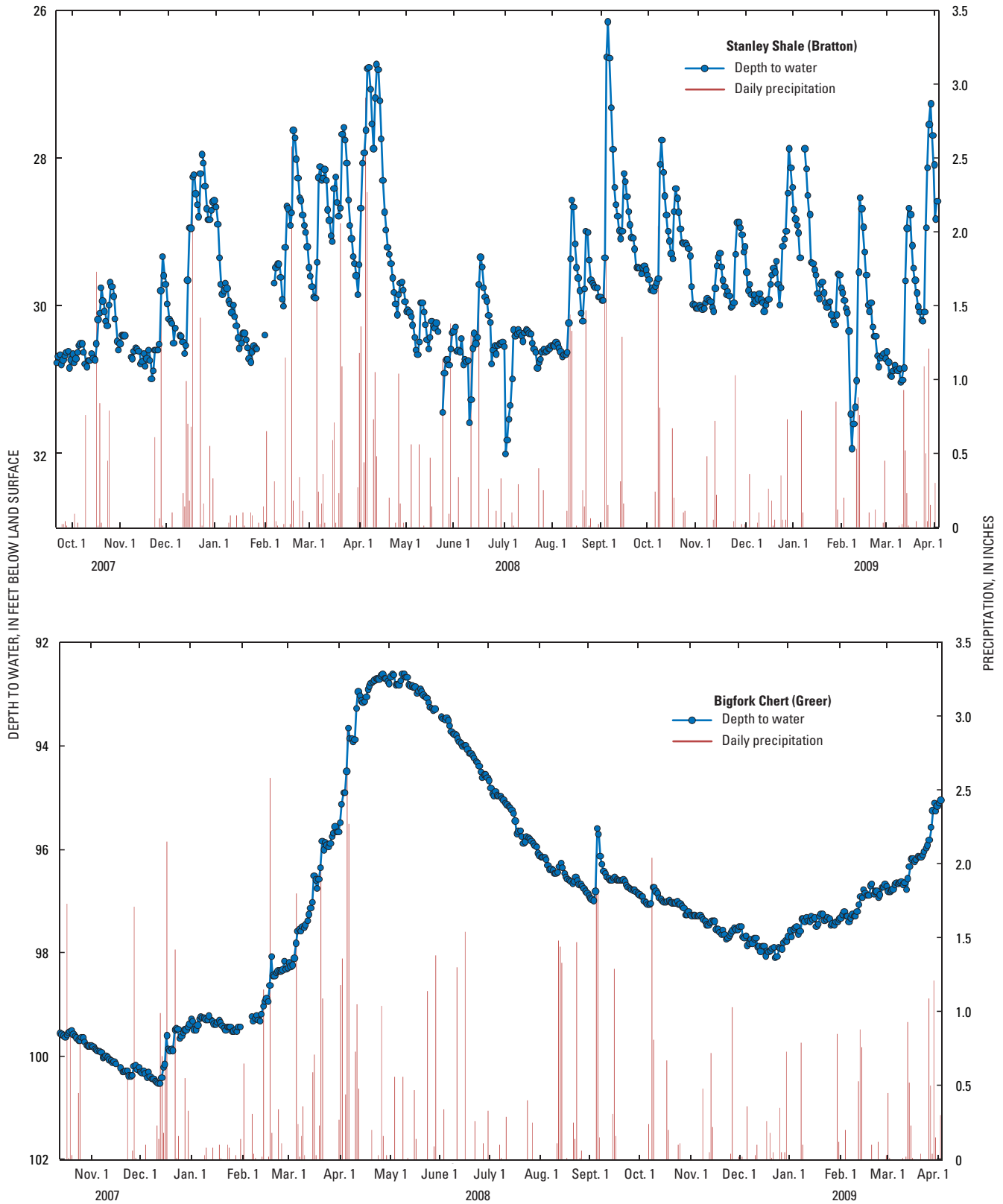
The differing water-level responses of these two wells to individual rain events and to seasonal variation in rainfall are a result of the differing storage and permeability characteristics of the shale and chert formations. The brittle nature and intense fracturing of the Bigfork Chert resulted in substantially greater fracture porosity as compared to the fracturing in the Stanley Shale. The greater storage and permeability of the fractured chert allowed greater storage of recharging rain water with lower water-level increases for individual rain events. The lower permeability and secondary porosity in the Stanley Shale resulted in rapid filling of the fractures, followed by rapid water-level declines driven by the steep gradients induced during filling of the fractures. These differences in permeability correspond directly to differences in observed yields for wells in these formations. The well completed in the Stanley Shale (Bratton site), which penetrated 140 ft of saturated thickness, can be pumped dry within 30 minutes of pumping at less than 3 gal/min; however, an observation well drilled in the Bigfork Chert (Greer site), which penetrated only 20 ft of saturated thickness, maintained a rate of 20 gal/min with negligible drawdown over a period of 30 minutes.

Three other sites were instrumented with long-term, continuous monitoring for water level and temperature. Existing wells at these sites were completed in the Stanley Shale (Thornton site), the Arkansas Novaculite (Thomas site), and the Bigfork Chert (Panther Valley site) (fig. 5). Hydrographs for wells at these three sites corroborated the observations

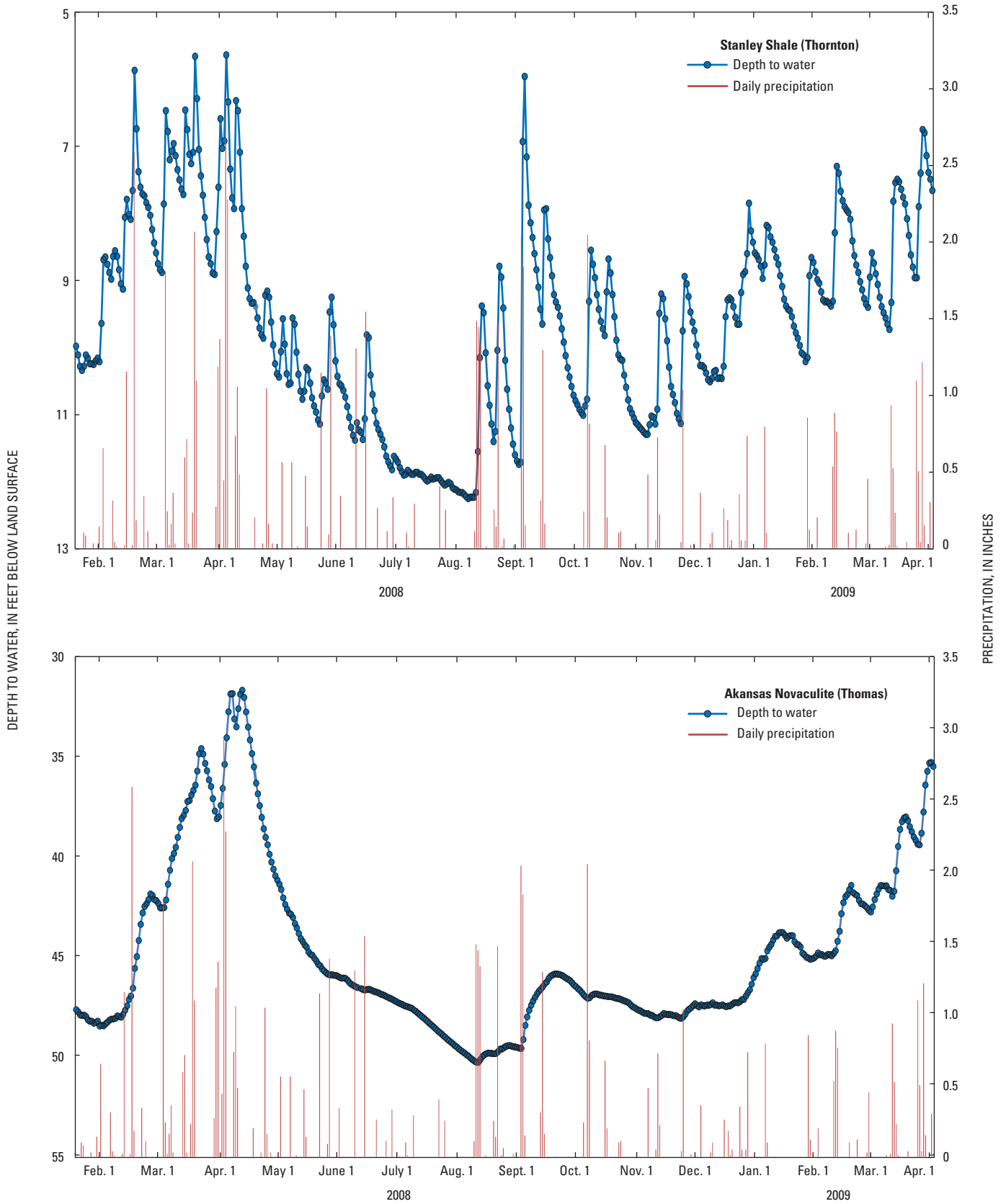


**Figure 4.** Short-term hydrographs of Bratton and Greer wells and daily precipitation at Hot Springs (U.S. Geological Survey gaging station 07358280).

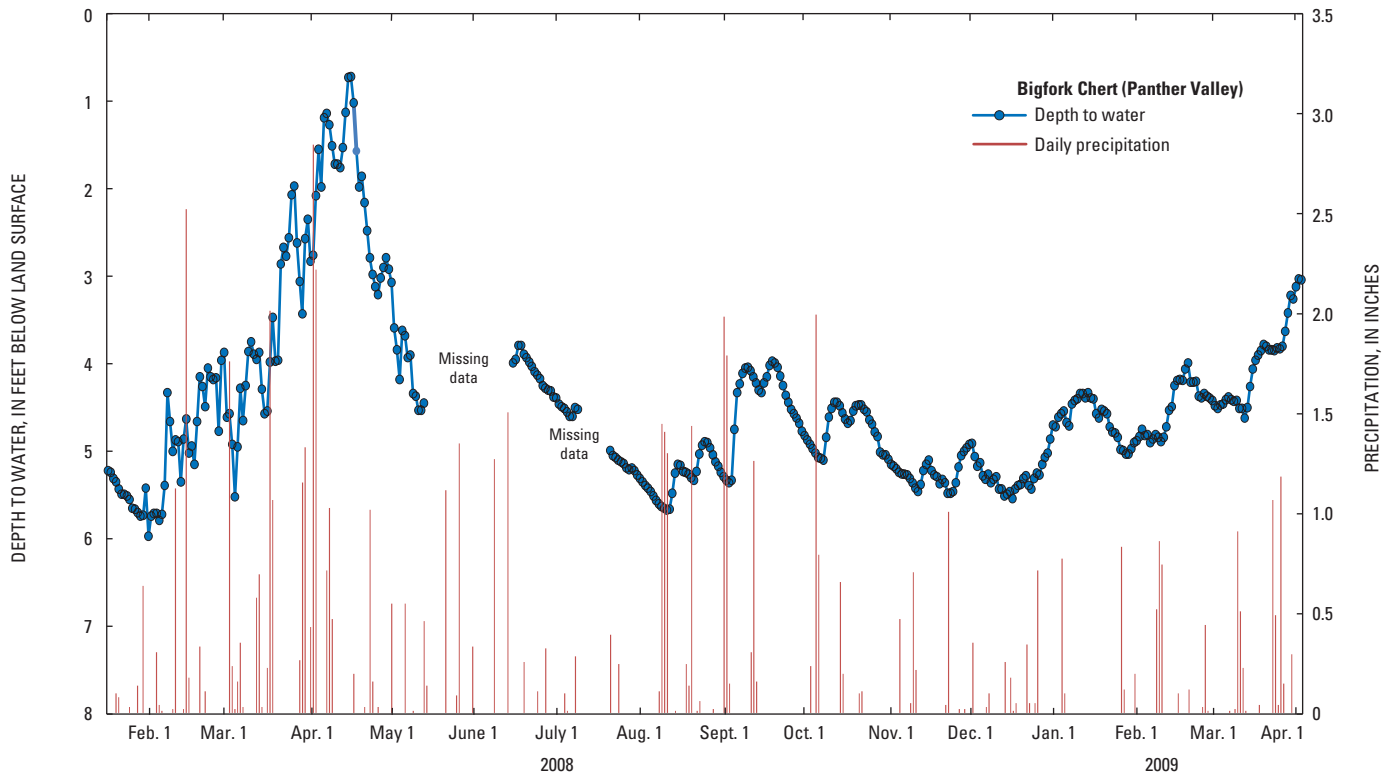




**Figure 5.** Seasonal hydrographs of Bratton, Greer, Thornton, Thomas, and Panther Valley wells and precipitation at Hot Springs (U.S. Geological Survey gaging station 07358280).



**Figure 5.** Seasonal hydrographs of Bratton, Greer, Thornton, Thomas, and Panther Valley wells and precipitation at Hot Springs (U.S. Geological Survey gaging station 07358280).—Continued



**Figure 5.** Seasonal hydrographs of Bratton, Greer, Thornton, Thomas, and Panther Valley wells and precipitation at Hot Springs (U.S. Geological Survey gaging station 07358280).—Continued

in regard to porosity and storage in the Stanley Shale and Bigfork Chert from the two wells discussed in the previous paragraph. Water-level increases of 5.5 ft and 16.5 ft are noted from approximately January 2008 through April 2008 for the wells completely in the Bigfork Chert (Panther Valley site) and Arkansas Novaculite (Thomas site), respectively, with a steady decline from approximately May 2008 through August 2008, followed by a steady increase beginning in January 2009, which corresponds to the rainy season in Arkansas. However, the well completed in the Stanley Shale (Thornton site) had large water-level increases in response to individual rain events (up to 3 ft for consecutive day rain events), but consistently fell back to a relative base level, which generally fluctuated between 9 to 11 ft below the land surface for the period of measurement, similar to the well completed in the Stanley Shale at the Bratton site.

In summary, characteristics of storage and secondary fracture porosity were interpreted from yields observed in individual wells completed in the Bigfork Chert and Stanley Shale; from hydrographs produced from continuous measurements of water levels in wells in the Arkansas Novaculite, the Bigfork Chert, and Stanley Shale; and from a potentiometric-surface map constructed using water levels in wells throughout the study area. The data gathered from these three separate exercises corroborate findings from earlier reports (Purdue, 1910; Purdue and Miser, 1923; Albin, 1965; Halberg and others, 1968) that fracture porosity is much greater in the Bigfork Chert relative to that in the Stanley Shale. At the scale that the

potentiometric map was developed, shallow groundwater flow is strongly influenced by surface topography with no discernable influence by faulting or other geological structural features. The Bigfork Chert generally is located along the hinge line of the topographically higher anticlinal ridges, and the higher groundwater elevations from the potentiometric-surface map indicate that exposures of Bigfork Chert serve as major recharge areas for the regional shallow groundwater system in the study area. Flow lines developed on the potentiometric-surface map indicated that flow moves from these elevated recharge areas and into streams within the synclinal valleys formed on exposures of the Stanley Shale. Therefore, groundwater flow follows topography, and there is no evidence of interbasin transfer of groundwater within the shallow flow system.

## Geochemistry and Comparative Analysis of the Shallow Aquifer and Thermal Water Systems

A groundwater-sampling program was conducted to determine water quality and geochemistry of shallow groundwater from the various shallow formations in the study area for comparison to the geochemistry of the hot springs in HSNP. The goal of this study component was collection of

water-quality data that would enable further characterization of shallow flow paths, identification of recharge source lithologies for shallow groundwater, and establishment of potential connections between shallow flow paths and deep flow paths of thermal waters within and outside of HSNP. Important information was gleaned from a general reconnaissance of the study area prior to the selection of sites for sampling and geochemical analysis. Because of the large amount of data presented in this section of the report, discussion of the data is divided into the following subsections for sake of clarity: reconnaissance, general geochemistry, trace metals, and isotope geochemistry.

### Reconnaissance

A reconnaissance of existing wells and springs in the study area was conducted during several trips between October 2006 and March 2007. Data gathered during the reconnaissance phase are found in Appendix 2 with statistical results of the data summarized below. These data enabled development and enhancement of a conceptual model for groundwater flow in the area and design of an efficient and effective geochemical sampling event.

Specific-conductance values collected from the well and spring reconnaissance showed low values for springs issuing from and wells completed in the quartz rock formations (Bigfork Chert, Arkansas Novaculite, and Hot Springs

Sandstone); all but one site exhibited specific-conductance values of less than 50  $\mu\text{S}/\text{cm}$  with a median of 30  $\mu\text{S}/\text{cm}$ . Specific conductance in wells completed in the shale formations (Stanley Shale, Womble Shale, and the undifferentiated Missouri Mountain Shale and Polk Creek Shale) ranged from 97  $\mu\text{S}/\text{cm}$  to 490  $\mu\text{S}/\text{cm}$  with a median value of 290  $\mu\text{S}/\text{cm}$ . The pH values observed for wells completed in shale formations ranged from 5.8 to 7.7 with a median value of 7.3; pH values for wells completed in quartz formations ranged from 3.6 to 5.9 with a median of 4.5.

The relation of pH and conductance of groundwater measured in 25 shallow wells during the reconnaissance was analyzed to assess the effects of geology on the field chemistry of groundwater in the study area (fig. 6). Values of pH increase with dissolution of mineral species with buffering capacity, particularly carbonate minerals, with a positive correlation in pH and conductance as a result. As such, the higher pH and conductance values were observed in groundwater samples from wells completed in the shale formations as a result of the greater abundance of carbonate and other acid-buffering minerals. Subsequent water-quality analyses revealed that all water samples from the shale formations in the study area were a calcium-bicarbonate water type (see “General Geochemistry” section). Rainwater in Arkansas typically is within a pH range of 4.7 to 4.8 standard units (National Atmospheric Deposition Program, 2009). Eight of the 10 wells completed in the quartz formations had pH values below that of rainwater.

