

Prepared in cooperation with (in alphabetical order)  
the Arkansas Natural Resources Commission, Arkansas Oil and Gas Commission,  
Duke University, Faulkner County, Shirley Community Development Corporation, and  
the University of Arkansas at Fayetteville, and  
the U.S. Geological Survey Groundwater Resources Program

## Shallow Groundwater Quality and Geochemistry in the Fayetteville Shale Gas-Production Area, North-Central Arkansas, 2011



Scientific Investigations Report 2012–5273

**Cover:**

**Left,** Drilling rig and equipment used in the Fayetteville Shale gas-production area, north-central Arkansas.

**Right,** Pond with synthetic liner used to store water at shale gas-production facility in the Fayetteville Shale area, north-central Arkansas.

**Bottom,** Freshwater pond and distribution lines for source water used in drilling and hydrofracturing in the Fayetteville Shale gas-production area, north-central Arkansas.

All photographs by Timothy M. Kresse, U.S. Geological Survey.

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

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## Conversion Factors

### Inch/Pound to SI

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi <sup>2</sup> )	259.0	hectare (ha)
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

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

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ).



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## Abstract

The Mississippian Fayetteville Shale serves as an unconventional gas reservoir across north-central Arkansas, ranging in thickness from approximately 50 to 550 feet and varying in depth from approximately 1,500 to 6,500 feet below the ground surface. Primary permeability in the Fayetteville Shale is severely limited, and successful extraction of the gas reservoir is the result of advances in horizontal drilling techniques and hydraulic fracturing to enhance and develop secondary fracture porosity and permeability. Drilling and production of gas wells began in 2004, with a steady increase in production thereafter. As of April 2012, approximately 4,000 producing wells had been completed in the Fayetteville Shale.

In Van Buren and Faulkner Counties, 127 domestic water wells were sampled and analyzed for major ions and trace metals, with a subset of the samples analyzed for methane and carbon isotopes to describe general water quality and geochemistry and to investigate the potential effects of gas-production activities on shallow groundwater in the study area. Water-quality analyses from this study were compared to historical (pregas development) shallow groundwater quality collected in the gas-production area. An additional comparison was made using analyses from this study of groundwater quality in similar geologic and topographic areas for well sites less than and greater than 2 miles from active gas-production wells.

Chloride concentrations for the 127 groundwater samples collected for this study ranged from approximately 1.0 milligram per liter (mg/L) to 70 mg/L, with a median concentration of 3.7 mg/L, as compared to maximum and median concentrations for the historical data of 378 mg/L and 20 mg/L, respectively. Statistical analysis of the data sets revealed statistically larger chloride concentrations ( $p$ -value  $< 0.001$ ) in the historical data compared to data collected

for this study. Chloride serves as an important indicator parameter based on its conservative transport characteristics and relatively elevated concentrations in production waters associated with gas extraction activities. Major ions and trace metals additionally had lower concentrations in data gathered for this study than in the historical analyses. Additionally, no statistical difference existed between chloride concentrations from water-quality data collected for this study from 94 wells located less than 2 miles from a gas-production well and 33 wells located 2 miles or more from a gas-production well; a Wilcoxon rank-sum test showed a  $p$ -value of 0.71.

Major ion chemistry was investigated to understand the effects of geochemical and reduction-oxidation (redox) processes on the shallow groundwater in the study area along a continuum of increased rock-water interaction represented by increases in dissolved solids concentration. Groundwater in sandstone formations is represented by a low dissolved solids concentration (less than 30 mg/L) and slightly acidic water type. Shallow shale aquifers were represented by dissolved solids concentrations ranging upward to 686 mg/L, and water types evolving from a dominantly mixed-bicarbonate and calcium-bicarbonate to a strongly sodium-bicarbonate water type.

Methane concentration and carbon isotopic composition were analyzed in 51 of the 127 samples collected for this study. Methane occurred above a detection limit of 0.0002 mg/L in 32 of the 51 samples, with concentrations ranging upward to 28.5 mg/L. Seven samples had methane concentrations greater than or equal to 0.5 mg/L. The carbon isotopic composition of these higher concentration samples, including the highest concentration of 28.5 mg/L, shows the methane was likely biogenic in origin with carbon isotope ratio values ranging from -57.6 to -74.7 per mil. Methane concentrations increased with increases in dissolved solids concentrations, indicating more strongly reducing conditions with increasing rock-water interaction in the aquifer. As such, groundwater-quality data collected for this study indicate that groundwater chemistry in the shallow aquifer system in the study area is a result of natural processes, beginning with recharge of dilute atmospheric precipitation and evolution

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of observed groundwater chemistry through rock-water interaction and redox processes.

### Introduction

Gas production in the Fayetteville Shale area of north-central Arkansas has provided important economic benefits for the State and the individual counties (University of Arkansas, 2008); however, local citizens and citizen groups have voiced numerous concerns regarding potential public health and environmental effects associated with gas production. Issues important to citizens include potential effects to surface-water and groundwater quality, noise, traffic, road damage, and air pollution. These concerns parallel those voiced in other newly developed shale-gas production areas throughout the country, where oil and gas development is moving into communities where residents have no prior history and experience with these activities and the potential effects to their local resources, infrastructure, health, and culture (New York Times, variously dated).

One of the most common concerns is related to perceived degradation of groundwater quality in domestic wells. Appropriate groundwater-quality data to address groundwater concerns are lacking, and up through the summer of 2010, no water-quality sampling had been performed to confirm or deny anecdotal evidence of groundwater contamination in Arkansas from gas-production activities. The purpose of this study by the U.S. Geological Survey, in cooperation with the Arkansas Natural Resources Commission, Arkansas Oil and Gas Commission, Duke University, Faulkner County, Shirley Community Development Corporation, the University of Arkansas at Fayetteville, and the U.S. Geological Survey Groundwater Resources Program, was to sample groundwater from domestic wells, document groundwater quality and geochemistry, and investigate potential effects to groundwater quality from gas-production activities in Faulkner and Van Buren Counties, Arkansas.

The Mississippian Fayetteville Shale serves as an unconventional gas reservoir across north-central Arkansas. The thickness of the Fayetteville Shale ranges from approximately 50 to 550 feet and varies in depth from approximately 1,500 feet to 6,500 feet below the ground surface (Southwestern Energy, 2012). Primary permeability in the Fayetteville Shale is very low, as is typical of dense shales, and economic extraction of gas has been made possible by advances in horizontal drilling and hydraulic fracturing of the formation, which are techniques that enhance secondary fracture porosity and permeability and maximize connectivity and gas yield to the production well (King, 2012). These technological advancements have made possible hydrocarbon production from formations that previously were not economically viable drilling targets and have expanded oil and gas industry operations into areas where such operations did not exist. Shale gas development in Arkansas began in 2004, and production has increased steadily thereafter. As of April

2012, approximately 4,000 producing gas wells had been completed in the Fayetteville Shale (Arkansas Oil and Gas Commission, 2012).

Gas-well drilling and completion activities in the Fayetteville Shale have the potential to affect water quality in shallow aquifers through the loss of fluids used in every step of gas production, including drilling, hydraulic fracturing, and storage and handling of flowback water. Transport pathways for surface-derived contaminants include potential leakage from earthen pits used to store drilling, hydraulic fracturing, and flowback fluids, leakage from pipes, and losses from pond overflows and spills during transport (King, 2012). Water contamination can possibly be associated with hydraulic fracturing through changes in the permeability of the shale gas formation and overlying geological units because of the hydraulic fracturing process, migration of hydraulic fracturing fluids through existing vertical fractures that connect to the shallow aquifer (Warner and others, 2012), and, more likely, upward migration of gas and pressurized fluids through poorly cased and grouted sections of the shale-gas well bore (Atlantic Council, 2011; King, 2012). Hydraulic fracturing in a properly cased and cemented wellbore has been cited as the lowest risk for shallow groundwater contamination in the entire well-development process (King, 2012). The potential for migration of fracturing fluids can increase where the target formation is shallower, thus reducing the separation distance between the gas-production zone and the shallow groundwater, or where increased hydraulic connectivity exists through deep faulting zones (Warner and others, 2012).

### Purpose and Scope

The purpose of this report is to describe general water quality and geochemistry of shallow groundwater in the Fayetteville Shale gas-production area in north-central Arkansas and evaluate the potential effects, if any, from activities related to shale-gas drilling and production. Groundwater wells were sampled during 2011 in two counties of north-central Arkansas: Van Buren County and Faulkner County. This report presents and assesses field and inorganic water-quality data, including major ions, trace metals, methane gas, and selected isotopes. Any constituents, notably organic compounds, that might have been added to fracturing fluids for gas drilling were not analyzed for this study.

### Description of Study Area

The study area is located in north-central Arkansas in Van Buren and Faulkner Counties; four of the sampling locations were slightly outside of these two counties but near to the county lines (fig. 1). The Fayetteville Shale gas-production area is approximately 2,500 square miles, and wells sampled for this study were distributed across an approximate area of 850 square miles or about one-third of the total gas-production area.

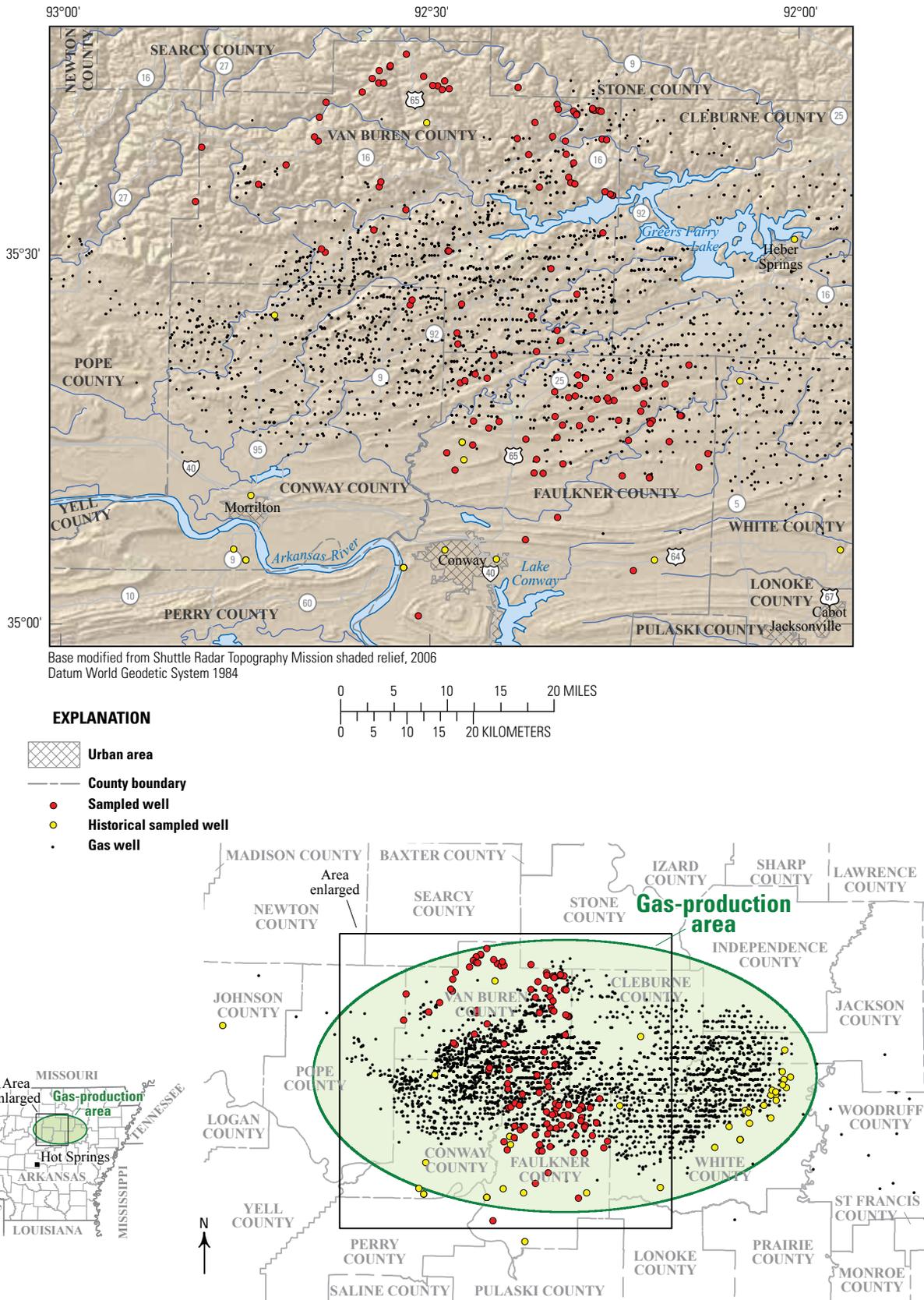


Figure 1. Location of the Fayetteville Shale study area sampling sites and gas-production wells.

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The study area is characterized by a rugged and mountainous landscape to the north and rugged and rolling landscape to the south. Van Buren County is mostly rural with a population density of 24 persons per square mile and has an economy dominantly based on small industry, cattle farming, and tourism (U.S. Census Bureau, 2012a). Although Faulkner County has a much larger population density of 175 persons per square mile, three colleges, and comparatively larger towns than Van Buren County, Faulkner County remains 50 percent rural (U.S. Census Bureau, 2012b). As such, both counties have outlying rural areas where water is supplied solely by domestic water wells.

### Overview of Hydrogeologic Setting

Surface and subsurface geological formations of interest in the study area are composed of Pennsylvanian and Mississippian sandstone and shale formations with occasional thin limestone units. From oldest to youngest, these formations include the Mississippian Fayetteville Shale and the Boyd, Hale, and Atoka Formations of Pennsylvanian age (fig. 2).

The exposed and shallow subsurface geologic formations serving as local aquifers for Van Buren and Faulkner Counties are a series of dominantly shale and sandstone strata of the Hale, Boyd, and Atoka Formations (fig. 2). Subsurface geology, particularly with respect to lateral facies within the Fayetteville Shale, was poorly defined prior to natural-gas development. The Pitkin Limestone conformably overlies the Fayetteville Shale along the Ozark uplift, but is absent on well logs that were examined in the eastern Arkoma Basin (Ratchford and others, 2006). As such, shales of the Hale Formation rest on top of the Fayetteville Shale, which presented challenges to early mapping activities in selecting the top of the Fayetteville Shale; however, consistent characteristic response on gamma ray, resistivity, and conductivity logs eventually provided confident determination of the contact, allowing for a better definition of the subsurface geology in the gas-production area (Ratchford and others, 2006).

The Fayetteville Shale is a black, fissile, concretionary, clay shale, which contains pyrite and silica replacement fossils in some intervals (McFarland, 2004). The Fayetteville Shale ranges in thickness from 50 to 550 feet in the gas-production area and dips from north to south in the subsurface at altitudes of 0 feet above the National Geodetic Vertical Datum of 1929 (NGVD 29) to -6,500 feet NGVD 29 in the western part of the study area, and approximately -1,500 to -7,500 feet NGVD 29 in the eastern part of the study area. The highly organic-rich facies within the Fayetteville Shale is present in the middle and lower part of the formation. Vitrinite reflectance falls within 1.93 to 5.09 percent, which corresponds to the dry-gas window (Ratchford and others, 2006).

The Hale Formation is made up of two members: the lower is the Cane Hill Member, which is typically composed

of silty shale interbedded with siltstone and thin-bedded, fine-grained sandstone, and the upper is the Prairie Grove Member, which is composed of thin to massive limey sandstone. The Hale Formation is up to 300 feet in thickness (McFarland, 2004). The Cane Hill Member of the Hale Formation is exposed in the extreme northern part of Van Buren County (fig. 2).

