# **Aquifers of the Interior Highlands**

The Interior Highlands of northern and western Arkansas have less reported groundwater use than other areas of the State. This reflects a combination of processes including: (1) prevalent and increasing use of surface water, (2) less intensive agricultural uses, (3) lower population and industry densities, (4) less potential yield of the resource, and (5) lack of detailed reporting. Reported use in 2010 for all aquifers of the Interior Highlands was approximately 115 Mgal/d, 1.5 percent of the total reported groundwater use in Arkansas of 7,873.75 Mgal/d. The various aquifers of the Interior Highlands generally occur in shallow, fractured, wellindurated, structurally modified bedrock of this mountainous region of the State. Rocks of the Interior Highlands are characterized by secondary, relatively low-porosity fractures and bedding planes. By comparison, the relatively flat-lying, unconsolidated sediments of the Coastal Plain have greater porosity, storage, and yields because they are composed of coarse-grained, uncemented sands and gravels. The laterally expansive and relatively continuous Coastal Plain aquifers contrast markedly with the more discontinuous aguifers and ancient bedrock in the highlands. The Interior Highlands have experienced multiple episodes of structural modification, uplift, and erosion causing truncation, dissection, and excision. Consequently, yields of aquifers in the Interior Highlands are lower, and domestic supply is the dominant use. Surface water is the greatest supplier when large volumes are required for population growth and industry.

Disparity in total water use for aquifers in the Coastal Plain and Interior Highlands arises from the major uses of groundwater in Arkansas. For example, irrigation use, which is almost solely from the Mississippi River Valley alluvial aquifer in eastern Arkansas, accounts for nearly 94 percent of the total groundwater used in the State. Thus, groundwater use from all other aquifers is insignificant compared to irrigation. Unfortunately, the magnitude of use for irrigation overshadows the important use of groundwater for thousands of households, numerous small-community supply systems (parks, stores, and small communities), and livestock supply, among other uses in the Interior Highlands.

Spatial trends in groundwater geochemistry in the Interior Highlands differ greatly from trends for aquifers in the Coastal Plain. In the Coastal Plain, the prevalence of long regional flow paths results in regionally predictable and mappable geochemical changes. In the Interior Highlands, groundwater flow paths are short and topographically controlled (from hilltops to valleys) within relatively small watersheds. Thus, dense data coverage from numerous wells would be required to effectively characterize these groundwater basins and define small-scale geochemical changes along any given flow path. Small-scale potentiometric-surface maps constructed in the Interior Highlands confirm the dominant control of topography on groundwater-flow directions (Leidy and Morris, 1990b; Kresse and Hays, 2009). Changes in geochemistry dominantly are related to rock type and residence time along individual flow paths.

The aquifers of the Interior Highlands are discussed from youngest to oldest in the following sections: the Arkansas River Valley alluvial aquifer, Ouachita Mountains aquifer, Western Interior Plains confining system, the Springfield Plateau aquifer, and the Ozark aquifer. The Western Interior Plains confining system, Springfield Plateau aquifer, and Ozark aquifer are regional hydrogeologic units, and regional nomenclature is adhered to in this report. The reader should refer to figure 5 for locations of cities and counties discussed in this section.

## Arkansas River Valley Alluvial Aquifer

The alluvial deposits of the Arkansas River are one of the most important sources of water in the Arkansas Valley section of the Ouachita Province. This water provides a valuable source of irrigation and public-supply use. Groundwater in alluvium of the Arkansas River Valley, hereinafter referred to as the Arkansas River Valley alluvial aquifer, is considered a distinct aquifer from approximately the State border at Fort Smith to Little Rock. In the Mississippi Alluvial Plain in eastern Arkansas, it is difficult to distinguish between groundwater from the alluvial deposits of the Arkansas River and those of the Mississippi Alluvial Plain. Consequently, all alluvial deposits east of Little Rock are considered part of the Mississippi River Valley alluvial aquifer.

The following sections provide information on the geohydrology and geochemistry of groundwater from the Arkansas River Valley alluvial aquifer. Much of this information was summarized from available historical and recent publications, which provide more detailed information.

# Geologic Setting

The Arkansas River Valley region is a synclinorium generally lying between dipping rocks of the Boston Mountains to the north and the highly folded rocks of the Ouachita Mountains to the south. Alluvial deposits overlie consolidated rocks along the Arkansas River and its major tributaries. They comprise terrace and flood-plain deposits that occur along the river in discontinuous segments 3-43 mi in length and 1-5 mi across the river valley (fig. 3). In some locations, the alluvium and terrace deposits are absent, and the river is bordered by consolidated rocks of the Interior Highlands (Bedinger and others, 1963; Cordova, 1963). Tops of older terraces lie 50 ft or more above the present flood plain and consist of interbedded gravel, clay, and sand. Younger terrace deposits lie 20-40 ft above the present flood plain and are composed of a coarsening downward sequence of clay, sand, and gravel. Flood-plain alluvial deposits consist of gravel, sand, silt, and clay. Younger terraces typically are hydraulically well connected with alluvium, whereas older terraces have bases far above the surface of the adjacent

alluvium (Bedinger and others, 1963). The alluvial deposits typically are about 40 ft thick near Fort Smith and thicken downstream to about 80 ft near Little Rock (Cordova, 1963).

The alluvium represents several environments of deposition and characteristic deposits including point bar, swale, channel fill, natural levee, and backswamp. These can be distinguished on the basis of lithologic character and topographic expression. Infiltration of rainfall is an important source of groundwater recharge. Recharge is higher in areas that are underlain by the highly permeable point-bar and natural-levee deposits, and lower in backswamp and channelfill deposits (Bedinger and others, 1963). Lithologic logs near Van Buren were used to determine why some wells did not have sufficient yield for use as irrigation water (Tim Kresse, U.S. Geological Survey, unpub. data, 2013). Percent sand thickness was calculated from each available log and overlain onto a photomosaic map to examine the areal distribution of sand thickness in relation to geomorphologic features (fig. 94). Several abandoned channels were identified from the map, and a consistent association was noted between higher sand percentages near the river on the point-bar (concave) side of abandoned channels and lower sand percentage on the convex side of the channel. Point-bar and channel deposits are located on the concave side and are characterized by coarser, higherpermeable deposits. Backswamp areas are located on the convex side of the channel and are characterized by finer, less permeable deposits. Modern-day point-bar deposits are easily recognizable on figure 94 as lighter colored sands and gravels on the concave side of the Arkansas River meander bend. The distribution of these deposits of varying permeability was in agreement with anecdotal information from farmers about the distribution of productive wells in the area and the proximity of low-permeable zones during irrigation well pumping (Tim Kresse, U.S. Geological Survey, unpub. data, 2013).

## Hydrologic Characteristics

Recharge to the Arkansas River Valley alluvial aquifer primarily is by downward percolation of precipitation in addition to leakage from the river (Bedinger and others, 1963; Kilpatrick and Ludwig, 1990a). Recharge in the vicinity of the Atkins well field (Pope County), which is underlain largely by backswamp deposits, was about 3 in/yr, whereas the average rate of recharge in nearby channel deposits was about 10 in/yr (Bedinger and others, 1963). Although absent locally beneath some channel-fill deposits, in most places 30-60 ft of saturated sand and gravel are present. The saturated thickness generally increases with distance downstream from Fort Smith. Wells completed in the sands and gravels in the lower part of the Arkansas River Valley alluvial aquifer are capable of yielding 300-700 gal/min of water and predominantly are used for sources of irrigation and public supply (Bedinger and others, 1963; Kilpatrick and Ludwig, 1990a). Water levels range from approximately 5 to 30 ft below the ground surface (Kilpatrick and Ludwig, 1990a). Transmissivity values range from 5,348 to 21,390  $ft^2/d$ , and

storage coefficient ranges from 0.0001 to 0.009 (Bedinger and others, 1963).

Groundwater in the Arkansas River Valley alluvial aquifer is largely unconfined. Historically, the water table sloped toward the river and larger tributary streams during normal and low river stages. During high river stages, the groundwater gradient is reversed with groundwater flowing away from the river. Local water-table highs are common beneath the more permeable surface materials where recharge rates are high. Locally, pumping can modify the shape of the water-table surface. Pumping for irrigation historically has had little pronounced effect because irrigation wells are widely spaced and pumpage is small. Withdrawals for public supply are nearly continuous and are concentrated in small areas. Bedinger and others (1963) noted that pumping for public supply near Atkins had a pronounced effect on the water table. The well fields near Ozark (Franklin County) and Dardanelle (Yell County), which are near the river, also had cones of depression extending from well fields to the river, which induced recharge from the river. Kline and others (2006), Kresse and others (2006), and Kresse and Clark (2008) also documented influx of river water into the Dardanelle well field. However, geochemical mixing curves indicated that a maximum of only 20 percent of the groundwater from the public-supply well was river water with greatly reduced mixing in other wells. They also noted that some wells near the river in adjacent well fields with similar production history showed very little, if any, influx of river water based on the same mixing approaches.

Bedinger and others (1963) contended that only when continuously pumping public-supply wells are in close proximity to the river will any appreciable influx of water occur from the Arkansas River. Similar findings were noted in southeastern Arkansas (Kresse and Clark, 2008). The lowest chloride concentrations occurred in wells next to the Arkansas River, in spite of intensive local and regional irrigation pumping, with the highest concentrations in backswamp deposits further from the river. Kresse and Clark (2008) hypothesized that recharge predominantly occurred through coarse natural levee and channel deposits near the river in this area, similar to that proposed for the Arkansas River Valley alluvial aquifer in the western part of the State.

## **Groundwater-Flow Simulation Models**

The groundwater-flow system of the Arkansas River Valley alluvial aquifer south of Dardanelle in Yell County was simulated by Kline (2003). A two-layer model was developed to characterize groundwater flow and to investigate the degree of groundwater connectivity with the Arkansas River. Results indicated that groundwater pumping induced flow from the river into the aquifer. Further work by Kline and others (2006) and Kresse and others (2006) used hydrographs and geochemical data to quantify the degree of interaction between groundwater and the Arkansas River and validate the results of the model.



Image from Arkansas State Land Information Board, 2006 Natural Color County Mosaic Universal Transverse Mercator, zone 15 North American Datum of 1983

Figure 94. Percent sand calculated from lithologic logs for the Arkansas River Valley alluvium in west-central Arkansas.

# Water Use

Groundwater from the Arkansas River Valley alluvial aquifer is, and historically has been, an important source of irrigation and public supply. Currently (2013), only the cities of Dardanelle and Maumelle are using the Arkansas River Valley alluvial aquifer as a source of public-supply water. In the past, the cities of Atkins, Dardanelle, Morrilton, and Ozark used the aquifer for public supply, but of these cities, only Dardanelle has continued and expanded the use of the aquifer as a sole public-supply water source. Bedinger and others (1963) described the use from these four systems and calculated the remaining development potential of the Arkansas River Valley alluvial aquifer based on aquifer thickness, extent, and average yields. During 1959, Atkins used three wells that yielded about 75-250 gal/min and pumped about 162,000 gal/d; Dardanelle used three wells that vielded about 300 gal/min and pumped about 225,000 gal/d; Morrilton used four wells that yielded about 200-500 gal/min and pumped about 681,000 gal/d; and Ozark used five wells to pump about 300,000 gal/d. Assuming natural recharge to the aquifer of 10 in/yr, Bedinger and others (1963) calculated that 130 Mgal/d could be pumped from the aquifer without overdraft of groundwater storage or inducting water from the river. In 1959, groundwater was pumped at an average rate of 3.2 Mgal/d from the aquifer, which is less than 3 percent of the amount regionally available from natural recharge (Bedinger and others, 1963).

Dardanelle continues to depend solely upon groundwater for public supply. Drilling efforts were part of the plan for continued long-term use of the aquifer. A review of data from 2003 through 2009 revealed total withdrawals increased from 1.1 to 2.2 Mgal/d with production from nine wells completed at depths of about 65 ft with each well pumping about 200 gal/min. Total reported use for Dardanelle in 2010 was 2.03 Mgal/d. In 2010, Dardanelle installed a horizontal interceptor well system 300 ft from the river that produced more than 2.5 Mgal/d. The interceptor well consists of a 13-ft by 16-ft caisson installed 45 ft below ground level with five 12-inch diameter lateral screens ranging from 150 to 250 ft in length. The collector well system replaced the nine production wells in January 2011 as the city's primary water supply, but the nine wells are maintained as a backup water supply. A pumping rate of more than 3.0 Mgal/d from the interceptor well was reported in 2012 (Bill Smith, Dardanelle Water Works, oral commun., 2012). With improved directionaldrilling techniques and innovative well design, Dardanelle has demonstrated that groundwater from the Arkansas River

Valley alluvial aquifer may contain great potential as a valuable and productive water supply in other areas along the river.

In Maumelle, pumping from the Arkansas River Valley alluvial aquifer began in 1941 when wells were installed to provide water for the production of ammonium picrate (picric acid); water use continued until the plant was deactivated in March 1945. In 1972, the city of Maumelle converted those wells for public supply and installed two additional wells. Nine additional wells were installed to provide water for the growing municipality from 1995 through 2012 (Barry Heller, Maumelle Water Management, oral commun., 2013). Maumelle currently (2013) pumps from 13 wells completed in the Arkansas River Valley alluvial aquifer with a reported average use of 2.74 Mgal/d in 2010 (Terrance W. Holland, U.S. Geological Survey, written commun., 2013).

In addition to its important use as a source for publicsupply water, the Arkansas River Valley alluvial aquifer continues to be a valuable source for irrigation along the Arkansas River. In 2010, the reported irrigation use was 2.6 Mgal/d, which was pumped from 34 wells for approximately 2,960 acres of cropland (Terrance W. Holland, U.S. Geological Survey, written commun., 2013).

# Water Quality

## General Geochemistry and Water Quality

Groundwater in the Arkansas River Valley alluvial aquifer is generally of good quality and appropriate for most uses, although elevated iron concentrations can require treatment for public supply and other uses. Values of pH ranged from 4.9 to 9.5 with a median of 8.0 (table 40). The relatively high median pH value results from the dissolution of carbonate minerals in the alluvial deposits. Groundwater from the aquifer principally has been identified as a calciumbicarbonate type and is characterized by wide variations in dissolved-solids concentrations (Bedinger and others, 1963; Kresse and others, 2006). Data compiled for this report confirm this dominant calcium-bicarbonate water type and contain more analyses of total anions (bicarbonate, chloride, sulfate) than for total cations (calcium, magnesium, sodium, potassium). Bicarbonate was greater than 50 percent in 462 of 493 (94 percent) samples. Calcium was greater than 50 percent for 75 of 81 (93 percent) samples having sufficient cation data for calculation of the dominant cation.

## 254 Aquifers of Arkansas—Protection, Management, and Hydrologic and Geochemical Characteristics of Groundwater

**Table 40.** Descriptive statistics for selected chemical constituents in groundwater from the Arkansas River Valley alluvial aquifer in western Arkansas.

[mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Constituent or characteristic	Minimum	Median	Maximum	Standard deviation	Number of wells
Calcium (mg/L)	0.5	58	433	60.4	143
Magnesium (mg/L)	1.69	16	70	10.4	139
Sodium (mg/L)	0.9	14	236	34.8	117
Potassium (mg/L)	0.08	1.6	48	5.12	102
Bicarbonate (mg/L)	8.0	231	1,050	150	503
Chloride (mg/L)	1.0	12	980	52.3	661
Sulfate (mg/L)	0.2	17	253	26.8	518
Silica (mg/L)	0.18	22	39.5	7.77	66
Nitrate (mg/L as nitrogen)	0.01	1.1	67	8.63	457
Dissolved solids (mg/L)	88	319	887	152	88
Iron (µg/L)	0.05	70	15,500	1,300	336
Manganese (µg/L)	0.13	338	1,360	403	17
Arsenic (µg/L)	0.03	0.76	6.8	1.78	15
Hardness (mg/L as calcium carbonate)	20	240	1,300	134	570
Specific conductance (µS/cm)	89	507	2,920	273	655
pH (standard units)	4.9	8.0	9.5	0.6	649

## Nitrate

Nitrate concentrations in the Arkansas River Valley alluvial aquifer ranged from 0.01 to 67 mg/L with a median of 1.1 mg/L in 457 samples (table 40). The median concentrations for all other aquifers in Arkansas, with the exception of the Springfield Plateau and Ozark aquifers, were less than 0.3 mg/L. The shallow depths and relatively high recharge to the aquifer are consistent with increased vulnerability to surface (for example, fertilizer and manure) and near-surface (for example, septic tanks) sources of nitrogen. Out of 457 samples with nitrate analyses, 58 (12.7 percent) had concentrations exceeding the Federal MCL of 10 mg/L. The greatest density of elevated nitrate concentrations was along the western (Crawford County) and the eastern (Conway, Faulkner, Pope, and Yell Counties) extents of the aquifer (fig. 95). The lower concentrations of nitrate in the central part of the aquifer (Franklin, Johnson, and Logan Counties) are hypothesized in this report to result from denitrification. Further evidence for denitrification as a control on nitrate concentrations in this part of the aquifer is provided in the discussions of iron, arsenic, and sulfate.



**Figure 95.** Spatial distribution of selected chemical constituents in groundwater from the Arkansas River Valley alluvial aquifer in western Arkansas.