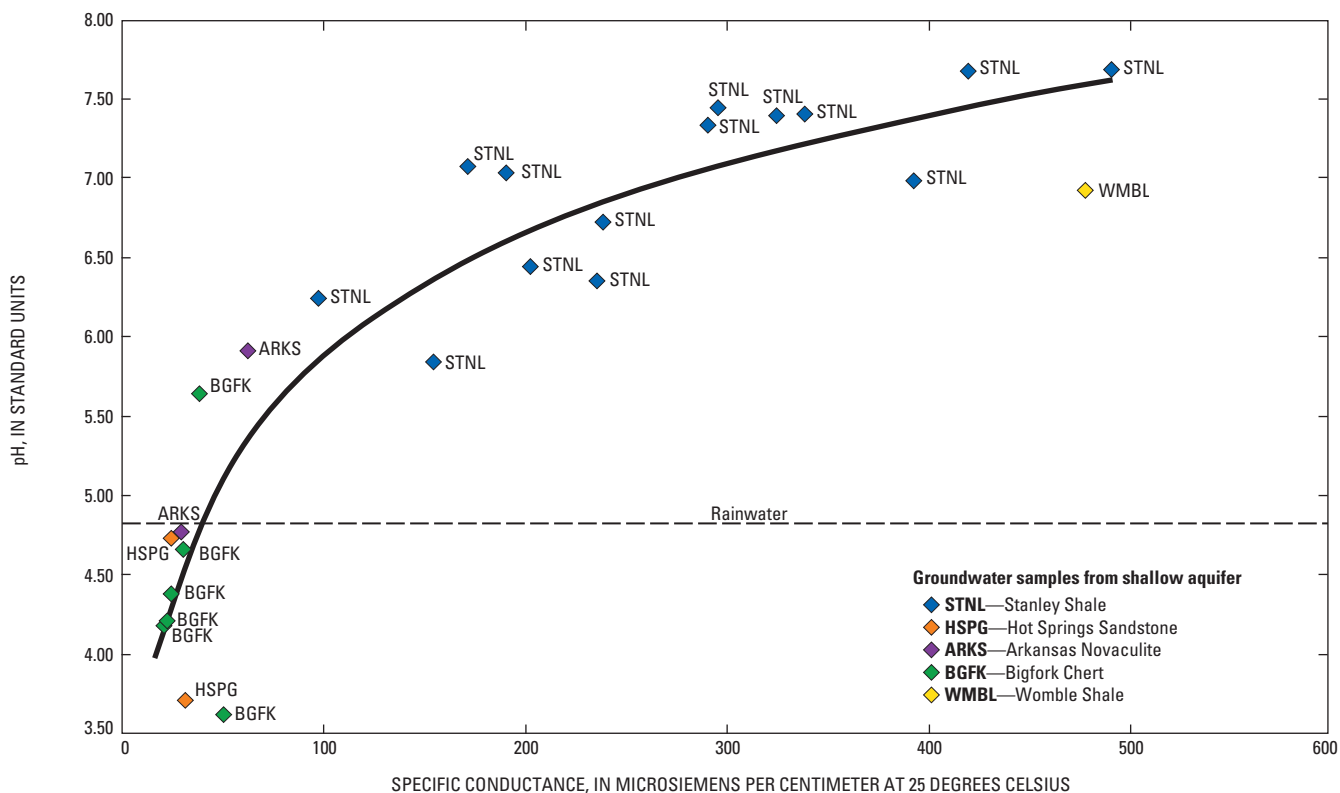


Figure 6. Specific conductance and pH values for groundwater samples from wells completed in shallow aquifers in the study area.

In the carbonate-poor soils and rock units of the quartz formations, carbonic acid, formed by dissolution of soil-gas carbon dioxide, resulted in decreased pH relative to rainwater. Equilibrium constants show carbon dioxide generally to be far more abundant than carbonic acid in solution (Appelo and Postma, 1999), and gases, which exsolved and caused bubbles to form in sampling tubes during sampling of water from the quartz rocks in the study area, were interpreted as carbon dioxide gas.

The apparent lack of carbonates in the quartz formations, evidenced by groundwater chemistry, is supported by early mineralogical studies (Weed, 1902). Chemical tests performed by Weed (1902) on novaculites in the study area showed that they consist of nearly pure silica, and that the silica is pure quartz and not amorphous silica. Numerous rhomboidal cavities were observed in novaculite rock, which corresponded in form and position to calcite inclusions found in the rock. The cavities were speculated to have formed by the dissolution and removal of the calcite (Weed, 1902). Purdue and Miser (1923) describe the upper division of the Arkansas Novaculite as being composed of massive, highly calcareous novaculite, and the Bigfork Chert as containing small quantities of calcite and pyrite. However, the poor buffering capacity implied by field measurements of water from the quartz formations indicates that these formations were noncalcareous in the study area or that weathering at the surfaces of the fractured rock and flushing by recharge water over time has removed the calcite, eliminating any buffering capacity for infiltrating slightly acidic rainfall.

## General Geochemistry

Based on results from the initial field reconnaissance, 15 shallow wells and 2 cold-water springs were sampled for a more comprehensive suite of constituents to evaluate geochemistry for the shallow groundwater system. Four of the wells were completed in the Stanley Shale, two wells in the Hot Springs Sandstone, one well in the Arkansas Novaculite, seven wells in the Bigfork Chert, and one well in the Womble Shale. One of the two cold-water springs sampled for the investigation issued from the Stanley Shale (ArScenic Spring) and the other from the Bigfork Chert (Sleepy Valley Spring). Additionally, 10 hot springs in HSNP were sampled for the investigation; all of which emerged from the Hot Springs Sandstone. Sampling of all sites took place from September 9 through September 13, 2008. Review of an earlier report by Bryan (1922) revealed three springs in Montgomery County that were listed as thermal springs. Two of these thermal springs (Bryan, 1922), Caddo Gap and Little Missouri Spring, hereinafter referred to as the western hot springs, were located in the field and sampled in June 2008.

A statistical summary of selected analytes from the sampling of 15 shallow wells and 2 cold-water springs in the study area (divided into quartz and shale formations), 10 hot springs in HSNP, and the 2 western hot springs is shown in table 2.

The complete set of analyses for all samples is found in appendix 1. The laboratory analyses substantiate the geochemical contrast between groundwater from the quartz formations and groundwater from the shale formations initially indicated by the field reconnaissance data. For the quartz formations, total dissolved solids (TDS) concentrations, as expected from the low specific conductance values, were very low with a median concentration of 23 mg/L, whereas median TDS concentration for groundwater from the shale formations was 153 mg/L. To illustrate the uniquely low ionic strength of the quartz groundwater, the median specific conductance of 30  $\mu\text{S}/\text{cm}$  for these waters compares very closely with distilled, membrane filtration, or reverse-osmosis bottled water available commercially, which typically ranges from 10 to 25  $\mu\text{S}/\text{cm}$  (North Dakota State University, 1992; Emerson Process Management, 2004). Calcium and bicarbonate concentrations for samples from quartz formations also were low, exhibiting median values of 0.4 mg/L and 5 mg/L, respectively. Silica, with a median concentration of 10.7 mg/L, generally constituted the greatest proportion by weight of the TDS.

A Piper diagram constructed using the major ion chemistry, in milliequivalents per liter, for all water samples revealed substantial scattering for the percentage distribution of cations and anions for groundwater samples from the quartz formations (fig. 7); such a distribution is likely the result of the low ionic strength for the water where small concentration changes can considerably affect percent ion contributions. Because of the low buffering capacity and low TDS concentrations in groundwater from the quartz formations, even small changes resulting from various processes including chemical reactions, evapotranspiration, cation exchange, and the quantity, distribution, and solubility of mineral assemblages, can greatly affect the resulting ion percentages. Water type for groundwater from the quartz formations also varied widely with sodium and calcium as the major percentage of cations in milliequivalents per liter and sulfate, chloride and bicarbonate as the major percentage of anions in milliequivalents per liter.

The shale formations, the hot springs in HSNP, and the western hot springs in Montgomery County all exhibited strongly calcium-bicarbonate water type (fig. 7). The chemistry of the hot springs of HSNP was remarkably consistent; the 10 springs appear to be represented by a single point on figure 7. Most analytes for the hot springs show similarity with the shale formations in exhibiting elevated concentrations; important exceptions to this similarity in water chemistry being low sodium and chloride concentrations (table 2), which compared more closely to the quartz formations. Because the Bigfork Chert and Arkansas Novaculite have been identified as the reservoir rock for recharge to the hot springs, the chemical composition for the hot springs would be expected to be closer to the chemistry of samples from the quartz formations. One potential explanation for the higher TDS, pH, calcium, and bicarbonate concentrations observed for the hot springs relative to those of the quartz formations is dissolution of unweathered calcium carbonate in the Big Fork Chert and Arkansas Novaculite at depth. However, trace metal

**Table 2.** Selected chemical characteristics for samples collected from shallow groundwater in study area.

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; <, less than; --, not measured; E, estimated]

Characteristics	Quartz formations (11 samples)						Shale formations (6 samples)						Hot springs (10 samples)						Western hot springs			
	Mini- mum		Mean		Median		Mini- mum		Mean		Median		Mini- mum		Mean		Median		Little Missouri Spring (1 sample)		Caddo Gap Spring (1 sample)	
	Mini- mum	Maxi- mum	Mean	Median	Mean	Median	Mini- mum	Maxi- mum	Mean	Median	Mean	Median	Mini- mum	Maxi- mum	Mean	Median	Value	Value	Value	Value		
Dissolved oxygen, mg/L	0.5	8.3	3.6	3.2	0.5	0.7	1.0	0.6	0.6	---	---	---	---	---	---	---	4.0	---	4.0	1.5		
pH	3.6	6.1	4.6	4.4	5.8	6.6	7.4	6.6	6.6	7.5	7.2	7.2	6.3	7.5	7.2	7.2	6.2	---	6.2	6.7		
Total dissolved solids, mg/L	11	43	25	23	141	179	273	153	153	184	179	179	173	184	179	179	73	---	73	149		
Specific conductance, µS/cm	17	63	34	30	154	260	477	228	228	316	298	298	284	316	298	298	98	---	98	233		
Calcium, mg/L	0.01	7.6	1.9	0.4	12	39	78	36	36	46	45	45	42	46	45	45	17	---	17	35		
Sodium, mg/L	0.7	9.2	2.0	1.5	1.7	10.7	14.8	11.4	11.4	4.0	3.9	3.9	3.7	4.0	3.9	3.9	1.6	---	1.6	4.2		
Bicarbonate, mg/L	1	20	8	5	83	187	249	164	164	167	158	160	151	167	158	160	62	---	62	133		
Chloride, mg/L	1.0	3.0	1.9	1.7	2.2	5.6	11.2	3.8	3.8	1.9	1.8	1.8	1.8	1.9	1.8	1.8	1.6	---	1.6	3.2		
Silica, mg/L	7.2	13.5	10.2	10.7	10.7	19.8	31.3	17.0	17.0	41.3	40.0	39.8	39.6	41.3	40.0	39.8	11	---	11	22		
Sulfate, mg/L	1.0	13.5	4.6	3.5	6.2	20.4	35.4	22.7	22.7	7.8	7.5	7.5	7.3	7.8	7.5	7.5	5.3	---	5.3	4.8		
Aluminum, µg/L	2.5	214	47.6	27.4	1.2	6.8	29.8	2.4	2.4	13.3	3.5	1.2	1.6	13.3	3.5	1.2	---	---	---	---		
Barium, µg/L	0.05	27	12	9	13	59	146	35	35	143	123	138	35	143	123	138	---	---	---	---		
Lithium, µg/L	<0.6	6.8	1.4 <sup>1</sup>	0.6	2.9	9.1	18.3	5.9	5.9	5.0	4.7	4.7	4.2	5.0	4.7	4.7	---	---	---	---		
Iron, µg/L	E4	2,510	491	38	12	186	611	127	127	25	9.5 <sup>1</sup>	<6	<6	25	9.5 <sup>1</sup>	<6	---	---	---	---		
Manganese, µg/L	<0.2	60	18 <sup>1</sup>	12	42	377	1,115	113	113	229	162 <sup>1</sup>	213	<0.2	229	162 <sup>1</sup>	213	---	---	---	---		
Strontium, µg/L	<0.4	40.5	8.7 <sup>1</sup>	4.0	91	226	324	222	222	108	104	106	99	108	104	106	37.1	---	37.1	83		

<sup>1</sup> Mean calculated by substituting one-half of the laboratory reporting level for censored values.

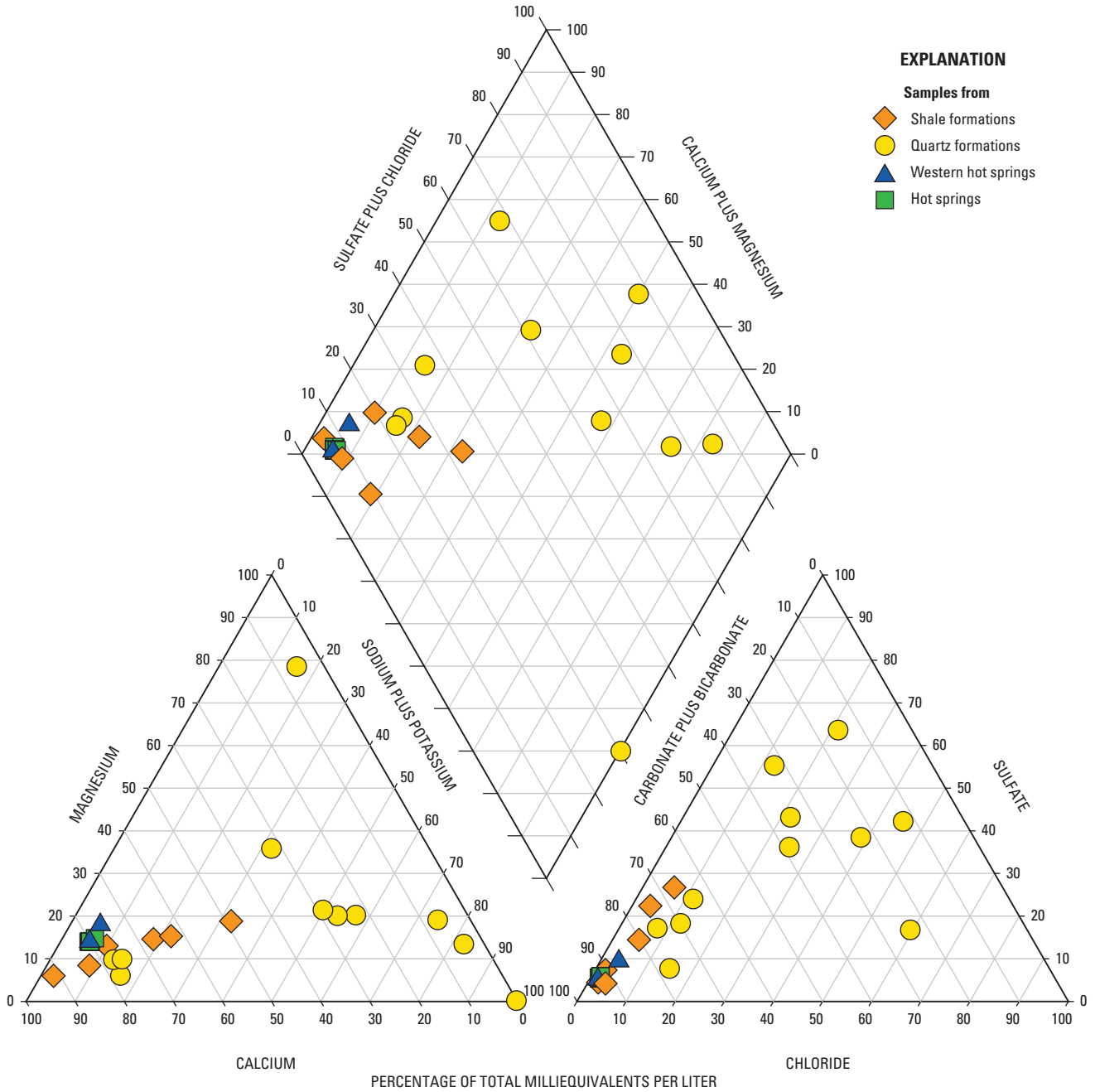


Figure 7. Piper diagram of major cations and anions from shallow groundwater and thermal water samples.

concentrations of the hot springs, including barium, lithium, manganese, and strontium, generally were substantially higher than those of the quartz groundwater and more similar to the shale formation groundwater. Hot springs water chemistry is likely a result of rock/water interaction in the shale formations in the deeper sections of the groundwater flow path to the hot springs with the initial, low ionic strength character inherited from shallow recharge through quartz formations being modified by passage through the shales at depth. This observation for the hot spring chemistry is in agreement with the conceptual model of flow for the hot springs, whereas, the water must traverse shale sequences to exit through the Hot Springs Sandstone (table 1), likely along thrust-fault conduits that bring water up from depth (Bedinger and others, 1979). Substantial contributions to recharge near the surface are not expected from the shale formations because of relatively low permeability, low fracture porosity, and limited storage associated with the shale formations and the lack of outcrop at elevations sufficiently high to drive flow to the hot springs.

The two western hot springs issue from the exposures of Arkansas Novaculite, and results from the field reconnaissance in the study area indicate that these springs also would have water chemistry similar to that of water samples from the quartz rock formations in the study area (low pH, TDS, calcium, and bicarbonate); however, analyses revealed a chemistry closer to that of water from shale formations rather than from the quartz formations (table 2, figs. 7 and 8). The high values of pH and specific conductance and high concentrations of calcium and bicarbonate match more closely with those of water from the shale formations rather than from the Arkansas Novaculite and other quartz formations. Because the springs have a thermal component, a plausible explanation is that the water is a mixture of shallow groundwater from the Arkansas Novaculite and deep flow path thermal water that has traveled along fracture zones at depth, interacting with shale formations to modify the water chemistry in similar fashion to that for the hot springs in HSNP.

A series of box plots were constructed for selected analytes to provide a visual representation of the distribution of concentrations for each site type and the relation of water chemistry between the four site types: the hot springs in HSNP, the quartz formations, the shale formations, and the two western hot springs (fig. 8). The box distribution of concentrations for samples collected from the hot springs in HSNP show the very consistent water chemistry for the 10 hot springs and little variability in samples collected from the quartz formations as compared to water from the shale formations, which show considerable range for most of these analytes (fig. 8). Plots for TDS, calcium, and bicarbonate (fig. 8) show the similar, relatively high concentrations for the thermal water (hot springs in HSNP and western hot springs) and the shale formations with much lower concentrations for water from the quartz formations. The overall similarity in appearance for TDS, calcium, and bicarbonate is explained by the fact that calcium and bicarbonate concentrations are derived stoichiometrically from the dissolution of calcium carbonate

minerals and that calcium and bicarbonate account for the majority of dissolved constituents contributing to the TDS concentration for the thermal water and the shale formations. The wide range of TDS, calcium, and bicarbonate concentrations in the shale formations is explained by varying degree of rock-water interaction along shallow, cold-water flow paths and increased dissolution of carbonate as slightly acidic recharge waters are buffered.

Because median constituent concentrations for the hot springs generally compare more closely to the median concentrations in shales, rather than the maximum shale concentrations (fig. 8) as one might expect for waters evolving along a very long flow path, this provides further argument against recharge through surficial shales as being an important part of the recharge to the hot springs in HSNP. To illustrate, if hot springs water was recharging through surficial shales and traveling a long shale-dominated flow path, the increased opportunity for greater rock-water interaction would lead to TDS concentrations that approach the maximum constituent concentrations observed for shales; this is not the case for the hot springs waters. This observation better supports a shale geochemical influence arising from consistent, well constrained rock-water interaction along a shorter flow path, such as is thought to occur as the waters of the hot springs move out of the quartz formations then move through faults traversing the shales at depth.