The Boyd Formation in its type locality in northwestern Arkansas is formally divided into five members, two of which are limestone. The limestone members are absent in the study area, and the Boyd Formation will be discussed as undifferentiated for purposes of this report. The lower two-thirds of the Boyd Formation consist dominantly of very thin- to thinly-bedded sandstone with shale interbeds. The upper Boyd Formation is dominantly shale with interbedded sandstone that is commonly calcareous; the sandstone units can reach thicknesses of up to 80 feet (Rains and Hutto, 2011). Total thickness for the Boyd Formation can exceed 400 feet in the study area. Exposures of the Boyd Formation are found in northern Van Buren County (fig. 2).

The Atoka Formation in the study area consists of a sequence of thick shales that are interbedded with typically thin-bedded, very fine-grained sandstone. The Atoka Formation is unconformable with the underlying Boyd Formation and can reach a thickness of up to 25,000 feet in the Ouachita Mountains (McFarland, 2004). The Atoka Formation is exposed throughout Faulkner County and the southern part of Van Buren County (fig. 2).

Unlike large regional aquifer systems in Arkansas that yield large quantities of water for multiple uses and span across several States, shallow groundwater in the study area is derived from formations that together comprise the Western Interior Plains Confining System for the underlying Ozarks Plateaus aquifer system. Regionally, geohydrologic properties for the collective formations within this confining system are represented dominantly by low-permeability shale with minor occurrences of relatively permeable sandstone, limestone, and coal (Imes and Emmett, 1994). No one formation within this confining system, even where representing a source of local water supply, forms a distinct aquifer regionally, and the regional designation as a confining unit indicates that on a regional scale these formations impede the vertical flow of water and confine the underlying aquifers.

Locally exposed rocks in the study area have an upper, relatively permeable surface formed by fractures providing secondary permeability, whereas approximately 300 feet below the land surface this situation is contrasted by the consolidated, compacted, and less permeable lower part of the confining system. Generally, groundwater is replenished by precipitation that infiltrates the ground in upland areas and percolates to the water table, where it then flows downgradient toward lowland areas and discharges into perennial streams (Imes and Emmett, 1994). As such, a conceptual groundwater flow model for the study area is one controlled by expansion fractures with limited groundwater storage and yields sufficient for use almost solely as domestic supply, and flow

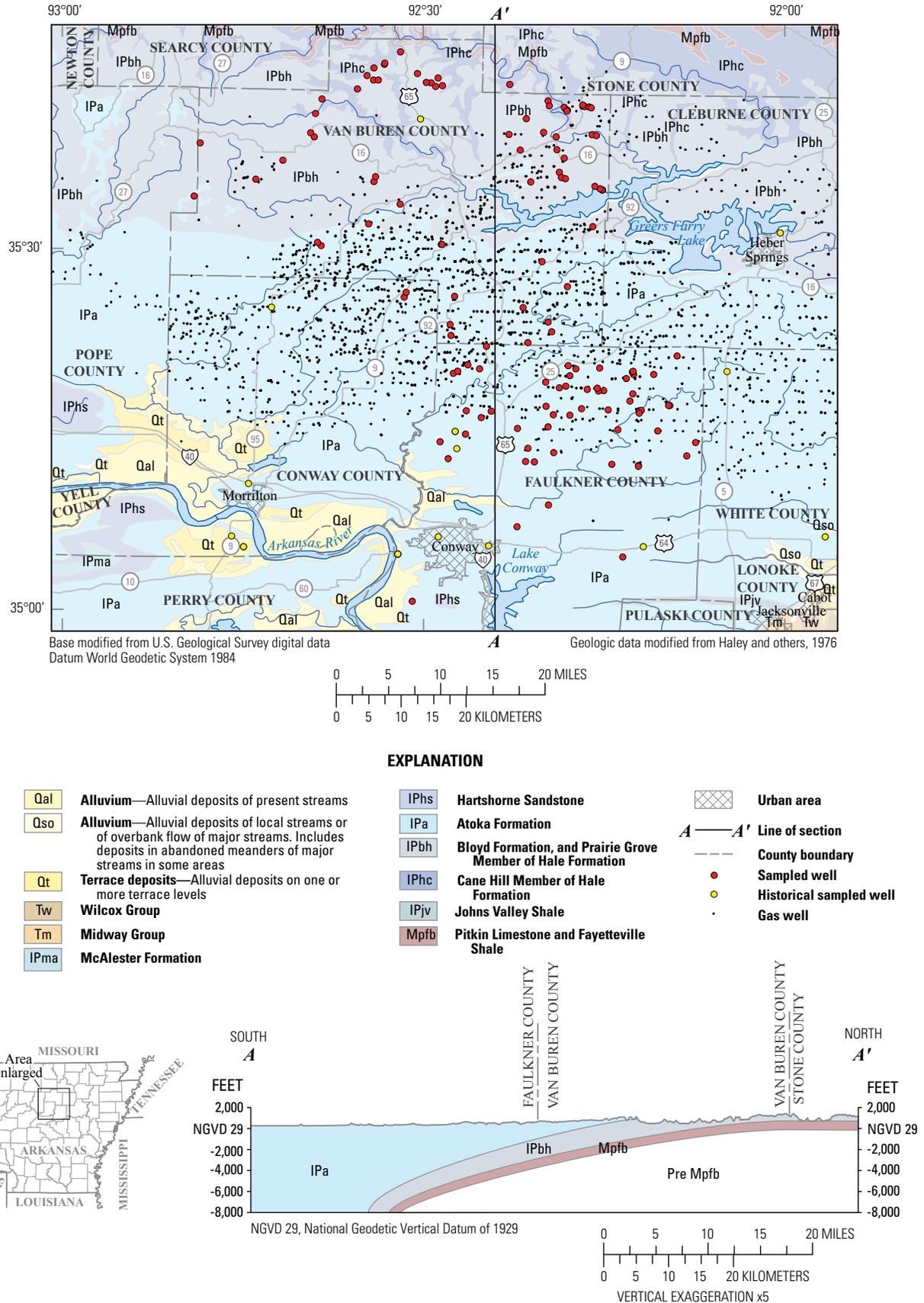


Figure 2. Geology of the Fayetteville Shale study area with generalized geologic cross section.

paths confined by small-scale topographic boundaries with short flow paths from elevated areas to valley floors in small stream systems.

Because of the interbedded nature of the sandstone, siltstone, and shale rocks, the lack of detailed geologic maps, infrequent outcrops, and poor to nonexistent well-log records, difficulties arise when attempting to determine rock type penetrated by individual domestic water wells, in addition to identifying the rock type for the dominant water-producing zone for each well. Water-quality data collected for this study, in addition to field observations, led to a cursory understanding of water type related to possible rock types, and this is discussed in greater detail in the section titled “Rock-Water Interaction.”

Where information was available for domestic wells sampled during this study, water wells range in depth from approximately 25 feet to 385 feet and average approximately 85 feet in the study area. Because the shallow aquifer system is formed in dominantly sandstone and shale strata of the Hale, Bloyd, and Atoka Formations with limited primary porosity, fractures formed from expansion of these rocks with uplift and weathering provide secondary fracture porosity and yields that are sufficient only for domestic water supply. Several wells were described by owners as going dry during excessive pumping, particularly during drought periods, based on information obtained during reconnaissance and sampling activities for this study. Separation distance is often used in shale-gas production areas to describe the distance between the zone of gas production and the zone of freshwater production for shallow wells. Because the maximum known depth for any one well was 385 feet and assuming a conservative estimate of 500 feet for possible deeper wells in the area, then based on the cited production depths for production from the Fayetteville Shale (1,500 – 6,500 feet; Southwestern Energy, 2012), the separation distance between shallow groundwater and the gas producing zone varies from approximately 1,000 to 6,000 feet.

## **Water Sample Collection and Analysis Methods**

Well selection for this study was dictated largely by project cost considerations. To reduce costs in the form of reconnaissance activities, designated persons from each county collected pertinent information from well owners interested in having their well sampled and participating in the study. Because well owners concerned with perceived changes in the quality of water from their well water (taste, appearance, and other aesthetic effects) were the most likely residents to participate, as evidenced in conversations at the time of sampling, the study exhibited some degree of bias toward the sampling of potentially affected wells in the gas-production area.

Water-quality samples were collected from a total of 127 domestic wells; 71 wells in Van Buren County were sampled in July 2011 and 56 wells in Faulkner County were sampled in October and November 2011. All samples were collected by U.S. Geological Survey (USGS) personnel using standard methods described by Radtke and others (2005), Rounds (2006), and Wilde (2004, 2006a, 2006b). Field measurements made at the time of sampling included pH, temperature, and specific conductance. All samples were analyzed for major cations and anions, and trace elements by Duke University, Durham, N.C. Major anions were determined by ion chromatography, major cations by direct current plasma optical emission spectrometry (DCP-OES), and trace-elements by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer (ICP-MS). Dissolved solids concentrations were computed as the sum of the major constituents: calcium, sodium, magnesium, nitrate as nitrogen, sulfate, bicarbonate, silica, and iron.

Additional samples for dissolved methane analysis were collected from 20 wells in Van Buren County and 31 wells in Faulkner County. All samples were collected following an Isotech Laboratories protocol (Isotech Laboratories, Inc., 2012a), and all bottles were supplied by Isotech. After purging the well until stabilization of pH, temperature, and specific conductance, a 5-gallon bucket was filled with water. Sample bottles were filled from the sample supply hose and then immersed in the bucket, where a minimum of two volumes of water was displaced from each bottle prior to capping underwater with a septum cap. This process ensured that no atmospheric methane contamination occurred in the sample bottle. After collection, samples were packed on ice and shipped overnight to the laboratory. Samples from Van Buren County were analyzed by Isotech Laboratories in Champaign, Ill., using chromatographic separation. For samples with sufficient methane, the carbon isotopic ratio ( $^{13}\text{C}/^{12}\text{C}$ ) was analyzed by combustion and dual-inlet isotope ratio mass spectrometry. This ratio is reported as  $\delta^{13}\text{C}$ , in parts per thousand ( $\text{‰}$ , or “per mil”). Detailed laboratory methodology and quality control information is available from Isotech Laboratory, Inc. (2012b). Samples from Faulkner County were analyzed at the Duke Environmental Isotope Laboratory. Methane and  $\delta^{13}\text{C}$  were determined by cavity ring-down spectroscopy (CRDS). Headspace equilibrations and extractions and concentration calculations were performed by a modification of the method of Kampbell and Vandegrift (1998).

Data quality for inorganic chemical constituents was based on laboratory results for performance-evaluation samples provided by the USGS Standard Reference Sample (SRS) program. The USGS distributes SRS samples semi-annually for laboratory performance comparison purposes. Approximately 100 laboratories participated in the SRS program during 2012 (U.S. Geological Survey, 2012a). Results from these laboratories are compiled and evaluated using non-parametric statistics. For each inorganic constituent, the median reported concentration is considered the most

probable value (MPV), and the spread of data is estimated by F-pseudosigma (Fps), which is the interquartile range divided by 1.349. If the data distribution is normal, Fps equals standard deviation for a normal distribution, but is not as strongly affected by outliers. A Z-value is calculated for each result:

$$Z = (\text{lab result} - \text{MPV}) / \text{Fps}$$

If Z is greater than 3 or less than -3, the laboratory result is significantly different from the MPV ( $p < 0.01$ ), and the accuracy of analysis for this constituent at this laboratory is questionable. The Duke University laboratory participated in the spring and fall 2012 SRS events; results of which are shown in appendix 1. Z-values were less than -3 for molybdenum and antimony in the spring and for silver in the fall. Therefore, all results for these three constituents were deleted from the data set discussed in this report, and none of these results were entered into the USGS National Water Information System (NWIS) database (U.S. Geological Survey, 2012b).

Performance-evaluation results were not available for methane and  $\delta^{13}\text{C}$ , so data quality was evaluated based on reproducibility. For Isotech Laboratories, the standard deviation of internal standards for  $\delta^{13}\text{C}$  was 0.081‰ and for duplicates was 0.077‰ for 2011. Methane concentrations in water samples are calculated using Henry's Law from the compositional analysis of methane in the headspace gas. As such, quality control data are available only for methane in the gas phase. The standard deviation of internal standards for methane gas for 2011 by Isotech Laboratory was 0.281 mole percent. For the Duke Environmental Isotopes Laboratory, relative standard deviation of dissolved methane concentrations determined by CRDS on field duplicates was 9.8%. Standard deviation of  $\delta^{13}\text{C}$  measurements determined by CRDS for eight field duplicate samples ranged from a minimum of 0.07‰ to a maximum of 1.0‰ with a mean 0.55‰, resulting in a relative standard deviation of 1.7%. All these results were considered to be an indication of acceptable accuracy.

The non-parametric Wilcoxon rank-sum test analysis (Helsel and Hirsch, 1992) was used to identify significant differences between concentrations in two groups of samples. This analysis does not depend on the distributions of data within each group and is not affected by outliers. For computing the test statistic, censored values are assigned the lowest rank. A p-value of less than 0.05 for the test was considered sufficient evidence of a significant difference between the groups.

Linear correlation was used as a primary means to evaluate the relation between pairs of variables in the historical data set. The squared correlation coefficient ( $R^2$ ),

computed as a value between 0 and 1, is a measure of the percent of variation in one variable that is accounted for by variation in the other variable. The closer  $R^2$  is to 1, where a linear relation is appropriate based upon inspection of the graph, the better the fit and accounting of the variation in the response variable (Helsel and Hirsch, 1992). None of the variables included in this correlation analysis had any censored values.

## Shallow Groundwater Quality and Geochemistry

Numerous challenges exist in defining background groundwater quality and natural variation and range for shallow groundwater constituents in the study area. These challenges include differentiating natural from anthropogenic sources of contamination, identifying sources of potential effects on groundwater quality, identifying transport pathways for potential contaminants, understanding natural variation from chemical reactions and microbially mediated processes in the aquifer, and numerous other variables involved in groundwater contamination studies. Compounding these challenges in the Fayetteville Shale gas-production area is the paucity of existing groundwater-quality data by which to establish background groundwater-quality conditions. Additionally, many existing sources of contaminants are present throughout the area that could affect shallow groundwater quality, including domestic, agricultural, small industrial, and urban sources.

Because little to no monitoring had been conducted prior to drilling and gas production in the study area, interpretation of water-quality data collected from individual wells after gas production relies heavily on comparative analysis. One approach is to compare contaminant source-water chemistry to that of shallow groundwater to establish indicator constituents unique to the source water. The difficulty with this type of comparison is that many of the shallow domestic wells are completed in shale or influenced by shale chemistry, as are waters from the gas-producing formation. Two other comparative analysis approaches include: (1) statistical comparison of historical, pregas development shallow groundwater-quality data collected in the gas-production area to water-quality data collected for this study, and (2) comparison of groundwater-quality data in similar geologic and topographic areas outside of the gas-production area to data collected from wells within the gas-production area. To achieve the most rigorous characterization of groundwater-quality conditions and identify potential changes to water quality, all three of these approaches were applied in this study.

## Historical Groundwater Quality and Geochemistry

Historical groundwater-quality data were retrieved from the USGS NWIS database (U.S. Geological Survey, 2012b) for six counties that contain the bulk of permitted and active gas production wells: Cleburne, Conway, Faulkner, Independence, Van Buren, and White Counties. The NWIS database yielded 43 sites with samples collected from 1951 through 1983 (table 1; appendix 2) prior to any shale-gas drilling activities. No data were noted in Independence County and one of the wells plotted in Johnson County. These data were limited with respect to trace metal chemistry and many of the major ions. The most frequently analyzed constituent was chloride, which can be important as an indicator of migration of production waters into shallow groundwater.