## Iron and Arsenic

Iron concentrations in the Arkansas River Valley alluvial aquifer ranged from 0.05 to 15,500  $\mu$ g/L with a median of 70  $\mu$ g/L (fig. 96; table 40). For 336 samples with iron analyses, only 37 (11 percent) exceeded the Federal secondary drinking-water regulation of 300 µg/L. Iron concentrations ranged from 155 to 15,500  $\mu$ g/L with a median of 2,955  $\mu$ g/L near Van Buren. The large median iron concentration likely indicates iron-reducing conditions and dissolution of iron oxyhydroxides (Chappelle and others, 2009). In this area, arsenic concentrations ranged from 0.38 to 6.8 µg/L with a median of 1.3  $\mu$ g/L; all concentrations were below the drinking-water standard of 10 µg/L (U.S. Environmental Protection Agency, 2009). Iron correlated positively to arsenic with an R<sup>2</sup> value of 0.76, indicating reduction of iron oxyhydroxides as a possible source of arsenic. Ironreducing conditions were similarly noted in the aquifer near Dardanelle by Kresse and others (2006). A review of waterquality data from the Dardanelle area (Kresse and others,

2006) also revealed a positive correlation between iron and arsenic with an R<sup>2</sup> value of 0.77. Arsenic concentrations ranged as much as 19  $\mu$ g/L in this area. Kresse and Fazio (2003) provided evidence for reductive dissolution of iron oxyhydroxides as the source of elevated iron and arsenic in the Mississippi River Valley alluvial aquifer along the Arkansas River in southeastern Arkansas. Detailed studies by Sharif and others (2008a, b) confirmed reductive dissolution of iron oxyhydroxides as the source of elevated iron and arsenic concentrations in this area. Holocene-age alluvial deposits contain abundant dissolved organic matter that provides a substrate for microbial respiration. This substrate results in utilization of electron acceptors such as oxygen, nitrate, iron oxyhydroxide, and sulfate thus increasing reducing conditions in the deeper sections of the aquifer. Reduction of iron oxyhydroxides likely is the source of elevated iron and arsenic concentrations in the Arkansas River Valley alluvial aquifer in the western part of the State.



Figure 96. Interquartile range of selected chemical constituents in groundwater from the Arkansas River Valley alluvial aquifer in western Arkansas.

The spatial distribution of iron concentrations shows that the highest density of elevated iron concentrations, similar to that of nitrate, occurred in the western and eastern parts of the aquifer (fig. 95). All but one iron concentration in the central part of the aquifer were less than 100 µg/L. This suggests that the more energetically favorable terminal electron acceptors-oxygen, nitrate, and iron oxyhydroxides-have been exhausted, and geochemical conditions have evolved to favor sulfate-reducing conditions and the precipitation of ironsulfide minerals. The inverse relation of iron and sulfate in the aquifer supports the theory of iron-sulfide mineralization as a control on iron in solution (fig. 97). Where iron-oxide supply has been exhausted in an aquifer and an appreciable sulfate and an organic substrate are available for sulfate-reducing bacteria, sulfate will be reduced to hydrogen sulfide, which quickly reacts with the soluble iron. Chapelle and others (2009) noted that sulfide was inversely related to dissolved iron, reflecting the rapid reaction kinetics of iron with hydrogen sulfide to produce relatively insoluble iron-sulfide minerals. Because sulfate concentrations are much greater than iron concentrations throughout most aquifers, any appreciable reduction of sulfate can remove a large fraction of the soluble iron.

## Sulfate

Sulfate concentrations generally were low throughout the Arkansas River Valley alluvial aquifer and ranged from 0.2 to 253 mg/L with a median of 17 mg/L (fig. 96; table 40). Of 518 samples with sulfate data, 470 (91 percent) had concentrations less than 50 mg/L, and 295 (57 percent) had concentrations less than 20 mg/L. Only one sample (253 mg/L) had a concentration greater than the secondary drinking-water regulation of 250 mg/L. In areas with sulfate concentrations exceeding approximately 30 mg/L, iron is virtually absent (less than 50  $\mu$ g/L), suggesting sulfate reducing conditions in areas with higher sulfate concentrations (fig. 97). No discernible trends were noted in the spatial distribution of sulfate concentrations.



Figure 97. Relation of iron and sulfate concentrations in groundwater from the Arkansas River Valley alluvial aquifer in western Arkansas.

## Chloride

Chloride concentrations in the Arkansas River Valley alluvial aquifer ranged from 1.0 to 980 mg/L with a median of 12 mg/L (fig. 96; table 40). Only 4 of 661 samples with chloride analyses exceeded the Federal secondary drinkingwater regulation of 250 mg/L; however, 32 samples exceeded 100 mg/L and are elevated as defined for this report. Bedinger and others (1963) hypothesized that natural variation in dissolved-solids content, salinity, and water type was related more to the movement of water from adjacent or underlying formations than from movement of groundwater within the alluvium. However, Kresse and others (2006) indicated that increases in salinity and dissolved-solids concentrations were the direct result of the type of deposits penetrated by wells in the aquifer in the Dardanelle area. They showed that groundwater in underlying formations was of better quality with lower salinity than water in the Arkansas River Valley alluvial aquifer. Higher chloride and dissolved-solids concentrations were noted for wells in two different areas of the aquifer: (1) areas with deposits having a higher percentage of clay and located further from the river, which correlates to areas of backswamp deposits, and (2) areas near to and directly affected by influx of higher salinity water from the Arkansas River. Trend lines for bromide and chloride concentrations in each area reflected differences in the source of salinity. Groundwater in backswamp areas contained higher bromide/chloride ratios and plotted along a trend line associated with evapotranspiration (fig. 98). Conversely, groundwater between the river and public-supply wells in the Dardanelle area had lower bromide/chloride ratios and plotted along a line with river water as an end member. Chloride concentrations in the river averaged approximately 200 mg/L during the study (Kresse and others, 2006), and the production well closest to the river had a maximum chloride concentration of 112 mg/L. Petersen (1988) provided a summary of water quality for four sites on the Arkansas River for 1975 through



**Figure 98.** Relation of chloride and bromide concentrations in groundwater samples from the Arkansas River Valley alluvial aquifer near Dardanelle, Arkansas (from Kresse and Clark, 2008).

1985 and showed maximum chloride concentrations ranging from 220 to 550 mg/L with means ranging from 90 to 150 mg/L for the four sites.

Kresse and Clark (2008) noted a relation between groundwater quality and the type of deposits that compose the Mississippi River Valley alluvial aquifer south of the Arkansas River in southeastern Arkansas. This was based on geochemical data for approximately 2,500 irrigation wells completed in the Mississippi River Valley alluvial aquifer south of the Arkansas River from Little Rock to the Mississippi River. This analysis showed that the lowest chloride concentrations were in wells completed in coarsergrained levee and channel deposits that tend to lie closest to the Arkansas River. The highest chloride concentrations were in wells completed in finer-grained backswamp deposits located away from the river (see Mississippi River Valley alluvial aquifer). Kresse and Clark (2008) hypothesized that a combination of rapid recharge and advective flushing in the relatively coarser channel and levee deposits near the river maintained low chloride concentrations in groundwater, which closely reflect that of evaporated rainwater. The fine-grained, clay-rich deposits associated with backswamp areas likely restrict recharge, induce increased ratios between evapotranspiration and recharge, and experience minimal flushing of salts concentrated during evapotranspiration. Although the spatial variability of various types of deposits is on a smaller scale for the Arkansas River Valley alluvium in the Interior Highlands, it is likely that restricted recharge through the lower permeable deposits results in groundwater of higher dissolved-solids concentration.

The highest chloride concentrations in the Arkansas River Valley alluvial aquifer generally occurred at further distances from the Arkansas River from Fort Smith to Little Rock. This situation is hypothesized to be the result of evapotranspiration in backswamp areas at greater distances from the river as proposed by Kresse and others (2006) and Kresse and Clark (2008). In the isolated areas where chloride concentrations were elevated next to the river, including an area in Franklin County, past pumping associated with public supply was likely the cause. In other words, past pumping for public supply resulted in the induced influx of water from the river into the alluvial aquifer. Bedinger and others (1963) also noted that pumping at the well fields in Dardanelle and Ozark had induced infiltration of river water into the aquifer.

In summary, groundwater in the Arkansas River Valley alluvial aquifer is of overall good quality, with the exception of elevated iron concentrations that often require treatment for use in public-supply systems. Chloride concentrations can be slightly elevated in backswamp areas or where influenced by an influx of water from the Arkansas River. Only 4 of 661 samples with chloride analyses exceeded the Federal secondary drinking-water regulation of 250 mg/L. Reducing conditions in various parts of the aquifer were hypothesized as controls on the distribution and concentration of nitrate, iron, and sulfate.

# **Ouachita Mountains Aquifer**

A thick sequence of Paleozoic rock formations in the Ouachita Mountains serves as an important source of groundwater supply for domestic users, in addition to a limited number of small commercial- and community-supply systems. The shallow saturated section of the combined formations in the Ouachita Mountains will hereinafter be referred to as the "Ouachita Mountains aquifer" (tables 2 and 4). Renken (1998) used a similar nomenclature in his listing of the "Ouachita Mountains aquifer" as a minor aquifer of Segment 5 (Arkansas, Louisiana, and Mississippi) of the Ground Water Atlas of the United States. Assignment of boundaries for various aguifers of Arkansas, and particularly those of the Ouachita Mountains, can be a daunting task. The Ouachita Province includes two sections: the Arkansas (River) Valley and the Ouachita Mountains (table 2). The Arkansas Valley lies between dipping rocks of the Boston Mountains to the north and the highly folded and deformed rocks of the Ouachita Mountains to the south and includes geologic formations that extend into both areas (fig. 3; Cordova, 1963; Kilpatrick and Ludwig, 1990a). Waterresources investigations in the Ouachita Mountains generally included an area south of the Arkansas Valley (Albin, 1965; Renken, 1998), which resulted in an arbitrary divide that omitted large, continuous exposures of formations that cross the divide to the north, particularly in Sebastian and Logan Counties. Some of these formations are included in Ouachita Mountains and Arkansas Valley sections and also extend into the Boston Mountains north of the river. For example, the Atoka Formation is exposed across a large part of the Boston Mountains physiographic region and is a major formation of the Western Interior Plains confining system. It extends as far south as Scott County in the heart of the Ouachita Mountains physiographic region (Haley and others, 1993).

Physiographic province and section boundaries often do not coincide with geologic or hydrologic boundaries. The Arkansas Valley section as identified on physiographic and regional hydrogeologic maps (Fenneman, 1938; Albin, 1965; Renken, 1998) includes formations that more appropriately belong to the Boston Mountains section of the Ozark Plateaus to the north or the Ouachita Mountains section of the Ouachita Province to the south. Including these formations as part of the Arkansas Valley for this report would result in (1) reproducing geologic, hydrologic, and water-quality discussions for either region in a separate section on the Arkansas Valley; (2) arbitrary boundaries of the Arkansas Valley cutting through continuously exposed formations (and possible groundwater flow paths) properly belonging to other sections; and (3) omitting important information, such as spatial water-quality trends or groundwater flow paths for aquifers in the Ouachita Mountains or Boston Mountains by arbitrary divides imposed by those defining the Arkansas Valley. For purposes of this report, the Arkansas River and associated alluvial deposits serve as a southern limit of the Western Interior Plains confining system (coinciding with

the Boston Mountains section) and the northern limit of the Ouachita Mountains. Therefore, the Ouachita Mountains aquifer includes all formations extending north to the Arkansas River (and associated alluvial deposits), west to the State line, and south and east to the boundary with the Coastal Plain.

# Geology

Rocks forming the Ouachita Mountains aquifer are dominantly of sedimentary origin, ranging in age from Cambrian to Middle Pennsylvanian (table 4). These rocks were deposited by a regionally extensive sinking trough (geosyncline) that extended at minimum from central Oklahoma to central Arkansas. The geosyncline formed throughout most of the Paleozoic Era accounting for approximately 46,000 ft of accumulated sediment deposited in the trough. Lithification and compression of the sediments at a later time formed shales, sandstone, conglomerates, limestone, chert, and novaculite, ultimately resulting in deformation of a complexly folded and thrust-faulted arch (anticlinorium).

Orogenic activity into the Middle Pennsylvanian Epoch formed the rocks into a complexly folded and thrust-faulted anticlinorium in which many of the folds were broken by thrusts or high-angle reverse faults. The folds were overturned to the south, resulting in the dips off the fold axes to the north (Purdue, 1910; Albin, 1965; Stone and Bush, 1984). A long period of epeirogenic uplift and erosion subsequently occurred resulting in the present-day mountains (Albin, 1965; Stone and Bush, 1984). The present-day physiography is represented by long even-crested ridges and flat-intermontane basins. The higher ridges and crest-forming rocks typically consist of the more resistant quartz formations (Albin, 1965; Kresse and Hays, 2009). Major faults are essentially parallel to trends of the axes of folds, which generally lie along east-west trending lines throughout the Ouachita Mountains. Consequently, wells of similar water-yielding capacity typically lie on east-west trends relative to each other. The best places to drill wells in the Ouachita Mountains generally are on the flanks of anticlines (in synclinal valleys) and off the noses of plunging anticlines (Albin, 1965; Halberg and others, 1968).

# Hydrologic Characteristics

Formations in the Ouachita Mountains are dominated by thick sequences of shale, siltstones, and quartz (sandstone, chert, novaculite), with minor occurrences of carbonates and other rocks. Similar lithologies coupled with structural modification have created an extremely high degree of hydraulic connectively between the formations. The rock sequence serves effectively as a single aquifer from a regional perspective, and a detailed discussion of lithology and depositional environment for each formation is not provided. For additional information, the reader is directed to Purdue and Miser (1916), Albin (1965), Halberg and others (1968), Stone and Bush (1984), and McFarland (2004). Primary porosity in rocks of the Ouachita Mountains was greatly decreased by compaction and lithification as sediments filled the synclinal trough and compression occurred during orogenic episodes. Secondary porosity and permeability are provided by faults, joints, fractures, bedding planes, and other structural features. These secondary permeability features generally result in low yields compared to unconsolidated sediments of Coastal Plain aquifers. Groundwater yields generally are sufficient for only domestic use. Groundwater geochemistry reflects the dominant aquifer rock types, with better quality water generally produced from quartz formations and poorer quality water from shale formations.

Groundwater availability afforded by secondary-porosity processes is strongly dependent on the degree of fracturing related to the tensile strength of the rock (Albin, 1965; Halberg and others, 1968; Stone and Bush, 1984; Cole and Morris, 1986; Kresse and Hays, 2009). Quartz formations such as the Bigfork Chert and Arkansas Novaculite are very brittle and prone to dense fracturing. Most researchers working in the Ouachita Mountains identified the Bigfork Chert as the most productive water-bearing formation in the region (Albin, 1965; Halberg and others, 1968; Stone and Bush, 1984; Cole and Morris, 1986; Kresse and Hays, 2009). Well yields have a fairly large range depending on individual formations and lithology but typically are low throughout the aquifer. Albin (1965) noted that most wells yielded less than 10 gal/min, and yields more than 50 gal/min were rare. The maximum recorded yield of 350 gal/min was for a well completed in the Bigfork Chert. Wells continuously yielding more than 10 gal/min for a week generally were considered "large-yield" wells. Wells in Hot Spring County generally yielded from 2 to 7 gal/min, with a few wells yielding 20 gal/ min or more (Halberg and others, 1968). The average pumping rate measured in this area was 21 gal/min with a reported maximum of 40 gal/min. A well completed in the Bigfork Chert in Garland County was pumped at 30 gal/min over a 3-day period, resulting in drawdown of only 1–2 inches (Kresse and Hays, 2009). Specific capacities ranged from 0.1 to 9.0 (gal/min)/ft of drawdown (Albin, 1965; Halberg, 1968), and transmissivities ranged from 134 to 2,674 ft<sup>2</sup>/d (Albin, 1965). In spite of the few relatively high reported yields cited above, all publications cautioned that the aquifer should not be considered as a source of water supply unless the required quantity was small (Albin, 1965; Halberg and others, 1968; Stone and Bush, 1984).

Most wells in the Ouachita Mountains aquifer are less than 100 ft deep but can be as much as 700 ft deep. Static water levels generally are less than 20 ft below land surface, and flowing-artesian wells are common throughout the region (Albin, 1965; Kresse and Hays, 2009). Pumping water levels may be as much as 150 ft below land surface in the deepest wells. Of the 35 wells surveyed in Garland County, 83 percent were less than or equal to 200 ft deep, and all were less than 400 ft deep (Kresse and Hays, 2009). Of these wells, 25 were located in valleys and had a mean depth of 16 ft compared to a mean depth of 75 ft for wells located at higher elevations. Generally, wells in the valleys were completed in the Stanley Shale and those at higher elevations were completed in the Bigfork Chert.

Seasonal water-level fluctuations in the Ouachita Mountains aguifer generally were less than 10 ft. Larger fluctuations are common in abnormally wet or dry years because the groundwater reservoirs generally have small storage capacities and are recharged by rapid infiltration of local precipitation (Albin, 1965). Kresse and Hays (2009) collected water-level data for seven wells (two Stanley Shale, one Hot Springs Sandstone, three Bigfork Chert, and one Arkansas Novaculite) from October 2007 through April 2009. Substantial water-level rises occurred for the quartz formations compared to the shale formations from December through May (wet season), reflecting greater storage in the guartz formations. Smaller rises in water levels were noted for wells in the quartz formations compared to shale formations for individual rain events. However, water levels slowly increased to maximum overall rises of 8-15 ft during the wet season in the quartz formations. Conversely, there were only episodic increases and decreases relative to a similar base level for wells in shale formations throughout this same period. Kresse and Hays (2009) hypothesized that the brittle nature and intense fracturing of the quartz formations resulted in substantially greater fracture porosity compared to shale formations. This provided greater permeability and storage for the quartz formations, with the result of an overall large rise in water levels in the wet season and smaller rises during individual rain events. The lower permeability and secondary porosity in the shale formations resulted in rapid filling of the fractures and causing large, short-term waterlevel rises, followed by rapid water-level declines driven by steep hydraulic gradients. Aquifer tests for several wells in both types of formations confirmed that yields and storage properties were substantially lower in the shale formations than in the quartz formations.