Sulfate concentrations (fig. 8) were greatest in the shale formations relative to all other site types. Lower sulfate concentrations in the hot springs relative to the shale formations may be the result of sulfate-reducing conditions and precipitation of iron-sulfide minerals at depth, which is supported by the extremely low and nondetectable concentrations of iron in the hot springs (table 2 and fig. 8). Sulfate reduction also was reported as a possibility by Bell and Hays (2007), whose sulfur isotope analyses provided results indicative of this microbially mediated process.

Silica concentrations (fig. 8) were highest for the hot springs relative to the other site types and can be explained by the increased solubility of quartz and other silica minerals with increased temperatures at depth (Fournier and Rowe, 1966). For the shallow groundwater samples, the variability in silica is a function of the silica phase present in the rock. Because silica in the quartz rocks is present dominantly in the form of pure quartz (Weed, 1902), the mineral form of silica that has the lowest solubility in typical groundwater (Hem, 1989), silica concentrations were lowest in cold-water groundwater samples from the quartz rocks. The presence of amorphous and cryptocrystalline silica, common silica forms in typical shales, likely explains the greater cold-water silica concentrations in the shale formations.

Aluminum concentrations (fig. 8) were highest in the quartz formations relative to the other site types, and are explained by the increased solubility of aluminum at lower pH values rather than rock type (fig. 9). Aluminum solubility and concentrations increase substantially at pH values approaching 4.0 (Hem, 1989). The median pH of groundwater from 11 sites



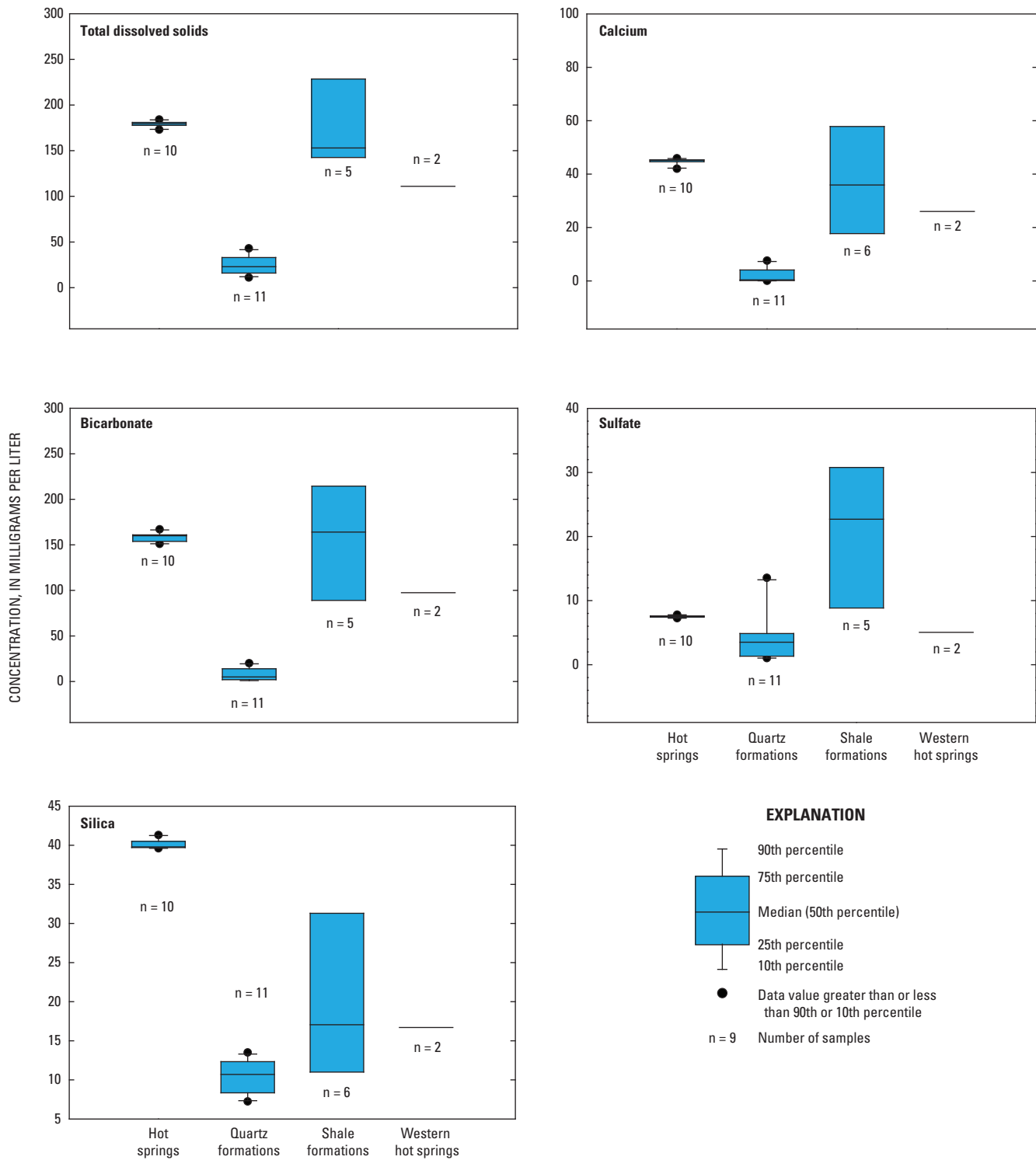


Figure 8. Distribution of concentrations of selected constituents from shallow groundwater and thermal water samples.

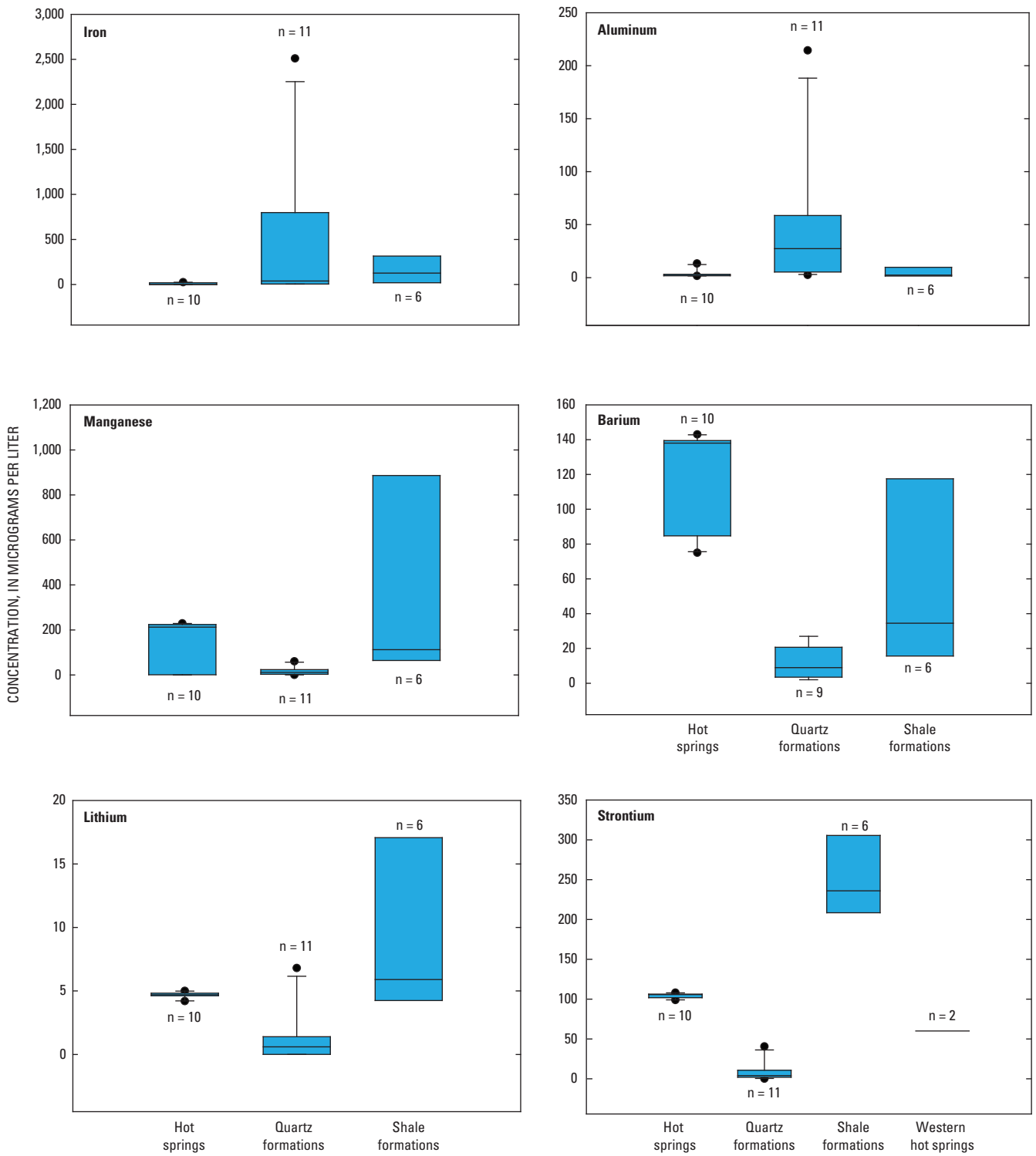
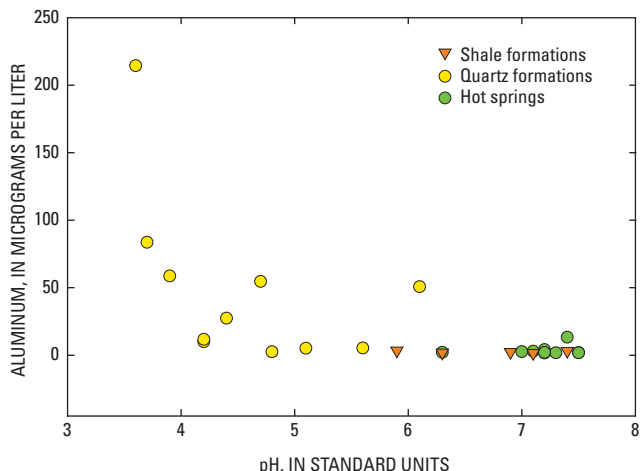


Figure 8. Distribution of concentrations of selected constituents from shallow groundwater and thermal water samples.—Continued



**Figure 9.** pH and aluminum concentrations for groundwater samples from study area.

in the quartz formations at the time of sampling was 4.4, and 6 of the 11 samples had pH values of 4.4 or less. A detailed discussion of additional trace metal concentrations related to the major site types is presented in the next section.

## Trace Metals

Concentrations for various trace metals were compared to those documented in previous studies, to ascertain potential mineral sources, and to provide additional information on the chemistry of the shallow groundwater system as related to that of the hot springs in HSNP. Trace metals provide useful adventitious tracers for understanding groundwater flow paths. Important potential sources for trace metals are organic-rich black shales and igneous rocks and fluids. Both of these sources are present in the Ouachita Mountains. The presence of economically viable ore emplacements, and the great historical interest in and development of economic metal ore deposits in the Ouachita Mountains, highlights the abundant presence of metals and the importance of the role of hydrology and geologic framework in metals movement and distribution at local to regional scales.

Early prospect mining for valuable minerals occurred throughout the Ouachita Mountains, including some unsuccessful gold prospects, from the mid 1800s to 1980. Prospects were worked on veins of pyrite and marcasite in 1830, 1915, and 1916. Traces of lead, zinc, and silver were associated with quartz veins and manganese deposits, and one quartz vein in the Arkansas Novaculite and lower Stanley Shale, with associated minerals of galena, sphalerite, chalcopyrite, pyrite and other minerals, was discovered in the 1890s and worked for several years (Stone and Bush, 1984). Native copper is found in veins in the Arkansas Novaculite. The various iron, manganese, and other ores in the Ouachita Mountains are potential

sources for, or are likely genetically related to, trace metal occurrence in groundwater throughout the region.

Wagner and Steele (1985) reported on metal concentrations in groundwater of the Ouachita Mountains as related to mineral deposits based on 91 samples, predominantly from springs in the area, and their analyses including the following elements: lithium (Li), barium (Ba), strontium (Sr), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), cobalt (Co), nickel (Ni), lead (Pb), mercury (Hg), and antimony (Sb). Primary mineralization near the study area included Mn deposits (found dominantly in the Arkansas Novaculite), containing up to 1 percent by weight of each of the base metals Co, Ni, Cu, and Zn. Four barite (barium sulfate) mining districts were present near the study area in the lower Stanley Shale (Wagner and Steele, 1985). Analyses from Wagner and Steele (1985), for samples from shallow groundwater in an area, which encompassed the study area for this report, are shown in table 3 and compared to metal concentrations analyzed from samples of shallow groundwater in the study area.

Most metal concentrations measured in samples in the shallow groundwater in the study area of this report were within the ranges of metal concentrations from Wagner and Steele (1985) (table 3). Median concentrations for most trace metals from Wagner and Steele (1985) were between the median concentrations listed for the quartz and shale formations; except for median Co, Ni, and Pb concentrations, which were higher in the analyses from Wagner and Steele (1985) than those from the study area shale and quartz formations. However, because the median concentrations for the shale and quartz formations are lower than the laboratory reporting level for Pb (10 µg/L) from Wagner and Steele (1985) (table 3), the higher median concentration for the data from Wagner and Steele (1985) may simply be a laboratory reporting level artifact. In general, because Wagner and Steele (1985) did not differentiate formation type in their data, it is reasonable that median concentrations for most metals would be between those differentiated by formation type.

Median and maximum concentrations for Mn, Ba, Li, and Sr were greater in groundwater from the shale formations than in groundwater from the quartz formations in the study area (fig. 8, table 3). Barite deposits occur most frequently in the Stanley Shale and likely account for the higher Ba concentrations in samples from shale formations. Higher Mn median concentrations were noted in the shale formations as compared to the quartz formations, and demonstrate that Mn mineralization may be more prevalent in the shale formations in the study area. Lithium is associated with Mn ore deposits, and the greater Li concentrations coincide with the greater Mn concentrations in the shale formations. Strontium is the most commonly substituted element for Ba in the barite structure (Crecelius and others, 2007) and also is commonly substituted for calcium in carbonate minerals. Strontium ores are associated with the Stanley Shale in Howard County (Stroud and others, 1969; Wagner and Steele, 1985) and possibly account for the greater Sr concentrations in samples from the shale formations compared to those from quartz formations.

**Table 3.** Comparison of trace metal concentrations from Wagner and Steele (1985) to concentrations from samples collected from shallow groundwater in the study area.

[µg/L, micrograms per liter; <, less than; --, not measured]

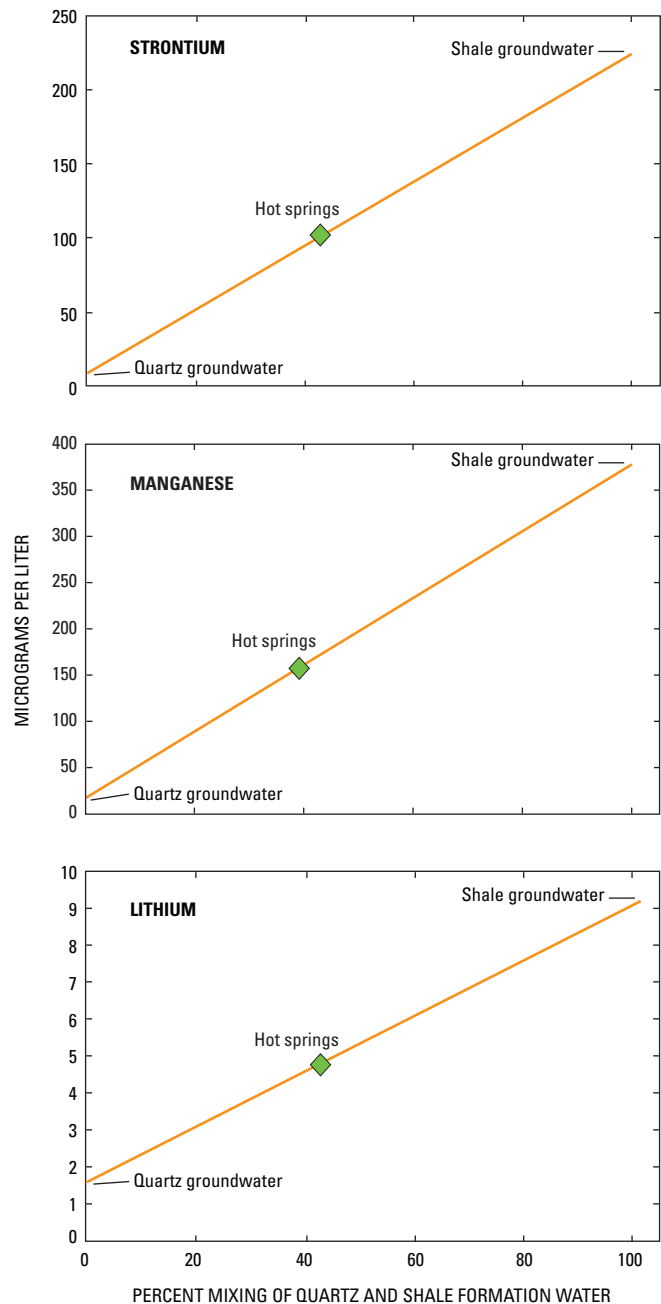
	Iron (µg/L)	Manganese (µg/L)	Zinc (µg/L)	Copper (µg/L)	Cobalt (µg/L)	Nickel (µg/L)	Mercury (µg/L)	Lead (µg/L)	Lithium (µg/L)	Barium (µg/L)	Strontium (µg/L)
median	56	21	18	3.2	5	9	<0.1	10	2.3	11.5	44
range	2-5,220	1-1,220	2-144	1-85	<2-31	2-39	<0.1-2.1	<10-37	<1-70	<1-70	1-2,200
Wagner and Steele (1985)											
median	38	12	32	3.4	0.8	2.1	--	0.67	0.6	9	4.0
range	4-2,510	<0.2-60	0.5-198	<0.4-446	<0.04-3.9	0.05-14	--	<0.12-50	<0.6-6.8	2-27	<0.4-41
Quartz formations											
median	127	113	10	1.2	1.1	2.5	--	0.14	5.9	35	222
range	12-611	42-1,115	<0.3-114	<0.4-20	0.08-2.5	0.46-7.8	--	<0.12-1.7	2.9-18.3	13-146	91-324
Shale formations											

Although median Fe concentrations were greater for samples from the shale formations compared to those from the quartz formations, maximum concentrations (in addition to three of the greatest concentrations) were noted in samples from the quartz formations. The range and median concentrations for Cu were greater in the quartz formations than in the shale formations. Copper primarily is associated with Mn ores found in the Arkansas Novaculite (Stone and Bush, 1984; Wagner and Steele, 1985), and the greatest concentration of Cu (446  $\mu\text{g/L}$ ) was in a groundwater sample from a well completed in the Arkansas Novaculite.