Production water commonly is termed “flowback” or “produced” by the Fayetteville Shale gas industry, which basically are accounting terms used by the industry to denote early and later return of emplaced hydraulic fracturing fluids. Produced water normally is a term reserved for formation water associated with oil and gas reserves that are brought to the surface with oil or gas and must be separated and removed at the surface. Fluid recovery rates following hydraulic fracturing are highest during the first 2-3 weeks, and diminish greatly after that time (King, 2012). Because of the shorter residence time in the producing formation (less rock-water interaction), initial flowback is normally of lower salinity than the low-volume, later-return produced water. The Fayetteville Shale is a dry formation, and yet water brought to the surface

with gas is probably a blend of injected hydraulic fracturing fluids, residual formation salts, and naturally occurring formation brine. The produced water salinity is a key factor to determine the relative proportion of low saline flowback water and typically highly saline formation water. A progressive increase in salinity of the produced water with pumping time of the shale-gas well reflects an increasing fraction of the producing formation water component. Over a longer time period, the saline formation water component consists of a larger fraction of the return flow. This report refers to “flowback water” as an intermediate stage following hydraulic fracturing relative to “produced water” that represents long-term flow fluid production associated with gas production.

Chloride can serve as an early indicator of infiltration of production water into the shallow aquifer system for several reasons: (1) chloride is a conservative constituent in groundwater; it does not react with other minerals or adsorb to clays or organics, and also is highly soluble; and (2) chloride is elevated in gas-production waters associated with the Fayetteville Shale—flowback water has chloride concentrations that vary from approximately 2,500 to 5,000 mg/L and produced water can range upward to greater than 20,000 mg/L (Arkansas Oil and Gas Commission, unpublished data, April 4, 2012), similar to that of seawater. All but one historical sample included analysis of chloride.

The highest chloride concentration from the historical dataset was 378 mg/L; two samples had concentrations greater than 200 mg/L, and six samples had concentrations between 100 and 200 mg/L. The median chloride concentration was 20 mg/L (table 1). Nineteen of the historical samples were from wells identified as completed in the Atoka

**Table 1.** Descriptive statistics for selected water-quality constituents from historical data collected from 1951 through 1983 from 43 wells in the Fayetteville Shale gas-production area, north-central Arkansas.

[ $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter;  $\mu\text{g}/\text{L}$ , micrograms per liter; <, less than]

Parameter	Number of samples	Number of censored values <sup>1</sup>	Minimum	25th percentile	Median	75th percentile	Maximum
pH (standard units)	27	0	5.9	6.6	6.8	7.4	8.2
Conductance ( $\mu\text{S}/\text{cm}$ )	41	0	32	236	378	602	1,840
Calcium (mg/L)	23	0	7.9	19	23	43	107
Magnesium (mg/L)	23	0	0.30	5.8	9.1	20	211
Sodium (mg/L)	23	0	2.0	13	24	51	145
Bicarbonate (mg/L)	24	0	6.0	71	125	256	980
Sulfate (mg/L)	26	0	0.8	4.4	10	22	255
Chloride (mg/L)	42	0	1.6	5.6	20	64	378
Iron ( $\mu\text{g}/\text{L}$ )	20	10	<10	<10	< 10	85	6,300
Manganese ( $\mu\text{g}/\text{L}$ )	8	0	10	58	120	188	600

<sup>1</sup>Data are reported as less than a censoring limit.

Formation, whereas 18 samples were associated with the Boyd Formation. The median chloride concentration for samples from the Atoka Formation was 22 mg/L, which was similar to the median chloride concentration of 19 mg/L for samples from the Boyd Formation. Statistical analysis of the difference in chloride concentrations for samples from each formation using Wilcoxon rank-sum test analysis (Helsel and Hirsch, 1992) revealed no significant differences ( $p$ -value = 0.78) based on geology, suggesting that the groundwater geochemistry in each formation results from similarities in the rock type and mineralogy for these formations (that being interbedded sandstone and shale).

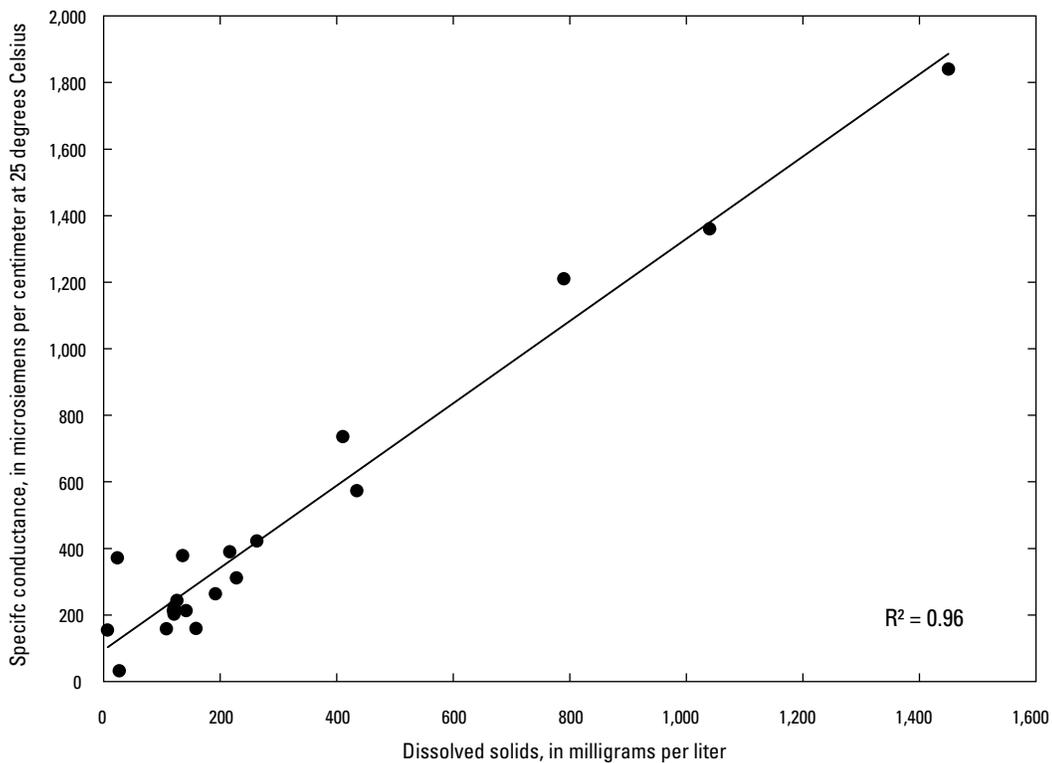
A full suite of major ions was available for only 16 of the 43 samples from the historical data. A comparison of calculated dissolved solids concentration and specific conductance demonstrated a good linear relation with a  $R^2$  value of 0.96 (fig. 3). More importantly, a cation/anion balance was calculated for the 16 samples with complete major ion chemistry with all but 2 samples having less than 3.5 percent charge-balance error. A linear relation was established between total cations and total anions in milliequivalents per liter with a  $R^2$  value of 1.00 and a slope of 0.99 (fig. 4). These quality-assurance checks warrant a high degree of confidence in the laboratory analyses. The groundwater generally is characterized by bicarbonate as the

major anion, ranging from a calcium-bicarbonate to sodium-bicarbonate water type. Three of the samples had chloride as the major anion (greater than 50 percent of the total anions in milliequivalents per liter), and one sample was a calcium-sulfate water type.

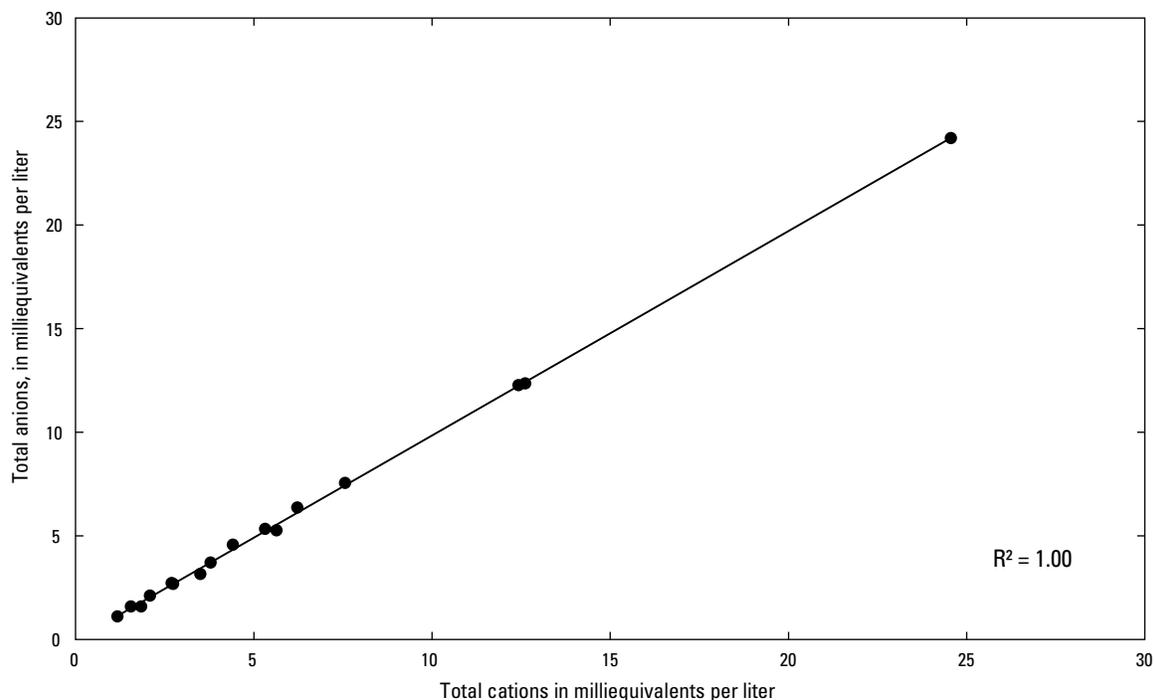
## Current Study Groundwater Quality and Geochemistry

### Groundwater Quality and Spatial and Temporal Comparative Analysis

The inorganic water-quality analyses for 127 groundwater samples collected for this study were compared to national drinking water standards (U.S. Environmental Protection Agency, 2009). A statistical summary of selected constituents from the water-quality data collected for this study is reported in table 2, and a complete list of the water-quality analyses is available in appendix 3. The primary drinking-water maximum contaminant level for nitrate (10 mg/L as nitrogen) was exceeded in 2 of the 127 samples. Sources of nitrate in the study area observed during reconnaissance and sampling activities included septic systems, animal waste, and fertilizers. Secondary drinking-water standards were exceeded



**Figure 3.** Relation between dissolved solids concentrations and specific conductance values for historical data (1951–83) in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 4.** Relation between total cation and anion milliequivalent concentrations for historical data (1951–83) in the Fayetteville Shale gas-production area, north-central Arkansas.

for iron in 55 samples and manganese in 74 samples, with standards of 0.3 mg/L and 0.05 mg/L, respectively. These secondary standards are non-enforceable limits based on aesthetic qualities of water including taste, odor, and staining properties of water. Iron and manganese are found in most rock types, have solubility characteristics that are controlled dominantly by changes in reduction-oxidation (redox) reactions, and are found in elevated concentrations in aquifers throughout Arkansas (Kresse and Fazio, 2002). Chloride has a secondary drinking-water standard of 250 mg/L; all concentrations were less than this concentration established for taste threshold. In general, shallow groundwater in Van Buren and Faulkner Counties is of good quality with respect to use as a drinking-water source, though taste and staining problems are unavoidable where untreated water contains elevated concentrations of iron, manganese, and other metals as a result of geochemical and microbiological processes in the aquifer.

Water-quality data collected for this study were compared to historical analyses, and comparisons using water-quality data for this study also were made between wells located less than 2 miles and wells located greater than 2 miles from active gas-production wells to assess potential effects from gas-production activities. Chloride, as stated in the previous section, can be an important indicator constituent and would be one of the first breakthrough constituents in a plume

of contamination from gas-production waters. Chloride concentrations from data collected for this study ranged from approximately 1.0 mg/L to 70 mg/L, with a median concentration of 3.7 mg/L (table 2). Boxplots were constructed from data collected for this study and from historical analyses for an overall comparison of water quality between the two sets (fig. 5), and generally show higher concentrations for all major ions in the historical analyses compared to analyses determined from this study. Maximum and median chloride concentrations in groundwater samples collected for this study were substantially lower than historical groundwater maximum and median chloride concentrations (tables 1 and 2). Application of the Wilcoxon rank-sum test showed significantly higher chloride concentrations ( $p$ -value < 0.001) in the historical data compared to chloride concentrations for this study. Other major ion and trace metal concentrations also were lower in samples collected for this study than in samples collected historically (tables 1 and 2; appendixes 2 and 3).

Much of the difference for the two data sets can be attributed to sampling a larger geographic area for the historical data (six counties compared to two counties for this study), although sampling sites for both data sets were collected from the same shallow aquifer system (dominantly the Atoka and Bloyd Formations). Only eight historical sites are located in the study area, which provide too small

**Table 2.** Descriptive statistics for selected water-quality constituents from data collected in 2011 from 127 wells in Van Buren and Faulkner Counties, Arkansas.[ $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius;  $\text{mg}/\text{L}$ , milligrams per liter;  $\mu\text{g}/\text{L}$ , micrograms per liter; <, less than]

Parameter	Number of samples	Number of censored values <sup>1</sup>	Minimum	25th percentile	Median	75th percentile	Maximum
pH (standard units)	127	0	4.2	5.9	6.5	7.1	8.6
Conductance ( $\mu\text{S}/\text{cm}$ )	127	0	13	101	250	339	909
Calcium ( $\text{mg}/\text{L}$ )	127	16	<2.1	5.6	17	35	88
Magnesium ( $\text{mg}/\text{L}$ )	127	4	<0.6	2.1	4.2	8.5	46
Sodium ( $\text{mg}/\text{L}$ )	127	20	<2.1	3.4	9.1	24	159
Bicarbonate ( $\text{mg}/\text{L}$ )	127	4	<2.0	47	130	196	527
Sulfate ( $\text{mg}/\text{L}$ )	127	10	<0.5	1.6	4.3	9.7	151
Chloride ( $\text{mg}/\text{L}$ )	127	0	0.94	2.3	3.7	7.6	70
Iron ( $\text{mg}/\text{L}$ )	127	38	<0.05	<0.05	0.19	0.51	5.7
Manganese ( $\mu\text{g}/\text{L}$ )	127	29	<15	19	96	286	4,370

<sup>1</sup>Data are reported as less than a censoring limit.