Because of the similar rock types in the Boston and Ouachita Mountains regions, groundwater flow within both of these systems is likely explained by a similar conceptual model. Kresse and others (2012) proposed a general conceptual model explaining groundwater flow for a part of the Boston Mountains. They hypothesized that flow was controlled by secondary-porosity features (fractures, bedding planes), which provide limited groundwater storage and low yields generally sufficient only for domestic supply, and that flow paths were confined by small-scale topographic boundaries with short flow paths from elevated areas to valley floors in individual, small-scale watersheds. Topographic basins in the Ouachita Mountains generally are defined by the folded strata resulting in synclinal and anticlinal basins. Consequently, Halberg and others (1968) postulated that flow directions would reflect the structural geology, orientation, and hydraulic connection of the major east-west trending faults and likely have little interbasin flow of groundwater. Kresse and Hays (2009) tested this postulation using water levels from 53 shallow (less than 400 ft deep) wells and 24 springs

in Garland County to construct a potentiometric-surface map. The map indicated a high degree of topographic control on shallow groundwater flow, with groundwater flow confined to individual synclinal and anticlinal basins. This observation adds support to the conceptual model of groundwater flow of topographically controlled, short flow paths within local watersheds in the Ouachita Mountains aquifer.

## Water Use

Determination of accurate values for the amount of water used from the Ouachita Mountains aquifer is difficult, and reported total use from the aquifer should be viewed with caution. The greatest use of groundwater from the Ouachita Mountains aquifer is for domestic supply. Domestic wells and wells producing less than 50,000 gal/d are exempt from reporting requirements; consequently, various methods that are used to estimate domestic water use commonly result in an underestimation of total groundwater use from the aquifer. Although Albin (1965) noted overall low yields and stated that wells in the aquifer that yield more than 10 gal/min are considered "large-yield wells," some wells can yield between 10 and 50 gal/min, which are more than sufficient for many communities. Records from the ADH indicate that 72 wells are used by camps and other recreational areas, conference centers, rest areas, stores, and even sources of public supply. Five separate communities used wells completed in the Atoka, Bigfork Chert, Stanley Shale, and Arkansas Novaculite Formations for purpose of public supply. This demonstrates that many formations within the Ouachita Mountains aquifer are capable of supplying sufficient volumes of water for a small community.

# Water Quality

Past research indicated that groundwater in the Ouachita Mountains aquifer primarily is of a mixed calcium- and sodium-bicarbonate type and chemically is suitable for most domestic and farm uses. However, some groundwater exhibited high hardness and contained concentrations of iron, manganese, chloride, and nitrate in excess of concentrations recommended for various uses. The most common complaint from domestic users was that the groundwater can be hard and high in iron (Albin, 1965; Halberg and others, 1968; Cole and Morris, 1986; Kresse and Hays, 2009).

## General Geochemistry and Water Type

Bicarbonate was the dominant anion in 90 of 116 samples (78 percent) with complete anion (chloride, sulfate, bicarbonate) analyses and was greater than 50 percent of the total anions in 78 of the 116 samples (67 percent) for the Ouachita Mountains aquifer. The remaining samples had chloride or sulfate as the dominant anion or were of a mixed type. For samples with complete cation (calcium, magnesium, sodium, potassium) analyses, calcium was the dominant cation in 59 of 125 samples (47 percent) and greater than 50 percent in 37 of 125 samples (30 percent). Sodium was the dominant cation in 48 of 125 samples (38 percent) and greater than 50 percent in 23 of 125 samples (18 percent). The remaining samples generally had magnesium as the dominant cation. Therefore, groundwater is predominantly a calcium-bicarbonate type throughout the aquifer. Generally, samples with the highest percent sodium occur in the southern part of the aquifer in wells completed in the Stanley Shale and in the northern part in wells completed in the shale-rich Atoka and McAlester Formations (fig. 99). These areas represent the transition from a calicium-bicarbonate to a sodium-bicarbonate or a sodium-chloride water type.

Values of pH for the Ouachita Mountains aquifer ranged from 3.3 to 8.6 in 137 samples with a median of 7.0 (table 41). To better assess the extreme variability of pH, it is useful to understand the difference in geochemistry of the source rocks, which are dominantly shale and quartz. A study by Kresse and Hays (2009) in Garland County revealed substantial differences in groundwater geochemistry based on rock type. Low specific-conductance values were noted for groundwater from quartz formations (Bigfork Chert, Arkansas Novaculite, and Hot Springs Sandstone). All but one sample exhibited values less than 50 µS/cm with a median of 30 µS/cm. These low specific-conductance values reflect a low dissolved-solids concentration attributable to the low solubility of quartz and the lack of carbonate minerals. Specificconductance values for the shale formations (Stanley Shale, Womble Shale, and the undifferentiated Missouri Mountain Shale and Polk Creek Shale) ranged from 97 to 490 µS/cm with a median of 293 µS/cm. These high specific-conductance values reflect high dissolved-solids concentrations attributable to the abundance of carbonate and other soluble minerals in the shale rocks. Values of pH in groundwater from shale rock ranged from 5.8 to 7.4 with a median of 6.6. Conversely, pH values in groundwater from quartz rocks ranged from 3.6 to 6.1 with a median of 4.4. Increased pH was attributed to dissolution of mineral species with buffering capacity, particularly carbonate minerals, resulting in a positive correlation of pH and conductance (Kresse and Hays, 2009).

Spatial patterns of pH and specific conductance generally followed formation outcrop patterns for the Ouachita Mountains aquifer. Generally, the lowest pH values (3.3–5.0) were from the eastern part of the aquifer, where the Bigfork Chert, Arkansas Novaculite, and Hot Springs Sandstone Formations have extensive outcrop. High pH values (8.1–8.6) occur in the south, dominantly represented by wells completed in the Stanley Shale, and also occur in the western and northern parts of the aquifer, where shale-dominated rocks of the Atoka Formation predominate in outcrop. A few of these wells also were completed in the shale-rich McAlester Formation (fig. 99).





 Table 41.
 Descriptive statistics for selected chemical constituents in groundwater from the Ouachita Moutains aquifer in western

 Arkansas.

Enn or /I	milligrama	mon liton		miorograma	monlitor		miorodi		agentime at an at 2	5 degrees	Coloina
IIII2/L.	mmingrams	ber mer.	$u_2/L$ .	micrograms	ber mer	. us/cm	. IIIICIOSI	lemens ber	centimeter at $2$ .	J degrees	Cersius
L 0 ,	0	r · · · ,	1.0 ,		F	,		· · · <b>r</b> ·			

Constituent or characteristic	Minimum	Median	Maximum	Standard deviation	Number of wells
Calcium (mg/L)	0.04	13.9	303	30.7	136
Magnesium (mg/L)	0.01	4.25	307	27	136
Sodium (mg/L)	0.67	12	284	41.1	135
Potassium (mg/L)	0.08	1.2	24	3.88	124
Bicarbonate (mg/L)	1.0	89	511	107	118
Chloride (mg/L)	0.9	7.0	500	62.1	152
Sulfate (mg/L)	0.02	9.15	535	56.1	137
Silica (mg/L)	1.1	13.2	46.8	11.1	102
Nitrate (mg/L as nitrogen)	0.01	0.14	15	3.17	101
Dissolved solids (mg/L)	14	152	953	152	125
Iron (µg/L)	0.05	170	14,000	2,320	108
Manganese (µg/L)	0.13	71.8	2,600	403	86
Arsenic (µg/L)	0.03	0.03	7.2	1.76	41
Hardness (mg/L as calcium carbonate)	0	62	410	82	116
Specific conductance (µS/cm)	15	241	3,050	401	157
pH (standard units)	3.3	7.0	8.6	1.2	137

Specific conductance values follow the same general trend represented by pH values. The lowest conductance values (15-50 µS/cm) occur in the eastern part of the aquifer, represented by the quartz formations listed above. A generally increasing trend in conductance occurs in the southern part of the aquifer, represented by wells dominantly completed in the Stanley Shale with numerous samples having conductance values ranging from 250 to 500 µS/cm. Lower values (ranging from 15 to 100  $\mu$ S/cm) in the southern part of the aquifer were from wells completed in the Jackfork Sandstone. The highest specific conductance values (ranging from 1,000 to  $3,050 \,\mu\text{S/cm}$ ) were from wells completed in the Atoka Formation in Scott County (fig. 99). The Atoka Formation is dominantly shale rock with some traceable sandstone units in the Ouachita Mountains. In general, the spatial distribution of pH and specific conductance values reflected source-rock types (Kresse and Hays, 2009).

Groundwater from quartz formations generally has lower conductance values than shale formations, reflecting lower dissolved-solids concentrations. This indicates that groundwater from quartz formations of the Ouachita Mountains aquifer is a highly desirable drinking-water source from the standpoint of hardness issues; however, the corresponding low pH values can present other problems related to leaching of metals in plumbing fixtures. Certain trace metals have solubility values that increase substantially at low pH values. These metals can be leached from pumps, pipes, fixtures, and other metallic parts of the waterdistribution system, which leads to higher concentrations that affect taste, pitting and corrosion of pipes, and staining of plumbing fixtures (Hem, 1989). Dissolved aluminum and copper were higher in groundwater from the quartz formations than in groundwater from shale formations as a result of the low pH in groundwater from quartz formations. This interpretation was substantiated by an inverse correlation of these metals with pH from a regression analysis.

#### Nitrate

Nitrate concentrations in the Ouachita Mountains aquifer ranged from 0.01 to 15 mg/L with a median of 0.14 (table 41), which reflects the generally low nitrate concentrations throughout the aquifer. Out of 101 samples with nitrate analyses, 40 had concentrations less than 0.10 mg/L and 72 were less than 1.0 mg/L. Only 4 of the 101 samples had concentrations exceeding the Federal MCL of 10 mg/L as nitrogen. No regional spatial trend was found in the distribution of nitrate. Although low concentrations can be found throughout the aquifer, a greater number of low (0.01)to 0.10) concentrations occur in the eastern part of the aquifer. Generally, decreasing nitrate concentrations were related to increasing well depth rather than to spatial variability. reflecting the differences in vulnerability based on regolith thickness, rock type, and other surface features. Nitrate concentrations greater than 2.0 mg/L occurred in wells less than 200 ft deep. Correlation of nitrate concentrations with nitrogen sources was outside the scope of this report and was not addressed in previous reports.

#### 264 Aquifers of Arkansas—Protection, Management, and Hydrologic and Geochemical Characteristics of Groundwater

#### Iron

Iron concentrations in the Ouachita Mountains aquifer ranged from 0.05 to 14,000  $\mu$ g/L with a median of 170  $\mu$ g/L (fig. 100; table 41). No spatial pattern was noted for iron; high and low concentrations occurred in shale and quartz formations. Iron is abundant in numerous minerals in alluvial sediments and sedimentary rocks throughout Arkansas. Controls on solubility generally are related to changes in redox zonation, which can result in dissolution or precipitation of various iron-rich minerals based on the presence or absence of oxygen and the availability of electron donors and acceptors. Although iron was cited as problematic for wells completed in the Ouachita Mountains aquifer (Albin, 1965; Halberg and others, 1968; Cole and Morris, 1986; Kresse and Hays, 2009), no studies currently (2013) have been completed to identify iron sources and transport pathways. Higher concentrations of some trace metals (barium, lithium, manganese, and strontium) are noted in shale formations, whereas other trace metals occur in higher concentrations from quartz formations related to the low pH values (Wagner and Steele, 1985; Kresse and Hays, 2009). Although no relations were noted for the spatial distribution or sources of iron, evidence shows some control on iron solubility by possible sulfate reduction as described in the next section.



**Figure 100.** Interquartile range of selected chemical constituents in groundwater from the Ouachita Mountains aquifer in western Arkansas.

## Sulfate

Sulfate concentrations generally were low throughout the Ouachita Mountains aguifer. Of 137 samples, 72 wells (53 percent) had concentrations less than 10 mg/L, 124 wells (91 percent) had concentrations less than 50 mg/L, and only 1 well had a concentration greater than the Federal secondary drinking-water regulation of 250 mg/L. Sulfate was substantially greater in shale formations than in quartz formations in the Ouachita Mountains aquifer (Kresse and Hays, 2009). Grouping all data by aquifer codes confirmed that concentrations greater than 10 mg/L (up to 535 mg/L) generally occurred in groundwater from the Stanley Shale, McAlester Formations, and Atoka Formation (51 of 88 combined analyses greater than 10 mg/L). Nevertheless, low concentrations can be found throughout the aquifer in groundwater from all formations. This is demonstrated by the low concentrations throughout the southern part of the aquifer, an area with numerous wells completed in the Stanley Shale. The lowest concentrations (generally less than 5 mg/L) generally occurred in the Bigfork Chert, Arkansas Novaculite, Hot Springs Sandstone, and Jackfork Sandstone (only 6 of 44 combined analyses more than 10 mg/L).

Various constituent relations suggest that sulfate reduction in groundwater from shale formations may serve as a control on iron solubility. Iron and sulfate had inverse correlations with nitrate, indicating that denitrification occurred prior to iron and sulfate reduction. Nitrate concentrations greater than 0.5 mg/L occurred where iron concentrations generally were less than 1,200  $\mu$ g/L. Iron concentrations greater than approximately 500  $\mu$ g/L with corresponding nitrate concentrations more than 0.5 mg/L normally represent mixing of groundwater from different zones in the aquifer, which is typical of open-hole completions in bedrock aquifers (fig. 101*A*). Nitrate concentrations were greater than 0.5 mg/L for sulfate concentrations generally less than 30 mg/L (fig. 101*B*).

Sulfate concentrations in the Ouachita Mountains aquifer were inversely correlated with iron concentrations (fig. 101C). The reduction of sulfate to hydrogen sulfide is directly related to the abundance of available sulfate. Studies have shown that dissolved iron (Fe<sup>2+</sup>) and hydrogen sulfide (H<sub>2</sub>S) tend to be inversely related according to a hyperbolic function. When Fe<sup>2+</sup> concentrations are high, H<sub>2</sub>S concentrations tend to be low and vice versa, which reflects the rapid reaction kinetics of Fe<sup>2+</sup> with H<sub>2</sub>S to produce relatively insoluble ferrous sulfides (Chapelle and others, 2009). The transition from iron- to sulfate-reducing conditions occurs when higher sulfate concentrations are available for sulfate-reducing bacteria to produce sulfide, and the resulting precipitation of iron-sulfide minerals acts as a sink for soluble iron. Kresse and others (2012) provided evidence for the geochemical evolution of redox zonation in similar shale formations in the Boston Mountains area. A series of reduction steps from denitrification, through iron reduction, and ultimately to sulfate reduction occurred with increasing dissolved-solids

concentrations, corresponding to increasing residence time in the aquifer.

Elevated (more than 2.0 mg/L) nitrate concentrations in the Ouachita Mountains aguifer dominantly occurred in association with dissolved-solids concentrations less than 200 mg/L (fig. 101D). Iron concentrations greater than 2,000 µg/L occurred in association with dissolvedsolids concentrations less than 250 mg/L (fig. 101E). When dissolved-solids concentrations exceeded 250 mg/L, all but one of the iron concentrations were less than 200  $\mu$ g/L. Although it appears that nitrate and iron concentrations overlap, the inverse correlation between iron and nitrate (fig. 101A) indicates that redox zonation varies for dissolvedsolids concentrations less than 200 mg/L, depending on conditions along local flow paths in different parts of the aquifer. Sulfate concentrations increased with increasing dissolved solids, and sulfate concentrations exceeding 50 mg/L (up to 535 mg/L) occurred where dissolved-solids concentrations were greater than 250 mg/L (fig. 101F). All of these relations support a conceptual model of redox zonation that fits the theory by Kresse and others (2012) for shale formations in the Boston Mountains. Shale formations are rich in labile organic material, which drives the reduction of initially oxygenated water by aerobic and anaerobic bacteria. These redox processes proceed sequentially from the most to the least energetic microbially mediated reaction (Appelo and Postma, 1999). Oxygen is the first terminal electron acceptor, followed by nitrate, manganese oxide, iron oxyhydroxide, sulfate, and carbon dioxide. Data indicate that nitrate and iron reduction dominate the redox zonation for dissolved-solids concentrations less than 250 mg/L. Concentrations of nitrate and iron appear to overlap along the continuum of increasing dissolved-solids concentrations (representing increased residence time in the aquifer) between approximately 100 and 200 mg/L. Because nitrate reduction precedes iron reduction, this relation appears to violate redox zonation theory. However, the inverse correlation of iron and nitrate (fig. 101A) shows that elevated concentrations for these constituents are mutually exclusive. Either process can be dominant in this region based on the abundance and availability of the respective electron acceptors and dissolved organic matter. Dissolved-solids concentrations more than 250 mg/L are characterized by: (1) the virtual disappearance of iron and nitrate, (2) the dominance of higher sulfate concentrations, and (3) hypothesized sulfate-reducing conditions. This corresponds closely with groundwater-quality data from shale formations in the Boston Mountains (Kresse and others, 2012), which indicate that sulfate reduction dominates over iron reduction for dissolved-solids concentrations exceeding approximately 290 mg/L (see "Western Interior Plains Confining System" section). Therefore, geochemical evolution of groundwater in shale formations appears to be similar throughout the Ouachita Mountains and Interior Highlands. This model of redox zonation accounts for controls on iron solubility, which was not evident from a review of the spatial distribution of iron concentrations or relation to geologic formations.



**Figure 101.** Relation of concentrations for *A*, nitrate and iron; *B*, nitrate and sulfate; *C*, sulfate and iron; *D*, nitrate and dissolved solids; *E*, iron and dissolved solids; and *F*, sulfate and dissolved solids in groundwater from the Ouachita Mountains aquifer in western Arkansas.