Comparisons of trace metal concentrations of samples from the hot springs in HSNP with shallow groundwater in the study area are difficult to explain because of the lack of knowledge of mineralization, diagenesis, and other important processes at depth in the deep flow system of the hot springs in HSNP. However, inspection of water geochemistry often can provide important information in regard to possible processes resulting from water/rock interactions. For example, concentrations of Fe were above the laboratory reporting level of 6  $\mu\text{g/L}$  in all shallow groundwater samples in the study area and ranged upward to 2,510  $\mu\text{g/L}$ ; however, Fe concentrations in all of the samples from the hot springs were less than or equal to 25  $\mu\text{g/L}$  and concentrations in 6 of the 10 samples from the hot springs were below a laboratory reporting level of 6  $\mu\text{g/L}$  (table 2). Potentially reducing conditions in the deep flow system may result in precipitation of FeS, which is stable in reducing conditions, and may account for the lower Fe concentrations. Bell and Hays (2007) investigated isotope chemistry of the hot springs in HSNP and indicated potential sulfate ( $\text{SO}_4$ ) reduction based on sulfur isotope analyses, which provides some evidence that both Fe- and  $\text{SO}_4$ -reducing conditions exist within the hot springs flow system.

Reducing conditions at depth additionally may explain elevated Ba concentrations in the hot springs. Barium concentrations were greatest in the hot springs compared to shallow groundwater samples from the quartz and shale formations. Dissolution of barite (and other minerals containing Ba) along a long flow path and transport of dissolved Ba and  $\text{SO}_4$  into Fe- and  $\text{SO}_4$ -reduction zones at depth can result in FeS formation and would tend to differentially remove Fe and  $\text{SO}_4$  with respect to Ba, thus increasing Ba in solution relative to other metals.

A review of general geochemistry (see previous subsection) indicated that the chemistry of samples from the hot springs in HSNP may represent a mixture of water from the shale and quartz formations. Where metal concentrations were substantially greater in the shale formations as compared to the quartz formations and the hot springs, relations were investigated using mixing curves. Mixing curves were developed for Sr, Mn, and Li concentrations, which were greatest in the shale formations (fig. 10). Mean concentrations for each of the major rock types were used to construct the mixing curves. For each of these metals, the hot springs represent an approximate 40-percent contribution of water from the shale formations and a 60-percent contribution of water from the quartz formations.



**Figure 10.** Mixing curves for strontium, manganese, and lithium for groundwater from the shallow aquifer in the study area and the hot springs of Hot Springs National Park.

As such, the mixing curves provides a method for describing and quantifying the mixture of water from the quartz and shale formations that is required to produce the chemistry of water in the hot springs in HSNP. Various processes, however, including evidence for both Fe- and  $\text{SO}_4$ -reducing conditions at depth, occur along the flow path and can affect the chemical fingerprint with respect to some of the chemical constituents.

## Isotope Geochemistry

Isotopic data enabled further comparison of groundwater in the study area with that of the HSNP system.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  provide evidence of the distinctive nature of the quartz and shale formation groundwaters and information on sources and recharge characteristics for quartz and shale groundwaters and for the hot springs in HSNP. Quartz formation groundwater isotope data define a strong and distinct trend (fig. 11) with linear regression describing a relation for these data of:

$$\delta^2 H_{CQ} = 6.96 \delta^{18} O_{CQ} + 8.25, \quad r^2 = 0.88 \quad (2)$$

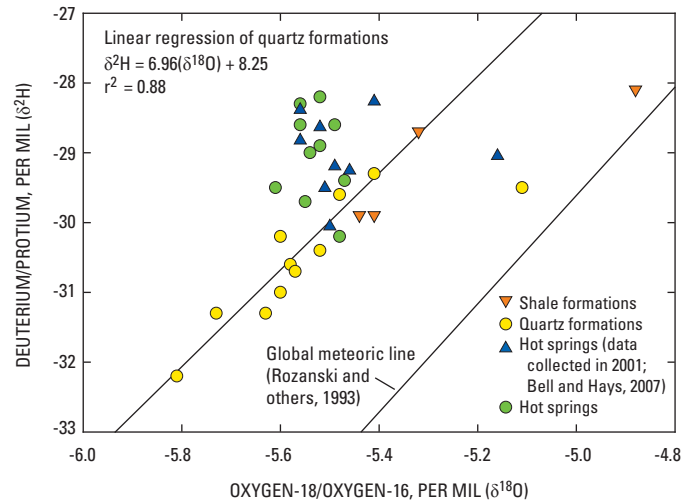
where

$\delta^2 H_{CQ}$  is the  $\delta^2 H$  of the quartz formation groundwater,  
 $\delta^{18} O_{CQ}$  is the  $\delta^{18} O$  of the quartz formation groundwater,  
 and  
 $r^2$  is the regression coefficient.

Comparison criteria for analysis of meteoric water lines include slope—which provides information on humidity and effects of evaporation in the area where precipitation is occurring—and deuterium excess, defined as  $d = \delta^2 H - 8 \delta^{18} O$ , where  $d$  is the deuterium excess. Deuterium excess provides information on humidity at the site of original vapor formation; the global meteoric water deuterium excess is about 10.8‰ (Clark and Fritz, 1997; Rozanski and others, 1993). Groundwater data collected for this study yield a trend that plots with a deuterium excess of 14.1‰, a value slightly more than 3‰ greater than the global meteoric water line deuterium excess of 10.8‰ (fig. 11), likely indicating that the marine vapor source for area recharge has a lower humidity than the global average of 85 percent (Clark and Fritz, 1997). The quartz formation groundwater trend exhibits a slope of 6.96, slightly less than the global average of 8.1 and essentially identical to the nearest available local meteoric water line (for the Fayetteville area— $\delta^2 H = 6.95 \delta^{18} O + 10$ ; (E. Pollock, University of Arkansas Stable Isotope Laboratory, written commun., 2009), and indicates lower humidity during precipitation as compared to the global average. One quartz formation sample is strongly displaced to the right of the quartz formation groundwater trend, indicating strong evaporation.

Shale groundwater  $\delta^2 H$  and  $\delta^{18} O$  values exhibit no notable correlation. Shale groundwater isotope data all plot in the isotopically heavier end of quartz formation groundwater trend, and most shale data plot to the right side of the trend; as such, oxygen isotopic compositions are heavy relative to hydrogen isotopic compositions for the samples. These observations indicate that shale formations received recharge during a relatively warmer time of year and were subject to greater evaporation than were the quartz formation groundwaters.

Hot springs isotopic compositions range from  $\delta^{18} O$  of -5.61 to -5.16‰ and  $\delta^2 H$  of -30.2 to -28.2‰, showing no discernable trend. Most of the hot springs data plot near or above the quartz formation groundwater-regression line at the isotopically heavy end. This position makes any attempt at relating



**Figure 11.** Hydrogen and oxygen isotopic compositions for groundwater samples from the study area.

hot spring water isotopic composition to current groundwater recharge isotopic compositions difficult. Hot springs isotopic compositions are not explained by high-temperature rock-water interaction, evaporation (each of which would cause isotopic compositions to be displaced to heavier oxygen isotopic compositions to the right of the plot), or mixing of quartz formation or shale groundwater (giving an intermediate value). These data indicate that the more ancient component of water discharging from the hot springs is meteoric water, but meteoric water that fell to earth under slightly different climatic conditions prevalent more than 4,000 years ago (Bedinger and others, 1979); distribution of the data potentially indicates that precipitation occurred under higher humidity conditions (giving a higher local meteoric water line slope) or that marine source vapors were generated under conditions of lower humidity (higher deuterium excess). Most (five of six) of the hot springs that plot near the quartz formation groundwater trendline were noted by Bell and Hays (2007) to exhibit relatively large components of locally derived, short flow-path cold-water recharge—further highlighting the distinctive character of the ancient, thermal component of the hot springs.

Characterization of Sr geochemistry and analysis of Sr isotopic signatures were conducted, comparing groundwater samples from the hot springs in HSNP, shallow groundwater samples in the study area from the quartz and shale formations, and samples from the western hot springs. Strontium isotopic data were used in concert with other geochemical data to discern geochemical signatures that can provide information on recharge origin of the two geothermal waters (western hot springs and the hot springs in HSNP) and whether these groundwater systems share any physical hydraulic connection.

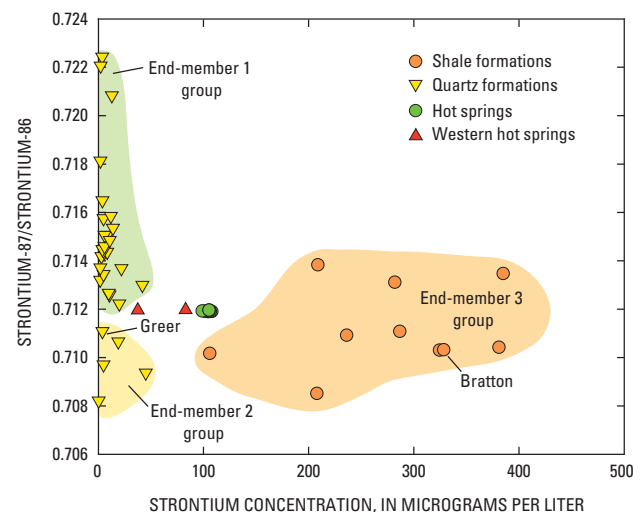
Strontium ( $\text{Sr}^{2+}$  in ionic form) is a divalent, reactive, and soluble metal that behaves similarly to calcium in chemical interactions and substitutes for calcium in many minerals; of particular importance for the HSNP region of the Ouachita Mountains is the substitution and occurrence of Sr in carbonates and sulfates (such as barite). Like  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  is soluble

and reactive and participates in water-rock reactions; Sr<sup>2+</sup> is a trace component of most rocks and most groundwater. Strontium ores have been described and mined in the Ouachita Mountains (Wagner and Steele, 1985). Strontium has four naturally occurring isotopes: <sup>84</sup>Sr, <sup>86</sup>Sr, <sup>87</sup>Sr and <sup>88</sup>Sr. Strontium isotopic compositions are reported as <sup>87</sup>Sr/<sup>86</sup>Sr ratios. Strontium isotopic ratios (<sup>87</sup>Sr/<sup>86</sup>Sr) are a useful indicator of water-rock interaction, and a valuable tracer for groundwater source and movement. As groundwater interacts with rock matrix, the water brings Sr into solution and adopts the rock Sr isotope signature. Aquifer-framework minerals often have distinctive Sr content and specific Sr isotopic signatures that can be picked up by water, enabling identification of recharge sources, transport pathways, and mixing. Unlike oxygen isotopes and other light stable isotopes, Sr isotopes are not subject to fractionation, and Sr isotopic signatures are determined only by Sr input (Clark and Fritz, 1997). Sr geochemical analysis of Hot Springs recharge area rocks provided very specific information on thermal water sources, pathways, and relations. Fifty-two groundwater samples were characterized for Sr geochemistry, including 10 samples from hot springs in HSNP, 16 Bigfork Chert, 10 Arkansas Novaculite, 4 Hot Springs Sandstone, 9 Stanley Shale, 2 Silurian/Ordovician undifferentiated shales, and 1 Womble Shale sample.

Groundwater Sr concentration and isotopic data from the hot springs in HSNP, quartz formations, and shale formations indicate three end-member data groupings (fig. 12): (1) high isotopic ratio (ranging from about 0.712 to 0.723), low Sr concentration quartz rocks; (2) low isotopic ratio (ranging from about 0.708 to 0.712), low Sr concentration quartz rocks, and (3) mid-range isotopic ratio, high-concentration shales; and one intermediate grouping—the hot springs in HSNP. The quartz formations of end-member groupings 1 and 2 exhibit a narrow range of concentration, 0.4 to 42 µg/L, and a very broad range of isotopic compositions—defining the isotopic composition end members for the quartz formations from a maximum of 0.7224 to the minimum of 0.7082. The shale grouping, group 3, exhibits a relatively broad range of concentrations (106 to 385 µg/L), and a narrow range of isotopic compositions from 0.7085 to 0.7138. Samples from the hot springs exhibit very tight ranges for concentration and isotopic composition (96 to 108 µg/L, and 0.712, respectively). The hot springs samples are generally intermediate to the end member 1 and end member 2 groups in isotopic composition but have considerably greater concentrations (fig. 12 and fig. 8); hot springs samples are intermediate to group 1 end member and group 3 end member for isotopic composition and Sr concentration. Isotopic composition-concentration relations indicate that the geochemistry of hot springs in HSNP is controlled predominantly by contribution from rock-water interaction with group 1 quartz formations and group 3 shale formations. Sr chemistry and isotopic composition corroborate general geochemistry and trace metals results.

The quartz mineralogy predominated rocks constitute one of the most remarkable groundwaters in the region by exhibiting some of the lowest TDS and most minimally buffered pH values to be found in natural, uncontaminated groundwater (Hem, 1989). The shale formations exhibit a geochemistry typical of regional shale groundwater—high TDS concentrations provided by the soluble and reactive mineral matrix of the rock and well buffered pH values. The hot springs in HSNP gain their distinctive chemical signature along a complex flow path through varying formation types. Low ionic strength rainwater recharges through the minimally soluble and reactive Bigfork Chert and Arkansas Novaculite, garnering an initial, baseline Sr chemical and isotopic signature (as well as a general geochemical and trace metal signature). This recharging water reacts with more soluble shales further along the flow path, altering the signature. This process is not purely a mixing process but a dissolution/reaction-based geochemical evolution, and a degree of understanding of the relative contributions along the two distinctive flow path segments can be derived from an assessment using simple, hyperbolic mixing analyses. For isotopes, mixing of two end members does not result in a number of mixtures that fall on a straight line in concentration-isotopic ratio space. Instead, the isotope ratio of the mixture is weighted by the concentration of Sr in each end member. More generally, the weighting of ratios in the mixture is controlled by the denominator of the ratio, in this case <sup>86</sup>Sr, causing mixtures to plot on a hyperbola whose curvature is dependent upon the difference in concentration of the two end members.

To explore the respective contributions of the quartz and shale formations and whether more complex controls are important in setting hot springs geochemistry, a simple hyperbolic mixing equation (Faure, 1986) was used to model hot springs Sr geochemistry. Sr concentration and isotopic



**Figure 12.** Strontium concentration and strontium isotope values for groundwater samples from the study area.

composition end-member values of 20  $\mu\text{g/L}$  and 0.7185 (quartz formation end member 1) and 265  $\mu\text{g/L}$  and 0.71083 (shale formation end member) were input. The hot springs plot on the hyperbolic mixing line derived from these quartz and shale formation end member Sr values—probably indicating that simple dissolution processes predominate over more complex geochemical reactions, which would result in displacement of the hot springs from the mixing line. The mixing model analysis indicated that the Sr geochemistry of the hot springs results from an approximately 35-percent contribution from the shales and a 65-percent contribution from the quartz formations. Thus, as the recharge waters move out of the quartz formations and into shales along the thermal flow path, the original quartz formation geochemical signature is overprinted to a considerable degree by the shales, resulting in a mixed signal. Evidence of this shale geochemical influence also is seen in major ion and trace metal chemistry as discussed earlier, and similar mixing percentages to that calculated for strontium isotopic data were shown on mixing curves for the trace metals Sr, Mn, and Li (fig. 10).

The highly fractured nature of all formations exposed at the surface of the study area and the Ouachita Mountains in general, creates a hydrologic environment favoring a high degree of mixing and integration of different flow lines. Additionally, these fractured strata present an extremely challenging environment for drilling and, ultimately, sampling of isolated zones. This combination of effects results in great difficulty in acquiring samples from discrete zones, such as is desired from the newly discovered thermal zones at the Bratton and Greer sites. It should be noted that optimally, isolated samples of the thermal waters at the Bratton and Greer sites would be the most desirable and most definitive for geochemical signature interpretation; however, isolated thermal water samples proved impossible to collect within constraints of the project. Thus, all of the samples available for interpretation were mixed samples. Interpretations using mixed samples are informative and useful and are in fact a common part of chemical hydrologic study, and, as such, interpretations presented here are useful and sufficient to addressing the questions posed, although initial objectives were to acquire discrete-zone samples.

The newly discovered thermal water sites, Bratton and Greer, did not exhibit notable similarity with the hot springs in HSNP with respect to Sr chemistry, but look geochemically like the groundwater of the local outcropping formations: the Stanley Shale in the case of Bratton and the Bigfork Chert for Greer. Median Sr concentration and isotopic composition for the two wells at the Bratton site is 327  $\mu\text{g/L}$  and 0.7103, respectively. Median Sr concentration and isotopic composition for the three wells at the Greer site are 4  $\mu\text{g/L}$  and 0.7106, respectively (fig. 12); these waters differ markedly from the hot springs in HSNP. The two very different Sr isotopic and geochemical signatures observed for the new thermal water sites do not provide evidence of any direct hydraulic connection with the springs in HSNP.

## Physical and Chemical Characteristics of Thermal Waters in the Ouachita Mountains

This section describes the physical and chemical characteristics of the various sources of thermal water outside of the HSNP boundaries and provides a conceptual model for the generation of thermal water at these various sites. In examining the characteristics of thermal waters in the Ouachita Mountains, it is useful to review the key components of the most widely accepted model accounting for the source, flow history, and hydrogeologic framework for the hot springs in HSNP. The combined thickness of the formations in the study area ranging from the Bigfork Chert, which has been identified as the predominant formation recharging the hot springs flow system, upward to and including the youngest exposed formation in the study area, the Stanley Shale, is greater than 10,000 ft, not including the 1,500-ft Womble Shale. The folding and extreme dips of the formations in the study area additionally plunge these formations to great depths. Bedinger and others (1979) presented a model that showed a required depth of 4,500 ft to 7,500 ft at geothermal gradients of 0.6°C to 1.0°C per 100 ft, respectively, to attain maximum projected source temperatures of 63°C to 68°C at depth as calculated from silica concentrations in the hot springs. These depths are easily achieved in view of the formation thicknesses and regional dips of 40 degrees and greater. With mean temperatures of approximately 62°C for the hot springs (Bedinger and others, 1979), the water must rise fairly rapidly along faults to prevent excessive cooling on the waters path to the surface. The hot springs emerge at the nose of a southwest plunging anticline along a major mapped thrust fault (fig. 2). A review of the geology outside the area of the hot springs revealed that similar geological conditions are replicated throughout the Ouachita Mountains. Similar to the hot springs, the Bratton and Greer well sites are on or near the nose of a southwest plunging anticline, and faulting is near to or directly bisecting the locations of the well sites (fig. 2). Hence, the model for development of the hot springs in HSNP serves as an analog for explaining the occurrence of thermal water at these locations.