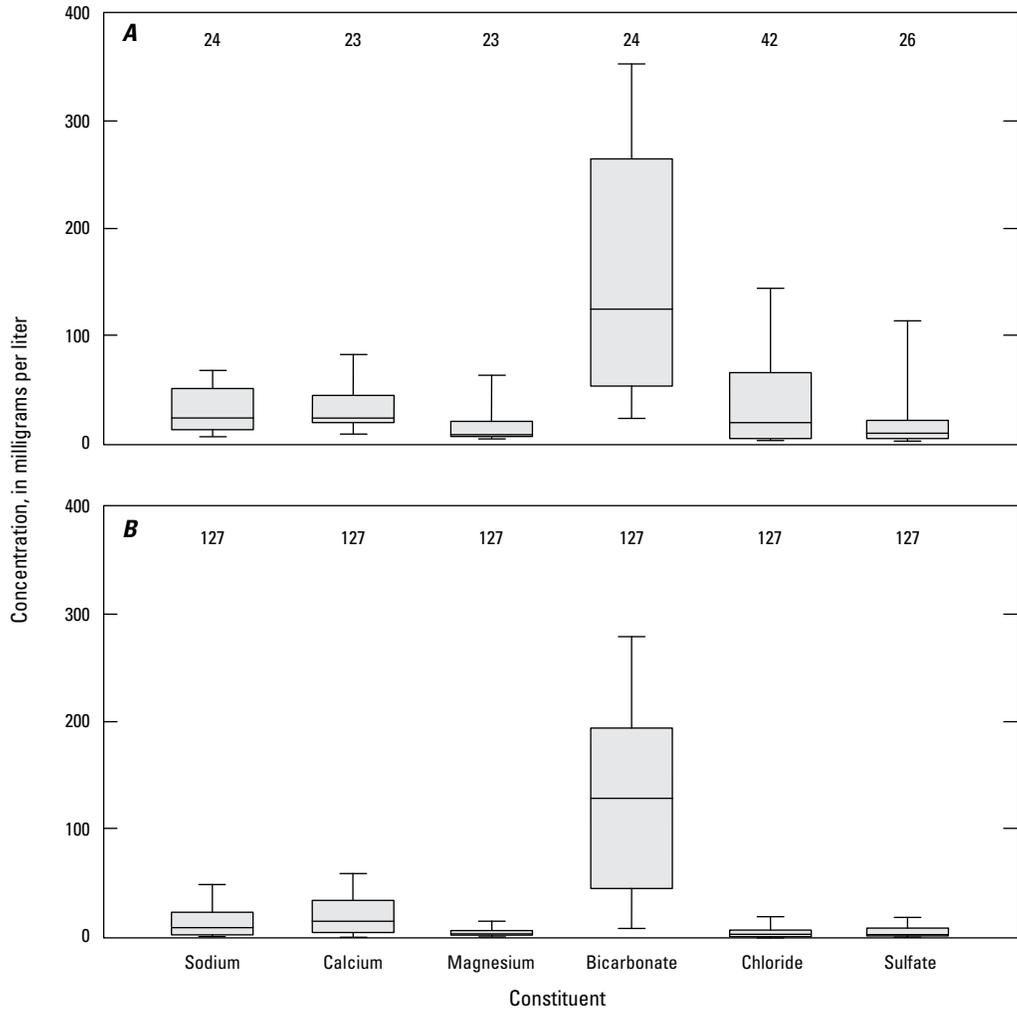
a number of samples for a meaningful statistical analysis. The historical data for the larger spatial extent of the gas-production area provide a snapshot of the range and variability of groundwater geochemistry, but should not be used for strict comparison to current data as the same wells were not sampled for both periods—thus no inference should be made that water quality has improved since the earlier period represented by the historical data. The historical data contain concentrations for chloride (and other constituent concentrations) that are larger than that of the new data and reveal the wider range of constituent concentrations that occur in groundwater from similar rock formations in the gas-production area of north-central Arkansas. As such, the historical data can be used to establish a general benchmark with which to examine possible variations in the water chemistry induced from natural processes and compare them to potential effects from contamination by shale-gas production waters.

In addition to comparison of historical water-quality data to data collected for this study, comparisons of chloride concentrations collected for this study were made between 94 domestic-well sample sites less than 2 miles from active gas-production wells (63 wells less than 0.5 mile from a gas-production well; 29 of which were less than 0.25 mile from a gas-production well) and 33 domestic-well sample sites greater than 2 miles (maximum distance of 16 miles) from gas-production wells. The 2-mile threshold was chosen as a conservative estimate for the length of possible plume migration based on average and maximum gasoline-contaminant plume lengths of 0.06 and 1.5 miles,

respectively (Ruiz-Aguilar and others, 2003; Falta, 2004), in addition to the fact that average and maximum length of horizontally-drilled and fractured lateral wells are 0.8 and 1.5 miles, respectively (Arkansas Oil and Gas Commission, 2012). A Wilcoxon rank-sum test showed no significant difference between the two groups ( $p$ -value = 0.71). The median chloride concentration for wells less than 2 miles from the nearest production wells was 3.7  $\text{mg}/\text{L}$ ; whereas, the median chloride concentration for wells greater than 2 miles from the nearest production well was 3.7  $\text{mg}/\text{L}$ . As such, using two comparative analysis methods (historical and distance) as initial screening tools for potential effects to water quality from gas-production activities within the western third of the shale-gas production area showed no evidence of migration of gas-production water into shallow groundwater based solely on the data gathered from the wells sampled in this study.

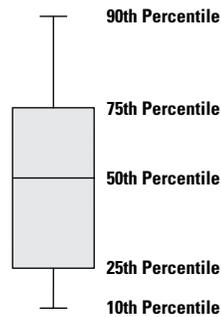
## Groundwater Geochemistry and Geochemical Evolution

In addition to the comparative analysis discussed in the above section, geochemical analyses can help identify potential outliers in the data and potential effects from gas-production activities as compared to natural geochemical processes. Data from individual well sites may be inferred to represent the chemistry of groundwater at a specific location along a groundwater flow path, and together with data from numerous other wells, provide information on geochemical evolution in the shallow groundwater system in the study area.



**EXPLANATION**

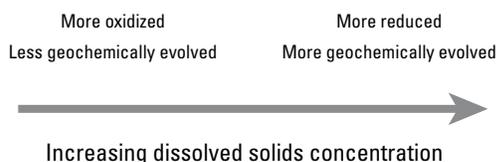
24 Number of values



**Figure 5.** Selected constituents for *A*, historical data and *B*, data from 127 wells in the Fayetteville Shale gas-production area, north-central Arkansas.

Describing the geochemical evolution of groundwater resulting from physical, chemical, and microbial processes in shallow aquifer systems with respect to increasing rock-water interaction provides a framework to understand geochemical and hydrological processes. A valuable proxy for increased rock-water interaction is increasing dissolved solids concentrations, particularly constituents that are not derived from only evapotranspiration of recharged water. Thus, how individual chemical constituents or relations between constituents change with increasing dissolved solids concentrations can reveal an overall pattern of geochemical conditions, water-chemistry controls, and specific chemical and biochemical reactions along a continuum of increased rock-water interaction. Chemical reactions are predicated on traveltime (slower traveltime leads to increased opportunity for rock-water processes to occur), availability of reactive minerals, electron donors and acceptors, charged substrates, and other variables (Appelo and Postma, 1999). The following section investigates relations between various chemical constituents to establish one possible model for the evolution of geochemistry in the shallow groundwater system in the study area.

Rainwater in Arkansas has a mean pH value of 4.7 and average dissolved solids concentrations below 3 mg/L (Kresse and Fazio, 2002). Rainwater is highly undersaturated with respect to most mineral phases and as such dissolves minerals as it percolates through soil and moves through aquifer host rock, thus increasing the dissolved solids concentration of soil pore water and groundwater. In aquifers with sufficient labile organic matter and reduced mineral phases such as pyrite, as is typical of surficial shale formations in the study area, oxygen carried to the subsurface with the percolating rain water is consumed as carbon and mineral phases are oxidized, and groundwater will tend to become more reduced along the flow path (Chapelle, 2001). Geochemical evolution of shallow groundwater in the study area can be visualized to represent a transition with increased rock-water interaction (represented by increasing dissolved solids concentration) of less geochemically evolved groundwater to more geochemically evolved groundwater and from a more oxidized water to a more reduced water (fig. 6).



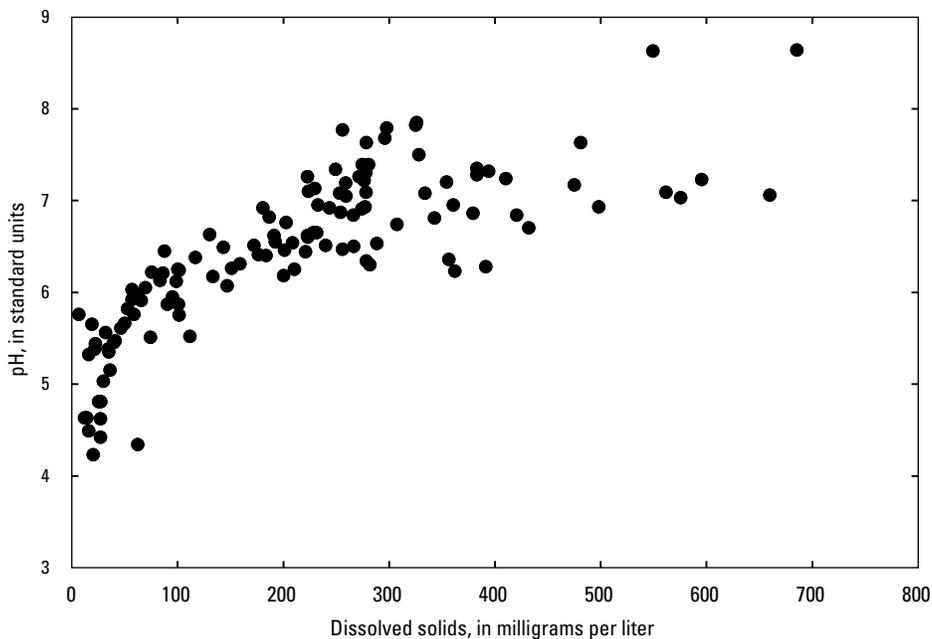
**Figure 6.** Conceptual model of geochemical evolution of groundwater with increased rock-water interaction represented by increasing dissolved solids concentrations.

## Rock-Water Interaction

Most aquifer systems in Arkansas exhibit a strongly calcium- or sodium-bicarbonate groundwater type (Arkansas Department of Environmental Quality, 1996). As limestone and other carbonate rocks are dissolved along the flow path, acids are buffered and pH increases concurrently with dissolved load. This process may be illustrated graphically by the relation between increasing pH values and dissolved solids concentrations (fig. 7). The interpretation that this process is controlled by dissolution of carbonate rock is supported by the relation between bicarbonate and dissolved solids concentration (fig. 8a), which shows a positive linear relation of increasing bicarbonate concentrations with increasing dissolved solids concentrations. Generally increasing, but weakly linear, trends were noted for sulfate and chloride compared to increasing dissolved solids concentrations, as well. Sulfate concentrations generally are less than 20 mg/L for dissolved solids concentrations less than 300 mg/L, with elevated concentrations up to 151 mg/L occurring at dissolved solids concentrations greater than 300 mg/L (fig. 8b); chloride concentrations greater than 20 mg/L occur only where dissolved solids concentrations exceed 200 mg/L (fig. 8c) with concentrations upward to 70 mg/L.

The relation of major cations (calcium, magnesium, and sodium) with dissolved solids concentrations shows that, similar to bicarbonate, calcium (fig. 8d) and magnesium (fig. 8e) correlate more tightly with increasing dissolved solids concentrations than sodium (fig. 8f); carbonate rocks dominantly have calcium and magnesium as the major cations constituting rock chemistry. Summing calcium with magnesium yielded only a slight improvement for the relation and linearity of fit with increasing dissolved solids concentrations. A better relation should be expected after combining the constituents based on the strong linearity of the bicarbonate-dissolved solids relation, if dissolution of a calcium plus magnesium carbonate is proposed as the dominant source for these constituents. Cation exchange—specifically the exchange of calcium for sodium on the clay mineral exchange sites—can be shown to account for the variability of calcium and sodium in solution and the poor relation between calcium and magnesium with dissolved solids.

In addition to dissolution and precipitation of minerals in the aquifer source rock, cation exchange is one of the more important rock-water interactions affecting chemical constituents in solution. This process occurs where groundwater is in contact with clays and weathered shale surfaces (Langmuir, 1997). Clays carry a negative electrostatic charge, which gives these materials a measurable capacity to hold cations. Cation exchange capacity (CEC) is highly dependent upon pH—higher pH gives a higher CEC; thus dissolution of carbonate minerals increases CEC by buffering pH and drives exchange of calcium for sodium as calcium and magnesium are released during carbonate mineral dissolution. Generally, cations with higher valence will preferentially



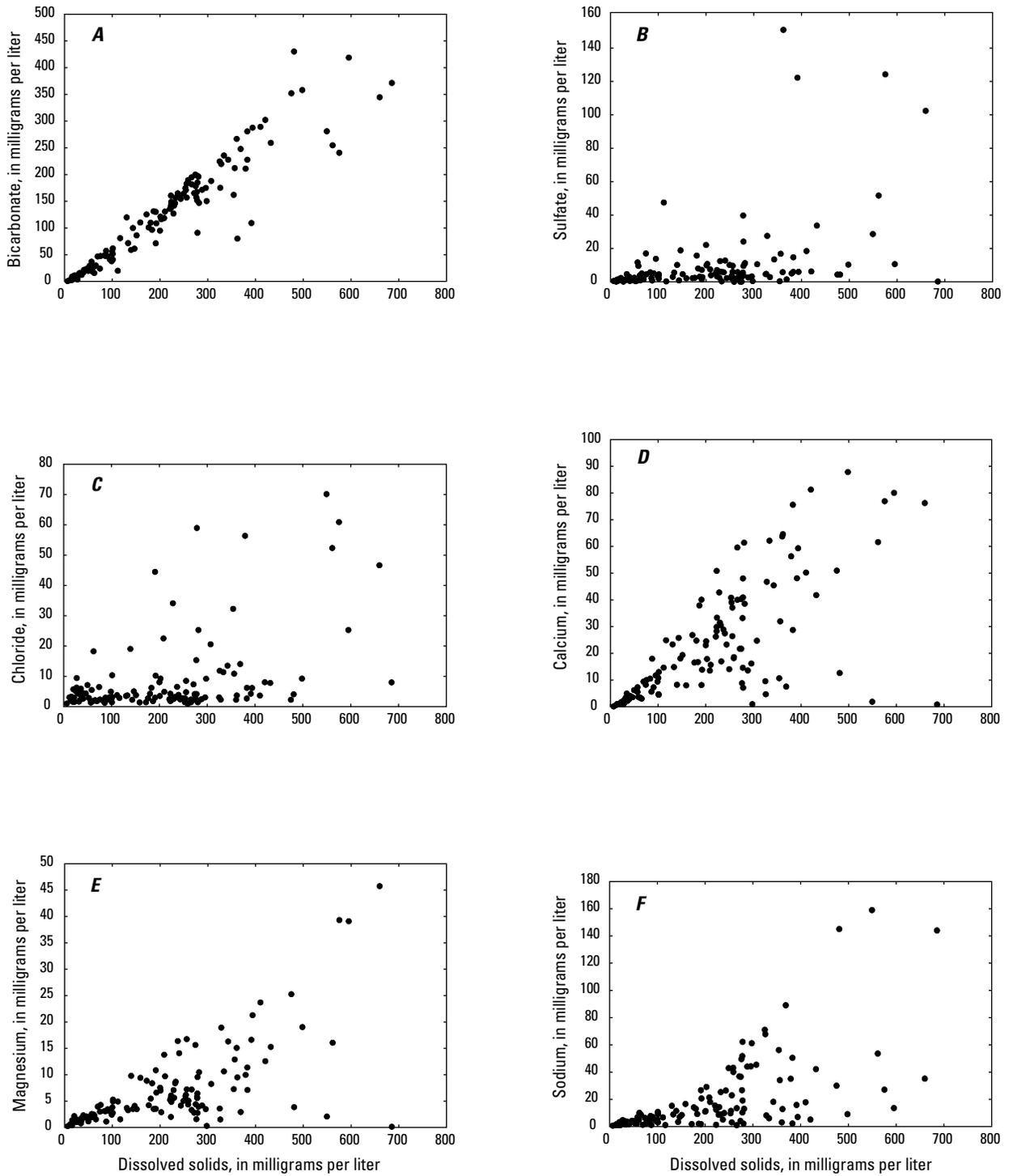
**Figure 7.** Relation between dissolved solids concentrations and pH values from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

occupy exchange sites over those of a lower valence. As such, calcium ions in solution ( $2^+$  charge) will replace sodium ions ( $1^+$  charge) at the exchange site, releasing the sodium ion into solution. As this process continues along a flow path, more and more calcium ions exchange for sodium at the exchange site, resulting in an increase of sodium ions in solution at the expense of calcium.