## Chloride

High salinity can be a problem in some aquifers, especially for some of the Tertiary and Cretaceous aquifers of the Coastal Plain, but chloride concentrations were low throughout the Ouachita Mountains aquifer. Shale formations formed from marine deposits often retain residual salts. Through the process of uplift and erosion, coupled to continuous flushing by meteoric water over time, much of the original salinity is often flushed from the aquifer. However, wells that penetrate low-porosity, hydraulically isolated zones that still retain high levels of chloride often result in production of slightly brackish water.

Chloride concentrations in the Ouachita Mountains aquifer ranged from 0.9 to 500 mg/L with a median of 7.0 mg/L (fig. 100; table 41). Out of 152 samples, 143 (94 percent) had concentrations that were less than 100 mg/L, 117 (77 percent) were less than 25 mg/L, and only 3 samples exceeded the Federal secondary drinking-water regulation of 250 mg/L. Chloride concentrations, similar to sulfate, generally increased with an increase in dissolved solids. All chloride concentrations more than 50 mg/L occurred at dissolved-solids concentrations greater than 200 mg/L. Extremely low chloride concentrations occur in the eastern part of the aquifer. The greatest density of elevated (greater than 100 mg/L) chloride concentrations occur in Scott County. Wells in this area are completed in the shale-dominated rocks of the Atoka Formation. For quartz formations, only 1 of 44 samples had a concentration that was greater than 10 mg/L (54 mg/L), and 38 of the 44 samples were less than 10 mg/L.

In summary, groundwater quality in the Ouachita Mountains aquifer is good with respect to Federal primary drinking-water standards. Problems in regard to taste, staining, and other aesthetic properties are related to elevated levels of iron, which is a common complaint among domestic users. Geochemical data indicate that an important control on iron solubility is sulfate reduction, which occurs dominantly in groundwater with dissolved-solids concentrations greater than 250 mg/L. Nitrate was somewhat elevated (greater than 1.0 mg/L) in numerous wells; however, only 4 of 101 samples exceeded the Federal MCL of 10 mg/L. Concentrations more than 1.0 mg/L generally occurred in wells less than 200 ft in depth. As is the case with most aquifers, shallow groundwater is more vulnerable to surface sources of contamination.

# Western Interior Plains Confining System

The Boston Mountains (fig. 3) are represented by a group of formations that comprise dominantly fractured shale and sandstone rocks, which are characterized by low secondary porosity and permeability with resulting low yields. Regional hydrogeologic framework studies (Imes and Emmett, 1994) characterize this system of formations as a regional confining unit, referred to as the Western Interior Plains confining system (table 5). Although regionally designated as a confining system, these formations are important locally as valuable sources of water supply. Unfortunately, there are no reports that view this collection of rocks as a regional aquifer system because of the dominance of shale formations and low well yields. However, historical reports discuss hydrologic characteristics and water quality for individual formations in this system of rocks. Historical and current USGS water-use reports use the term "rocks of Paleozoic age, undifferentiated" to refer to the total reported groundwater use from all shallow rock formations of the Interior Highlands, including those of the Ouachita Mountains, the Boston Mountains, and the Ozark and Springfield Plateaus regions. Although this report retains the accepted regional nomenclature of Western Interior Plains confining system for this system of formations, it is implied and often referred to in the following discussion as an important aquifer system in Arkansas.

# **Geologic Setting**

The Western Interior Plains confining system comprises 11 different predominantly clastic (sand, siltstone, shale) formations of Upper Mississippian and Pennsylvanian age (tables 2 and 5). These formations are relatively thin in the northern Boston Mountains and thicken considerably to the south at rates of approximately 180 ft/mi. Total thickness of the formations is more than 6,000 ft beneath the Arkansas River Valley (Imes and Emmett, 1994). The lithology and hydrogeological characteristics of these formations are very similar. Consequently, a detailed discussion of each formation is not integral to the understanding of this shallow aquifer system. For additional information on the stratigraphy of the individual formations composing the confining system, the reader is referred to McFarland (2004). A general knowledge of the basic rock types is sufficient to understanding the hydrologic characteristics and geochemistry of groundwater from the Western Interior Plains confining system.

## Hydrologic Characteristics

The Western Interior Plains confining system (fig. 3) consists of alternating sequences of low-permeable shale and siltstone, and low- to moderate-permeable sandstone, with minor occurrences of limestone and coal. Regionally, the confining system impedes the flow of water to and from the underlying Springfield Plateau aquifer (Imes and Emmett, 1994). The designation of these combined formations as a "confining system" is a consequence of the marked permeability contrast between the high porosity karst limestone of the Springfield Plateau aquifer compared to the low fracture porosity in the Western Interior Plains confining system. Porosity in the well-indurated clastic rocks of the Western Interior Plains confining system is dependent upon weathering and resultant fracture development. Chemical and physical weathering processes result in the development of secondary porosity through expansion and fracturing of the rocks. Fractures tend to exhibit denser distribution and larger apertures near the surface because of unloading expansion

that is a mechanical response to decreased compressive stress as overlying rocks are eroded and removed. The hydraulic properties of the Western Interior Plains confining system exhibit low primary porosity, secondary porosity from fractures associated with compression, uplift and weathering, and low yields that rarely exceed 1–5 gal/min, similar to that of the shale- and sandstone-dominated Ouachita Mountains aquifer.

Imes and Emmett (1994) noted that local groundwaterflow systems in the Western Interior Plains confining system are dominantly present in the upper 300 ft of the weathered confining system. This is because fractures generally have a larger aperture near the surface and diminishing width with depth. Porosity and permeability generally decrease to a magnitude insufficient to support production from wells at depths more than approximately 300 ft (Cordova, 1963; Kilpatrick and Ludwig, 1990b; Imes and Emmett, 1994; Kresse and others, 2012). Kresse and others (2012) reported on 58 wells in the central part of the Western Interior Plains confining system with depths ranging from 25 to 385 ft with a median of 87 ft. Many wells in the Western Interior Plains confining system often go dry during pumping, particularly during drought periods (Cordova, 1963; Kresse and others, 2012). The quantity of groundwater available in the Western Interior Plains confining system is related directly to the density, size, openness, and degree of interconnection of fractures (Cordova, 1963).

Groundwater generally is recharged by precipitation that infiltrates in upland areas, percolates to the water table, flows downgradient toward lowland areas, and discharges into streams (Imes and Emmett, 1994). A conceptual model of groundwater flow for the Western Interior Plains confining system is controlled by expansion fractures with limited groundwater storage and has sufficient yields almost solely for use as domestic supply. Groundwater flow paths are constrained by small-scale topographic boundaries with flow from elevated areas to valley floors in small stream systems (Cordova, 1963; Imes and Emmett, 1994; Kresse and others, 2012). Regional hydraulic heads and flow gradients probably have changed little since predevelopment because of the poor hydraulic connection between lower and higher permeability zones. Water-level measurements in any one well represent averages of all the water-yielding layers in the Western Interior Plains confining system (Imes and Emmett, 1994).

Because of the low porosity of the Western Interior Plains confining system, well yields generally are sufficient only for household, small public-supply, and nonirrigation farm uses. Cordova (1963) noted that most wells yielded less than 60 gal/min, which is the maximum yield in the Western Interior Plains confining system. Thicker sandstone units in the Atoka Formation and the Batesville Sandstone in the eastern part of the confining system commonly yield 5–10 gal/min to wells less than 300 ft deep (Albin and others, 1967a). Kilpatrick and Ludwig (1990b) also noted that yields typically are less than 10 gal/min. Well yields for 16 shallow wells in southwestern Washington County ranged from 2 to 19 gal/min (Muse, 1982). Water levels in the Western Interior Plains confining system typically range from near land surface to approximately 50 ft below land surface. Seasonal fluctuations are approximately 10 ft with drawdowns from pumping as much as 45 ft (Cordova, 1963; Albin and others, 1967a).

## Water Use

Difficulties exist when attempting to gather information on use of groundwater in the Interior Highlands. Before development of surface-water resources, wells were common throughout the region for domestic and livestock supply and less common for public supply, commercial, and industrial purposes (Purdue and Miser, 1916; Cordova, 1963; Albin and others, 1967a; Lamonds, 1972). Because domestic and publicsupply systems serving less than 50,000 gal/d are not required to report their groundwater use, there is no way to accurately quantify the number of domestic and livestock wells currently in use. Thirteen wells were reported as completed in the Atoka Formation of the Western Interior Plains confining system in 2010 (Terrance W. Holland, U.S. Geological Survey, written commun., 2013). These wells were mainly used for public supply or parks. Several schools, stores, parks, and some commercial businesses also withdraw water from the Western Interior Plains confining system (Lyle Godfrey, Arkansas Health Department, written commun., 2012).

# Water Quality

Little groundwater-quality monitoring has been done in the past related to the Western Interior Plains confining system. Most water-resource investigations in the Ozark Plateaus have concentrated on the Springfield Plateau and Ozark aquifers. Kilpatrick and Ludwig (1990a) reported that overall geochemistry in the area is closely related to the mineral concentration of the rock, although no detailed discussions were provided to explain this observation. The water was described as a calcium-magnesium-bicarbonate type, hard, and high in iron, with areas of slightly saline water and occasional high nitrate concentrations (Kilpatrick and Ludwig, 1990a).

Groundwater in formations of the Western Interior Plains confining system was noted to have bicarbonate as the principal anion with sodium, calcium, or magnesium dominating the cations dependent on the formation type (Cordova, 1963). Lamonds (1972) stated that groundwater ranged from a calcium- to a sodium-bicarbonate type with dissolved-solids concentrations ranging from 20 to 1,200 mg/L. Dissolved-solids concentrations for groundwater in sandstones of the Atoka Formation typically ranged up to 200 mg/L, whereas groundwater from shale formations typically had dissolved-solids concentrations greater than 200 mg/L. Cordova (1963) attributed sodium- and magnesium-chloride water types to proximity of hydrocarbon accumulations and attributed the sulfate water type to oxidation of pyrite. Cordova also noted that iron concentration varied widely, ranging from nondetectable to 19 mg/L. Odors of hydrogen sulfide and iron staining on plumbing fixtures were the major complaints of household residents (Cordova, 1963).

Albin and others (1967a) reported on water resources of Jackson and Independence Counties, which are located in the eastern extent of the Western Interior Plains confining system. Analyses for the Atoka Formation indicated that groundwater generally was of good quality with low concentrations for most chemical constituents; though, in a few areas, the water was hard with elevated iron concentrations. The poorest quality groundwater was noted in groundwater from the Fayetteville Shale, which contained elevated concentrations of iron, sodium, sulfate, chloride, and dissolved solids relative to other formations (Albin and others, 1967a). Lamonds (1972) also noted that groundwater from black shale can be high in sulfide and sulfate.

The primary scope of previously described earlier reports was a general assessment of the quantity and quality of surface and subsurface waters throughout the State. Detailed geochemical evaluations to assess rock/water interactions and microbially mediated processes affecting geochemical evolution of groundwater, in addition to anthropogenic sources affecting groundwater quality, were outside the scope of these earlier reports. Recent groundwater studies (Kresse and Hays, 2009; Kresse and others, 2012; Warner and others, 2013) collected a more extensive and comprehensive geochemical database. These recent studies also provided an analysis of isotopic compositions to better understand rock/water interactions and evolution of groundwater geochemistry with respect to rock type in the Interior Highlands. These recent studies confirmed the poor quality of groundwater quality from shale formations and showed marked differences in the geochemistry of groundwater from quartz formations (sandstone, chert, and novaculite) and shale formations in the Interior Highlands.

## General Geochemistry and Water Type

There is no definitive spatial trend for various chemical constituents in the Western Interior Plains confining system, which contrasts markedly with the strong trend noted for most of the aquifers of the Coastal Plain. One explanation for the lack of spatial trends is the predominance of relatively short, local flow paths, and small fracture size. These affect groundwater residence time and the amount of flushing in the Western Interior Plains confining system. The nature of the alternating geologic formations and differing associated mineralogies across the areal extent of the Western Interior Plains confining system are also a factor.

A detailed analysis of groundwater geochemistry in the central part of the Western Interior Plains confining system was performed by Kresse and others (2012) as part of an assessment of potential effects of gas-extraction activities in the Fayetteville Shale. This study used groundwater data from 127 wells completed dominantly in the Atoka and Bloyd Formations. Out of 282 groundwater samples compiled for this report, 260 (92 percent) samples were from the Atoka (191 samples) and Bloyd (69 samples) Formations, with the remaining 22 samples distributed among other formations. Because Kresse and others (2012) reported on groundwater quality and geochemistry using data dominantly from the Atoka and Bloyd Formations, their study can be used to explain the variation in geochemistry for most of the Western Interior Plains confining system, as these two formations constitute the greatest area of exposure throughout the confining system.

Much of the variation in groundwater geochemistry within the Western Interior Plains confining system can be explained by the dominant geology in the region, which mainly consists of alternating shale and sandstone units. In most areas, shale dominates the lithology with minor occurrences of thin sandstone units within any one vertical section. In some other areas, thicker sandstone units occur. Distinct geochemical differences were noted in groundwater extracted from shale compared to groundwater extracted from quartz formations in the Ouachita and Boston Mountains areas, which are dominated by these clastic lithologies (Kresse and Hays, 2009; Kresse and others, 2012). These differences in groundwater geochemistry were definable, reproducible, and consistent across both areas and were controlled by mineralogy. This is primarily related to the presence or absence of carbonate minerals, as well as redox zonation for a given section of aquifer penetrated by each well. Much of the following discussion on the evolution of geochemistry in the Western Interior Plains confining system is taken from Kresse and Hays (2009) and Kresse and others (2012).

Similar to most aquifers in Arkansas, groundwater in the Western Interior Plains confining system generally is a strong bicarbonate water type. Bicarbonate accounted for more than 50 percent of the total anions in 202 of 249 (81 percent) samples with complete anion (chloride, sulfate, bicarbonate) analyses. Eighty-three of these 202 samples had percent bicarbonate exceeding 90 percent. Bicarbonate concentrations ranged up to 980 mg/L with a median of 129 mg/L (fig. 102; table 42). For samples with bicarbonate as the dominant anion, groundwater ranged from calcium- and calcium-magnesiumbicarbonate to a sodium-bicarbonate water type. Bicarbonate concentrations increased with increasing dissolved-solids concentrations. This relation indicates that dissolution of carbonate minerals accounts for the increasing bicarbonate concentrations, which drives the concomitant increases in dissolved solids (fig. 103A). Shale formations in the Western Interior Plains confining system have abundant carbonate minerals because the source sediments accumulated in marine environments (McFarland, 2004). Similarly, increasing values of pH correlated to increasing concentrations of bicarbonate and dissolved solids (figs. 103B, C).



**Figure 102.** Interquartile range of selected chemical constituents in groundwater from the Western Interior Plains confining system in northern Arkansas.

 Table 42.
 Descriptive statistics for selected chemical constituents in groundwater from the Western Interior Plains confining system in northern Arkansas.

[mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Constituent or characteristic	Minimum	Median	Maximum	Standard deviation	Number of wells
Calcium (mg/L)	0.1	16.4	160	24.9	262
Magnesium (mg/L)	0.07	4.98	211	17.1	262
Sodium (mg/L)	0.9	12.3	844	74.7	257
Potassium (mg/L)	0.13	0.8	11	1.87	128
Bicarbonate (mg/L)	2.0	129	980	137	256
Chloride (mg/L)	0.9	5.0	1,100	78.2	282
Sulfate (mg/L)	0.02	4.7	1,030	80.6	267
Silica (mg/L)	0.18	11	47.7	8.2	252
Nitrate (mg/L as nitrogen)	0.01	0.09	18	1.95	214
Dissolved solids (mg/L)	7.0	176	2,460	346	129
Iron (µg/L)	0.05	27	13,800	2,410	163
Manganese (µg/L)	0.13	100	4,370	519	218
Arsenic (µg/L)	0.03	0.03	16.9	1.28	200
Hardness (mg/L as calcium carbonate)	4.0	73	1,100	131	195
Specific conductance (µS/cm)	13	267	3,500	388	280
pH (standard units)	3.5	6.6	8.8	1.1	266



**Figure 103.** Relation of *A*, dissolved solids and bicarbonate; *B*, bicarbonate and pH; *C*, dissolved solids and pH; *D*, calcium plus magnesium/bicarbonate and sodium/chloride; *E*, dissolved solids and sulfate; and *F*, dissolved solids and chloride in groundwater from the Western Interior Plains confining system in northern Arkansas.

Similar to most aquifers in Arkansas, recharge of slightly acidic precipitation with a mean pH value of approximately 4.7 (Kresse and Fazio, 2002) is neutralized with the dissolution of carbonate minerals. This results in increasing pH values along a continuum of increased residence time with resultant increasing dissolved-solids concentrations in the Western Interior Plains confining system (Kresse and Fazio, 2002; Kresse and Hays, 2009; Kresse and others, 2012). Values of pH ranged from 3.5 to 8.8 (table 42), and 16 samples had pH values less than 4.7. Values of pH lower than the pH of rainwater are attributed to formation of carbonic acid by dissolution of carbon dioxide with recharging precipitation in the unsaturated zone of carbonate-free sandstone units (Kresse and Hays, 2009; Kresse and others, 2012). Bicarbonate concentrations and pH values show no clearly discernible spatial trends. However, some groupings of lower values for pH (for example, in extreme southern Van Buren County; fig. 104) suggest that wells may be producing from areal extensive sandstone units. Similarly, a grouping of higher pH values in northern Faulkner County may indicate wells completed in predominately shale rocks (fig. 104).