### Bratton Site Characterization

Several exercises were conducted to investigate the nature of the thermal component of water at the Bratton site, including pumping events and geophysical logging for the Bratton domestic well and a monitoring well installed near the domestic well. On March 13, 2006, following the initial report of the discovery of thermal water in the domestic well, USGS personnel recorded well-water temperatures during a 2-hour pumping event. A maximum of 31°C was measured initially, followed by a steady decrease in temperature with the



temperature never dropping below 21.7°C during the pumping period. Mean temperature for shallow groundwater in the area is approximately 17°C. This simple exercise provided evidence of a weak, low-yield component of thermal water flow for which the thermal signature was dampened by a greater cold-water contribution during pumping. The thermal water likely moved through a discrete fracture set in communication with a deep flow path, while the cold-water component was likely supplied by fracture sets representing short flow paths in direct communication with the surface.

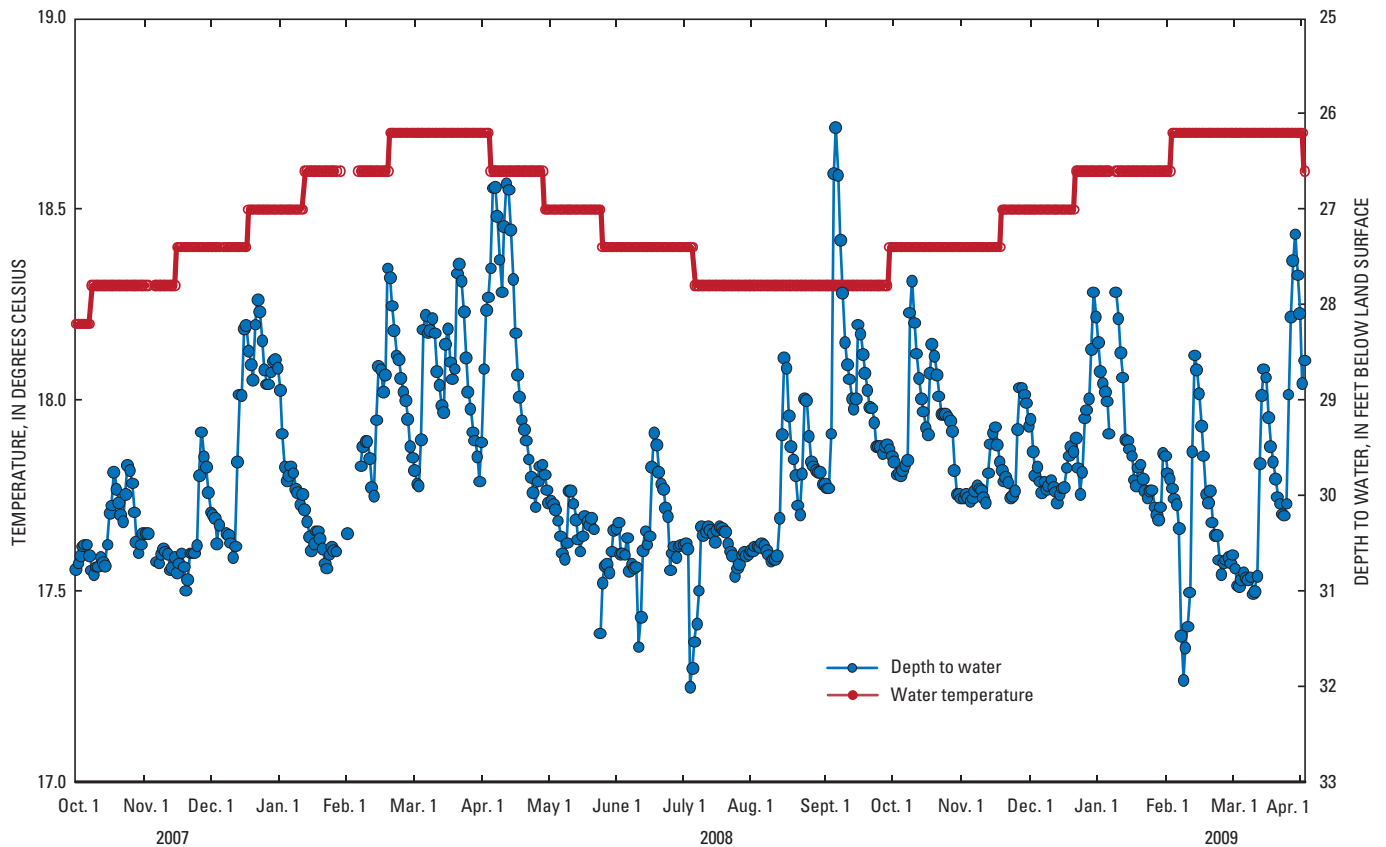
Geophysical borehole logging was conducted on January 29, 2007, which included a temperature and flow profile obtained using an electromagnetic (EM) flowmeter. The temperature profile indicated a uniform temperature of approximately 17.8°C (64°F) to approximately 100 ft, at which point temperatures began to increase to a maximum temperature of 21.1°C (70°F) at a depth of approximately 130 ft (fig. 13a). Temperature rapidly decreased to 18.3°C (65°F) at a depth of approximately 150 ft, where it remained relatively constant to the completion depth of 205 ft. Numerous fracture sets were noted from review of the acoustic televiewer log (dark sinusoids on fig. 13a) to depths of approximately 160 ft, at which point a lack of apparent fractures was noted to the completion depth of 205 ft. The fact that the temperature drops during pumping of the well suggests that the dominant component of flow is a cold-water contribution, and that the warm-water component is a weaker flow zone. A flow profile was generated using an EM flowmeter under ambient and pumping conditions in the well. The EM flowmeter profile showed the greatest flow entering the well between 90 to 120 ft and a negative component of flow from 130 to 140 ft. As such, individual flow components upward to 0.3 gal/min were moving into the well bore from 90 to 120 ft; whereas below this point, flow was moving out into the formation. A profile also was generated for specific conductance, which showed an increase in specific conductance within the same zone as the temperature increase. The increase in specific conductance indicates that the thermal component of flow is enriched in dissolved solids relative to other flow zones in the well and provides evidence that this component of flow comes from a longer flow path.

A monitoring well was drilled on June 27-28, 2007, approximately 20 ft from the original Bratton domestic well. The intention of drilling the monitoring well was to isolate the zone of thermal water contribution for estimating flow and for sampling and analyzing water quality. The well was drilled to a depth of 165 ft. Driller-estimated flows of 90 gal/min occurred at approximately 80 ft with no appreciable gain in flow below that depth. On June 28, 2007, geophysical logging was performed on the monitoring well, which was an open-hole completion at the time of logging (fig. 13b). A high temperature of 21.1°C (70°F) near the surface was the result of radiant warming with the high summer temperatures. Temperature dropped steadily to approximately 15.0°C (59°F) at a depth of approximately 100 ft and remained at this temperature from 100 to 120 ft, at which point temperatures begin to

increase to a temperature of 15.5°C (60°F) near a depth of 140 to 145 ft; this is interpreted to be the zone of thermal water contribution. Temperatures then decreased to a minimum of 15.0°C (59°F) at approximately 155 ft, where it remained to the completion depth of 165 ft. The increase in temperature occurred at a similar depth as that recorded in the domestic well, and the monitoring well was screened from 130 to 150 ft in order to isolate the zone of interest.

Several short-term (less than 3 hours) pumping episodes were conducted on the well with approximate yields of 1.5 gal/min; pumping rates greater than 1.5 gal/min were not sustainable. Hydraulic connection between the domestic well and the monitoring well were evident from water-level decreases of greater than 1 ft observed in the monitoring well when the domestic well was being pumped. Although the domestic well was not used as a continuous domestic supply, the owner did intermittently use the well, resulting in sudden drops in water levels observed in the real-time data for the monitoring well. Although the monitoring well was screened over the interval (130–150 ft) demonstrating a slight increase in temperature, which correlated to a similar depth for the temperature increase in the domestic well, the real-time temperature measurements of water in the monitoring well never rose above 18.7°C for the period of measurement, considerably less than the maximum temperatures observed for the Bratton domestic well. However, these measurements were made approximately 20 ft below the water surface, which was the location of the transducer that records water level.

A 3-hour pumping event was conducted on the monitoring well on May 20, 2008, and revealed only slightly greater temperatures ranging from 19.1°C to 19.6°C. Although these temperatures were slightly higher than the real-time temperatures measured at the transducer approximately 10 ft below the water surface for the period of measurement, the temperatures were far below the temperatures recorded in the domestic well, and indicate a much weaker component of thermal flow to the monitoring well than in the domestic well. Despite the proximity of the monitoring well to the domestic well (20 ft) and careful, deliberate drilling and completion, the monitoring well was not as effectively connected to the thermal-water fracture sets providing thermal flow. Temperature of water in the monitoring well was noted to increase from November 2007 through March 2008, contrary to the response of other shallow wells in the area, which exhibit a decrease in water temperature during the cold season from November through March (fig. 14). Because water levels are higher during the fall and winter months, which coincides with the period of higher water temperature, these data are interpreted to indicate that higher heads in the recharge area for the deep flow system providing the thermal water moves a larger component of thermal water through the shallow aquifer system during the wet season. Temperatures began to drop in the observation well after March 2008 during the spring and summer months, only to begin to increase once again in November 2008. These data indicate that during the wet season, water-level increases and the greater pressure heads in the higher elevation



**Figure 14.** Hydrograph of temperature and water level in the monitoring well at the Bratton site.

thermal-water recharge areas on exposures of the Bigfork Chert and Arkansas Novaculite result in a rapid pressure response through the system and increased flows in the down-gradient end of the flow path. The observations from study of the Bratton site lead to an understanding that has broader application and implications across the Ouachita Mountains for the occurrence of thermal flow systems.

Temperature was monitored in the Bratton domestic well at the Bratton site during a 3-hour and 20-minute pumping event on May 20, 2008. Continuous temperature monitoring yielded valuable information regarding the zone of thermal contribution in the domestic well. Water temperatures peaked at a value of 36.4°C, 4 minutes into the purging event, and began dropping thereafter to a low of 18.8°C after 1 hour and 15 minutes of purging at 2 to 3 gal/min. This latter result was in contrast with the earlier tests on March 13, 2006, when temperature never dropped below 21.7°C. Interestingly, during the May 20, 2008 test, after water temperature dropped to the minimum of 18.8°C, a slug of red, Fe-precipitate rich, turbid water appeared in the collection bucket over a period of a couple of minutes, after which the water returned to a clear condition. Following the breakthrough of the turbid water, water temperatures began to rise to a maximum of 23.8°C and remained above 22°C for the remainder of the purging event. A red, Fe-oxyhydroxide precipitate was noted to have settled at the bottom of the discharge monitoring bucket.

In groundwater systems, Fe occurs in one of two oxidation states: reduced, very soluble divalent ferrous Fe ( $\text{Fe}^{+2}$ ) or oxidized insoluble trivalent ferric Fe ( $\text{Fe}^{+3}$ ) (Appelo and Postma, 1999). Under reducing conditions typical of deep flow-path waters,  $\text{Fe}^{+2}$  predominates, is very mobile, and is carried with migrating groundwater. Under shallow groundwater conditions where free oxygen is available, Fe is oxidized to the insoluble  $\text{Fe}^{+3}$  form, creating Fe oxyhydroxide precipitates (such as hematite and goethite). Precipitation of Fe oxides and other minerals, including carbonate and silica minerals, at these deep flow path/shallow flow path redox interfaces is common for hot springs, and these precipitates often are observed to restrict flow, sometimes temporarily—ending when plugs are pushed out by changes in head or other agitation and sometimes permanently—resulting in repositioning of spring emergence points, such as is common in HSNP and other thermal springs (Bryan, 1922; Yeatts, 2006). The slug of Fe-precipitate laden water may have originated as a fracture-plugging Fe oxyhydroxide precipitate at the redox interface of the shallow subsurface of the well, temporarily sealing fractures conveying thermal water and reducing thermal-water flow and temperature of water in the well. The lowering of the water table and surging and concomitant turbulence in the well during pumping are thought to have unseated the weakly bound Fe-precipitate plug, resulting in an increase in the thermal flow component and increased temperatures.

## Greer Site Characterization

The appearance of thermal water at the Greer site was discovered on June 6, 2007, during a well reconnaissance in the early phase of the study. The site is approximately 3 miles from the hot springs in HSNP. Water periodically is pumped from the 185-ft well into a large holding tank for domestic use. However, a spigot available at the well head is used for watering vegetation at the home during the spring and summer months, and water is delivered directly from the pump into the spigot and hose. The owner reported that during the first use of the water from the spigot in May 2007 the water felt warm to the touch and remained warm during a long watering episode, though this phenomena had not been observed in the previous 5 years use of the well.

During this initial visit, USGS personnel pumped water from the spigot directly into a bucket and measured temperature over a 30-minute period. A maximum temperature of 26.6°C was attained during the early stage of pumping, followed by a steady decline to 22.4°C after 5 minutes of pumping, with temperature fluctuating between 24°C and 25°C throughout the remainder of the purging period. Variable temperatures during the purging event indicated mixing of both cold water and thermal water contributions to the well bore, similar to that at the Bratton site. The Greer site presented numerous difficulties in determining the zone of contribution for the thermal component of water and the temporal and variable nature of fluctuating temperature signatures in the well. Geophysical logs showed the well to be cased to the completion depth of 185 ft—through the likely zones of interest. As such, no information could be obtained from the geophysical logging to determine zones of flow, temperature profiles, stratigraphic and geologic data, and other data that might elucidate the thermal component of flow to the well.

Installation of a new, open-borehole monitoring well next to the Greer domestic well was attempted for the purpose of providing access to the subsurface for borehole geophysical logging, determining the zone of thermal water contribution, and providing for discrete zone sampling. Two well-installation attempts proved problematic as a result of continual caving and collapse in the highly fractured Bigfork Chert. The borehole was advanced to a depth of 120 ft, whereupon a constant infilling of rock material prevented further penetration, even after numerous attempts to clean the borehole and continue drilling. Decisions were made to complete the well at a depth of 120 ft, and begin a new hole. A second borehole, nearer to the domestic well, was advanced to a depth of 155 ft before continual collapse of rock material forced drilling termination and completion at this depth. No attempt was made to log either open hole because of concerns of losing costly logging equipment in the unstable borehole. With completion of the two additional wells, three wells were available for monitoring of temperature and water quality at depths of 120 ft, 155 ft, and 185 ft. Similar water levels in all three wells demonstrated the hydraulic connection between the various

depths with no apparent confinement or isolation between the water-producing zones.

Continuous monitoring of water level and temperature in the 155-ft well from October 2007 and March 2009 showed only a slight increase in water temperature from 16.6°C to 16.8°C. Continuous monitoring of the 185-ft domestic well from June 2008 to March 2009 also showed little variation in temperature with only a slight increase from 15.8°C to 16.0°C. Purging of all three wells during a water-quality sampling event on September 5-7, 2007, resulted in final purged-water temperatures that ranged from approximately 18.0°C to 19.0°C for all three wells. Elevated temperatures have not been reported by the well owner since the original measurements in June 2007, and continuous and periodic measurements have not revealed elevated temperatures in any of the three wells.

There are several explanations for the appearance and temporal nature of the occurrence of a thermal component of water in the domestic well at the Greer site. An active quarry with associated blasting is approximately 0.75 mile east of the Greer site. Changes in the hydrologic system associated with dewatering and removal of fine-grained material from fractures at the quarry may have altered groundwater flows near the quarry. The generation of fractures greater than a few tens of feet from blasting activities is not anticipated from the literature review on the effects of blasting, and minor changes in flow regimes by dislodging sediment-plugged fractures during blasting may become quickly sealed over time by fine-grained material and chemical precipitates.

Another explanation for the temporal nature of the occurrence of a thermal component of flow in the domestic well at the site may be that a large influx of cold water during high water-level periods associated with shallow recharge may dampen the thermal component of flow. However, water-level increases and decreases over the period of continuous monitoring of two wells at the site did not result in changes in water temperature.

Similar to the discovery of Fe-oxyhydroxide precipitation and apparent sealing of fractures within the thermal zone at the Bratton site, another explanation is that fractures associated with transport of thermal water in the domestic well at the Greer site may have sealed with time. This explanation, however, does not fit with the timing as the thermal-zone fractures would most likely be open when first encountered during the drilling process, with sealing over time resulting from changes in the redox conditions initiated by the presence of the well with the associated surface communication and continual influx of oxygen into the borehole.

The most likely scenario is that the initial discovery of the apparent thermal water component at the Greer site coincided with a 3-year drought, more extreme than any in the past 50 years (which covers the period of the existence of the Greer well) that ended as this study was starting (National Climatic Data Center, 2009). Data from the National Climatic Data Center (NCDC) showed 26 of 36 months in drought status

from the NCDC Palmer Drought Severity Index data with 12 months of moderate to extreme drought. This period of minimal local cold-water system recharge may have enabled a short-lived ability to detect the small thermal-water contribution that was subsequently overridden by increased cold-water recharge as the drought ended.

### Thermal Springs Outside of Study Area

A review of Ouachita Mountains region literature identified four thermal springs outside of the study area, three of which are in Montgomery County and one in Pike County (fig. 15). These springs range from approximately 30 to 50 miles from the hot springs in HSNP. Three of the springs, Caddo Gap, Redland Mountain, and Little Missouri Springs, were listed in Bryan (1922). Temperatures for Caddo Gap and Little Missouri Springs measured in 1915 were 34.5°C and 23.3°C (Bryan, 1922), respectively, and measurements made in June 2008 revealed similar temperatures of 33.8°C and 23.4°C, respectively. For comparison, surface-water temperatures in the Caddo River and the Little Missouri River at the time of sampling were 21.8°C and 19.5°C, respectively. Caddo Gap Spring issues from small fractures in the bedrock directly beneath the surface of the Caddo River. Little Missouri Spring issues as a series of seeps in a sand and cobble bank approximately 5 ft from the Little Missouri River. Similar to measurements made at the hot springs in HSNP from the late 1800s to the present date, which have showed no discernable long-term trend (Bedinger and others, 1979; Bell and Hays, 2007), the measured temperatures at Caddo Gap and Little Missouri Springs have shown relatively stable temperature with time. The lack of temperature variation in the hot springs in HSNP and thermal springs as far as 50 miles from the hot springs indicates that these springs arise from hydrogeologic systems that provide continuous and stable flow of thermal water and also indicates a degree of comparability between the hydrologic systems providing for these disparately located occurrences of thermal water.