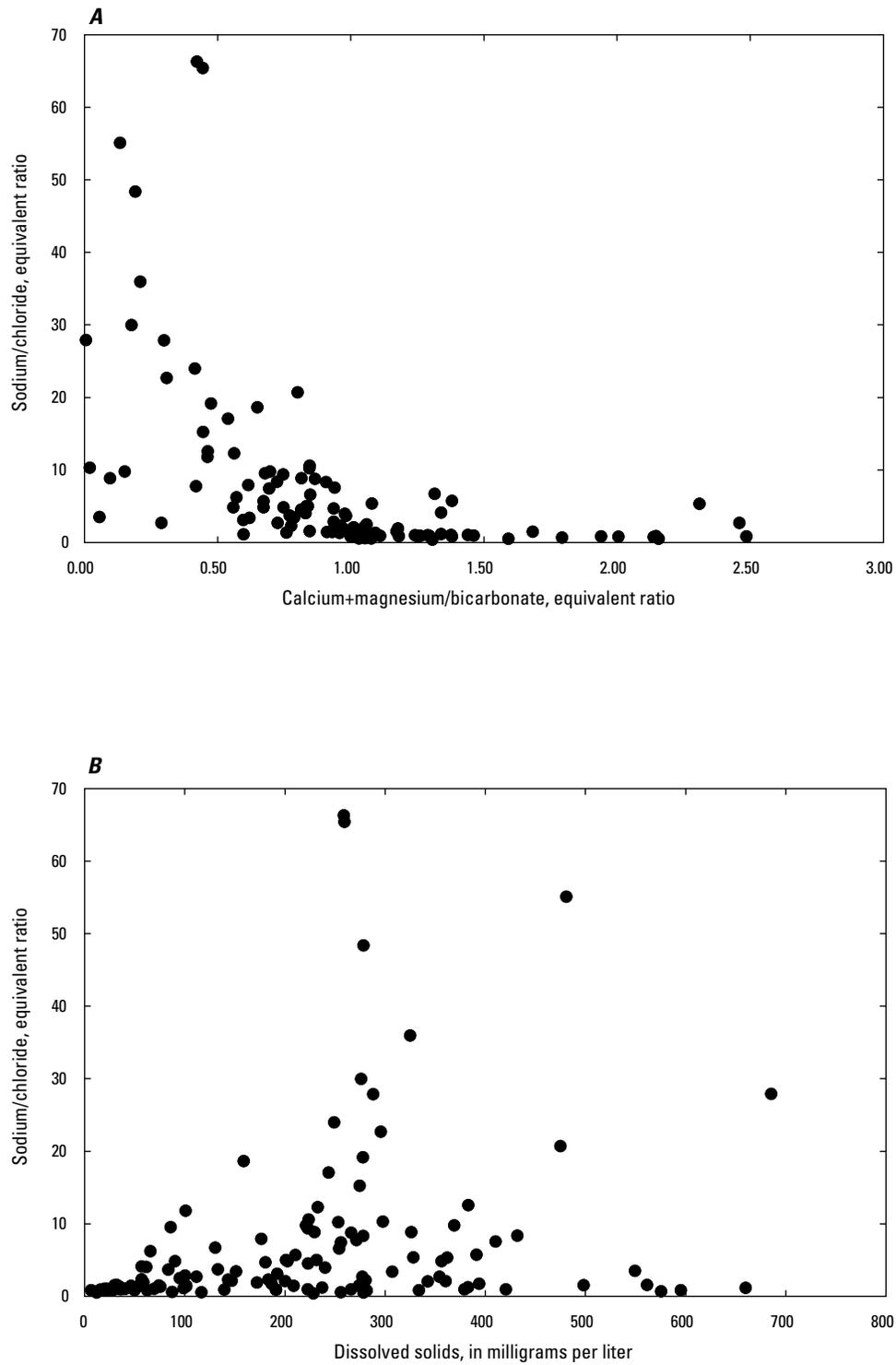
Concentrations reported in milliequivalents per liter take both the charge and weight of an individual ion into consideration, allowing a comparison of the number of ions in solution. Dissolution of a sodium-chloride salt in water will yield an equal number of sodium and chloride ions in solution, thus having an equivalent ratio of one; similar stoichiometric relations also hold for dissolution of carbonate rock and other minerals. Assuming most sodium and chloride is derived from dissolution of the parent salt and calcium, magnesium, and bicarbonate are derived from dissolution of carbonate minerals, a comparison of ratios for the common cations and anions theoretically would plot at 1.0 on both axes, given that no reactions take place, adding or removing ions to or from solution. In aquifer systems, however, rock-water interaction can appreciably alter the chemical composition of the groundwater.

A review of the relation between sodium/chloride and calcium plus magnesium/bicarbonate equivalent ratios suggests that cation exchange is actively occurring in the shallow aquifer (fig. 9a), with increasing sodium/chloride

ratios resulting in decreasing calcium plus magnesium/bicarbonate ratios. Sodium concentration in solution will continue to increase as cation exchange progresses; chloride is a conservative ion that does not participate in reactions in the system and remains invariant in concentration unless further dissolution occurs. As such, increasing cation exchange results in sodium/chloride ratios greater than 60 times what is expected from simple dissolution of sodium-chloride salts (fig. 9a). The increase in sodium from cation exchange observed in samples for this study was large enough to result in 28 samples being categorized as sodium-bicarbonate water type. With respect to chemical evolution along the continuum of increasing rock-water interaction in the aquifer, sodium/chloride ratios are found to increase with increasing dissolved solids concentrations (fig. 9b). For low dissolved solids waters (less than approximately 50 mg/L dissolved solids), the sodium/chloride ratio is approximately 1.0, suggesting dissolution of a sodium-chloride salt with no cation exchange occurring between calcium and sodium in the aquifer system. The ratios begin to increase markedly at dissolved solids concentrations greater than 50 mg/L, showing that cation exchange progresses with increases of sodium in solution with increasing rock-water interaction. Sodium/chloride ratios near 1.0 for the lower dissolved solids concentration waters are attributed to sandstone as the source rock, as explained in the following section.



**Figure 8.** Relation between dissolved solids concentrations and *A*, bicarbonate, *B*, sulfate, *C*, chloride, *D*, calcium, *E*, magnesium, and *F*, sodium concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

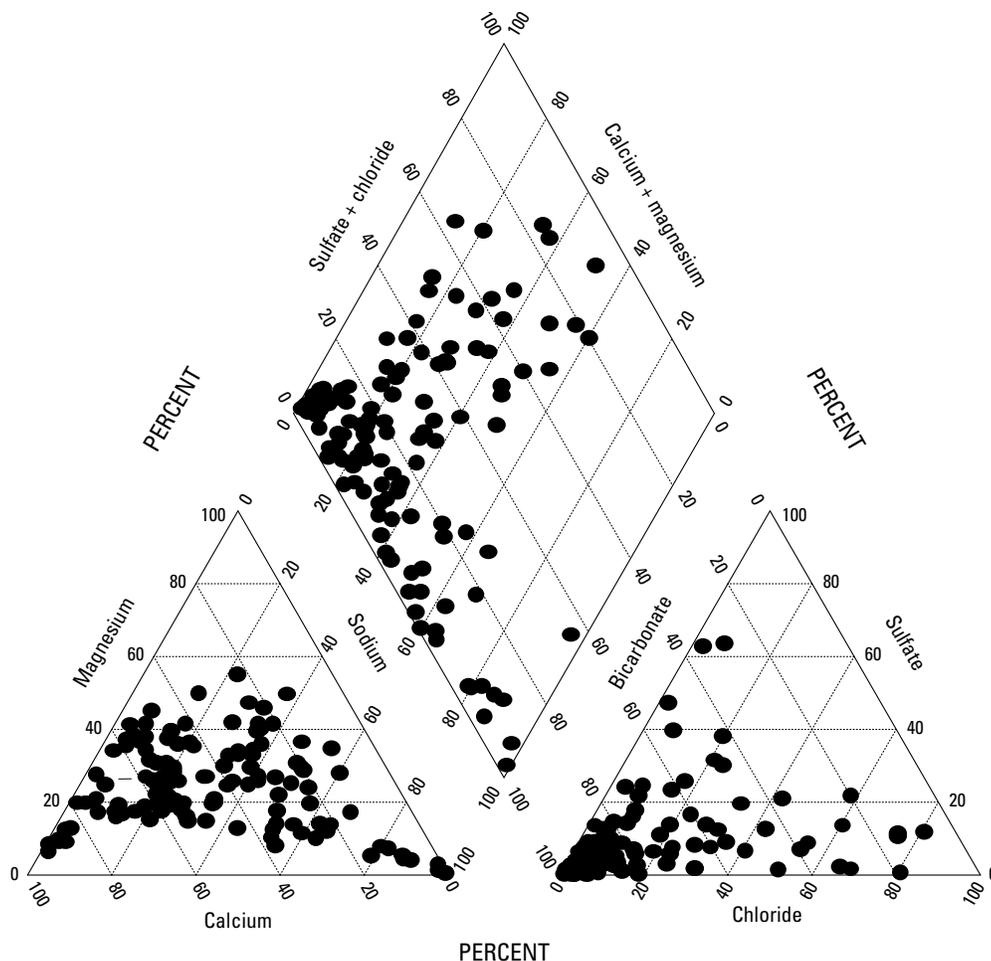


**Figure 9.** Relation between sodium/chloride ratios and *A*, calcium plus magnesium/bicarbonate ratios constructed using milliequivalent concentrations and *B*, dissolved solids concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

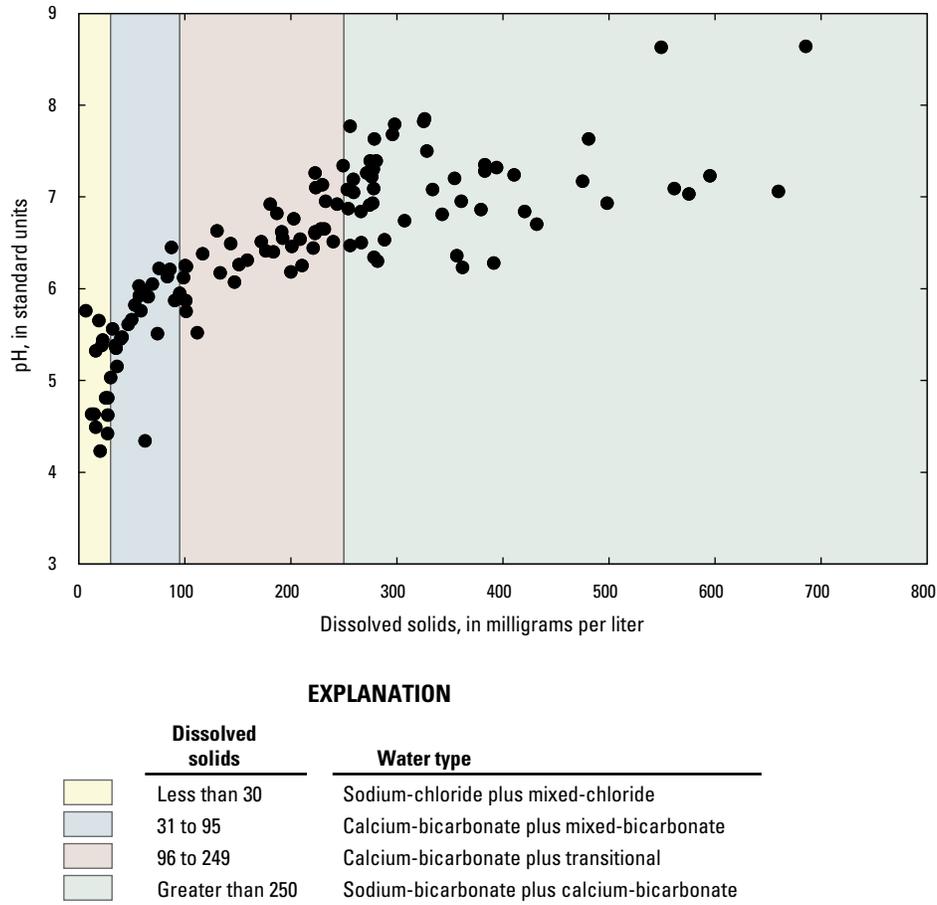
Water type was determined for each of the samples using milliequivalent concentrations to calculate percentage of total cations for each of the major cations (calcium, magnesium, and sodium) and percentage of total anions for each of the major anions (bicarbonate, chloride, and sulfate). A trilinear diagram was constructed to show the general distribution and trend for the major cations and anions for each sample (fig. 10). The trilinear diagram, particularly the lower left triangle, shows the general distribution of ions and an overall trend from a calcium-bicarbonate type water to a sodium-bicarbonate water.

A general plotting of water types along the defined continuum of increasing dissolved solids concentrations shows that the major ion chemistry of the shallow groundwater is not random but follows a predictable regular pattern based on rock type and rock-water interaction. The pH values were very low, ranging from 4.2 to 5.8, in groundwater samples

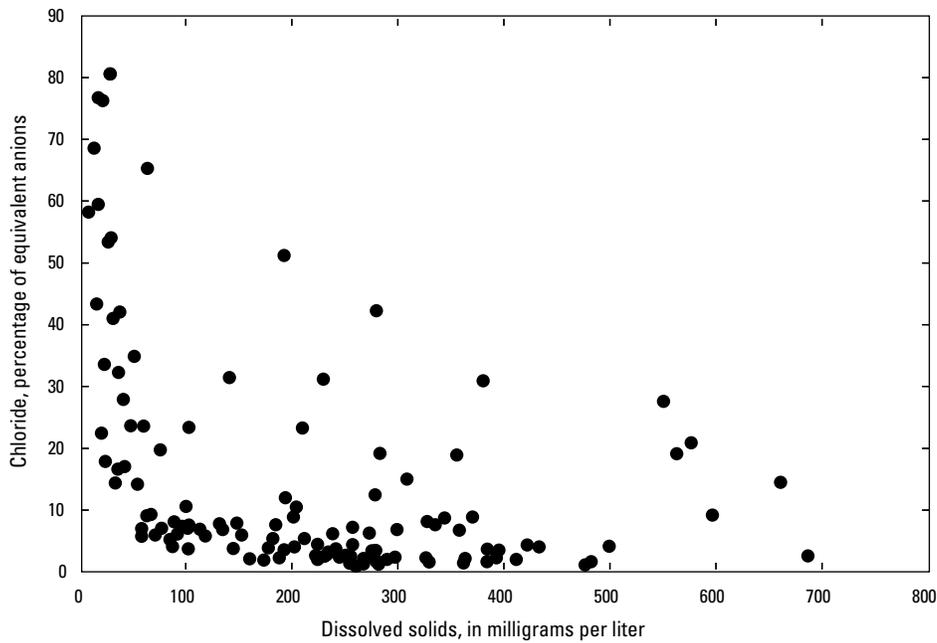
with dissolved solids concentrations less than approximately 30 mg/L (fig. 11). In addition, these low dissolved solids samples are represented dominantly by water types with chloride as the major anion (all but two samples with chloride as the major anion occur where dissolved solids concentration was less than 30 mg/L) and, together with the low dissolved solids and low pH values, resemble an evaporated rainwater with addition of silica and minor trace metals (Kresse and Fazio, 2002). A comparison of percent chloride (of the total anions in milliequivalents per liter) and increasing dissolved solids concentrations shows the dominance of chloride in the lower dissolved solids groundwater, whereas percent chloride generally declines as carbonate dissolution, and resultant increasing bicarbonate concentrations, begins to dominate the chemistry of the groundwater with increasing dissolved solids concentrations (fig. 12).