In addition to mineral dissolution, cation exchange is one of the more important rock/water interaction processes affecting groundwater geochemistry and resulting water type. Cation exchange occurs when groundwater is in contact with clays and weathered shale surfaces. Kresse and others (2012) showed that sodium/chloride equivalent ratios were inversely correlated to calcium plus magnesium/bicarbonate ratios. This suggests that cation exchange was actively occurring in the Western Interior Plains confining system, increasing sodium while decreasing calcium in solution. Data compiled for this report showed a similar relation between these two ratios for the Western Interior Plains confining system (fig. 103D). The lowest sodium/chloride ratios occur in groundwater with the lowest dissolved-solids concentrations and lowest pH values. Sodium/chloride ratios increase with increasing dissolved solids, indicating that cation exchange progresses with increasing residence time in the aquifer. Ultimately, this results in sodium/chloride equivalent ratios nearly 70 times the oneto-one ratio resulting from dissolution of sodium-chloride salts (Kresse and others, 2012).

#### Nitrate

Nitrate concentrations in the Western Interior Plains confining system ranged from 0.01 to 18 mg/L as nitrogen with a median of 0.09 mg/L (table 42). Of 214 samples with nitrate data, 169 (79 percent) were less than 0.5 mg/L and 186 (87 percent) were less than 1.0 mg/L, reflecting the overall low nitrate concentrations in groundwater from the Western Interior Plains confining system. Only two samples had nitrate concentrations exceeding the Federal MCL of 10 mg/L as nitrogen. Generally, higher nitrate concentrations occurred near the southern boundary of Van Buren County in the same area as wells with low pH values (fig. 104) and, therefore, low dissolved-solids concentrations (fig. 103*C*). An inverse relation noted for nitrate and dissolved solids confirmed this

observation in that most nitrate concentrations are more than 1.0 mg/L when dissolved-solids concentrations are less than 125 mg/L. Kresse and others (2012) similarly noted that nitrate concentrations were highest in groundwater samples with low pH and low dissolved-solids concentrations. Low pH and low dissolved-solids concentrations in groundwater were noted by Kresse and others (2012) as occurring in poorly buffered sandstone units. This suggests that sandy soils developed in these areas have increased permeability and concomitantly increased vulnerability to surface and shallow subsurface (for example, septic systems) sources of nutrients. By comparison, clayey soils developed in regions of weathered shale outcrops have less permeable soils that retard transport of nutrients to the water table. Kresse and others (2012) also showed inverse correlations of nitrate with iron and manganese concentrations. This suggests that nitrate is removed from the system by denitrification with increased residence time along the flow path. These relations suggest that the occurrence and distribution of nitrate is related to degree of vulnerability associated with soils of varying permeability, reduction of nitrate with increased residence time in the aquifer, or a combination of both processes. No relation was noted between well depth and nitrate in the Western Interior Plains confining system. For many of the aquifers in the Coastal Plain, nitrate generally was inversely correlated to well depth.

## Iron

Iron concentrations in the Western Interior Plains confining system ranged from 0.05 to 13,800  $\mu$ g/L with a median of 27  $\mu$ g/L (fig. 102; table 42). Iron concentrations were below the Federal secondary drinking-water regulation of 300  $\mu$ g/L in 120 of 163 (74 percent) samples. Groupings of concentrations exceeding 500  $\mu$ g/L generally occur in Faulkner County and into eastern Conway County and similarly throughout Cleburne and White Counties (fig. 104). However, wells with high iron concentrations occur next to wells with low concentrations, indicating the lack of a welldefined and consistent spatial distribution trend. The lack of any spatial trend suggests that the occurrence of iron is a function of mineralogical and reduction-oxidation processes occurring with increased residence time along localized and relatively short groundwater flow paths.

Kresse and others (2012) showed that dissolved iron was lowest (less than 500 µg/L) in groundwater with dissolved solids less than 60 mg/L, generally correlating to regions with high nitrate concentrations. Iron concentrations increased with increasing dissolved-solids concentrations up to approximately 290 mg/L and decreased for dissolved-solids concentrations greater than 290 mg/L. Arsenic concentrations had similar trends with increasing dissolved solids. Kresse and others (2012) hypothesized that sulfate reduction dominates redox zonation at dissolved solids more than 290 mg/L, removing iron from solution with the precipitation of iron sulfide minerals. For a more detailed discussion, see the later section "Conceptual Model of Groundwater Geochemical Evolution."



**Figure 104.** Spatial distribution of selected chemical constituents in groundwater from the Western Interior Plains confining system in northern Arkansas.

## Sulfate

Sulfate concentrations generally were low throughout the Western Interior Plains confining system. Only three samples were higher than the secondary drinking-water regulation of 250 mg/L. Sulfate concentrations ranged from 0.02 to 1,030 mg/L with a median of 4.7 mg/L (fig. 102; table 42). Out of 267 samples, 243 (91 percent) had concentrations less than 50 mg/L. Cordova (1963) attributed sulfate in groundwater to oxidation of pyrite; however, Kresse and others (2012) hypothesized that appreciable sulfate concentrations results from gypsum dissolution. Sulfate concentrations increased with increasing dissolved-solids concentrations (fig. 103E). For dissolved-solids concentrations less than 100 mg/L, sulfate was less than 10 mg/L. For dissolved-solids concentrations between 100 and 200 mg/L, sulfate was less than 25 mg/L. All sulfate concentrations greater than 50 mg/L occurred at dissolved-solids concentrations greater than 200 mg/L. This is a region that was shown by Kresse and others (2012) to be under iron- and possibly sulfate-reducing conditions in which pyrite would be stable. Additionally, increases in sulfate generally correlated to increases in calcium/bicarbonate equivalent ratios more than 1.0 and up to 8.0. This correlation suggested that excess calcium not accounted for by dissolution of carbonate minerals may be derived from dissolution of gypsum.

#### Chloride

Chloride concentrations generally are low in groundwater throughout the Western Interior Plains confining system. Chloride concentrations ranged from 0.9 to 1,100 mg/L with a median concentration of 5.0 mg/L (fig. 102; table 42). Out of 282 samples, 195 (69 percent) were less than 10 mg/L, and only 5 samples exceeded the Federal secondary drinkingwater regulation of 250 mg/L. Residual salinity from the marine environment in which shales of the Atoka and Bloyd Formations were deposited generally has been flushed over time by infiltrating precipitation. In low permeability zones or hydraulically isolated areas that have not been flushed over time, higher salinity water can be released into the well bore. This raises chloride concentrations above the generally low concentrations found across much of the Western Interior Plains confining system. Chloride concentrations increase with increasing dissolved solids (fig. 103F). This suggests that higher chloride concentrations in groundwater are more likely in regions of more evolved groundwater with a longer residence time along a given flow path, affording greater rock/ water interaction over time.

## Conceptual Model of Groundwater Geochemical Evolution

A general analysis of abundant groundwater geochemical data enabled the development of a conceptual model for the evolution of groundwater geochemistry in the shallow Western Interior Plains confining system. Kresse and others (2012) used nonparametric statistical analysis to show that groundwater from the Atoka and Bloyd Formations have a similar geochemistry. This suggested that the geochemistry in both formations results from similarities in mineralogy of the interbedded sandstone and shale. Because 92 percent of the samples compiled for this report were from these formations, this general model may be applied to the system as a whole and is discussed in more detail in the following paragraphs.

Kresse and others (2012) evaluated data from 127 groundwater samples primarily from the Atoka and Bloyd Formations to construct a geochemical model for evolving water type. A plotting of water types along a continuum of increasing dissolved solids showed that major ion geochemistry is not random but follows a predictable pattern based on rock type and rock/water interaction. The continuum of increasing dissolved solids represents increased residence time in the aquifer system. The lowest pH values, ranging from 4.2 to 5.8, occurred in groundwater with dissolved-solids concentrations less than approximately 30 mg/L (fig. 105). Although chloride concentrations increased with increasing dissolved-solids concentrations, chloride was found to be the dominant anion almost solely for dissolved-solids concentrations less than 30 mg/L. The geochemistry of these samples resembled that of evaporated rainwater with minor addition of silica and trace metals (Kresse and Fazio, 2002). Much of this groundwater is theorized to be derived from carbonate-free sandstone units. Similar findings were noted in the Ouachita Mountains aquifer near Hot Springs (Garland County), where well-defined, thick sequences of quartz formations and shale formations allowed the association of unique groundwater chemistry for each rock type. Groundwater from the quartz formations was soft and acidic (7 of 11 samples had pH values less than 4.7 and 3 samples were less than 4.0), indicating a quartz source rock with little to no buffering capacity (Kresse and Hays, 2009).

In general, groundwater with dissolved-solids concentrations greater than 30 mg/L had bicarbonate as the dominant anion and shale as the dominant rock type. Groundwater with dissolved-solids concentrations between 31 and 95 mg/L exhibited a mixture of calcium-bicarbonate and mixed-bicarbonate water types. For groundwater with dissolved-solids concentrations between 96 and 249 mg/L, calcium-bicarbonate was the dominant water type in 24 of the 40 samples. A majority of the remaining samples had increasing sodium percentages and sodium as one of two major cations representing groundwater transitioning toward sodium as the dominant cation. For groundwater with dissolved-solids concentrations greater than 250 mg/L, 20 of 51 samples were a sodium-bicarbonate water type with sodium percentages ranging from 52 to 99 percent of the total cations. The remaining samples primarily were calcium-bicarbonate water types with a few transitional water types (fig. 105).

Kresse and others (2012) described the effects of reduction-oxidation (redox) processes in the Western Interior Plains confining system using redox-sensitive inorganic constituents and methane for 51 groundwater samples.



**Figure 105.** Relation between dissolved-solids concentrations and pH values with a depiction of the evolution of chemical water types for groundwater from the Western Interior Plains confining system in northern Arkansas (from Kresse and others, 2012).

Using the same continuum of increased residence time for groundwater to investigate evolution of redox zonation in the aquifer system is informative and enables refining of the geochemical model. Shale formations in the Western Interior Plains confining system are rich in labile organic material, which drives the reduction of oxygenated water by aerobic and fermentation bacteria. As recharging water enters an aquifer system having abundant organic matter, oxygen first will be used as a terminal electron acceptor; followed by nitrate, manganese oxide, iron oxyhydroxide compounds, and sulfate; and finally carbon dioxide with the generation of methane. Depending on the available supply of electron donors (carbon) and electron acceptors (oxidizers), redox zonation can stop at any point along this continuum or proceed through each sequence to methane production (Kresse and others, 2012).

Kresse and others (2012) noted that the highest nitrate concentrations occurred for groundwater with dissolved-solids concentrations less than approximately 100 mg/L. Conversely, the highest iron concentrations occurred in association with

dissolved-solids concentrations greater than 90 mg/L. Data compiled for this report confirmed that nitrate concentrations generally were less than 0.5 mg/L for dissolved-solids concentrations greater than 100 mg/L. For dissolved-solids concentrations greater than approximately 90 to 100 mg/L, nitrate has been consumed, resulting in the prevalence of manganese- and iron-reducing conditions. Iron and manganese had well-defined inverse correlations with nitrate, thus confirming this assumption. As nitrate is depleted, iron and manganese oxides are reduced, releasing iron and manganese into solution. Iron concentrations generally increased to approximately 290 mg/L, at which point, iron concentrations steadily decreased to low and nondetectable concentrations for dissolved solids exceeding 500 mg/L (fig. 106A). Arsenic concentrations (fig. 106B) behaved in a similar fashion. Kresse and others (2012) hypothesized that beyond a dissolved-solids concentration of 290 mg/L, sulfate reduction dominates over iron reduction with free sulfide combining with iron (and arsenic) to precipitate as iron-sulfide minerals.



**Figure 106.** Relation between dissolved-solids concentrations and *A*, iron and *B*, arsenic concentrations in groundwater from the Western Interior Plains confining system in northern Arkansas.

Biogenic methane was detected in 32 of 51 samples with 7 of the samples having methane concentrations greater than 0.5 mg/L (maximum of 28.5 mg/L). Methane concentrations increased with increasing dissolved-solids concentrations. Concentrations greater than 1.0 mg/L generally occurred at dissolved-solids concentrations more than 475 mg/L. Therefore, the conceptual model for geochemical evolution in the Western Interior Plains confining system is one where increased groundwater residence time in the shallow aquifer system drives rock/ water interaction, particularly cation exchange. This results in transitioning from a calcium- to a sodium-bicarbonate water type along the flow path. Microbial-mediated redox zonation similarly transitions with increasing residence time in the aquifer through oxygen consumption; reduction of nitrate, iron and manganese oxides, and sulfate; and eventually to the production of biogenic methane (Kresse and others, 2012).

In summary, water quality generally is good throughout the Western Interior Plains confining system. Groundwater with elevated iron, nitrate, sulfate, and chloride occurs in localized areas, depending on rock type and position along a flow path. Groundwater varies from a soft, slightly acidic type, typically encountered in wells completed in sandstone rocks, to a calcium-and sodium-bicarbonate water type dependent on the amount of cation exchange in the groundwater system. Reducing conditions are found throughout the Western Interior Plains confining system, predominantly for groundwater from shale rock, with a complete redox zonation from nitrate-reducing conditions to production of methane.

# **Springfield Plateau Aquifer**

The Springfield Plateau aquifer (fig. 3) lies within the Springfield-Salem Plateaus section of the Ozark Plateaus (fig. 3; tables 2 and 5) and comprises a sequence of limestone and cherty limestone of Mississippian age. The Ozark Plateaus (Ozarks) are a region of unique and complex hydrogeology and physiography. The Ozarks are characterized by a predominantly mantled karst terrain where aquifer anisotropy and heterogeneity, and variability in aquifer hydraulic characteristics are the norms. This variability is noted on a small spatial scale where (1) groundwater-flow velocities vary from 10-6 ft/s to several feet per second, (2) a well may produce 0.01 gal/min or 1,000 gal/min, (3) groundwater chemistry may not reflect interaction with the aquifer matrix compared in one location and nearby may be mineral saturated and actively precipitating authigenics, (4) surface-derived contaminants may be effectively ameliorated within a short distance or may travel great distances with little to no attenuation, and (5) a subsurface may be essentially lifeless or home to numerous cave-related species. Groundwater flow and quality within the Ozark Plateaus are controlled by (1) the lithologies of the rocks exposed at the surface that convey

groundwater flow; (2) stratigraphic relations of these different lithologies; and (3) geologic structure, including the physical modifications to the rocks that have occurred over time.

# **Geologic Setting**

The Ozarks are referred to locally and regionally as the "Ozark Mountains." Geologic structure of the Ozarks, however, is characterized by a lack of any intense modification over an expanse of geologic time; therefore, the Ozarks generally are not considered a true mountain range. The great topographic relief in the area results from erosional dissection of the plateaus that has been controlled to a degree by presence of structural features such as faults and fracture zones as well as by lithology. The Ozarks were formed by a structural dome that has been uplifted during several periods since Precambrian time (Nunn and Lin, 2002; Tennyson and others, 2008; Cox, 2009). The core of the dome is in southeastern Missouri. Sedimentary units in Arkansas drape off of the southern and southwestern margins of the dome with gentle regional dips generally ranging from 10 to 100 ft/mi and steeper dips being common near faults (Frezon and Glick, 1959). Widespread extensional fracturing, jointing, and faulting of Ozarks' rocks occurred with uplift (Hudson and Cox, 2003), creating secondary porosity that has provided key nucleation points for initiation of dissolution of the carbonate rocks and karst development.

The karstic bedrock of the region is overlain by weathered regolith that greatly varies in thickness from near zero in many areas to more than 100 ft. Areas of low topographic relief, including plateau tops and valley floors, tend to have greater thicknesses of regolith. Steep areas tend to have lesser thicknesses of regolith, although thicknesses are variable within all areas. The regolith mantles the underlying karst topography, which typifies the Ozarks' karst and distinguishes the region from classic occurrences of karst elsewhere. The regolith is a clay-rich, typically low-permeable unit that contains variable amounts of chert. This material is derived from weathering of the original Mississippian and, in some areas, Pennsylvanian capping units and comprises refractory impurities and weathering products-predominantly chert and clay. The regolith generally is present as a silt-loam surface soil overlying a clay-loam subsoil, which can vary from being well-drained and exhibiting moderate permeability to very tight with low permeability. Chert constitutes up to 90 percent of the regolith in some areas. The chert is present from sand to boulder size and is present as remnant layers that remain in weathered soil profiles. These layers often create barriers to infiltration of recharge water. Where present in considerable thickness, the regolith is a strong impediment to infiltration of precipitation and leakage from surface water, protecting the underlying karst aquifer from rapid input of surface-derived contaminants. However, the variable thickness of the regolith and the variable clay content render the protective qualities of the regolith somewhat sporadic throughout the Ozarks.

The Boone Formation comprises the Springfield Plateau aquifer (Imes and Smith, 1990; Imes and Emmett, 1994) and is exposed across most of the Springfield Plateau. However, outlier remnants of confining clastics are observed in the southern area of the Springfield Plateau where the upper Mississippian section is represented by the Batesville Sandstone and the Fayetteville Shale (Adamski and others, 1995; table 5). These sandstone and shale units typically are well-cemented and exhibit low matrix porosity and permeability but exhibit moderate porosity and permeability where weathered or highly fractured. Owing to the predominance of low-permeable shale and sandstone, the Upper Mississippian and Pennsylvanian strata are included in the Western Interior Plains confining system hydrogeologic unit to the south in the Boston Mountains (Imes and Smith, 1990; Imes and Emmet, 1994; Adamski and others, 1995).

The Boone Formation has a thickness of about 200–500 ft (McFarland and others, 1979) but is variably eroded across the plateau. The basal St. Joe Limestone Member of the Boone Formation is a relatively pure limestone. Above the St. Joe, the Boone Formation contains abundant chert, which can exceed 70 percent of the interval. Matrix porosity and permeability of the Boone Formation are very low (Stanton, 1993), but where fracturing has occurred, carbonate dissolution has greatly enhanced porosity and permeability (Nunn and Lin, 2002). Solutioning of the fractures ultimately created the karst terrain that typifies the area.