A comparison of temperatures was made between the various thermal waters observed in this study, including the hot springs in HSNP, and shallow groundwater in the study area to evaluate the spatial differences in temperature (table 4). Although 30 miles from the hot springs in HSNP, Caddo Gap Spring is the same temperature as the water from the domestic well at the Bratton site, which is only 5 miles from the hot springs in HSNP. Similarly, Little Missouri Spring is 50 miles from the hot springs in HSNP and has a similar temperature to water in the domestic well at the Greer site. The spatial distribution of similar temperatures in similar geologic settings (nose of plunging anticlines; fig. 15) indicates that other thermal waters may exist throughout the Ouachita Mountains within these settings that have yet to be discovered, at or near land surface.

**Table 4.** Comparison of temperatures from thermal water in Ouachita Mountain region to shallow groundwater in study area.

Water source	Approximate temperature (degrees Celsius)
Shallow groundwater	17
Hot springs of Hot Springs National Park	62
Bratton site	34
Greer site	25
Little Missouri Spring	23

## Implications and Conceptual Model for Thermal System Analogs in Ouachita Mountains

At the 1:500,000 scale represented by the Arkansas State geologic map (Haley, 1976), thermal water generally is located in similar geologic settings, although the thermal waters emanate from three different formations: the Stanley Shale (Bratton site) including the Hot Springs Sandstone Member of the Stanley Shale (the hot springs in HSNP), the Bigfork Chert (Greer site), and the Arkansas Novaculite (Caddo Gap, Redland Mountain, Barton, and Little Missouri Springs) (fig. 15). These thermal waters tend to be found along the nose of plunging anticlines and closely align with mapped thrust faults where detailed regional geologic maps were available. Because shallow flow systems have been identified as being restricted to the regional surface watershed boundaries, the deep flow systems for thermal water are likely unique to the local hydrologic and geologic setting and represent an analog to the geologic framework model for propagation of groundwater to the hot springs in HSNP.

Concerns related to pirating of water from the hot springs flow system in HSNP because of blasting near the Bratton and Greer sites were not supported by the data gathered for this study. No physical hydraulic connection was found between these thermal sites and the hot springs at HSNP, and the waters exhibited different geochemical composition and different isotopic and trace metal signatures. The newly discovered thermal sites (Bratton and Greer sites) appear to be low-volume systems in comparison with the springs in HSNP, and the sites are separated by distance and geological and hydrological boundaries. Thermal-water sites across the Ouachita Mountains appear to represent discrete systems that are associated with a specific set of hydrologic and geologic conditions, which occur at numerous locations across the region and are viewed as analogs to the hot spring flow system in HSNP rather than connected components of the same hydraulic system. Several variables, including permeability

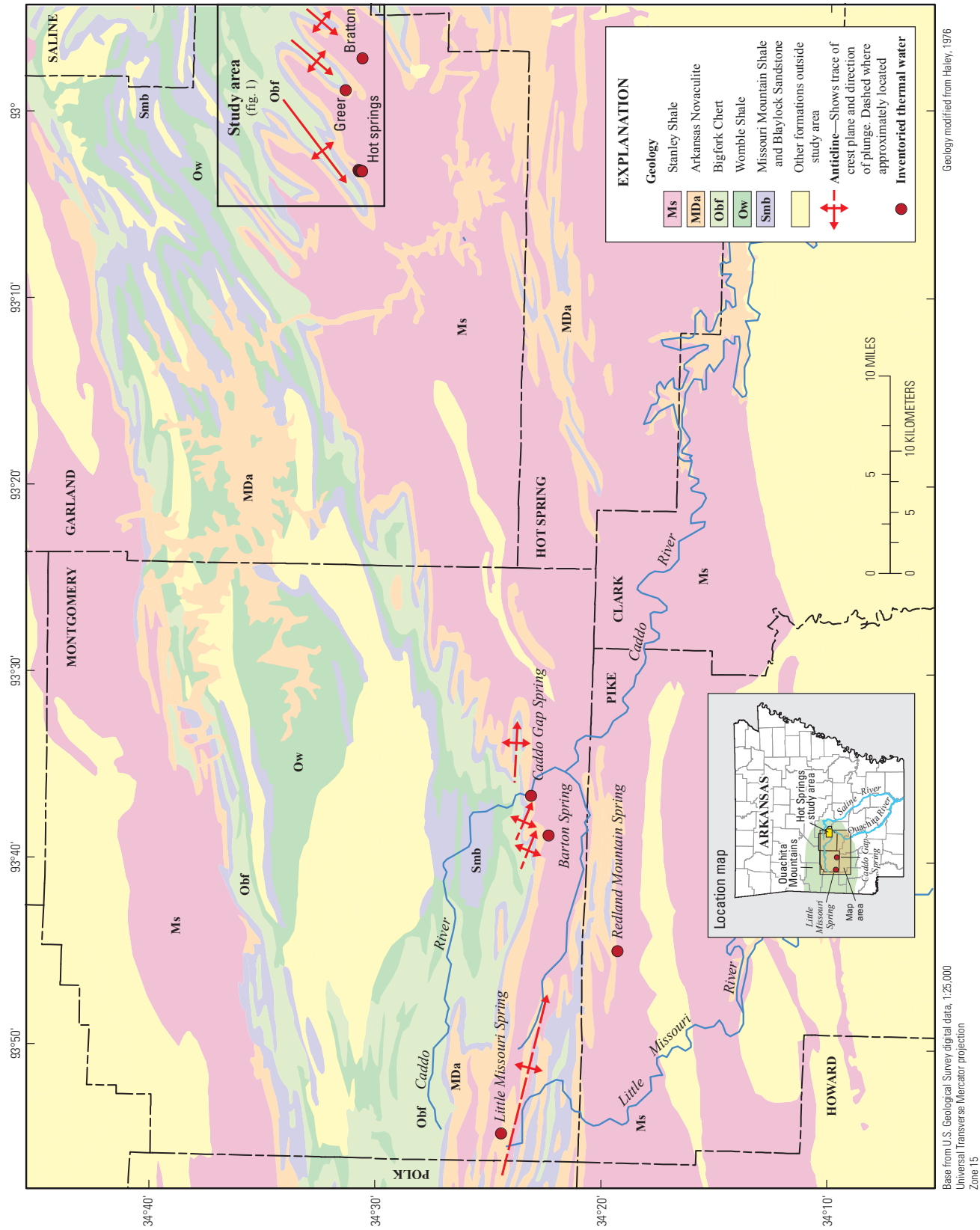


Figure 15. Geology associated with thermal sites in Ouachita Mountains region of western Arkansas.

along faults, downward and upward flow rates, pressure head at the recharge areas, plunging depth of the combined formations, and various other geologic and hydraulic factors affect the amount and associated temperatures of thermal waters emerging at the surface in the various thermal system locations. Although the mechanism for generation of thermal water appears to be very similar for the described thermal water occurrences throughout the Ouachita Mountains, the temperature of these waters will vary at the land surface where they issue as springs or along subsurface fractures intersected by shallow wells.

This conceptual model of the occurrence of thermal waters outside of HSNP is consistent with the observations and information gathered from data collected at the Bratton site. Although temperatures were lower in the monitoring well than in the domestic well at the Bratton site, isolation of the fracture zones contributing the thermal component of flow to the monitoring well provided important data leading to implications regarding recharge in the deep flow system. During the wet season, water-level increases and the greater pressure heads in the higher elevation thermal-water recharge areas on exposures of the Bigfork Chert and Arkansas Novaculite result in a rapid pressure response through the system and increased flows in the downgradient end of the flow path. This increased contribution of hot water resulted in the increased water temperature in the well. In exhibiting this type of response, the Bratton site thermal flow system manifests as an important analog for the hot springs in HSNP, and observations and conclusions for the Bratton system provide important input for understanding and ultimately protecting and managing the HSNP hot springs system. An important and useful difference is that the Bratton system represents a smaller system with more limited recharge and less integration and averaging of flow input. Because of this, the system is more easily perturbed and smaller or shorter-term effects on the system can be more easily and quickly discerned than for the much larger HSNP system. Thus, seasonal influence of recharge-area head changes were observed in the Bratton system. It should be noted that discharge and temperature of individual springs in HSNP have never been monitored in tandem on a long-term basis, making recognition of seasonal and other influences on the HSNP hot springs flow system very difficult.

Similar to the Bratton system, the hot springs in HSNP are recharged by infiltrating rainwater through higher elevation exposures of Bigfork Chert and Arkansas Novaculite, and any changes in the recharge/runoff ratio in the recharge area could affect the discharge and temperature at the hot springs. Changes to surface and subsurface physical properties of hydraulic conductivity, porosity, storage, and fracture and flow-path connectivity and orientation can cause changes in system hydraulic head and pressure. As such, alterations of the hydraulic characteristics of the land surface resulting from land-use changes can affect changes in recharge and resultant pressures in the deep flow system that will propagate quickly along the flow path with rapid effect on the flow at the hot springs. This situation could arise as a result of a diversion of

surface runoff from the recharge area by installation of impermeable surfaces (road cuts, parking lots, buildings, and other manmade structures), removing soil and regolith, dewatering activities, changes in vegetation cover type and density, and additionally by changing, blocking, or opening fractures carrying water to depth in the host rocks within the recharge area. Decreased recharge will result in decreased hot spring discharge—decreasing the quantity of water available—and decrease average temperature of the springs. Because water flowing from the hot springs in HSNP includes a small, but important, component of cold-water recharge (surficial recharge proximal to the hot spring discharge area) (Bell and Hays, 2007), any decrease in the rate of geothermal discharge from the springs also would be accompanied by an immediate decrease in the temperature of the hot springs that would be much exacerbated during the wet season.

## Summary

A study was conducted by the U.S. Geological Survey in cooperation with the Arkansas State Highway and Transportation Department to characterize the contributing hydrogeology of newly discovered thermal water in a private domestic well 5.5 miles east of Hot Springs National Park, Hot Springs, Arkansas, and to determine the degree of hydraulic connectivity between the thermal water in the well and the hot springs in Hot Springs National Park. The initial water temperature in the well, which was completed in the Stanley Shale, was measured at 33.9°C and never dropped below 21.7°C after 2 hours of pumping. A second well with a thermal water component at a site 3 miles from the hot springs in Hot Springs National Park was discovered during a reconnaissance of the area. The well was completed in the Bigfork Chert and field measurement of well water revealed a maximum temperature of 26.6°C. Mean temperature for shallow groundwater in the area is approximately 17°C, and the occurrence of thermal water in these wells raised questions and concerns with regard to the timing for the appearance of the thermal water.

Concerns regarding the possible effects of blasting associated with highway construction near the first thermal well necessitated a technical review on the effects of blasting on shallow groundwater systems. Results from available studies indicate that propagation of new fractures near blasting sites is of limited extent. Safe levels of ground vibration from blasting range from a peak particle velocity of 0.5 to 2.0 in/sec for residential structures, and this range in vibrations appears to be safe for protection of groundwater wells ranging from 300-5,100 ft from blasting sites based on a review of pertinent studies. Although a possibility of rock collapse exists for uncased wells completed in highly fractured rock, as the vibrations can result in rock collapse, the propagation of newly formed large fractures that potentially could damage well structures or result in pirating of water from production wells appears to be of limited possibility based on review of relevant studies.

Characteristics of storage and secondary fracture porosity were interpreted from yields observed in individual wells completed in the Bigfork Chert and Stanley Shale; from hydrographs produced from continuous measurements of water levels in wells completed in the Arkansas Novaculite, the Bigfork Chert, and Stanley Shale; and from a potentiometric-surface map constructed using water levels in wells throughout the study area. The data gathered from these three separate exercises corroborate findings from earlier reports that fracture porosity is much greater in the Bigfork Chert relative to that in the Stanley Shale. At the scale that the potentiometric map was developed, potentiometric contours tend to mimic topography with no discernable influence on shallow groundwater flow by faulting or other geological structural features. The Bigfork Chert generally is located along the hinge line of the topographically higher anticlinal ridges, and the higher groundwater elevations from the potentiometric-surface map indicate that exposures of Bigfork Chert serve as major recharge areas for the regional shallow groundwater system in the study area. Flow lines developed on the potentiometric-surface map indicated flow from these elevated recharge areas along and into streams within the synclinal valleys formed on exposures of the Stanley Shale. Therefore, flow follows topography, and there is no evidence of interbasin transfer of groundwater within the shallow flow system.

A groundwater-sampling program was conducted to determine water quality and geochemistry of shallow groundwater from the various exposed formations in the study area for comparison to the geochemistry of the hot springs in Hot Springs National Park. Values of pH and conductance of groundwater were measured in 25 wells during an initial reconnaissance of the study area. The median pH was 7.3 for wells completed in shale formations and 4.5 for wells completed in quartz formations (novaculite, chert, and sandstone formations). Low specific-conductance values were measured for wells completed in the quartz formations; all but one site exhibited specific-conductance values of less than 50  $\mu\text{S}/\text{cm}$ , with a median of 30  $\mu\text{S}/\text{cm}$ , whereas wells completed in shale formations ranged from 97  $\mu\text{S}/\text{cm}$  to 490  $\mu\text{S}/\text{cm}$  with a median value of 290  $\mu\text{S}/\text{cm}$ . Based on results from the reconnaissance, 15 shallow wells and 2 cold-water springs were sampled to represent the water quality and geochemistry for the shallow groundwater system. For the quartz formations, total dissolved solids concentrations, as expected from the low specific conductance values, were very low with a median concentration of 23 mg/L, whereas the median concentration for groundwater from the shale formations was 184 mg/L. Ten hot springs in Hot Springs National Park were sampled for the study. Several chemical constituents for the hot springs, including pH, total dissolved solids, major cations and anions, and trace metals, show similarity with the shale formations in exhibiting elevated concentrations, though mean and median concentrations for most analytes were slightly lower in the hot springs compared to water from the shale formations. The chemistry of the hot springs is likely a result of rock/water interaction in the shale formations in the deeper sections of the

hot spring flow path with the initial, low ionic strength character inherited from shallow recharge through quartz formations being modified by passage through the shales at depth. Mixing curves for lithium, manganese, and strontium concentrations, which were greatest in the shale formations, revealed that the hot springs represent an approximate 40-percent contribution of water from the shale formations and 60-percent contribution of water from the quartz formations.

Oxygen, hydrogen, and strontium isotopes were included in the geochemical analysis of study area groundwater. Characterization of strontium geochemistry and analysis of strontium isotopic signatures were conducted, comparing groundwater samples from the hot springs in Hot Springs National Park, shallow groundwater samples in the study area from the quartz and shale formations, and samples from two western hot springs 30 to 50 miles west of Hot Springs in Montgomery County. Strontium isotopic data were used in concert with other geochemical data to discern geochemical signatures that can provide information on recharge origin of the two geothermal waters (western hot springs and the hot springs in Hot Springs National Park) and whether these groundwater systems share any physical hydraulic connection. Mixing model analysis indicated that the strontium geochemistry of the hot springs results from an approximately 35-percent contribution from the shales and a 65-percent contribution from the quartz formations, similar to that found from trace-metal analysis mixing curves. The newly discovered thermal water sites did not exhibit notable similarity with the hot springs in Hot Springs National Park with respect to strontium chemistry, but look geochemically like the groundwater of the local outcropping formations. The two very different isotopic and geochemical signatures observed for the new thermal water sites do not provide evidence of any direct hydraulic connection with the hot springs in Hot Springs National Park.

Plotting all thermal sites on the State geologic map showed that thermal water generally is located in similar geologic settings, although the thermal waters emanate from three different formations: the Stanley Shale including the Hot Springs Sandstone member of the Stanley Shale, the Bigfork Chert, and the Arkansas Novaculite. The thermal waters tend to be found along the nose of plunging anticlines and closely align with mapped thrust faults where detailed geologic maps were available. Because shallow flow systems have been identified as being confined within the regional surface watershed boundaries, the deep flow systems for thermal water are likely unique to the local hydrologic and geologic setting and represent an analog to the geologic framework model for propagation of groundwater to the hot springs in Hot Springs National Park. Concerns related to pirating of water from the hot springs in Hot Springs National Park because of blasting near the thermal well sites were not supported by the data gathered for this study. No physical hydraulic connection is evidenced; the waters exhibit different geochemical composition and different isotopic and trace metal signatures; the newly discovered thermal sites appear to be low-volume systems; and the sites are separated by distance and geological and hydrological

boundaries. Thermal-water sites across the Ouachita Mountains appear to represent discrete systems that are associated with a specific set of hydrologic and geologic conditions, which occur at numerous locations across the region, and are viewed as analogs to the hot spring flow system in Hot Springs National Park rather than connected components of the same hydraulic system. Although the mechanism for generation of thermal water appears to be very similar for the described thermal water occurrences throughout the Ouachita Mountains, the temperature of these waters will vary at the land surface where they issue as springs or along subsurface fractures intersected by shallow wells.