**Figure 10.** Percentage distribution of major ions from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 11.** Relation between dissolved solids concentrations and pH values with a depiction of the evolution of chemical water types from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 12.** Relation between dissolved solids concentration and chloride as percent of total anions in milliequivalents per liter from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

Many of the sites from which the lower dissolved solids samples were derived had outcropping sandstone formations nearby, and the wells appear to have been completed in sandstone rock with water chemistry that corroborates this observation. The sandstone is assumed to have little carbonate material in the host rock or weathered soil above the sandstone, thus having little to no buffering capacity and little opportunity for cation exchange as discussed in the preceding paragraph. Some samples were below the mean pH of 4.7 for rainwater in Arkansas (Kresse and Fazio, 2002), possibly as a result of entrainment of carbon dioxide in the soil zone leading to formation of carbonic acid. Similar findings were noted to the south of the study area near Hot Springs, Arkansas, where well-defined, thick sequences of quartz formations and shale formations allowed differentiation of groundwater chemistry from each rock type. Samples taken from wells completed in the quartz formations revealed a soft, acidic groundwater (7 of 11 samples with pH values less than 4.7; 3 samples less than 4.0), indicating a quartz source rock with little to no buffering capacity (Kresse and Hays, 2009). The interpretation established for groundwater data gathered in Hot Springs is thought to explain the observed low dissolved solids groundwater chemistry in Van Buren and Faulkner Counties.

Shale formations in the study area have abundant carbonate material, the source sediments for these rocks being accumulated in marine environments (McFarland, 2004). Groundwater moving through shale rock is quickly buffered along a given flow path with increasing pH and dissolved solids concentrations with dissolution of carbonate minerals. The groundwater samples with dissolved solids concentrations greater than 30 mg/L had bicarbonate as the dominant anion with the exception of three samples, two of which were a sodium-chloride water type and one calcium-sulfate water type. Samples with dissolved solids concentrations between approximately 31 and 95 mg/L exhibited a mixture of calcium-bicarbonate (each ion greater than 50 percent of total cations and anions, respectively) and mixed-bicarbonate (no dominance of calcium, magnesium, or sodium) water types (fig. 11).

For samples with dissolved solids concentrations between approximately 96 and 249 mg/L, calcium-bicarbonate was the dominant water type (24 of 40 of the samples), whereas the majority of the remaining samples had increasing sodium percentages and sodium as one of two major cations, thus representing a transitional water toward sodium as the dominant cation. For all samples with dissolved solids concentrations greater than 250 mg/L, 20 of 51 samples were a strongly sodium-bicarbonate water type—each constituent greater than 50 percent of the total cations or anions, respectively—with sodium percentages ranging from 52 to 99 percent of the total cations. The remaining samples were calcium-bicarbonate water types with a few transitional water types (fig. 11).

In summary, the model proposed for the predominant rock-water interactions controlling major-ion groundwater chemistry observed in the study area is primarily mineral dissolution and cation exchange. Rock-water interaction alters the chemical composition of shallow groundwater in the study area along a continuum represented by increasing dissolved solids concentrations. Groundwater samples from the relatively carbonate-free sandstone formations are represented by a low dissolved solids concentration (less than 30 mg/L), slightly acidic water type. Sandstones are predominated by low-solubility quartz with little or no carbonate minerals to buffer pH, resulting in the characteristic water chemistry. Groundwater from the shale formations in the study area contain abundant soluble carbonate minerals, which undergo dissolution to produce groundwater with a maximum dissolved solids concentrations of 686 mg/L and water type evolving from a dominantly mixed-bicarbonate and calcium-bicarbonate to a strongly sodium-bicarbonate water type as cation exchange reaches a maximum. This understanding of the chemical evolution of groundwater with increased opportunity for rock-water interaction has important implications to the occurrence of natural methane in study area groundwater, which is discussed in the following section.

### Reduction-Oxidation Processes

The subsurface environment hosts thriving microbial ecosystems, and these microbes sustain their life functions by participating in electron transfer through redox reactions. The microbes orchestrate electron transfer using organic carbon as an electron donor substrate or energy source and a sequence of decreasingly energy-yielding terminal electron acceptors, including in order of reaction energy: oxygen, nitrate, manganese oxides, iron oxyhydroxides, sulfate, and carbon dioxide (Appelo and Postma, 1999). These microbially mediated redox reactions affect many geochemical changes on solid-phase material and dissolved constituents in groundwater. Shale formations are rich in labile organic material, which drives the reduction of oxygenated water by aerobic and fermentation bacteria. Hydrogen is a waste product of the fermentation bacteria, which is then used by respiring microorganisms including nitrate reducers, manganese reducers, iron reducers, sulfate reducers, and methanogens (Chapelle, 2001). It is generally observed in both stream sediments and aquifers that redox processes proceed sequentially from the highest energy yield downward (Appelo and Postma, 1999). Therefore, as oxygenated water enters an aquifer system with abundant organic matter, oxygen will first be used as a terminal electron acceptor, followed by nitrate, manganese oxide, iron oxyhydroxide, sulfate, and finally carbon dioxide with the generation of methane. Depending on the available supply of electron donors and electron acceptors, redox zonation can stop at any point along this continuum or proceed through each sequence to methane production.

Evidence for various steps in the redox zonation described above is found in several relations observed for various dissolved constituents. Electron potential and hydrogen ion concentrations are commonly used surrogates to establish the redox zonation for groundwater within an aquifer system (Chapelle, 2001). Such data were not available for this study; however, general water-quality data often can provide strong corollary evidence for redox conditions. Evidence for reduction of iron and manganese oxides (and oxyhydroxides) often is inferred where each dissolved species has a concentration greater than 0.5 mg/L, as oxidized forms are extremely insoluble. Iron concentrations range upward to 5.7 mg/L with a median concentration of 0.19 mg/L, and manganese concentrations range upward to 4.4 mg/L with a median concentration of 0.12 mg/L. As such, elevated concentrations of these metals in solution indicate the presence of iron and manganese reduction throughout the shallow aquifer system. Elevated iron (fig. 13a) and manganese (fig. 13b) concentrations were mutually exclusive with elevated nitrate concentrations, confirming predicted redox zonation in the aquifer—nitrate-reducing bacteria take advantage of the more energetically favorable nitrate reduction reaction, thereby out-competing the manganese- and iron-reducing bacteria until dissolved nitrate is effectively depleted. In cases where both manganese and iron exceed 0.5 mg/L, nitrate is absent; whereas nitrate concentrations greater than 0.5 mg/L occur only where manganese and iron concentrations are less than 0.5 mg/L, indicating that onset of manganese and iron reduction has not occurred. Nitrate concentrations demonstrated an inverse relation with pH (fig. 14), suggesting that nitrate reduction is dominant only in the low dissolved solids concentration, low pH waters.

Evidence for sulfate reduction, while not directly measured by presence of sulfide gas species or hydrogen-ion concentration for this study, is found anecdotally in reports of sulfide odors from domestic well owners during reconnaissance and sampling activities. An interesting relation between iron and dissolved solids concentrations does provide some corollary geochemical evidence of sulfate reduction in the shallow aquifer system. In general, dissolved iron is absent (less than 0.5 mg/L) for dissolved solids concentrations less than 60 mg/L; it was shown that reduction of nitrate is dominant for these lower dissolved solids waters. Iron concentrations generally increase with increases in dissolved solids concentrations from 60 mg/L up to approximately 290 mg/L, at which point iron concentrations steadily begin to decline to low and nondetectable concentrations for dissolved solids concentrations exceeding 500 mg/L (fig. 15a); arsenic concentrations (fig. 15b) behave similarly. Sulfate reduction in the study area is theorized to dominate over iron reduction for dissolved solids concentrations greater than approximately 290 mg/L, and free sulfide in solution combines with both iron and arsenic in solution to precipitate as iron-sulfide minerals (with

varying amounts of arsenic and other trace metals), which are extremely stable in reducing conditions.

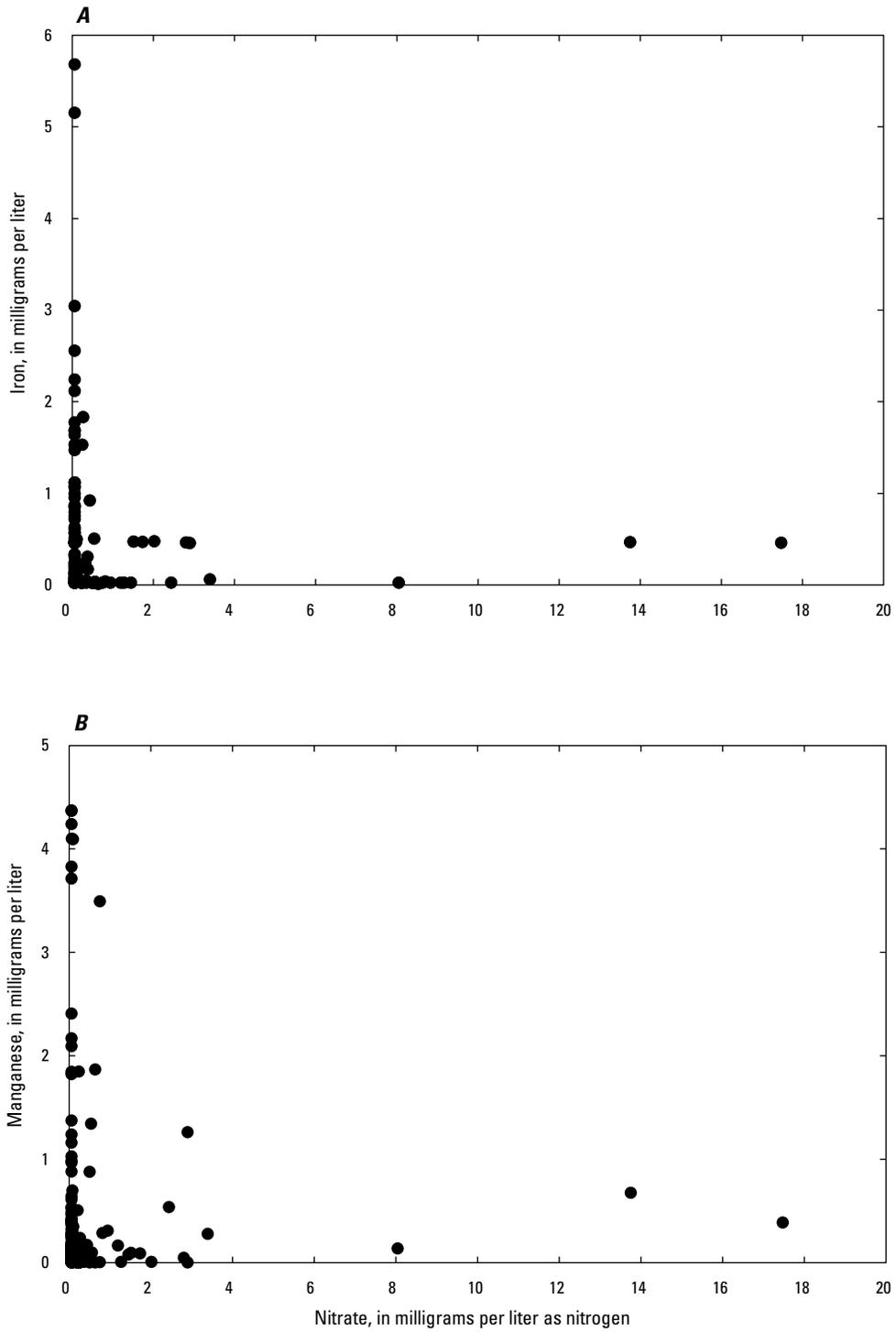
### Methane and Carbon Isotopes

Methane concentration and carbon isotopic composition were analyzed in 51 of the 127 samples collected for this study to investigate the potential for contamination of the shallow aquifer system by upward migration of methane along natural pathways (faults, fractures and other permeable avenues) and artificially created pathways associated with gas production (for example, a poorly cemented annulus section of a gas-production well). Osborn and others (2011) showed average and maximum methane concentrations in drinking wells in Pennsylvania increased to 19.2 and 64 mg/L, respectively, with proximity to gas-production wells, whereas dissolved methane in wells at neighboring nongas-production sites averaged 1.1 mg/L. Average carbon stable isotope,  $^{13}\text{C}/^{12}\text{C}$  ( $\delta^{13}\text{C}$ ), values of dissolved methane in shallow groundwater for the Osborn and others (2011) study were significantly less negative for active than for nonactive gas-production sites ( $-37 \pm 7$  per mil (‰) and  $-54 \pm 11$  ‰, respectively; *p*-value less than 0.0001).

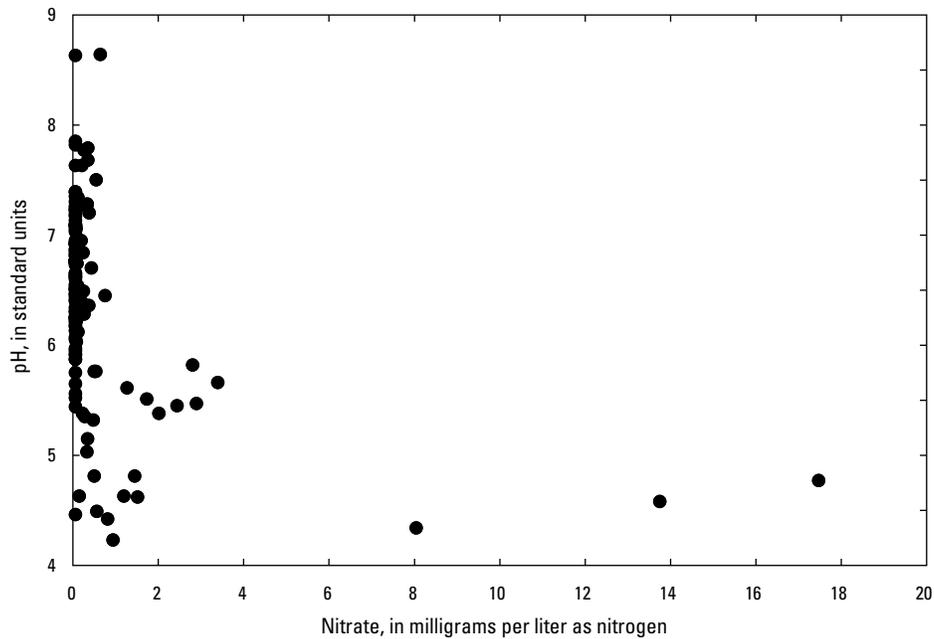
Methane is encountered in gas basins and shallow aquifers and can be derived from thermally or microbially driven reactions, generating thermogenic or biogenic gas, respectively (Bernard and others, 1977; Fuex, 1977; Schoell, 1980; Rice and Claypool, 1981; Grossman and others, 1989). Mixing of the forms can occur as highly mobile gas migrates upward along primary or secondary permeable pathways. Thermogenic gas is produced by the thermal decomposition (cracking) of longer chain hydrocarbon kerogen or oil at high burial temperatures. Biogenic gas is generated in the subsurface under anaerobic conditions by fermentative bacteria, acetogenic bacteria, and the Archaea methanogens.