Bedrock in the Ozarks shows evidence of multiple episodes of water movement and carbonate dissolution defining distinct karst development events through time (Stoffell and others, 2008). Exposure of Ordovician strata associated with the Ordovician-Mississippian unconformity resulted in dissolution and some paleokarst development. Widespread dissolution features associated with the lead and zinc ore-bearing fluids that moved from the Arkoma Basin (Leach and Rowan, 1986) are observed across the Ozarks region. Lead and zinc were mined commercially where faults conveyed mineral-saturated fluids up from depth. Hypogene indicators such as diagnostic calcite isotopic compositions (Brahana and others, 2009), collapse breccias (McKnight, 1935), and isotopic dating (Brannon and others, 1996) show that this episode of fluid movement and dissolution was a separate occurrence predating recent karst development. Exposure of Mississippian strata associated with the Mississippian-Pennsylvanian unconformity resulted in meteoric diagenesis followed by pedogenesis, regolith formation, and paleokarst development on the Pitkin Limestone (Webb, 1994). The Ozarks once again showed active karst development as uplift, denudation, and abundant precipitation; recharge initiated dissolution of soluble carbonate lithologies.

The recent period of dissolution and karst development has had a very visible impact on the modern karst land surface, controlling subsurface flow and ultimately the surface flow in the region. The hydrogeology of the region is typical of karst with focused flow paths that are well connected to the surface and deliver water from input to discharge points at streams and springs at velocities of tens to thousands of feet per day (Funkhouser and others, 1999; Mott and others, 2000; Hudson and others, 2005; Hudson and Turner, 2007). Abundant karst features are apparent-ponors, losing stream reaches, springs, caves, and sink holes. However, recent karst development often reactivated and followed previous dissolution-enhanced flow paths that originally developed during ancient exposure periods (such as at the Ordovician-Mississippian and the Mississippian-Pennsylvanian unconformities; Webb, 1994) or hypogene episodes (such as Mississippi Valley Type ore emplacement; Leach and Rowan, 1986; Brannon and others, 1996; Brahana and others, 2009). Another very important phenomenon caused by karst development is interbasin transfer of water. Dye tracing studies and observations of drainage-area and discharge relations show the abundant occurrence and transfer of groundwater across surface-water drainage-basin divides (Sullavan, 1974; Brahana and Davis, 1998; Mott and others, 2000). Consideration of interbasin movement of water is an important point for protection and management of groundwater because contributing zones are not apparent at the surface, and contaminants can be introduced into groundwater from unexpected locations. This interbasin transfer has been shown to be driven more by local hydraulic gradients than by interbasin structure and karst development (Mott and others, 2000).

# Hydrologic Characteristics

The Springfield Plateau aquifer generally is unconfined across the Springfield Plateau and confined in the Boston Mountains. The highly soluble nature of carbonate rocks of the Boone Formation has given rise to development of the distinctive karst terrain and pervasive occurrence of karst features, such as caves, springs, and sinkholes. There is hydraulic connection of surface water and groundwater as well as the variable aquifer characteristics that typify the area (fig. 107). Karst aquifers are typified by a bimodal distribution of porosity-primary matrix porosity and small fracture porosity. This results in low porosity values for individual small-scale samples that are pervasive through the aquifer matrix and constitute a large proportion of total porosity. Secondary fractures and dissolution-enhanced porosity are significant within focused areas but represent a smaller proportion of the total porosity. The control of these porosity types on permeability leads to two end-member flow types—diffuse and focused flow (Alley and others, 2002; Ghasemizadeh and others, 2012). The bimodal nature of karst porosity enables spring and stream base flow to be maintained. The slower diffuse flow allows for sustained groundwater input to streams and springs, even during dry periods. The faster focused flow provides extremely rapid response and short transit times for precipitation events. An observable and prominent feature associated with karst aquifers is caves,



- sinkholes - large aperature fractures
  - 4 Focused: indirect - losing stream
- Spring Evapotranspiration

8

9 Evapotranspiration
 10 Withdrawals

Figure 107. Conceptual model of karst hydrogeologic setting for the Springfield Plateau aquifer in northern Arkansas.

which serve as a window into the Springfield Plateau aquifer and allow the study of environments in the saturated and unsaturated zones. Large cavernous conduits and solution features allow for deep and rapid circulation of groundwater. Conduits and dissolution-enhanced fracturing help integrate flow to spring resurgences (Harvey, 1980). As a result, high-discharge springs are common throughout the exposed sections of the Springfield Plateau aquifer.

High hydraulic conductivities of as much as 1,000 ft/d (Stanton, 1993) associated with the Springfield Plateau aquifer result from the development of secondary porosity

through diagenetic processes, which particularly results from dissolution of bedrock along joints, fractures, and bedding planes rather than from primary, matrix-type porosity. Enhancement or enlargements of fractures, bedding planes, and conduits by carbonate dissolution is an active, ongoing process (Adamski and others, 1995). Hydraulic conductivity of matrix porosity blocks is much lower, on the order of 10<sup>-7</sup> ft/d or even less (Van den Heuvel, 1979; Peterson and others, 2002). Development of secondary porosity has produced anisotropic and heterogeneous hydraulic characteristics for the aquifer. The presence of smaller-scale matrix,

small-aperture fracture, and small-conduit porosity combined with the dissolution-enhanced conduits results in a bimodal permeability distribution. Water movement may be described relative to the two flow end members of diffuse flow and focused (conduit) flow previously defined. Because of the low rock-matrix hydraulic conductivity, a large fraction of groundwater transfer is through the focused-flow component of the aquifer (Imes and Smith, 1990; Kilpatrick and Ludwig, 1990b). Rapid input of surface water, rapid-flow velocities, rapid mass transfer, and minimal attenuation of contaminants are associated with this component of flow. More timeaveraged flow, maintenance of streamflows during dry periods, low-flow velocities, and effective attenuation of contaminants are behaviors associated with the diffuse component of flow.

Fracture and bedding-plane apertures typically decrease with depth as lithostatic pressure increases (Drogue, 1980). Correspondingly, groundwater storage, hydraulic conductivity, and well yields decrease with depth in the Springfield Plateau aquifer (Lamonds, 1972), and well depths rarely exceed 300 ft in the aquifer (Imes and Emmett, 1994). Most well depths associated with data compiled for this report were less than 200 ft. Average values of horizontal conductivity from groundwater simulations are 22 ft/d (Imes and Emmett, 1994) with vertical conductivities about an order of magnitude lower (Adamski and others, 1995). However, hydraulic conductivities as high as 886–2,100 ft/d occur locally (Vandike, 1997). Transmissivity values range from approximately 1,700 to 8,600 ft<sup>2</sup>/d (Imes and Emmett, 1994). Wells yields reflect the porosity types. Where wells intersect highly porous and permeable zones, yields of 10 gal/min to more than 100 gal/min are common. Where wells are completed in zones with little secondary development of porosity and permeability, well yields are typically less than 10 gal/min. Most wells yield less than 20 gal/min throughout the extent of the aquifer (Adamski and others, 1995; Peterson and others, 2002; McFarland and Prior, 2005; Gillip, 2007).

Most recharge to the Springfield Plateau aquifer is by infiltration of precipitation in the aquifer's outcrop area. Where confined, recharge occurs by leakage through overlying units (Adamski and others, 1995). Recharge to the aquifer occurs as diffuse and focused recharge (Alley and others, 2002; Healy, 2010). Diffuse recharge occurs by infiltration of precipitation through the overlying regolith; however, most potential recharge water moving through the soil zone is lost to evapotranspiration, particularly during the growing season (Brahana, 2011b). Diffuse recharge likely amounts to a small percentage of the total recharge compared to focused recharge through karst features such as sinkholes, fractures and conduits, and losing stream reaches (Alley and others, 2002; Brahana and others, 2005). The distribution of recharge is not well understood for the Springfield Plateau aquifer. Karst features allow for rapid recharge, thus allowing the influx of surface-derived contaminants into the aquifer with little attenuation (Jagucki and others, 2009). Consequently, karst

aquifers such as the Springfield Plateau aquifer have a high susceptibility to contamination.

Discharge from the Springfield Plateau aquifer is primarily through springs, withdrawals by wells, and interaquifer flow to the underlying Ozark aguifer system (Branner, 1937; Harvey, 1980; Brahana and Davis, 1998; Czarnecki and others, 2009; Hudson and others, 2011; Vardy, 2011). Seeps and springs are the predominant discharge points for the aquifer. Springs generally occur near the base of the Boone Formation coincident with structural lows and the underlying Ozark confining unit (Kilpatrick and Ludwig, 1990a; Adamski and others, 1995; Murray and Hudson, 2002; Bolyard, 2007; Hudson and others, 2011). Where the underlying Ozark confining unit is absent or incompetent, groundwater discharges from the Springfield Plateau aquifer to the underlying Ozark aquifer (Imes and Emmet, 1994). Groundwater withdrawals by pumping do not appear to have caused distinguishable differences in potentiometric surfaces over time in northern Arkansas (Gillip, 2007).

## Water Levels

Long-term groundwater-level measurements for the Springfield Plateau aquifer are limited. Only one record exists that has more than 15 years duration and was measured at an interval adequate to capture seasonal variability (fig. 108; see fig. 109 for location of the well). Direct correlation of seasonal water-level variations is weak ( $R^2 = 0.063$ ). The potentiometric surface (Imes and Emmet, 1994) reflects relatively higher groundwater levels in high-altitude areas such as Benton, Carroll, Boone, Washington, Madison, and Newton Counties. A lower potentiometric surface occurs in lower altitude areas west towards Oklahoma, south towards the Arkansas River Valley, and east towards the Mississippi Alluvial Plain. An NWIS query revealed 543 wells with both land-surface altitude and water-level data. The potentiometric surface for the aquifer generally reflects topography and exhibits a strong correlation with land-surface altitude ( $R^2 =$ 0.98). However, a regional correlation between land-surface altitude and groundwater level below land surface cannot fully explain groundwater movement in the Springfield Plateau aquifer at more localized scales. Small-scale variation in flow is the result of fractures, faults, conduits, and other structures that facilitate or vertically and laterally impede flow (Leidy and Morris, 1990b; Brahana and Davis, 1998; Turner and Hudson, 2008; Hudson and others, 2011). Numerous dyetracing studies have shown hydraulic connectivity across watershed divides (interbasin flow) (Adamski and others, 1995; Brahana and Davis, 1998; Adamski, 2000; Gillip, 2007; Brahana, 2011a, b). This connectivity can occur across considerable distances outside a given watershed (Mott and others, 1999; Murray and Hudson, 2002).



Figure 108. Water levels in a well completed in the Springfield Plateau aquifer in northern Arkansas.

## Water Use

The Springfield Plateau aquifer is widely used throughout northwestern Arkansas. Historically, the aguifer was used extensively for domestic, public-supply, commercial, and industrial purposes. Several towns were sited near areas of large springs, which were frequently used to power grain and lumber mills and to supply residents of the growing population. Several domestic and livestock wells were recorded in Carroll and Boone Counties (Brahana and others, 1991, 1993). At the time of this report (2013), numerous domestic and livestock wells were still in use. Because domestic and water-supply systems serving less than 50,000 gal/d are not required to report water use, total use of groundwater from the Springfield Plateau aquifer is unknown. The wider distribution of surface-water systems has largely supplanted use of the Springfield Plateau aquifer as a source of water supply. There were three public-supply wells in Carroll County reporting use from the Springfield Plateau in 2010. A limited number of small communitysupply systems, as well as restaurants, resorts, recreational vehicle parks, and shops, are registered as using this aquifer with ADH (Lyle Godfrey, Arkansas Department of Health, written commun., 2012).

# Water Quality

Groundwater quality resulting from rock/water interaction in the Springfield Plateau aquifer generally is good. The water can be used without treatment as an important source of water supply throughout the Ozarks, although low yields limit its use primarily to domestic supply. Iron is the most frequent naturally derived constituent exceeding Federal drinking-water regulations (Lamonds, 1972; Steele, 1981). Hardness related to dissolved carbonate minerals can present problems related to scaling of pipes, water heaters, and other plumbing fixtures (Lamonds, 1972; Leidy and Morris, 1990b; Imes and Emmett, 1994; Adamski, 2000). Surfacederived, anthropogenic contaminants primarily related to livestock agricultural activities also affect water quality as a result of rapid influx of surface water with little attenuation in many areas. The aquifer constitutes a large part of the karst landscape of the Ozark Plateaus. This karst network creates a hydrologic system of great complexity with intimate groundwater/surface-water interaction, which makes the system highly vulnerable to surface-derived contamination. Anthropogenic contaminant sources can affect the natural groundwater geochemistry and water quality. Common contaminants include nutrients, fecal bacteria, and pesticides.

Agriculture in the form of beef and dairy cattle, swine, and poultry operations accounts for the greatest land-use activity in this region. Contamination of the aquifer often is derived from these activities (Peterson and others, 2000). Nationally, Arkansas ranks second in poultry production, and the three top counties for agricultural sales in Arkansas are located in the northwestern region of the State (U.S. Department of Agriculture, 2010). Another common source of contamination is septic systems, which are the primary means of domestic waste treatment in rural and in many suburban areas in the Ozarks. The thin, poorly developed soils in the Ozarks make installation of effective, functioning septic systems a challenge, resulting in frequent contamination of groundwater. A vulnerability map created for Arkansas (Arkansas Soil and Water Conservation Commission, 1991) generally listed the entire Ozarks of northern Arkansas at the highest vulnerability index. The spatial distribution of karst features, as well as the variable thickness and composition of soils in the overlying regolith, results in variable vertical permeability and resultant variable vulnerability.

## General Geochemistry and Water Quality

The predominant carbonate rock hosting the Springfield Plateau aquifer is limestone. Numerous reports have documented the dominant calcium-bicarbonate water type resulting from dissolution of the parent rock (Lamonds, 1972; Leidy and Morris, 1990b; Imes and Emmett, 1994; Adamski, 1997; Huetter and others, 1997). Groundwater derives acidity from carbonic, nitric, sulfuric, and other acids formed from natural and anthropogenic sources of carbon dioxide, sulfur dioxide and hydrogen sulfide, and nitrogen oxides. Gas sources include vehicle, industrial, and other anthropogenic emissions, in addition to carbon dioxide and organic acids derived from plant respiration and organic-matter decay in soil. This acidity drives dissolution of limestone and resultant increases in dissolved calcium and bicarbonate concentrations (Wagner and others, 1975). Because limestone is the dominant rock type of the Springfield Plateau aquifer and dolomite is more common in the Ozark aquifer, researchers frequently use calcium/magnesium ratios to differentiate groundwater in these two aquifers. Dolomite has equal parts of calcium and magnesium, and groundwater from predominant dolostone formations composing the Ozark aquifer generally reflects this one-to-one ratio. These ratios are considerably higher in groundwater from limestone of the Springfield Plateau aquifer. Calcium/magnesium equivalent ratios for 134 samples from the Springfield Plateau aquifer ranged from 1.2 to 359 with a median of 17. This median ratio reflects the higher calcium/ magnesium ratio typical of groundwater from the Springfield Plateau aquifer. All ratios, except for the minimum of 1.2, were greater than 2.0, and all but 11 of the 134 samples were greater than 5.0. No strong spatial trend was evident in calcium/magnesium ratios, though a greater density of lower

ratios occurs near the contact of the Springfield Plateau with Ordovician-age formations of the Ozark Plateaus in Boone and Independence Counties (fig. 109). Limestone often contains varying amounts of magnesium. Consequently, lower calcium/magnesium ratios in some areas result from a higher admixture of magnesium in the limestone or migration of Ozark aquifer groundwater across the Chattanooga confining layer in areas where it is absent or incompetent. Additionally, some wells labeled as completed in the Springfield Plateau aquifer may penetrate and receive water from upper units of the Ozark aquifer. The relation of calcium and bicarbonate shows the overall strong calcium-bicarbonate type water of the Springfield Plateau aquifer. Calcium was strongly correlated to bicarbonate with an R<sup>2</sup> of 0.78. The addition of magnesium to this analysis improved the correlation by only a small degree to an R<sup>2</sup> of 0.81 (fig. 110).

Low pH from precipitation recharging the aquifer is quickly buffered by carbonate minerals in the overlying regolith and bedrock of the Boone Formation. Values of pH subsequently increase to values exceeding 6.0 throughout the aquifer. Values of pH ranged from 6.0 to 9.1 with a median of 7.2 (table 43). Sixty-seven percent (110 of 163 samples) of the samples had pH values greater than 7.0. No correlation was established between dissolved-solids concentrations and pH values, and the entire range of pH values was found throughout the range of dissolved-solids concentrations (58 to 515 mg/L), which strongly suggests that buffering occurs in the weathered regolith and unsaturated bedrock prior to recharging the aquifer. Knierim and others (2011, 2013) and Pollock and others (2011) characterized basic geochemical changes, nutrient and carbon alterations, and isotopic behavior as groundwater moved through soils into diffuse and focused karst flow paths in the Ozarks. They noted modification of acidity and behavior of soil and regolith as a storage zone for organic carbon and other nutrients. For example, median calcium concentrations in the soil and regolith zones for sites from two different study locales were 5.0 and 5.9 mg/L, respectively, and median dissolved inorganic carbon (predominantly bicarbonate) concentrations were 13.1 and 1.7 mg/L, respectively. These results indicated considerable modification of recharge water in the soil and regolith zones prior to reaching the epikarst. Pollock and others (2011) used hydrograph separation mixing models to rigorously quantify source-water contributions to streams in caves and flow from springs during storm events and to measure evolution of groundwater geochemistry. A key finding was the importance of the soil and regolith zone on groundwater chemistry very early on for karst flow paths. Soil and regolith were found to be of particular importance in controlling chemistry during high-flow events. A metadata analysis for this study showed no spatial correlation for the distribution of pH values throughout the aquifer based on data compiled for this report.