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## **Appendixes 1-2**

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**Appendix 1. Inorganic and isotopic water-quality data for samples collected in study area, Hot Springs, Arkansas.**

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; E, estimated; <sup>2</sup>H/H, deuterium/protium; <sup>18</sup>O/<sup>16</sup>O, oxygen-18/oxygen-16; <sup>13</sup>C/<sup>12</sup>C, carbon-13/carbon-12; <sup>87</sup>Str/<sup>86</sup>Str, strontium-87/strontium-86; ams, accelerator mass spectrometry; PMC, percent modern carbon; --, not measured]

Map number (figure 1)	Site identification number	Station name	Field name	Formation	Date collected	Time collected	Dis-solved oxygen (mg/L)	pH (field)	Specific conductance (µS/cm)	Water temperature (°C)	Hardness (mg/L as CaCO <sub>3</sub> )	Total dissolved solids (calculated) (mg/L)
1	343230093000701	02S19W24BCA1	Thomas	Arkansas Novaculite	9/12/2007	1100	6.8	4.8	29	16.5	12	12.7
3	343256092554201	02S18W22BBA1	Appel	Hot Springs Sandstone	9/10/2007	1500	5.5	3.9	23	20.0	1	6.8
5	343124092580301	02S18W30DDDI	Schnick	Hot Springs Sandstone	9/13/2007	1400	6.8	3.7	31	18.4	4	8.0
16	343056093001701	02S19W35ADD1	Thomton	Stanley Shale	9/11/2007	1200	1.0	6.3	235	18.7	85	113.2
24	343047092571101	02S18W32DAB1	Bratton	Stanley Shale	9/05/2007	1100	0.9	5.8	154	19.1	--	--
30	343224092562301	02S18W21CDB1	Sharp	Stanley Shale	9/10/2007	1300	0.5	5.9	184	18.3	68	109.6
34	343047092571201	02S19W32DAB2	Bratton2 (MW)	Stanley Shale	9/05/2007	1200	0.6	7.4	295	20.4	140	165.4
40	343238092555201	02S18W23ADB2	Bratton4	Bigfork Chert	9/11/2007	1400	8.3	4.2	17	17.1	1	3.9
41	343458092560201	02S18W04DBD1	Gates	Bigfork Chert	9/06/2007	1400	0.5	4.7	30	16.7	12	17.7
45	343350092560701	02S18W09DCD1	King	Bigfork Chert	9/07/2007	1500	5.7	4.2	22	19.5	5	8.9
46	343330092591101	02S19W13ADC1	Ester Trusty-Carlin	Bigfork Chert	9/07/2007	1200	0.5	3.6	50	17.5	0.1	18.8
49	343132092585401	02S18W30CCB1	Greer	Bigfork Chert	9/05/2007	1700	0.7	4.4	24	19.2	2	10.8
51	343132092585501	02S18W30CCB2	Greer (MW2)	Bigfork Chert	9/07/2007	1600	0.9	5.1	44	18.3	--	22.6
52	343132092585402	02S18W30CCB3	Greer (MW1)	Bigfork Chert	9/06/2007	1000	0.5	5.6	38	17.9	16	22.3
53	343511092580901	02S18W06ACD1	Rigsby	Womble Shale	9/07/2007	1000	0.5	6.9	477	19.5	230	262.5
60	343130093021901	AR-SCENICSPRING	ArScenic Spring	Stanley Shale	9/13/2007	1300	--	7.1	220	19.2	140	142.0
61	343211093011501	02S19W27AAB1SP	Sleepy Valley Spring	Bigfork Chert	9/13/2007	1016	--	6.1	63	19.2	21	30.2
83	342314093363301	04S24W19ABB1	Caddo Gap Spring	Arkansas Novaculite	6/18/2008	1015	1.5	6.7	233	33.8	96	149.0
84	343227093543501	04S27W08DDC1	Little Missouri Spring	Arkansas Novaculite	6/10/2008	1105	4.0	6.2	98	23.4	53	73.0
85	343048093031301	Quapaw Spring	Spring42	Hot Springs Sandstone	9/11/2007	817	--	7.0	286	61.2	130	137.6
86	343049093031301	Fordyce Spring	Spring46	Hot Springs Sandstone	9/10/2007	1411	--	7.2	297	57.4	130	140.8
87	343050093031201	DISPLAY SPRING	Spring33	Hot Springs Sandstone	9/13/2007	1532	--	7.2	298	55.8	130	136.6
88	343052093031301	HALE SPRING	Spring25	Hot Springs Sandstone	9/10/2007	850	--	7.1	302	62.5	130	140.6
89	343054093031201	SPRING 49	Spring49	Hot Springs Sandstone	9/12/2007	1555	--	7.4	290	61.8	130	136.8
90	343055093031301	SPRING 9	Spring9	Hot Springs Sandstone	9/11/2007	1009	--	7.5	311	62.1	130	139.0
91	343056093030901	SPRING 8	Spring8	Hot Springs Sandstone	9/12/2007	1045	--	7.5	284	61.9	130	140.1
92	343056093031101	02S19W33BCD2	Spring6	Hot Springs Sandstone	9/11/2007	1530	--	6.3	302	57.9	133	140.7
93	343057093031301	02S19W33CBB6SP	Spring17	Hot Springs Sandstone	9/11/2007	1330	--	7.3	290	54.0	120	132.8
94	343058093030901	SPRING 47	Spring47	Hot Springs Sandstone	9/12/2007	1000	--	7.2	316	61.3	140	144.0

**Appendix 1.** Inorganic and isotopic water-quality data for samples collected in study area, Hot Springs, Arkansas.—Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; E, estimated; <sup>2</sup>H/H, deuterium/protium; <sup>18</sup>O/<sup>16</sup>O, oxygen-18/oxygen-16; <sup>13</sup>C/<sup>12</sup>C, carbon-13/strontium-86; <sup>87</sup>Sr/<sup>86</sup>Sr, strontium-87/strontium-86; ams, accelerator mass spectrometry; PMC, percent modern carbon; --, not measured]

Map number (figure 1)	Station identification number	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Alkalinity (field) (mg/L as CaCO <sub>3</sub> )	Bicarbonate (field) (mg/L)	Carbonate (field) (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Silica (mg/L)	Hydrogen ion (calculated) (mg/L)	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)
1	343230093000701	0.31	2.62	1.00	10	13	0	1.02	1.48	E 0.1	10.7	0.01712	2.5	<0.06	<0.12
3	343256092554201	0.12	0.21	1.53	0	2	0	1.11	2.92	<0.1	9.08	0.11572	58.6	<0.06	<0.12
5	343124092580301	0.81	0.36	1.60	0	1	0	2.67	2.12	<0.1	7.76	0.19653	83.6	E 0.04	<0.12
16	343056093001701	27.16	4.01	10.83	78	95	0	22.71	2.86	0.21	31.3	0.00045	1.6	0.40	6.88
24	343047092571101	12.4	2.19	11.3	--	--	--	--	11.2	0.15	15.8	0.00146	29.8	<0.20	0.30
30	343224092562301	19.5	4.56	14.8	68	83	0	26.17	4.73	0.18	31.3	0.00116	3.1	E 0.06	1.70
34	343047092571201	44.7	5.92	14.3	149	180	0	11.50	2.57	0.18	18.3	0.00004	2.8	<0.06	1.60
40	343238092535201	0.3	0.14	0.69	0	1	0	1.32	0.98	<0.1	7.23	0.06659	9.9	<0.06	<0.12
41	343458092560201	4.1	0.34	0.91	11	14	0	4.11	1.49	0.1	8.34	0.02205	54.6	E 0.04	1.40
45	343350092560701	0.9	0.61	1.03	3	4	0	2.95	1.52	<0.1	8.38	0.06215	11.7	<0.06	<0.12
46	343330092591101	0.078	0.15	1.756	0	4	0.3	12.05	3.00	<0.1	12.33	0.242	214.4	0.55	2.09
49	343132092585401	0.39	0.21	1.12	4	5	0	4.87	1.83	<0.1	11.8	0.04202	27.4	0.07	1.10
51	343132092585501	0.01	0.01	9.17	14	17	0	3.51	1.71	0.17	13.5	0.00765	5.1	0.25	3.30
52	343132092585402	6.11	0.29	1.46	16	20	0	3.60	1.22	<0.1	10.8	0.00231	5.3	0.81	7.20
53	343511092580901	78.1	8.00	11.5	205	249	0	35.4	9.95	0.15	10.7	0.00012	2.0	0.24	0.49
60	343130093021901	51.1	2.03	1.68	135	164	0	6.19	2.23	0.14	11.1	0.00008	E 1.2	0.15	0.47
61	343211093011501	7.57	0.58	1.45	8	10	0	13.55	2.28	0.1	12.5	0.00076	50.7	0.09	0.13
83	342314093363301	34.7	2.14	4.16	109	133	--	4.78	3.18	0.18	22.2	--	--	--	--
84	343227093543501	17.3	2.48	1.61	51	62	--	5.31	1.63	0.13	11.2	--	--	--	--
85	343048093031301	45.2	4.84	3.95	127	154	0	7.79	1.93	0.14	39.8	0.0001	2.6	<0.06	0.52
86	343049093031301	45.4	4.83	4.01	132	161	0	7.46	1.86	0.14	40.4	0.00006	E 1.6	<0.06	0.39
87	343050093031201	45.2	4.78	3.7	126	153	0	7.66	1.82	0.15	41.3	0.00007	4.1	<0.06	0.43
88	343052093031301	45.3	4.83	3.92	132	161	0	7.48	1.83	0.13	39.7	0.00008	2.9	<0.06	0.40
89	343054093031201	44.4	4.72	3.75	128	156	0	7.25	1.84	0.14	40.8	0.00004	13.3	<0.06	0.44
90	343055093031301	44.7	4.79	3.88	131	159	0	7.53	1.77	0.13	39.8	0.00004	1.7	<0.06	0.38
91	343056093030901	44.8	4.78	3.88	132	161	0	7.49	1.84	0.13	39.6	0.00003	1.9	<0.06	0.39
92	343056093031101	45.3	4.82	3.91	132	161	0	7.53	1.86	0.13	39.89	0.00049	2.09	<0.06	0.32
93	343057093031301	42.0	4.81	4.04	124	151	0	7.60	1.87	0.13	39.7	0.00005	1.7	<0.06	0.38
94	343058093030901	45.9	4.88	3.91	138	167	0	7.32	1.84	0.13	39.7	0.00006	2.0	<0.06	0.38

**Appendix 1.** Inorganic and isotopic water-quality data for samples collected in study area, Hot Springs, Arkansas.—Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; E, estimated; <sup>3</sup>H/H, deuterium/protium; <sup>18</sup>O/<sup>16</sup>O, oxygen-18/oxygen-16; <sup>13</sup>C/<sup>12</sup>C, carbon-13/carbon-12; <sup>87</sup>Sr/<sup>86</sup>Sr, strontium-87/strontium-86; ams, accelerator mass spectrometry; PMC, percent modern carbon; --, not measured]

Map number (figure 1)	Station identification number	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)	Manganese (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)
1	343230093000701	0.7	<0.06	<8	<0.04	<0.12	0.32	31.6	38	0.67	6.8	60.4	<0.1	0.91	0.09
3	343256092554201	27	0.11	<8	0.05	<0.12	0.8	42	29	6.63	0.7	3.3	<0.1	1.4	0.11
5	343124092580301	20	0.06	E 5	<0.04	E 0.08	0.22	446	89	13.5	<0.6	4.7	<0.1	1.2	0.17
16	343056093001701	17	0.09	10	<0.04	0.09	2.5	0.4	216.4	<0.12	16.7	1115	1	2.7	0.12
24	343047092571101	108	0.18	28	<0.04	0.08	1.73	1.7	96	0.21	2.9	41.8	<0.4	2.3	0.09
30	343224092562301	18	0.10	11	<0.04	<0.12	2.1	2.1	611	0.8	18.3	810	0.3	7.8	<0.08
34	343047092571201	146	<0.06	15	<0.04	0.12	0.08	<0.4	158	<0.12	6	71.5	0.4	0.46	<0.08
40	343238092535201	5	<0.06	<8	<0.04	<0.12	0.16	0.9	E 4	0.16	<0.6	1.6	<0.1	0.42	0.12
41	343458092560201	2	<0.06	<8	0.23	<0.12	2.7	0.9	798	0.25	<0.6	12	0.4	8.7	<0.08
45	343350092560701	18	E 0.04	E 6	0.05	<0.12	0.44	15.6	E 5	1.74	<0.6	6.2	<0.1	2.1	0.20
46	343330092591101	21	0.09	E 4.7	0.108	0.22	2.40	89.7	696.6	50.13	0.8	17.1	0.5	14	0.25
49	343132092585401	2	E 0.03	E 5	0.36	<0.12	3.9	3.4	2510	14.2	0.6	23.6	<0.1	7.3	0.09
51	343132092585501	E 0.05	<0.06	9	<0.04	<0.12	<0.04	0.9	8	<0.12	1.4	<0.2	2.3	E 0.05	0.54
52	343132092585402	9	<0.06	E 4	0.04	0.13	1.8	<0.4	1220	<0.12	E 0.4	22.7	0.7	3.8	0.44
53	343511092580901	51	<0.06	56	0.12	<0.12	0.45	19.7	12	1.66	4.7	81.1	0.7	5.0	<0.08
60	343130093021901	13	<0.06	E 6	<0.04	<0.12	0.46	0.7	21	<0.12	5.8	144	0.2	1.3	0.36
61	343211093011501	8	E 0.05	E 6	0.08	<0.12	2.9	1.2	E 4	E 0.09	3.6	41.4	<0.1	11.4	<0.08
83	342314093363301	--	--	--	--	--	--	--	--	--	--	--	--	--	--
84	343227093543501	--	--	--	--	--	--	--	--	--	--	--	--	--	--
85	343048093031301	139	<0.06	11	<0.04	<0.12	0.16	E 0.4	18	<0.12	4.8	223	0.2	0.46	<0.08
86	343049093031301	138	<0.06	11	<0.04	<0.12	0.04	<0.4	14	<0.12	4.7	215	0.2	0.29	<0.08
87	343050093031201	143	<0.06	12	<0.04	<0.12	0.08	2.1	25	E 0.09	5	229	0.2	0.58	<0.08
88	343052093031301	141	<0.06	10	<0.04	<0.12	0.06	<0.4	20	<0.12	4.4	226	0.2	0.42	<0.08
89	343054093031201	111	<0.06	11	<0.04	<0.12	0.05	7.2	<6	0.39	4.9	140	0.3	0.85	<0.08
90	343055093031301	75	<0.06	11	<0.04	<0.12	<0.04	E 0.4	<6	<0.12	4.7	1.1	0.2	0.3	<0.08
91	343056093030901	138	<0.06	11	<0.04	<0.12	0.05	<0.4	<6	<0.12	4.7	213	0.1	0.32	<0.08
92	343056093031101	86	<0.06	11	<0.04	<0.12	<0.04	<0.4	<6	<0.12	4.8	<0.2	0.2	0.19	0.06
93	343057093031301	81	<0.06	10	<0.04	<0.12	<0.04	0.7	<6	<0.12	4.2	<0.2	0.2	0.19	<0.08
94	343058093030901	138	<0.06	11	<0.04	<0.12	0.05	E 0.23	<6	<0.12	4.7	212	0.2	0.33	<0.08



**Appendix 1.** Inorganic and isotopic water-quality data for samples collected in study area, Hot Springs, Arkansas.—Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; E, estimated; <sup>2</sup>H/H, deuterium/protium; <sup>18</sup>O/<sup>16</sup>O, oxygen-18/oxygen-16; <sup>13</sup>C/<sup>12</sup>C, carbon-13/carbon-12; <sup>87</sup>Sr/<sup>86</sup>Sr, strontium-87/strontium-86; ams, accelerator mass spectrometry; PMC, percent modern carbon; --, not measured]

Map number (figure 1)	Site identification number	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	<sup>2</sup> H/H (ratio per mil)	Tritium 2-sigma pCi/L	Tritium (pCi/L)	Uranium (µg/L)	<sup>18</sup> O/ <sup>16</sup> O (ratio per mil)	<sup>13</sup> C/ <sup>12</sup> C (ratio per mil)	Carbon-14 ams (percent error)	Carbon-14 (PMC)	<sup>87</sup> Sr/ <sup>86</sup> Sr
1	343230093000701	<0.1	2.33	<0.04	<0.04	31.6	-31	3.2	9	E 0.03	-5.60	--	--	--	0.72205
3	343256092554201	<0.1	1.81	<0.04	E 0.03	6.4	-31.3	3.2	7	<0.04	-5.73	--	--	--	0.71812
5	343124092580301	<0.1	6.63	<0.04	<0.04	39.1	-30.7	--	--	<0.04	-5.57	--	--	--	0.71435
16	343056093001701	<0.1	209	<0.04	0.05	10.23	-28.1	3.2	12	--	-4.88	-17.37	0.3	66.1	0.71383
24	343047092571101	<0.2	328	0.003	<0.10	7.3	--	3.2	9	0.09	--	-19.43	0.4	79.5	0.71032
30	343224092562301	<0.1	236	E 0.02	0.04	114	-29.9	--	--	0.06	-5.41	--	--	--	0.71092
34	343047092571201	<0.1	324	<0.04	0.05	<0.6	--	3.2	1	0.45	--	-12.7	0.2	23.7	0.7103
40	343238092555201	<0.1	1.87	<0.04	<0.04	4.3	-32.2	--	--	<0.04	-5.81	--	--	--	0.71319
41	343458092560201	<0.1	5.07	0.14	0.44	198	-29.6	--	--	E 0.03	-5.48	--	--	--	0.70969
45	343350092560701	<0.1	10.7	E 0.03	0.06	10.5	-29.3	--	--	<0.04	-5.41	--	--	--	0.71258
46	343330092591101	<0.1	3.02	0.4076	1.342	33.42	-30.4	3.2	9	0.040	-5.52	--	--	--	0.72242
49	343132092585401	<0.1	4.03	0.31	0.15	49.9	-30.2	3.2	7	<0.04	-5.60	-23.49	0.4	77.8	0.71107
51	343132092585501	<0.1	<0.4	E 0.03	0.56	E 0.48	-30.6	3.2	8	0.49	-5.58	-23.09	0.4	85.2	0.7082
52	343132092585402	<0.1	19.1	0.19	1.5	5.1	-31.3	3.2	8	0.13	-5.63	-22.14	0.4	78.6	0.71064
53	343511092580901	<0.1	287	0.1	0.15	26.7	-28.7	--	--	2.1	-5.32	--	--	--	0.71108
60	343130093021901	<0.1	208	<0.04	0.21	8.9	-29.9	--	--	0.10	-5.44	--	--	--	0.70851
61	343211093011501	<0.1	40.5	0.23	0.09	41.1	-29.5	3.2	7	<0.04	-5.11	--	--	--	0.70937
83	342314093363301	--	83.0	--	--	--	-29.4	3.0	2	--	-5.58	--	--	--	0.71211
84	343227093543501	--	37.1	--	--	--	--	--	--	--	--	--	--	--	0.7121
85	343048093031301	<0.1	106	0.04	0.06	1.2	-28.9	--	--	<0.04	-5.52	-14.03	0.2	36.6	0.71192
86	343049093031301	<0.1	108	0.04	E 0.03	<0.6	-28.6	--	--	<0.04	-5.49	-13.86	0.2	35.6	0.7119
87	343050093031201	<0.1	101	0.05	E 0.03	6.5	-30.2	--	--	<0.04	-5.48	-13.42	0.2	36.9	0.71191
88	343052093031301	<0.1	106	E 0.04	0.05	E 0.42	-29	--	--	<0.04	-5.54	-14.73	0.2	35.7	0.71196
89	343054093031201	<0.1	98.8	0.04	0.06	6.7	-29.7	--	--	<0.04	-5.55	-14.02	0.3	44.8	0.71192
90	343055093031301	<0.1	107	0.04	E 0.03	E 0.47	-28.2	3.2	0	<0.04	-5.52	-13.24	0.2	37	0.7119
91	343056093030901	<0.1	104	E 0.04	0.05	E 0.49	-28.3	3.2	0	<0.04	-5.56	-13.8	0.2	38.3	0.71189
92	343056093031101	<0.1	105	0.05	0.06	<0.6	-28.6	--	--	<0.04	-5.56	-13.87	0.2	36.3	0.71196
93	343057093031301	<0.1	102	E 0.03	E 0.03	0.6	-29.4	--	--	<0.04	-5.47	-13.51	0.2	40	0.7119
94	343058093030901	<0.1	106	E 0.04	0.22	E 0.37	-29.5	--	--	<0.04	-5.61	-13.3	0.2	36.2	0.7119

**Appendix 1.** Inorganic and isotopic water-quality data for samples collected in study area, Hot Springs, Arkansas.—Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °Celsius, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; E, estimated; <sup>2</sup>H/H, deuterium/protium; <sup>18</sup>O/<sup>16</sup>O, oxygen-18/oxygen-16; <sup>13</sup>C/<sup>12</sup>C, carbon-13/carbon-12; <sup>87</sup>Sr/<sup>86</sup>Sr, strontium-87/strontium-86; ams, accelerator mass spectrometry; PMC, percent modern carbon; --, not measured]