Depending upon the particular biogenic reaction pathway, the carbon isotopic composition of biogenic methane can be very light—enriched in  $^{12}\text{C}$  and depleted in  $^{13}\text{C}$ —yielding very low  $\delta^{13}\text{C}$  values. Typical biogenic methane  $\delta^{13}\text{C}$  values are less than  $-55$ ‰; thermogenic methane  $\delta^{13}\text{C}$  values typically are higher than  $-55$ ‰ (Schoell, 1980; Rice and Claypool, 1981; Grossman and others, 1989; Aravena and Wassenaar, 1993; Whiticar, 1999), providing a very useful indicator of gas source or origin. Zumberge and others (2012) analyzed 100 gas samples from gas-production wells in the Fayetteville Shale and reported  $\delta^{13}\text{C}$  values ranging from  $-41.9$  to  $-35.0$ ‰.

Methane was detected above the detection limit of 0.0002 mg/L in 32 of the 51 samples for this study, with concentrations ranging upward to 28.5 mg/L. Seven samples had methane concentrations greater than or equal to 0.5 mg/L. The carbon isotopic composition for all methane concentrations greater than 0.5 mg/L for this study, including the highest concentration of 28.5 mg/L, showed the methane was likely biogenic in origin with  $\delta^{13}\text{C}$  values ranging from  $-57.6$  to  $-74.7$ ‰.



**Figure 13.** Relation between nitrate and *A*, iron and *B*, manganese concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 14.** Relation between nitrate concentrations and pH values from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

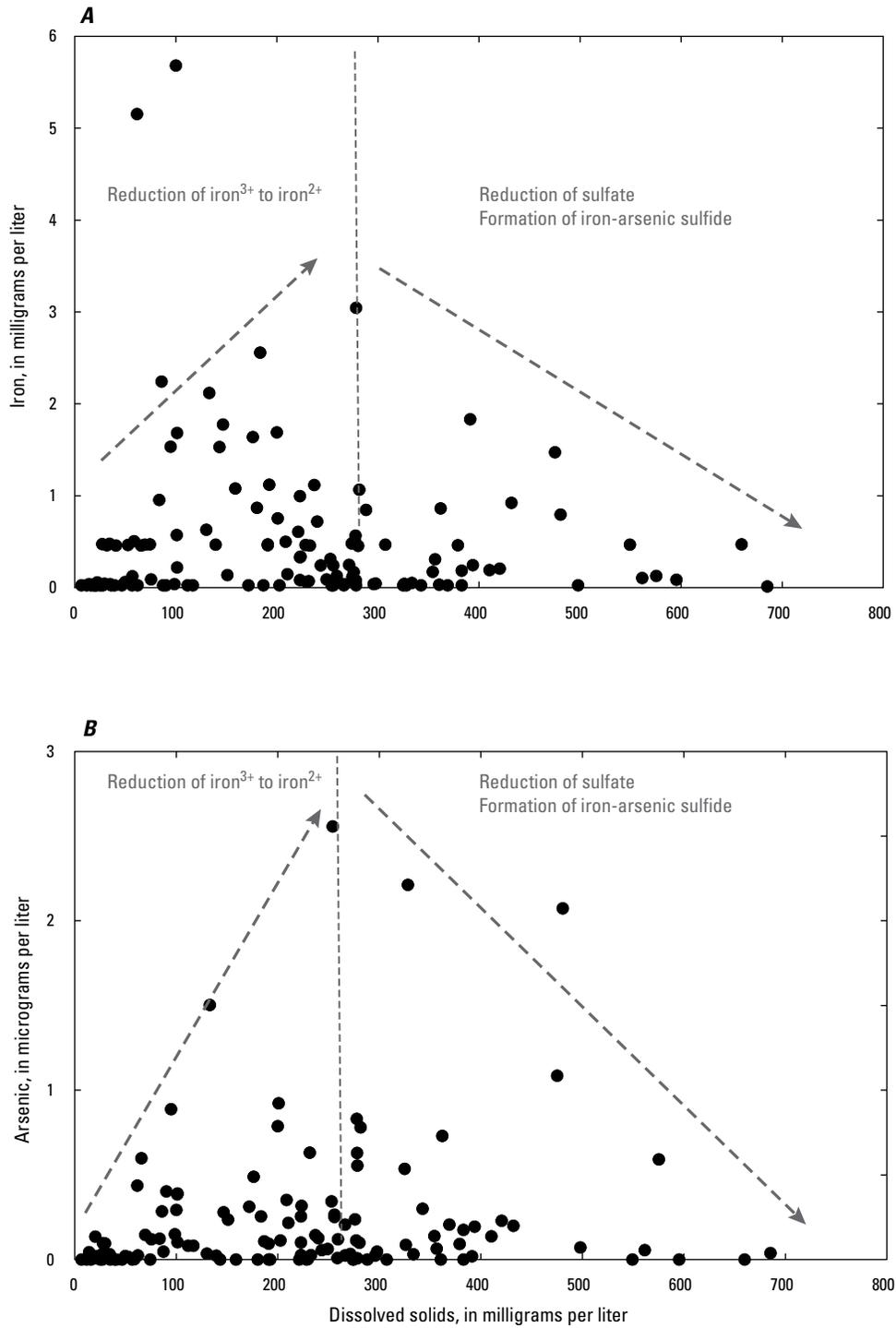
Of note to the discussion of the evolution of groundwater along a continuum of increased rock-water interaction in the aquifer, increases in methane concentrations were related to increases in dissolved solids concentrations (fig. 16), with the highest methane concentration of 28.5 mg/L occurring in conjunction with the highest dissolved solids concentration of 686 mg/L. As such, methane production follows the continuum established earlier and illustrated in figure 6—increased rock-water interaction in the shallow aquifer allows more time for geochemical processes, including cation exchange and a transition from a calcium- to a sodium-bicarbonate water type, and redox zonation transitioning through oxygen consumption, reduction of nitrate, iron and manganese oxides, sulfate, and eventually to the production of biogenic methane.

Although carbon isotope analyses revealed that methane in seven samples exhibiting concentrations greater than 0.5 mg/L was biogenic in origin, thermogenic methane signatures were noted in five samples that exhibited extremely low methane concentrations ranging from 0.012 to 0.324 mg/L with  $\delta^{13}\text{C}$  values ranging from -31.96 to -49.87. Two of these five wells were at distances of 5.2 and 7.3 miles from the nearest active production well.

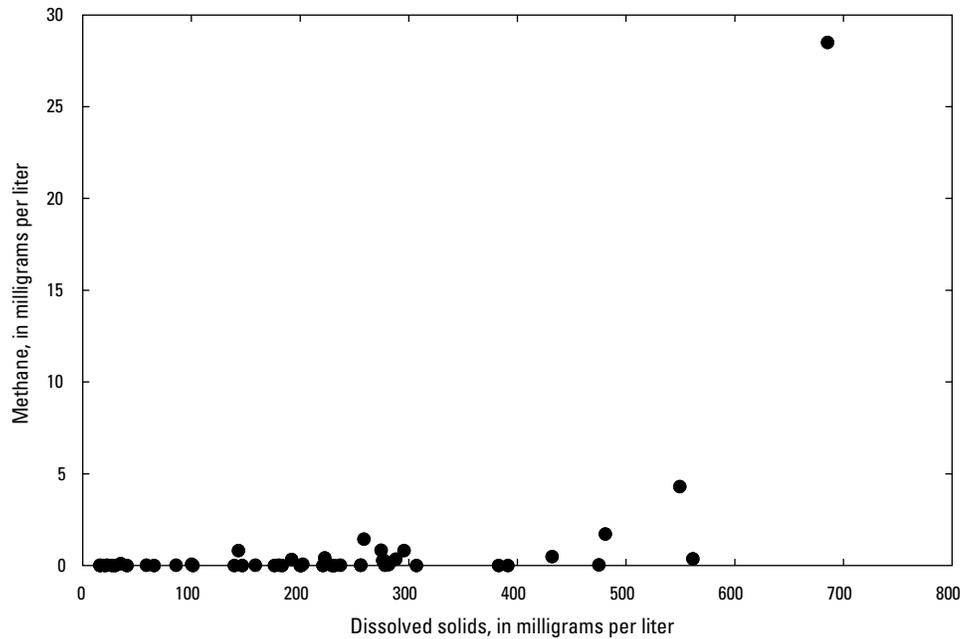
The most likely transport pathway for anthropogenically induced release of thermogenic methane into shallow groundwater occurs where methane gas travels up the well bore and out into shallow formations along poorly cemented annulus sections of the well bore near the surface. This situation has been described and confirmed by the gas

industry (Atlantic Council, 2011; King, 2012) and in soil-gas studies, where methane concentrations in soils were noted to occur near production pads and diminish to nondetectable concentrations at distances of greater than 30 feet from the pad (Naftz and others, 1998), indicating that the most likely anthropogenic release of methane is near gas-well bores.

Thermogenic methane can migrate to shallow aquifers and to the surface naturally, following pathways offered by faults, fractures, and other permeable zones (Warner and others, 2012; King, 2012). In conventional natural gas reservoirs, thermogenic methane migrates upward and is trapped by a confining low-permeability zone. If a confining layer is not 100 percent effective, methane can seep to the land surface through fractures and other permeable pathways. Documented cases of thermogenic natural gas in aquifers abound in areas overlying gasfields with reports of methane in groundwater prior to any drilling activities (Lohman, 1937) and anecdotes of flaring of tapwater being common prior to any gas development throughout the country (King, 2012). In addition, one of the primary exploration techniques for new, unexplored basins is the use of gas “sniffers” that detect methane leaking into the atmosphere in aerial overflights (Jones and others, 1999; Plummer, 1993). The fact that low levels of thermogenic methane were found in groundwater from domestic wells sampled for this study at great distances from production wells suggests that upward migration of thermogenic gas occurs naturally in the study area and can produce low thermogenic methane concentrations in the shallow aquifer.



**Figure 15.** Relation between dissolved solids concentrations and *A*, iron and *B*, arsenic concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 16.** Relation between dissolved solids and methane concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.

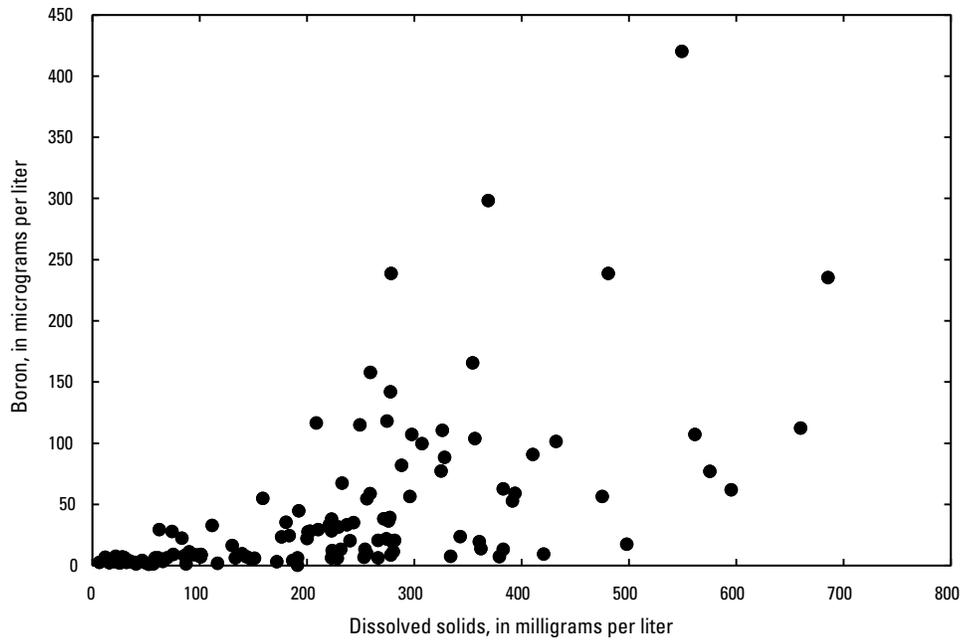
Thermogenic gas also occurs in the Atoka Formation, which overlies the Fayetteville Shale, in isolated areas within the Fayetteville Shale gas-production area, although it has been actively produced and occurs in abundance in the Atoka Formation in the western part of the State (Arkansas Oil and Gas Commission, 2012). The first gas well producing from the lower Pennsylvanian Morrow Group rocks in western Arkansas was drilled in 1949 to a total depth of 5,000 feet and penetrated rocks of Pennsylvanian, Mississippian, Devonian, Silurian, and Ordovician age (Lantz, 1950)—the gas producing zone being the Atoka Formation within the Morrow Group. Although the production of methane gas from the Atoka Formation in the Fayetteville Shale gas-production zone is limited (possibly loss of the methane over time through increased fracture pathways in the Fayetteville Shale production area), pockets of methane gas do occur in the Atoka Formation throughout the study area (Arkansas Oil and Gas Commission, 2012). As such, upward seepage of gas from the Atoka Formation is one possible source of the extremely low thermogenic methane concentrations observed in the shallow aquifer in the study area, as determined from the relatively heavy  $\delta^{13}\text{C}$  signatures.

### Trace Metals

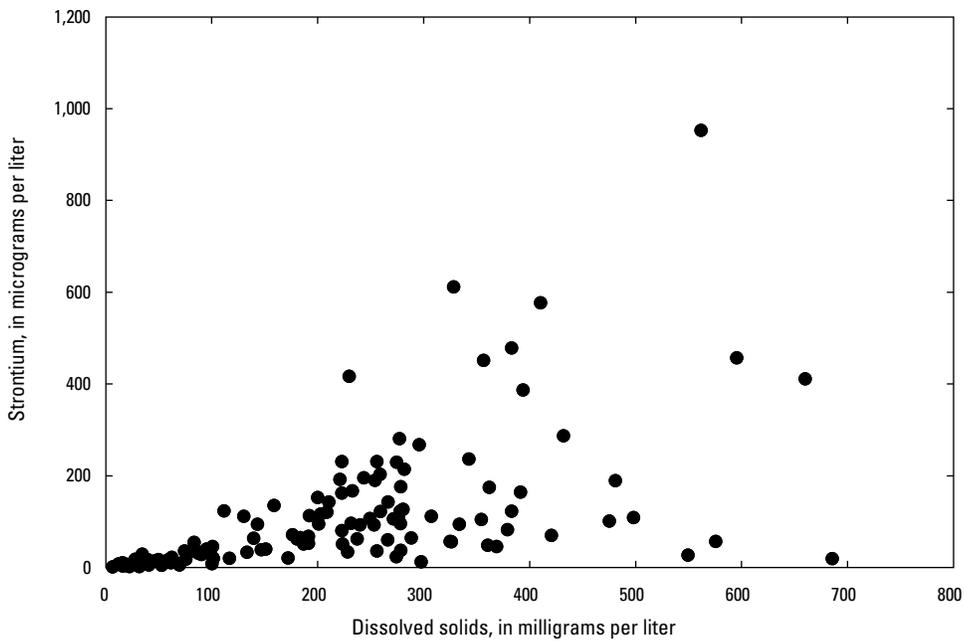
Trace metal concentrations appear to result from either rock-water interactions or the occurrence of low

pH water—higher metal concentrations occurring with enhanced metal solubilities at low pH (Hem, 1989). Boron increased with increasing dissolved solids with the highest concentration observed being 420 micrograms per liter ( $\mu\text{g/L}$ ). Boron was virtually absent (less than 5  $\mu\text{g/L}$ ) in samples with dissolved solids concentrations less than approximately 50 mg/L, indicating that shale formations, rather than sandstone formations, are the source rock for boron. All boron concentrations greater than 100  $\mu\text{g/L}$  occurred at dissolved solids concentrations exceeding 200 mg/L (fig. 17). Lithium and barium similarly showed positive, albeit weakly linear, trends with increasing dissolved solids concentration, and, similar to boron, tend to be related to groundwater in wells completed in shale formations.