Figure 109. Spatial distribution of calcium/magnesium ratios (from milliequivalent concentrations) in groundwater from the Springfield Plateau aquifer in northern Arkansas.



**Figure 110.** Relation of bicarbonate to *A*, calcium and *B*, calcium plus magnesium in groundwater from the Springfield Plateau aquifer in northern Arkansas.

**Table 43.**Descriptive statistics for selected chemical constituents in groundwater from the Springfield Plateau aquifer in northernArkansas.

[mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Constituent or characteristic	Minimum	Median	Maximum	Standard deviation	Number of wells		
Calcium (mg/L)	0.04	55	109	20.4	134		
Magnesium (mg/L)	0.01	1.7	21	3.31	134		
Sodium (mg/L)	0.2	4.3	51	6.38	132		
Potassium (mg/L)	0.1	1.2	15	1.58	132		
Bicarbonate (mg/L)	39	164	316	65	119		
Chloride (mg/L)	1.2	7.6	47	6.8	134		
Sulfate (mg/L)	0.48	3.9	90	11.2	134		
Silica (mg/L)	5.3	9.7	19	1.85	129		
Nitrate (mg/L as nitrogen)	0.01	1.8	20	2.77	166		
Dissolved solids (mg/L)	58	193	515	69	134		
Iron (µg/L)	0.05	5.6	3,300	338	126		
Manganese (µg/L)	0.13	0.13	1,410	198	129		
Arsenic (µg/L)	0.03	0.03	2.52	0.39	90		
Hardness (mg/L as calcium carbonate)	0.1	140	323	54	115		
Specific conductance (µS/cm)	102	349	693	112	161		
pH (standard units)	6.0	7.2	9.1	0.5	163		

Adamski (2000) noted that groundwater from springs and wells was geochemically different. In general, median concentrations of dissolved solids, calcium, magnesium, and bicarbonate were greater in samples from wells than from springs. Additionally, groundwater from wells was more saturated with respect to calcite than from springs. Springs typically receive a large component of flow from focusedflow conduits in the flow system. Rapid flow through large conduits in spring basins results in minimal contact with carbonate rock. This is because the size of the conduits (solution channels) and shorter residence times result in a lesser degree of rock/water interaction for springs. In contrast, the low yield of many wells indicates that most boreholes receive a large component of flow from the more diffuse part of the flow system. This diffuse flow is through small conduits and fractures and is characterized by lower permeability, increased residence time, and increased rock/water interaction (Adamski, 2000; Pollock and others, 2011; Knierim and others, 2013).

Water-quality monitoring during storm events substantiates the shorter residence time and reduced rock/ water interaction for groundwater moving through conduits that feed springs. Generally, concentrations of rock-derived dissolved constituents (for example, calcium, magnesium, and bicarbonate) have been observed to decrease substantially during storm events within hours of the storm. Conversely, concentrations of surface-derived constituents (for example, nitrate, chloride, phosphate, fecal bacteria) often increase over the rise and peak of storm events (Widmann, 1982; Steele and others, 1985; Adamski, 1987; Parr, 1987; Wickliff, 1988; Davis and others, 2000; Pollock and others, 2011; Knierim and others, 2013). Pollock and others (2011) described marked changes in groundwater chemistry for storm events compared to base-flow events. There was less rock/water interaction modifying recharging waters during the rapid input stormevent periods, but there was effective delivery of dissolved constituents such as nitrate from the surface and regolith zones. For example, median calcium and dissolved inorganic carbon concentrations were 38.4 mg/L and 24.8 mg/L, respectively, during base flow, and 20.3 mg/L and 11.8 mg/L, respectively, during times of stormflow. By comparison, the nitrate concentration did not change substantially but remained near 2.7 mg/L for base flow and stormflow. Nitrate remained essentially constant even as flows increased by orders of magnitude, indicating considerable transport of dissolved mass into and through the aquifer during storm events.

## Nitrate

The terms "elevated," "background," and "baseline" as applied to groundwater nitrate concentrations can, from a quantitative perspective, have different meanings in different comparative contexts and defining these terms as used for the discussion of nitrate in groundwater of the Ozarks is of great importance. The typical contexts are comparing watershed to watershed, within a watershed, between different land uses, land-use intensity, time steps, areas of differing scales, and between contaminant source inputs. One definition of "elevated" nitrate would be the Federal MCL of 10.0 mg/L as nitrogen, which was established based on potential health effects from consumption of high-nitrate water. This definition, however, does not address concentrations that are greater than background levels and can result in environmental effects, such as promotion of algal growth in streams.

Several studies of the Springfield Plateau aquifer have been conducted in areas that are dominantly forested and provide a better understanding of representative background nitrate concentrations in relatively pristine areas. Steele (1983) sampled 74 springs in three relatively pristine (forested) areas in northwestern Arkansas with mean and median nitrate concentrations of 0.32 mg/L and 0.15 mg/L as nitrogen, respectively. Steele and Adamski (1987) sampled 48 springs and noted that seasonal mean nitrate concentrations in dominant forested areas ranged from 0.16 to 0.40 mg/L for the same sites sampled in different seasons. None of these sites were completely forested because there were homes with septic systems located throughout the spring basin; therefore, a true background concentration is probably less than this range of concentrations. Kresse and others (2011) established what they considered a conservative estimate for a background nitrate concentration of 0.40 mg/L as nitrogen based on review of data in these previous studies. The term "elevated" nitrate as used in this report refers to nitrate concentrations exceeding the 0.40 mg/L background concentration estimated in the above studies.

Because soils are generally thin, rocky, and poorly suited for row-crop farming, poultry, cattle, and swine production is the predominant agricultural activity in the Ozarks. The karst terrain enables rapid infiltration of surface water into the subsurface, which renders groundwater highly vulnerable to surface-derived contamination. This results in widespread influx of nutrients and fecal bacteria from waste generated by agricultural activities and septic tanks. Nitrogen and phosphorus associated with these activities are the dominant nutrients posing environmental threats to surface and subsurface waters in the Ozarks. Because most of the phosphorus is strongly bound to clays and organic matter in soils, little phosphorus moves in the dissolved state. Conversely, nitrate is the most soluble form of nitrogen and is conservative in transport. Consequently, nitrate is more persistent than phosphorus in the subsurface and poses the largest threat to groundwater resources in the Ozarks.

Numerous studies in northwestern Arkansas have reported on the occurrence, sources, transport pathways, and fate of nitrate in the Springfield Plateau aquifer (Keener, 1972; Coughlin, 1975; MacDonald and others, 1976; Ogden, 1979; Cox and others, 1980; Leidy and Morris, 1990b; Davis and others, 2000). Most of these studies found a wide range of elevated nitrate concentrations with a small percentage that exceeds the Federal MCL of 10.0 mg/L. Most studies attributed nitrate contamination to an abundance of septic systems and chicken houses in northwestern Arkansas. Other studies have attributed elevated nitrate and other surfacederived contaminants to urban sources (Gillip, 2007; Kresse and others, 2011; Vardy, 2011). Concentrations of nitrate in 166 samples from the Springfield Plateau aquifer compiled for this report ranged from 0.01 to 20 mg/L with a median of 1.8 mg/L. Only three samples exceeded the Federal MCL of 10 mg/L. Contrary to most of the aquifers of the Coastal Plain, the occurrence of nitrate in the Springfield Plateau aquifer was not correlated with well depth. Concentrations of more than 5.0 mg/L as nitrate were found uniformly throughout the range of well depths from as shallow as 5 ft upwards to 250 ft.

Several variables can affect the transport of nitrate to the subsurface including nitrogen form and loading, soil type, regolith thickness, attenuation processes such as denitrification, plant uptake, as well as presence of karst features and other focused-flow pathways. A well-defined relation was noted for the Springfield Plateau aquifer between increases in agricultural land use and increases in nitrate. Adamski (1997) used regression analysis that revealed a positive correlation between nitrate concentrations and percent agricultural land use in 103 sampled sites across the Ozark Plateau in Arkansas, Kansas, Missouri, and Oklahoma. Kresse and others (2011) similarly applied regression analysis using groundwater samples from 823 sites (springs and wells) in northern Arkansas that showed a similar positive, though weak linear, correlation between the two variables. Although the sites included samples from groundwater throughout the Ozark Plateaus aquifer system, most were from the Springfield Plateau aquifer. Bar graphs also were employed to show a positive relation between increasing mean nitrate concentrations for 10 percent incremental increases in agricultural land use using the same dataset (fig. 111A). An overall mean nitrate concentration of 2.4 mg/L was exceeded by the mean nitrate concentration for agricultural land use that exceeded 40 percent. Most domestic wells that were sampled had a septic system nearby that could affect the groundwater sample from the well. Thus, inclusion of data from domestic wells can skew the analysis, regardless of surrounding land use. To overcome this problem, the regression of nitrate and land use was conducted for spring sites only, which generally would not be associated with nearby septic systems. The 254 spring sites in the database were extracted and similarly tested for relation to agricultural land use. For springs, a much more consistent stepwise increase in nitrate concentration was noted for increasing agricultural land use, indicating the well data were affected by septic systems. Hence, the water chemistry of springs better reflects the influence of increasing agricultural land use (fig. 111B). The mean nitrate concentration for all spring sites was 2.6 mg/L, which was exceeded for all agricultural land-use percentage categories more than 40 percent, similar to that of wells and springs. Higher mean nitrate concentrations occurred for each percent agricultural land-use category as compared to both wells and springs. The

spring data showed that effects on nitrate concentrations in groundwater were discernible at any level of agricultural land use. Even at the lowest agricultural land-use category from 0 to 10 percent, the mean nitrate concentration for 46 samples was 0.9 mg/L, almost twice the background concentration of 0.4 mg/L. This finding demonstrates the effects of even small land-use changes on the concentration of nitrate in groundwater and indicates that agricultural land use of more than 40 percent has an effect on groundwater quality in the Springfield Plateau aquifer.

Elevated nitrate concentrations in previous groundwater studies of the Springfield Plateau aquifer were attributed to karst features that allow rapid movement of groundwater with minimal attenuation of surface-derived contaminants. None of these studies, however, produced data to quantitatively test the influence of karst. One problem in assessing other variables affecting the occurrence and concentration of nitrate was the overriding variable of land use (Adamski, 1997; Kresse and others, 2011). To separately test the influence of karst terrain features on nitrate transport in dominant agricultural land-use areas, Kresse and others (2011) used the density of mapped sinkholes as a surrogate representing the degree of karst development in north-central Arkansas (Newton and Searcy Counties). Only springs were sampled to reduce the local influence of septic systems. Sampling locations were limited to agricultural land-use areas to remove land use as the main control on nitrate occurrence. Following these constraints, 34 springs were sampled in an area of highly developed karst as indicated by a high density of mapped sinkholes (Group I), and 22 springs were sampled in an area of less developed karst as indicated by an area devoid of mapped sinkholes (Group II). A statistically significant difference (p<0.01) occurred between the two groups; nitrate concentrations were greater for Group I springs. A weak point in the analysis was that total acres of agricultural land use were greater in Group I than in Group II, indicating that land use likely remained a controlling variable between the two sites. Regression analysis of nitrate concentrations from all springs did show a positive correlation to agricultural land use. To account for this land-use inconsistency, an analysis of covariance was conducted to investigate the importance of karst development as an additional important variable in nitrate occurrence. The analysis revealed that nitrate concentrations for Group I springs were greater than Group II springs for increasing agricultural land use (fig. 112). The occurrence of karst features accounted for approximately 12 percent of the variation between the two groups. This indicates that while nitrate concentrations in springs generally increase with increasing agricultural land use, concentrations generally are greater in areas where karst development (represented by sinkholes) is greater. The occurrence of sinkholes and other karst features thus provided more direct and rapid transport of contaminants to groundwater (Kresse and others, 2011).



**Figure 111.** Relation of agricultural land use in percent of total land use to mean nitrate concentrations in groundwater from *A*, wells and springs and *B*, springs in the Ozark Plateaus aquifer system in northwest Arkansas.



Figure 112. Analysis of covariance for nitrate concentrations and agricultural land use for Group I (highly developed karst) and Group II (less developed karst) springs.

Nitrate concentrations in the Springfield Plateau and Ozark aquifers have been compared in several studies, and higher mean and median concentrations have consistently been noted for the Springfield Plateau (Leidy and Morris, 1990b; Smith and Steele, 1990; Steele and McCalister, 1990, Adamski, 1997; Huetter and others, 1997; Kresse and others, 2011). For example, mean and median nitrate concentrations in 190 samples taken from the Springfield Plateau aquifer were 2.9 and 1.8 mg/L, respectively, compared to 0.47 and 0.10 mg/L, respectively, for 101 samples from the Ozark aquifer (Kresse and others, 2011). Most of the studies referenced above were in northwestern Arkansas, where the Ozark aquifer is confined and often overlain by exposures of the Boone Formation. Lower concentrations in the Ozark aguifer were attributed to protection from overlying formations. However, in areas of northeastern Arkansas and southeastern Missouri where the Ozark aquifer is exposed, mean and median nitrate concentrations remained low, similar to where the aquifer is confined (Kresse and others, 2011) (see section "Ozark Aquifer"). This finding suggests greater vulnerability to surface-derived contaminants for the Springfield Plateau aquifer compared to the Ozark aquifer. No definitive attributes have been identified to explain the higher vulnerability of the Springfield Plateau aquifer because the geology for both aquifers hosts abundant karst features (sinkholes, springs, and losing streams).

Recent research in northwestern Arkansas has been conducted at plot scale for assessing fate of nitrate in the Springfield Plateau aquifer (Peterson and others, 2002; Laincz, 2011). In these studies, nitrate transport was traced from its source through active microbial zones in soil, regolith, and epikarst, and ultimately into bedrock solution channels. The purpose was to determine controls on nitrate transport and the effectiveness of various zones in the aquifer system in removing nitrate. Results from one study indicated piston flow in the soil matrix with nitrate moving in pulses and the soil serving as a reservoir for nitrate (Peterson and others, 2002). Another study documented nitrate attenuation processes (denitrification) in the interflow zone between the soil and focused-flow (bedrock) zones, which can remove as much as 33 percent of infiltrating nitrate (Laincz, 2011).

#### Bacteria

The increasing occurrence of pathogens in groundwater from the Springfield Plateau aquifer has been one of the primary water-quality factors limiting its use (Knierim and others, 2013). The potential occurrence of pathogens in groundwater usually is indicated by surrogate measurement of indicator bacteria, for example fecal coliform, fecal streptococcus, and *Escherichia coli* (*E. coli*). Fecal indicator bacteria commonly are detected in groundwater from the aquifer and are detected with great frequency in springs, where conduit flow and rapid transport prevent effective filtering. Bacteria in springs and wells in northwestern Arkansas have been documented at rates ranging from 42 to 80 percent of the sampling sites (Keener, 1972; Coughlin, 1975; MacDonald and others, 1976; Ogden, 1979; Cox and others, 1980; Leidy and Morris, 1990b; Davis and others, 2000). Bacteria sources are related to agricultural and urban land use, and bacteria survival and transport in the aquifer are controlled by degree of karst development, hydrologic flow condition, and sediment concentrations (Marshall and others, 1998). Davis and others (2005) found that fecal-coliform bacterial concentrations, including E. coli, were controlled by groundwater-flow conditions with bacteria concentrations varying by several orders of magnitude from base-flow to storm-flow conditions. Bacteria concentrations in spring water rapidly increased during the rising limb of stormevent hydrographs prior to breakthrough of nitrate and other conservative constituents, and the concentrations declined prior to the falling limb of the storm. Bacteria likely resided within sediment in the groundwater system, and the bacteria flux was associated with resuspension of sediment during the onset of turbulent flow. The survival period for bacteria in groundwater was at least 4 months (Davis and others, 2005).

## Sediment

Sediment, especially clay, is a contaminant that is virtually nonexistent in clastic aquifers in the State but is an important contaminant in karst settings, particularly from an ecosystem standpoint. Sediment commonly is associated with karst environments in urban land-use settings of the Ozarks. Sediment also is important in facilitating bacterial transport (Marshall and others, 1998; Davis and others, 2005). Gillip (2007) described large volumes of sediment that moved through karst and caves near urban areas in northwestern Arkansas as development denuded the landscape, exposing and enabling mobilization of the clayey regolith. Individual storm events were observed to deposit more than 3 ft of sediment in caves with considerable effects on the karst ecosystems. Gillip (2007) also showed the dynamic nature of sediment transport in karst as noted by deposition followed by removal of sediment during succeeding lowerprecipitation events. Caving expeditions coupled with surface reconnaissance showed movement of sediment through fractures and conduits directly into caves during urbandevelopment activities (Phillip D. Hays, U.S. Geological Survey, written commun., 2013). Ting (2005) used europiumlabeled clays to demonstrate the effectiveness of suspendedphase transport in karst conduits and showed that the average transport velocity for a given mass of suspended material was more than the average transport velocity for dissolved material. Ting hypothesized that this discrepancy was the result of size exclusion and rapid preferential movement of suspended material through larger conduits.

## Pesticides

Because of the limited use of pesticides in the Ozarks relative to its pervasive use in row-crop areas of eastern Arkansas, very little sampling has been performed to document the occurrence of pesticides in groundwater from the Springfield Plateau aquifer. One regional study sampled for pesticides in groundwater from the Ozark Plateaus in Arkansas, Kansas, Missouri, and Oklahoma (Adamski, 1997). Pesticides were detected in 80 of 229 (35 percent) groundwater samples from 73 of 215 sites (9 sites in northern Arkansas). Twenty pesticides were detected, with a maximum of 5 detected in any one sample. The most commonly detected pesticides were tebuthiuron (31 samples), atrazine (30), prometon (25), desethylatrazine, a metabolite of atrazine (19), and simazine (18). These are herbicides that commonly are used on pastures and other noncrop areas. Pesticides were detected statistically (p<0.01) more often in groundwater from the Springfield Plateau aquifer than from the Ozark aquifer (Adamski, 1997). Pesticide detections additionally were related to nitrate concentrations in samples from agricultural sites. Median nitrate concentrations were statistically greater in samples with pesticide detections, further substantiating the increased vulnerability of the aquifer to surface contamination.