Map number (figure 1)	Site identification number	Station name	Field name	Formation	Date collected	Time collected	Strontium (ug/L)	<sup>87</sup> Sr/ <sup>86</sup> Sr
6	343034092581601	02S18W31DDB1	Smith	Stanley Shale	4/30/2008	930	385	0.71347
9	343150092565101	02S18W28BCB1	Bodi	Stanley Shale	4/30/2008	945	42	0.71298
19	343150092594901	02S19W25BCD1	Shinkle	Stanley Shale	4/29/2008	1040	282	0.71311
33	343050093000101	02S19W36CBB1	Artesian	Stanley Shale	4/30/2008	905	381	0.71042
62	343159092554601	02S18W27BBC1	Sangster Lane Spring	Arkansas Novaculite	4/28/2008	945	6	0.71458
63	343203092553901	02S18W27BBA1	Sangster Two	Missouri Mountain Shale	4/28/2008	1025	22	0.71367
64	343150092555301	02S18W28ADA1	Jerryrig Spring	Hot Springs Sandstone	4/28/2008	915	5	0.71574
65	343152092554101	02S18W27BCA1	Between Spring	Bigfork Chert	4/28/2008	1135	4	0.71648
66	343149092553101	02S18W27BDA1	Java Spring	Missouri Mountain Shale	4/28/2008	1210	11	0.71484
67	343219092553601	02S18W22CBD1	Thresher North	Bigfork Chert	4/28/2008	1500	12	0.71583
68	343214092553501	02S18W22CDB1	Thresher South	Bigfork Chert	4/28/2008	1340	20	0.71221
69	343057092572101	02S18W32ACC1	Amphitheater Spring	Stanley Shale	4/30/2008	820	106	0.71017
71	343209092553601	02S18W22CCD1	Tree Fall Spring	Missouri Mountain Shale	4/28/2008	1415	13	0.72082
72	343134092580501	02S18W30DAD1	Powerline Spring	Arkansas Novaculite	4/29/2008	1615	6	0.71505
73	343128092581901	02S18W30DCA1	Covenant Spring	Arkansas Novaculite	4/29/2008	1445	4	0.71446
74	343126092582601	02S18W30DCC1	Simmerman Spring	Arkansas Novaculite	4/29/2008	1505	3	0.71417
75	343155092583301	02S18W30BDA1	Panther Valley	Bigfork Chert	4/29/2008	1218	9	0.71505
77	343209092583101	02S18W30BAA1	Seth Spring	Bigfork Chert	4/29/2008	1325	10	0.71265
78	343211092582301	02S18W30ABB2	Sam Spring	Bigfork Chert	4/29/2008	1255	5	0.71343
79	343156093012101	02S19W27ADB1	Montanus Spring	Arkansas Novaculite	4/28/2008	1510	5	0.71444
80	343159093005301	02S19W26BCA1	Novastone Spring	Arkansas Novaculite	4/29/2008	950	14	0.71534
81	343158092585501	02S18W30BCB1	Thousand Spring	Bigfork Chert	4/29/2008	1115	6	0.71434
82	343218092585501	02S18W19CCC1	Denise Spring	Stanley Shale	4/29/2008	1155	2	0.71137
86	343049093031301	Fordyce Spring	Spring 46 - Fordyce	Hot Springs Sandstone	5/29/2008	915	101	0.71198
88	343052093031301	HALE SPRING	Spring 25	Hot Springs Sandstone	5/29/2008	845	106	0.71197
89	343054093031201	SPRING 49	Spring 49	Hot Springs Sandstone	5/29/2008	1035	96	0.71197
91	343056093030901	SPRING 8	Spring 8	Hot Springs Sandstone	5/29/2008	1110	101	0.71199
93	343057093031301	02S19W33CBB6SP	Spring 17	Hot Springs Sandstone	5/29/2008	1000	98	0.71197

**Appendix 2. Measurement site characteristics for Hot Springs well and spring reconnaissance.**

[NGVD 29, National Geodetic Vertical Datum of 1929: °C, degrees Celsius; μS/cm, microsiemens per centimeter at 25 degrees Celsius; --, not measured; 330ARKS, Arkansas Novaculite; 330HSPG, Hot Springs Sandstone; 330STNL, Stanley Shale; 350SLRN, Missouri Mountain Shale and Polk Creek Shale, undifferentiated; 364BGFK, Bigfork Chert; 367WMBL, Womble Shale]

Map number (figure 1)	Field name	Formation	Well/spring	Well/latitude	Longitude	Site identification number	Well depth (feet)	Water level (feet) below land surface	Water level altitude (feet) above NGVD 29	Temperature (°C)	Specific conductance (μS/cm)	pH	Date inventoried	Land-surface datum altitude (NGVD 29)
1	Thomas	330ARKS	Well	34.541750	93.002000	343230093000701	150	46.82	75.3	20.1	29	4.77	4/04/2007	800
2	House for sell	330ARKS	Well	34.520944	92.972194	343115092582001	--	--	--	20.6	62	5.91	6/02/2007	1,025
3	Appel	330HSPG	Well	34.548806	92.928250	343256092554201	35	7.63	702	18.5	24	4.73	4/02/2007	710
4	Stubbs	330HSPG	Well	34.511917	92.949333	343043092565801	--	Artesian	580	--	--	--	2/28/2007	580
5	Schnick	330HSPG	Well	34.523278	92.967583	343124092580301	300	236.16	754	17.0	31	3.70	4/05/2007	990
6	Smith	330STNL	Well	34.509417	92.971222	343034092581601	100	3.00	487	17.7	338	7.40	4/02/2007	490
7	Lantz	330STNL	Well	34.514194	92.964917	343051092575401	300	26.98	523	22.8	354	--	4/02/2007	550
8	Remont	330STNL	Well	34.516167	92.961111	343058092574001	130	28.45	482	19.1	419	7.67	4/02/2007	510
9	Bodi	330STNL	Well	34.530500	92.947583	343150092565101	90	20.34	580	18.0	97	6.24	4/02/2007	600
10	USNR (north)	330STNL	Well	34.507056	92.979556	343025092584601	--	7.73	522	--	--	--	2/27/2007	530
11	USNR (south)	330STNL	Well	34.506306	92.979972	343023092584801	253	7.35	518	--	--	--	2/27/2007	525
12	Uzick	330STNL	Well	34.508222	92.956278	343030092572201	--	12.59	517	--	--	--	2/27/2007	530
13	Wheeler	330STNL	Well	34.521889	92.921444	343119092551701	--	14.01	526	--	--	--	2/27/2007	540
14	Jones	330STNL	Well	34.534556	92.982028	343204092585501	--	4.28	526	--	--	--	2/28/2007	530
15	UNK (basement)	330STNL	Well	34.507167	92.952528	343026092570901	--	12.65	507	--	--	--	2/28/2007	520
16	Thornton	330STNL	Well	34.515500	93.004639	343056093001701	74	9.16	541	--	235	6.35	11/08/2006	550
17	Edwards	330STNL	Well	34.508611	93.005361	343031093001901	--	19.10	501	--	--	--	11/08/2006	520
18	Daniel	330STNL	Well	34.523417	93.000222	343124093000101	100	3.68	466	--	--	--	4/03/2007	470
19	Shinkle	330STNL	Well	34.530472	92.996833	343150092594901	130	17.00	583	--	--	--	4/03/2007	600
20	UNK (MHSL)	330STNL	Well	34.506167	92.984194	343022092590301	--	0.00	480	--	--	--	4/04/2007	480
21	McDougal	330STNL	Well	34.541361	92.981028	343229092585201	120	3.49	547	--	--	--	4/03/2007	550
22	Blackwell	330STNL	Well	34.542028	92.888750	343231092532001	75	3.83	716	--	--	--	4/05/2007	720
23	Rest area	330STNL	Well	34.536167	92.897833	343210092535201	48	17.56	667	18.9	181	--	11/16/2006	685
24	Bratton	330STNL	Well	34.513000	92.953167	343047092571101	200	--	--	--	155	5.84	11/08/2006	595
25	186 Bratton	330STNL	Well	34.509778	92.957694	343035092572801	197	--	--	--	--	--	11/14/2006	560
26	Cabinet shop	330STNL	Well	34.507917	92.958333	343029092593001	130	28.42	472	--	--	--	11/14/2006	500
27	Faye	330STNL	Well	34.510861	92.968694	343039092580701	--	18.85	501	18.0	392	6.98	6/02/2007	520
28	Jackson	330STNL	Well	34.544222	92.935139	343039092560601	--	--	--	18.0	--	7.33	6/02/2007	655
29	McCoy	330STNL	Well	34.545861	92.935694	343245092560801	--	66.66	618	17.9	490	7.68	6/02/2007	685
30	Sharp	330STNL	Well	34.540000	92.939778	343224092562301	--	6.24	619	18.1	202	6.44	6/02/2007	625

**Appendix 2. Measurement site characteristics for Hot Springs well and spring reconnaissance.—Continued**

[NGVD 29, National Geodetic Vertical Datum of 1929: °C, degrees Celsius; μS/cm, microsiemens per centimeter at 25 degrees Celsius; --, not measured; 330ARKS, Arkansas Novaculite; 330HSPG, Hot Springs Sandstone; 330STNL, Stanley Shale; 350SLRN, Missouri Mountain Shale and Polk Creek Shale, undifferentiated; 364BGFK, Bigfork Chert; 367WMBL, Womble Shale]

Map number (figure 1)	Field name	Formation	Well/spring	Latitude	Longitude	Site identification number	Well depth (feet)	Water level (feet) below land surface	Water-level altitude (feet) above NGVD 29	Temperature (°C)	Specific conductance (μS/cm)	pH	Date inventoried	Land-surface datum altitude (NGVD 29)
31	Chamness	330STNL	Well	34.521639	92.958028	343118092572901	45	--	--	16.9	190	7.03	6/02/2007	540
32	Stallones	330STNL	Well	34.520472	92.960972	343114092574001	--	16.05	544	17.5	171	7.07	6/02/2007	560
33	Artesian	330STNL	Well	34.513972	93.000389	343050093000101	--	--	485	18.9	324	7.39	6/02/2007	485
34	Bratton2 (MW)	330STNL	Well	34.512972	92.953250	343047092571201	165	30.77	564	--	295	--	7/03/2007	595
35	Thomas (USGS1)	350SLRN	Well	34.551472	92.993000	343305092593501	89	42.97	667	--	--	--	11/16/2006	710
36	Thomas (USGS2)	350SLRN	Well	34.551056	92.992944	343304092593501	106	50.48	665	--	--	--	11/16/2006	715
37	Smith Abrasives	350SLRN	Well	34.553417	92.989694	343312092592301	380	--	--	--	--	--	11/08/2006	700
38	Simmerman	350SLRN	Well	34.524583	92.975528	343129092583201	--	--	--	17.5	238	6.72	6/02/2007	680
39	Bratton3	350SLRN	Well	34.544472	92.899472	343240092535801	83	2.92	747	--	--	--	7/10/2007	750
40	Bratton4	350SLRN	Well	34.544000	92.897861	343238092535201	--	Artesian	795	18.0	17	4.18	7/10/2007	790
41	Gates	364BGFK	Well	34.582694	92.933917	343458092560201	--	7.08	543	--	30	4.66	2/27/2007	550
42	Stange	364BGFK	Well	34.55417	92.973944	343208092582601	208	134.80	625	--	--	--	2/27/2007	760
43	Belvedere C.C.	364BGFK	Well	34.547806	93.006861	343252093002501	--	63.80	671	17.3	23	--	2/27/2007	735
44	Weston	364BGFK	Well	34.578056	92.925361	343441092553101	--	10.93	609	--	--	--	2/28/2007	620
45	King	364BGFK	Well	34.564000	92.935194	343350092560701	--	Artesian	610	--	22	4.21	2/28/2007	610
46	Ester Trusty-Carlin	364BGFK	Well	34.558250	92.986278	343330092591101	50	25.58	644	16.6	41	3.62	4/04/2007	670
47	Weddock	364BGFK	Well	34.529333	92.979639	343146092584701	300	200.40	540	22.4	32	--	4/03/2007	740
48	Panther Valley	364BGFK	Well	34.531361	92.973472	343153092582401	54	7.43	573	18.1	--	--	10/26/2006	580
49	Greer	364BGFK	Well	34.525472	92.981556	343132092585401	185	95.95	609	23.8	24	4.4	6/02/2007	705
50	Bratton5	350SLRN	Well	34.547917	92.898306	343253092535401	180	51.64	738	17.2	298	--	7/10/2007	790
51	Greer2 (MW1)	364BGFK	Well	34.525472	92.981944	343132092585501	120	94.79	605	--	44	5.12	7/03/2007	700
52	Greer3 (MW2)	364BGFK	Well	34.525444	92.981528	343132092585402	155	96.89	608	--	38	5.64	7/03/2007	705
53	Rigsby	367WMBL	Well	34.586333	92.969278	343511092580901	--	8.08	532	--	477	6.92	2/28/2007	540
54	UNK (for rent)	367WMBL	Well	34.579222	92.979889	343445092584801	--	7.64	552	--	--	--	2/28/2007	560
55	Church	367WMBL	Well	34.589722	92.965333	343523092575501	100	9.53	520	--	--	--	4/05/2007	530
56	Loprinzi	367WMBL	Well	34.568583	92.821222	343407092491601	165	8.80	471	--	--	--	4/05/2007	480
57	Lyon	367WMBL	Well	34.573250	92.824111	343424092492701	150	12.62	432	--	--	--	4/05/2007	445
58	Fountain Lake	367WMBL	Well	34.603750	92.927722	343614092554001	--	Artesian	490	--	--	--	12/12/2006	490
59	Edds	367WMBL	Well	34.580583	92.874389	343450092522801	200	7.74	547	--	--	--	12/12/2006	555
60	ArScenic Spring	330STNL	Spring	34.525000	93.038611	343130093021901	--	--	--	19.2	273	7.10	9/13/2007	--

**Appendix 2. Measurement site characteristics for Hot Springs well and spring reconnaissance.—Continued**

[NGVD 29, National Geodetic Vertical Datum of 1929: °C, degrees Celsius; μS/cm, microsiemens per centimeter at 25 degrees Celsius; --, not measured; 330ARKS, Arkansas Novaculite; 330HSPG, Hot Springs Sandstone; 330STNL, Stanley Shale; 350SLRN, Missouri Mountain Shale and Polk Creek Shale, undifferentiated; 364BGFK, Bigfork Chert; 367WMBL, Womble Shale]

Map number (figure 1)	Field name	Formation	Well/spring	Well/spring	Latitude	Longitude	Site identification number	Well depth (feet)	Water level (feet) below land surface	Water-level altitude (feet) above NGVD 29	Temperature (°C)	Specific conductance (μS/cm)	pH	Date inventoried	Land-surface datum altitude (NGVD 29)
61	Sleepy Valley Spring	364BGFK	Spring	Spring	34.536389	93.020833	343211093011501	--	--	--	--	63	6.10	4/28/2008	640
62	Sangster Lane Spring	330HSPG	Spring	Spring	34.533181	92.92955	343159092554601	--	--	--	10.2	23	--	4/28/2008	805
63	Sangster Two Spring	364BGFK	Spring	Spring	34.534100	92.9274806	343203092553901	--	--	--	11.5	25	--	5/05/2008	740
64	Jerrying Spring	350SLRN	Spring	Spring	34.530639	92.9312806	343150092555301	--	--	--	9.4	19	--	5/05/2008	865
65	Between Spring	364BGFK	Spring	Spring	34.531150	92.9280611	343152092554101	--	--	--	10.9	20	--	5/05/2008	670
66	Java Spring	364BGFK	Spring	Spring	34.530319	92.9253194	343149092553101	--	--	--	10.6	20	--	5/05/2008	600
67	Thresher North	364BGFK	Spring	Spring	34.538600	92.9266806	343219092553601	--	--	--	9.5	20	--	5/05/2008	660
68	Thresher South	364BGFK	Spring	Spring	34.537239	92.9262611	343214092553501	--	--	--	--	--	--	5/06/2008	640
69	Amphitheater Spring	350SLRN	Spring	Spring	34.515706	92.9557222	343057092572101	--	--	--	15.6	232	--	5/06/2008	570
70	McClendon Spring	330ARKS	Spring	Spring	34.516325	92.9559639	343105092572001	--	--	--	16.9	222	--	5/06/2008	--
71	Tree Fall Spring	330ARKS	Spring	Spring	34.535831	92.9267611	343209092553601	--	--	--	10.1	22	--	5/07/2008	680
72	Powerline Spring	330ARKS	Spring	Spring	34.526153	92.9679639	343134092580501	--	--	--	13.9	20	--	5/07/2008	930
73	Covenant Spring	364BGFK	Spring	Spring	34.524481	92.9720694	343128092581901	--	--	--	14.2	10	--	5/07/2008	740
74	Simmerman Spring	364BGFK	Spring	Spring	34.523864	92.9738	343126092582601	--	--	--	14.6	16	--	5/07/2008	715
75	Panther Valley	364BGFK	Spring	Spring	34.531900	92.9759389	343155092583301	--	--	--	15.9	28	--	5/07/2008	565
76	Witness Spring	364BGFK	Spring	Spring	34.532492	92.9769056	343157092583701	--	--	--	10.8	147	--	5/07/2008	555
77	Seth Spring	330ARKS	Spring	Spring	34.535694	92.9753611	343209092583101	--	--	--	--	--	--	4/29/2008	630
78	Sam Spring	330ARKS	Spring	Spring	34.536306	92.9730556	343211092582301	--	--	--	--	--	--	4/29/2008	620
79	Montanus Spring	364BGFK	Spring	Spring	34.532250	93.0225278	343156093012101	--	--	--	15.5	13	4.09	4/28/2008	760
80	Novastone Spring	330STNL	Spring	Spring	34.532917	93.0146389	343159093005301	--	--	--	12.3	21	4.46	4/29/2008	860
81	Thousand Spring	330ARKS	Spring	Spring	34.532778	92.9821111	343158092585501	--	--	--	15.8	19	4.13	4/29/2008	590
82	Denise Spring	330ARKS	Spring	Spring	34.538194	92.9818611	343218092585501	--	--	--	16.5	18	4.05	4/29/2008	535
83	Caddo Gap Spring	330ARKS	Spring	Spring	34.387161	93.6092444	342314093363301	--	--	--	33.6	233	6.72	6/18/2008	590
84	Little Missouri	330ARKS	Spring	Spring	34.407403	93.9097222	343227093543501	--	--	--	23.5	98	6.17	6/10/2008	1,060

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