Strontium geochemical behavior is very similar to calcium, and small amounts of strontium can be incorporated in carbonate rocks (Appelo and Postma, 1999). Groundwater analyses indicated that sandstone rocks in the study area were effectively free of carbonates; as such, strontium is largely absent (less than 20  $\mu\text{g/L}$ ) for samples with dissolved solids concentrations less than 75 mg/L. Strontium concentration increased with increasing dissolved solids concentrations; strontium concentrations generally were less than 50  $\mu\text{g/L}$  for dissolved solids concentration less than 100 mg/L, and showed an upward trend thereafter with the greatest strontium concentration of 953  $\mu\text{g/L}$  occurring at a dissolved solids concentration of 562 mg/L (fig. 18).



**Figure 17.** Relation between dissolved solids and boron concentrations from data collected in the Fayetteville Shale gas-production area, north-central Arkansas.



**Figure 18.** Relation between dissolved solids and strontium concentrations from data collected in the Fayetteville Shale production area, north-central Arkansas.

Appreciable concentrations of aluminum, cobalt, copper, lead, nickel, and zinc concentrations were observed only in low pH waters. Because low pH waters contained low dissolved solids concentrations, these metals also were observed in groundwater with low dissolved solids concentrations. Because these metals often are associated with metal household plumbing (Hem, 1989), a potential source for these metals in domestic well-water systems is leaching of metals from well casing, plumbing, and associated metal-based sealants. Most elevated concentrations for these trace metals occurred at pH values below approximately 5.5 to 6.0, and concentrations dropped near to or below detection limits for pH values greater than 6.0.

## Limitations Associated with Data Interpretation

Although groundwater water-quality data from 127 domestic well-water samples indicate that resulting geochemistry appear to result from natural processes within the shallow aquifer, there are certain limitations to interpretation of the data, in addition to the implication that there are no apparent effects from gas-production activities. Because every domestic well within the Fayetteville Shale gas-production area was not sampled in studies to date, these findings do not preclude the possibility that one or more domestic wells may have some mixing of water associated with gas production from a spill or other fluid release into shallow groundwater; however, no evidence of such contamination was found for the spatial extent and timeframe covered by this study. Further, although the hydrogeologic model is one of relatively short groundwater flow paths confined by small-scale topographic boundaries with groundwater flowing from higher altitudes to valley floors (Imes and Emmett, 1994), the possibility of slow groundwater travel times could result in contaminants that had not reached sampled wells during the course of this study.

The most likely sources and transport pathways for contamination from gas-production activities are related to water-handling processes at the land surface, including leakage from temporary holding lagoons, pipe breaks and leaks, spills, and other water-handling activities related to drilling, storage, and transport of gas-production water. Difficulties in detecting minor contamination events with low mixing proportions arise because of the lack of a clear and distinct fingerprint for the source water and the fact that local groundwater chemistry is highly variable—making determination of mixing end-member compositions difficult—and that many shallow domestic wells are completed in shale formations, thus having source rock and rock-water interaction processes similar to the Fayetteville Shale. As such, care must be taken in simply comparing chloride concentrations in samples from domestic wells for current conditions (postgas production) to historical (pregas production) concentrations.

If a pregas-production chloride concentration was not known for a domestic well prior to postgas-production sampling, it is possible that minor mixing may have occurred with a release of production waters, but the final mix composition resulted in chloride concentrations within the range of historical analyses. For example, if groundwater extracted from a domestic well had a pregas-production average chloride concentration of 10 mg/L, simple mixing curves reveal that mixing of 10 percent gas-production water with a chloride concentration of 2,500 mg/L with 90 percent shallow aquifer water from the domestic well, would result in a postgas-production chloride concentration of approximately 250 mg/L in the domestic water supply, which is within the range of historical concentrations. Although pregas-production water-quality data were lacking for the wells sampled for this study, geochemical data presented a well-defined pattern of geochemical evolution based on natural rock-water interaction and microbially mediated processes, suggesting that the current water quality is derived from these natural processes within the shallow aquifer with no apparent effects from gas-production activities.

It should also be noted that additives in water used for hydrofracturing in the form of various organic compounds were not analyzed on samples collected for this study. Various organic compounds are added to hydrofracturing water for use as friction reducers, disinfectants (biocide), surfactants, scale inhibitors, and corrosion inhibitors (U.S. Environmental Protection Agency, 2004; King, 2012). These chemicals are a small part of the water formulation used for fracturing purposes and comprise upward to about 0.5 percent of the water. Much of the volume of chemicals injected into the well is absorbed on pipe and in the production formation, and chemicals returning from a well after a fracturing treatment are at a fraction (upward to about 40 percent for polymers) of the total volume pumped down the well (Friedmann, 1986). In transport with a contaminant plume, various retardation and destruction processes would further lessen the concentrations including biodegradation, dispersion, dilution, sorption, volatilization, chemical and biological stabilization, transformation, and destruction of contaminants (U.S. Environmental Protection Agency, 1999). As such, the chance of finding these compounds in a domestic well downgradient from a gas-production area is greatly reduced unless a domestic well is in close proximity to a gas-production area and the contaminant plume comprises a large part of the volume of the water in an affected well.

The Arkansas Department of Environmental Quality (ADEQ) operates a water-quality laboratory in North Little Rock, Arkansas, and analyzes samples using U.S. Environmental Protection Agency approved methods, in addition to participating in the biannual USGS SRS program. The ADEQ sampled 51 domestic wells (unpublished data) distributed throughout the Fayetteville Shale production area in 2011 for a suite of volatile organic compounds, including benzene, toluene, ethylbenzene, and xylene, using U.S. Environmental Protection Agency method 8260C, Volatile

Organics by Gas Chromatography/Mass Spectrometry (U.S. Environmental Protection Agency, 2012a). No organic compounds used as additives by the gas industry were detected in any of the samples. Chloroform, a common laboratory contaminant (Agency for Toxic Substances and Disease Registry, 1997), was detected in two wells, and three disinfection products (U.S. Environmental Protection Agency, 2012a), chloroform, dibromochloromethane, and bromodichloromethane, were found in one domestic well that used chlorine to disinfect the well (Roger Miller, Arkansas Department of Environmental Quality, written commun., September 18, 2012). These results provide supporting evidence that lack of organic chemistry data does not undermine investigative techniques using inorganic chemical constituents as a primary indication of contamination by waters used for hydrofracturing and other processes.

If any cases of groundwater contamination currently exist from the excursion of fluids used and produced by the shale-gas industry within the gas-production area, they are likely isolated and of limited extent. This supposition is supported by summary accounts of lengths of gasoline-contaminant plumes, which average less than approximately 300 feet (Ruiz-Aguilar and others, 2003; Falta, 2004) with maximum plume lengths of approximately 8,000 feet (Falta, 2004). Contamination of shallow groundwater by release of gas-production water of high salinity could result in greater plume lengths of the conservative chloride ion, which would depend on the source-water concentration, groundwater velocity, and dispersion values.

## Implications of Study Results

Although there are data limitations in all environmental studies, certain implications can be made from the data and interpretations associated with this study. Methods used to evaluate the data (comparison of historical with current data, comparison of data at different distances from gas-production wells, evaluation of geochemical trends using inorganic constituents and methane) revealed no indication of systemic, regional effects on shallow groundwater quality from shale-gas production. Comparative analyses demonstrated that maximum and median chloride concentrations for data from this study were below that of historical (prior to gas production) chloride concentrations, and, more importantly, that chloride concentrations for wells less than 2 miles from gas-production wells were not significantly different from chloride concentrations more than 2 miles from gas-production wells. Additionally, groundwater-quality data collected for this study indicated that groundwater chemistry in the shallow aquifer system in the study area is a result of natural processes, controlled by geochemical rock-water interaction and microbially mediated redox reactions.

Relations between various inorganic chemical constituents suggest a natural evolution of chemistry from a

low pH, low dissolved solids water in contact with sandstone formations that are poorly buffered with respect to carbonates to strongly calcium-bicarbonate and sodium-bicarbonate water types as a result of carbonate dissolution and cation exchange within shale formations. Redox reactions also proceed along this same evolutionary trend from more oxidized to more reducing conditions, resulting in the most strongly reduced condition in groundwater—production of methane—associated with the highest dissolved solids concentrations. This information indicated that natural processes can account for the geochemistry of the shallow groundwater in the study area.

The findings from this study were based on the sampling of 127 domestic wells in the western part of the shale-gas production area, representing approximately one-third of the entire gas-production area. These findings are similar to those of Nottmeier (2012), who sampled 100 wells distributed across the entire shale-gas production area in north-central Arkansas. Nottmeier (2012) also made comparisons to historical analyses and similarly attributed primary control of groundwater geochemistry to natural rock-water interaction. A review of groundwater inorganic chemistry with particular emphasis on chloride concentration was used for this study and that of Nottmeier (2012) to indicate that no regional effects on groundwater are apparent from activities related to gas production in the Fayetteville Shale in north-central Arkansas.

Results from this study represent a timeframe relatively early in the gas-production life cycle, and any contaminants released during production activities may not have had sufficient time to reach the sampled wells. As such, groundwater-quality data from this study describe current conditions at the date of sampling and do not address potential legacy problems, if any should occur in the future; however, these data provide a baseline range and variation of geochemistry for groundwater in the study area, which can be used to assess future potential changes to groundwater quality in the area of gas production from the Fayetteville Shale.

## Summary

The Mississippian Fayetteville Shale serves as an unconventional gas reservoir across north-central Arkansas, ranges in thickness from approximately 50 to 550 feet, and varies in depth from approximately 1,500 to 6,500 feet below the ground surface. Primary permeability in the Fayetteville Shale is severely limited, and successful extraction of the gas reservoir is the result of advances in horizontal drilling techniques and hydraulic fracturing that enhance and develop secondary fracture porosity and permeability. Drilling and production of gas wells began in 2004, with a steady increase in production thereafter. As of April 2012, approximately 4,000 producing gas wells had been completed in the Fayetteville Shale in Arkansas.

Gas-well drilling and completion activities in the Fayetteville Shale have the potential to affect water quality in shallow aquifers. Potential sources of contamination include fluids associated with the drilling operation and spent water from the fracturing process. Contaminant transport pathways include potential leakage from earthen pits used to store drilling mud and other process waters including hydraulic fracturing and flowback fluids, leakage from pipes, and losses from overflows, spills, and other unexpected releases. The process of fracture propagation during hydraulic fracturing adds a lesser but additional threat to shallow aquifer systems by creation of new fracture sets, enlargement of existing vertical fractures, and upward migration of pressurized fluids through poorly cemented annulus sections of the gas well. The potential for migration of gas-production fluids is greater where the gas-production zone is shallow or where deep faulting intersects the vertical or horizontal well bore.

Surface and subsurface geological formations of interest in the study area are comprised of Pennsylvanian and Mississippian sandstones and shales with occasional thin limestone strata. From oldest to youngest, these formations include the Mississippian Fayetteville Shale, and the Hale, Bloyd, and Atoka Formations of Pennsylvanian age. Domestic wells are completed in these Pennsylvanian formations with limited yields from secondary fracture permeability. In Van Buren and Faulkner Counties, 127 wells were sampled and analyzed for major ions and trace metals with a subset of the samples analyzed for methane and carbon isotopes.

Because little to no monitoring had been conducted prior to drilling and gas production, interpretation of water-quality data from domestic well-water samples following gas production relies heavily on comparative analysis. One type of comparative analysis is to compare source-water chemistry to that of shallow groundwater in the search of indicator constituents unique to the source (gas production) water. Difficulties with this type of comparison are that many of the shallow domestic wells are completed in or influenced by shale chemistry, similar to the source rock for production of gas. Two types of additional comparative analyses include the statistical comparison of historical shallow groundwater quality collected within the gas-production area to water quality collected for this study, and comparison of groundwater quality in similar geologic and topographic areas within and outside of the gas-production area.

Historical groundwater quality data from 43 wells were extracted from the U.S. Geological Survey National Water Information System data base for the six counties that comprise the bulk of permitted and active gas-production wells: Cleburne, Conway, Faulkner, Independence, Van Buren, and White Counties. Chloride serves as an early indicator of potential effects from gas-production water for several reasons: (1) chloride is very conservative in its transport, it does not react with other minerals, adsorb to clays or organics, and chloride salts are soluble at extremely high concentrations; and (2) chloride is elevated in the gas-production waters—initial flowback fluids vary from approximately 2,500 to 5,000

milligrams per liter (mg/L) and later produced waters range upward to greater than 20,000 mg/L. The highest chloride concentration from the historical dataset was 378 mg/L; two samples had concentrations greater than 200 mg/L, and six samples had concentrations between 100 to 200 mg/L. The median chloride concentration was 20 mg/L.

Chloride concentrations for the 127 groundwater samples collected for this study ranged from approximately 1.0 mg/L to 70 mg/L, with a median concentration of 3.7 mg/L and statistically were lower than chloride concentrations from the historical water-quality data. Major ions and trace metals additionally were lower in the data gathered for this study than in the historical analyses. Additionally, there was no statistical difference (Wilcoxon rank-sum p-value of 0.71) between groundwater quality for samples collected from 94 wells located less than 2 miles from gas-production wells and 33 wells located more than 2 miles from gas-production wells.

Major ion chemistry was investigated to understand the effects of geochemical and reduction-oxidation (redox) processes on the shallow groundwater in the study area along a continuum of increased rock-water interaction represented by increases in dissolved solids concentration. Groundwater in sandstone formations that are relatively carbonate free is represented by a low dissolved solids (less than 30 mg/L), slightly acidic water type. With the dissolution of carbonates in shale formations in the study area, dissolved solids concentrations increase upward to 686 mg/L, and water type evolves from a dominantly mixed-bicarbonate and calcium-bicarbonate to a strongly sodium-bicarbonate water type as cation exchange reaches a maximum.

Methane concentration and carbon isotopic composition were analyzed in 51 of the 127 samples collected for this study. Methane was detected above a detection limit of 0.0002 mg/L in 32 of the 51 samples, with concentrations ranging upward to 28.5 mg/L. Seven samples had methane concentrations greater than or equal to 0.5 mg/L. The carbon isotopic composition of these higher concentration samples, including the highest concentration of 28.5 mg/L, shows that the methane was likely biogenic in origin with stable carbon isotope ratio ( $\delta^{13}\text{C}$ ) values ranging from -57.6 to -74.7‰. Methane concentrations correlated to dissolved solids concentrations, indicating that increasing reducing conditions correspond to more geochemically evolved groundwater with increasing rock-water interaction.

Although preproduction water-quality data were lacking for the wells sampled for this study, geochemical data presented a well-defined pattern of geochemical evolution based on natural rock-water and microbially mediated processes, strongly suggesting that the resulting water quality is derived from these natural processes with no effects from gas-production activities. Results from the groundwater-quality monitoring activities for this study provide a baseline range and variation of geochemistry for the shallow groundwater in the study area, which can be used to assess future potential changes to groundwater quality in the area of gas production from the Fayetteville Shale.

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