## Iron

Iron concentrations in 126 samples from the Springfield Plateau aquifer ranged from 0.05 to 3,300 µg/L with a median of 5.6 µg/L (fig. 113; table 43). Only five samples had iron concentrations exceeding the Federal secondary drinkingwater regulation of 300 µg/L. Potential sources include: (1) iron mobilized from overlying regolith that contains abundant iron oxyhydroxide minerals that gives the unit its prevalent bright red coloration, (2) weathering of abundant pyrite that occurs in the Boone Formation limestone, and (3) iron sulfides associated with the Mississippi Valley Type ore mineralization that is common along fault zones in the Ozarks. The oxidation of iron-sulfide minerals as a source of iron is unlikely because of an observed inverse relation of iron and sulfate concentrations (graph not shown). Mobilization of iron from the regolith with onset of reducing conditions may explain elevated iron in isolated areas. This process is particularly common near landfills, waste lagoons, and other sources of abundant organic matter that provides a substrate for microbial activity using terminal electron acceptor processes (Hobza, 2005; Bolyard, 2007; Wagner, 2007). Regardless of the source, iron concentrations generally are low throughout the Springfield Plateau aquifer.



**Figure 113.** Interquartile range of selected chemical constituents in groundwater from the Springfield Plateau aquifer of northern Arkansas.

#### Chloride

Chloride concentrations for 134 sites in the Springfield Plateau aquifer ranged from 1.2 to 47 mg/L with a median of 7.6 mg/L (fig. 113; table 43). Imes and Emmett (1994) reported concentrations generally are less than 10 mg/L in the aquifer throughout the Ozark Plateaus. Several studies noted the co-occurrence of nitrate and chloride in the aquifer, indicating that chloride may be derived from the same sources as nitrate (Ogden, 1979; Davis and others, 2000; Kresse and others, 2011; Vardy, 2011). Although a positive linear relation was noted between nitrate and chloride for this report, considerable variation occurred with an R<sup>2</sup> of only 0.12. This indicates that attenuation processes affecting the transport and resultant concentration of nitrate in groundwater are not affecting chloride, which is nonreactive (conservative) in transport within the hydrologic system. No spatial trend was noted for chloride concentrations.

## Sulfate

Sulfate concentrations for 134 sites in the Springfield Plateau aquifer ranged from 0.48 to 90 mg/L with a median of 3.9 mg/L (fig. 113; table 43). Imes and Emmett (1994) noted that sulfate concentrations generally are less than 10 mg/L. No spatial trend was noted for sulfate concentrations. As noted for iron, an inverse relation of iron and sulfate concentrations tends to rule out oxidation of iron-sulfide minerals as a source of sulfate. Because all but one sulfate concentration greater than 20 mg/L had ratios of calcium plus magnesium divided by bicarbonate that were more than 1.0, dissolution of gypsum may account for the increased sulfate concentrations.

In summary, groundwater from natural rock/water interaction processes in the Springfield Plateau aquifer is generally of good quality. Because of the steep topography and poor soils in the Ozarks, agriculture in the form of beef and dairy cattle, swine, and poultry operations accounts for the greatest land-use activity. Nutrients, bacteria, and pesticides from agricultural activities, home septic systems, and infiltration of urban runoff are the dominant threats to groundwater quality in the aquifer. Numerous studies have documented elevated nitrate and fecal bacteria in groundwater from springs and wells. A positive correlation between agricultural land use and nitrate concentrations validates concerns over agricultural wastes and the vulnerability of the aquifer to anthropogenic contaminants. Recent studies have shown a direct correlation between areas of greater karst development and increased vulnerability of the aquifer to these agricultural waste sources. Inorganic constituents, including chloride, sulfate, and iron, generally were low throughout the aquifer, revealing a relative high quality of groundwater for all water-supply uses.

# **Ozark Aquifer**

The Ozark aquifer (fig. 3) is exposed and generally unconfined within the Salem Plateaus section of the Ozark Plateaus (Ozarks) province (table 2). The aquifer underlies and is confined below the Springfield Plateau aquifer in the Springfield Plateau and Boston Mountains regions of the Ozarks (tables 2 and 5). The aquifer comprises a sequence of formations predominated by dolostones along with minor limestone, sandstone, and shale intervals of Ordovician age. These formations contribute to the unique and complex hydrogeology and physiography of the Ozarks. The karst of the carbonates in the upper Ozark aquifer presents a physiographic and hydrologic environment in the Salem Plateau similar in aspect and complexity to that seen for the Springfield Plateau.

The upper, carbonate-dominated part of the Ozark aquifer comprises the Clifty Limestone, Penters Chert, Lafferty Limestone, St. Clair Limestone, Brassfield Limestone, Cason Shale, Fernvale Limestone, Kimmswick Limestone, Plattin Limestone, Joachim Dolomite, St. Peter Sandstone, Everton Formation, Powell Dolomite, Cotter Dolomite, and Jefferson City Dolomite (table 5). The carbonate-dominated limestones and dolomites of Ordovician age are the predominant waterbearing units of the upper part of the aquifer. This differs from the lower part of the aquifer in predominant lithologies, groundwater levels, exposure and confinement, yields, and geochemistry, and hereinafter will be commonly referred to in this report as the "upper Ozark aquifer." The lower part of the aquifer includes the confined Roubidoux Formation, Gunter Member of the Gasconade Dolomite, Van Buren Formation, Eminence Dolomite, and Potosi Dolomite. The combined Roubidoux and Gunter Member of the Gasconade Dolomite are the primary water-bearing units of the lower part of the aquifer in Arkansas and are predominated by sandstone lithology with abundant dolomite and shaly intervals common in the Roubidoux Formation. The combined water-bearing units of the Roubidoux and Gunter Member of the Gasconade Dolomite are referred to hereinafter in this report as the "lower Ozark aquifer." Similar to the Springfield Plateau aquifer, groundwater movement and groundwater quality of the Ozark aquifer are controlled by regional and local geology. Geologic factors include the presence and composition of the regolith mantle, the lithologies of the rocks that convey groundwater flow, stratigraphic relations of these different lithologies, and geologic structure.

# **Geologic Setting**

The fundamental structural feature defining the Ozark Plateaus is a broad dome that has been uplifted during several periods since Precambrian time to bring the plateaus to their current altitude (Nunn and Lin, 2002; Tennyson and others, 2008; Cox, 2009). The core of the dome is in southeastern Missouri. Sedimentary units in Arkansas lie along the southern and southwestern margins of the dome with gentle regional dips generally ranging from 10 to 100 ft/mi and steeper dips being common proximal to faults (Frezon and Glick, 1959). Regional extensional fracturing, jointing, and faulting of rocks in the Ozark Plateaus occurred with uplift of the formations (Hudson and Cox, 2003) creating secondary porosity that has provided key nucleation points for initiation of dissolution of the carbonate rocks and karst development. Topographic relief resulted from erosional dissection of the Ozark Plateaus rather than from intense folding and faulting. This erosion has been controlled to a degree by structural features such as faults and fracture zones as well as by lithology.

Regolith mantles most areas of the underlying karstic bedrock where the formations of the Ozark aquifer are exposed on the Salem Plateau. In many areas of the regolith, thickness varies from near zero to more than 100 ft and typically comprises a silt-loam surface soil overlying a clay-loam subsoil. The regolith usually is clay-rich, low in permeability, and impedes recharging water. The regolith mantling the Salem Plateau generally contains less chert than the regolith over the Springfield Plateau. This compositional difference may make the Salem Plateau regolith a more competent barrier to surface-derived contamination. This has been theorized to explain observational differences in lower nitrate concentrations in the Ozark aquifer compared to the Springfield Plateau aquifer (see "Water Quality" section below).

The younger Ordovician-age rocks constituting the upper Ozark aquifer only require a brief description because yield and water quality are similar throughout. The Fernvale Limestone is generally observed as a massive, zero to more than 100 ft in thickness, coarsely crystalline, light-gray to pink limestone present in the Ozarks of northern Arkansas. The Fernvale is very similar to the underlying Kimmswick, which is generally less than 50 ft in thickness. The Plattin Limestone is a gray, thin-bedded limestone and is usually less than 100 ft in thickness. The Joachim Dolomite is generally described as a fine-grained dolostone or dolomitic limestone with thin beds of shale. Sand is abundant at the base of the formation with thin sandstones commonly occurring above

the St. Peter Sandstone. The Joachim is absent in the western Ozarks and is as thick as 100 ft in the central and eastern Ozarks. The St. Peter Sandstone is usually observed as a massive-bedded, medium- to fine-grained, well-rounded, poorly cemented, white sandstone. The formation ranges from less than 1.0 ft to as much as 175 ft in thickness. The Everton Formation exhibits considerable spatial variation in lithologic character and comprises dolostone, sandstone, and limestone intervals in varying proportions. The Everton Formation includes members of thick, friable sandstone that are similar to the overlying St. Peter Sandstone. Thickness of the Everton Formation varies from about 300 ft to more than 650 ft. The Powell Dolomite usually is observed as a fine-grained, light to green-gray dolostone from less than 50 ft to more than 200 ft in thickness, with thin beds of shale, sandstone, and occasional chert. The Jefferson City and Cotter Dolomites constitute a thick interval of 1,000 ft or more of light- to dark-tan, fineto medium-grained dolostone with common chert and some thin beds of sandstone and shale. These two formations are indistinguishable in Arkansas (McFarland, 1998).

The lower Ozark aquifer comprises the Roubidoux Formation and the Gasconade Dolomite for which the Gunter Sandstone Member is the primary water-yielding unit. These formations do not crop out in Arkansas. The Roubidoux consists of dolomite, sandstone, and chert. The dolomite is light gray to brown in color, finely granular to medium crystalline, and is sandy and cherty at some locations (Caplan, 1960; Howe and Konig, 1961; Imes and Emmet, 1994; Adamski and others, 1995). The sandstones consist of discontinuous beds of white to light-gray, fine to medium quartz (Snyder, 1976; McDonald and others, 1977) and are loosely to well cemented by silica or carbonate materials (Caplan, 1960). The Roubidoux Formation ranges from 100 ft to more than 450 ft in thickness in northern Arkansas.

The Gunter Sandstone Member at the base of the undifferentiated Gasconade Formation represents the oldest Ordovician rock present in northern Arkansas and rests unconformably on the Cambrian Eminence Dolomite. The Gasconade Formation comprises light brownish-gray, fine- to medium-crystalline dolomites that frequently contain chert (Caplan, 1960; Prior and others, 1999). The upper part of the Gasconade Formation contains relatively small amounts of chert; however, the formation may contain as much as 50 percent chert by volume above the Gunter Sandstone Member (Prior and others, 1999). The Gasconade Formation ranges from about 300 to over 700 ft in thickness (Caplan, 1960; Melton, 1976). The Gunter Sandstone is mainly composed of white to light-gray, fine- to coarse-grained quartz sandstone and sandy dolostone (McQueen, 1931; Knight, 1954; Caplan, 1960; Melton, 1976; Snyder, 1976; MacDonald and others, 1977; Adamski and others, 1995; Imes and Emmet, 1994; Prior and others, 1999a). The sand generally is loosely cemented by silica or carbonate material (Grohskopf and McCracken, 1949). The Gunter Sandstone Member typically averages about 30 ft in thickness (Caplan, 1960; Melton, 1976; Prior and others, 1999) but is locally reported to be

approximately 100–120 ft in thickness (Caplan, 1960; Melton, 1976; Prior and others, 1999). The Gunter Sandstone Member may be locally absent (Caplan, 1960; Prior and others, 1999).

The tops and thicknesses of the Roubidoux Formation and the Gunter Sandstone encountered in wells in northern Arkansas were identified by Lamonds and Stephens (1969). Structural maps of the Roubidoux and the Gunter are presented by Caplan (1960), Lamonds (1972), Melton (1976), MacDonald and others (1977), and Prior and others (1999). A limited number of wells are drilled to the Roubidoux and the Gunter. As a result, data used to compile the structural maps are limited. Prior and others (1999) used 174 wells and provided the most comprehensive structural map available at this time (2013).

Karst-development processes and history are an important aspect of the geology controlling groundwater hydrology in the Ozarks. The exposed formations of the Ozark aquifer present an example of a dynamic and developing karst aquifer. Also evident are episodes of karst development through geologic time that results in overlap and interplay of recent and paleokarst features. Karst aquifers are typified by a combination of diffuse and focused flow. The slower flow occurs through diffuse flow paths and allows for sustained groundwater input to streams and springs, even during dry periods. Extremely rapid response and transit times occur during precipitation events and are provided through preferential flow paths and karst features. In karst systems, large cavernous conduits allow for deep and rapid circulation of recharge. Conduits and dissolution-enhanced fracturing help integrate flow to spring resurgences (Harvey, 1980). As a result, springs are common throughout the exposed sections of the Ozark aquifer.

Bedrock in the Ozarks shows evidence of multiple episodes of water movement and carbonate dissolution, which defines distinct karst-development events through time (Stoffell and others, 2008). Exposure of Ordovician strata associated with the Ordovician-Mississippian unconformity caused dissolution and initial paleokarst development. Widespread dissolution features associated with the lead and zinc ore-bearing fluids that moved from the Arkoma Basin (Leach and Rowan, 1986) are observed across the Ozarks region. Lead and zinc were commercially mined where faults conveyed mineral-saturated fluids up from depth. Hypogene indicators, such as diagnostic calcite isotopic compositions (Brahana and others, 2009), collapse breccias (McKnight, 1935), and isotopic dating (Brannon and others, 1996), show that this episode of fluid movement and dissolution was a separate occurrence predating recent karst development. The formations of the Ozark aquifer once again showed active karst development as uplift, denudation, and abundant precipitation, and recharge initiated further dissolution of the soluble carbonate lithologies.

The recent period of dissolution and karst development has had very visible impact on the modern karst land surface, on controlling subsurface flow, and ultimately on surface flow in the region. The hydrogeology of the region is typical of karst with focused flow paths that are well connected to the surface and delivers water from input to discharge points at streams and springs at velocities of tens to thousands of feet per day (Funkhouser and others, 1999; Mott and others, 2000; Turner and others, 2007; Hudson and others, 2011). Abundant karst features are apparent including ponors, losing stream reaches, springs, caves, and sink holes. However, recent karst development in the Ozark aquifer has often reactivated and followed previous dissolution-enhanced flow paths. These flow paths originally developed during ancient exposure periods (for example, at the Ordovician-Mississippian unconformity; Webb, 1994) or hypogene episodes (such as Mississippi Valley Type ore emplacement; Leach and Rowan, 1986; Brannon and others, 1996; Brahana and others, 2009).

# Hydrologic Characteristics

The upper Ozark aquifer is generally unconfined across the Salem Plateau and confined in the Springfield Plateau and Boston Mountains. The highly soluble nature of the carbonate rocks of the dolostones and limestones that comprise the upper Ozark aquifer has resulted in development of the hydrologically heterogeneous karst terrain. Karst features include caves, springs, and sinkholes, which result in the direct hydraulic connection of surface water and groundwater and create the highly variable aquifer characteristics that typify the area. In the upper Ozark aquifer, high hydraulic conductivity values typically result from secondary porosity created by dissolution of bedrock along joints, fractures, and bedding planes, rather than from primary, matrix-type porosity. Enhancement of fractures, bedding planes, and conduits by carbonate dissolution is an active, ongoing process (Adamski and others, 1995). Diagenetic processes have developed secondary porosity features and have produced anisotropic and heterogeneous hydraulic characteristics in the aquifer. At one end of the porosity-permeable continuum, smaller-scale matrix, small-aperture fracture, and small-conduit porosity give rise to diffuse groundwater flow in the aquifer. At the other end of the porosity-permeable continuum, dissolutionenhanced porosity creates the focused (conduit) groundwater flow. Because of the low rock-matrix permeability, a large fraction of groundwater transfer is through the focusedflow component of the aquifer (Imes and Smith, 1990). The rapid recharge of surface water, rapid flow velocities, rapid mass transfer, and minimal attenuation of contaminants are associated with this component of flow. The time-averaged groundwater flow, base flow of streams during dry periods, low groundwater-flow velocities, and effective attenuation of contaminants are behaviors associated with the diffuse component of flow.

In the unconfined upper Ozark aquifer, precipitation provides recharge to the aquifer where exposed. Recharge can be rapid and result in highly variable water levels, substantial seasonal changes, and groundwater-gradient reversals (Aley, 1988). In areas where the Ozark aquifer is overlain by the Springfield Plateau aquifer, most recharge occurs through downgradient flow originating in the outcrop area for the Ozark aquifer and leakage from the overlying Springfield Plateau aquifer. Leakage of water between the Springfield Plateau and Ozark aquifers is impeded by shales (primarily the Chattanooga Shale) and dense, low-permeable limestones and dolostones (Imes and Emmett, 1994; Adamski and others, 1995). In some areas, the Chattanooga Shale is absent and the potential is increased for hydraulic connection between the two aquifers.

Well yields are relatively low within the upper Ozark aquifer and are comparable to those of the exposed Springfield Plateau aquifer, reflective of the generally low permeability. Wells within the upper Ozark aquifer are generally less than 300 ft in depth (Lamonds, 1972) and have yields of approximately 5–10 gal/min (Lamonds, 1972; Leidy and Morris, 1990b). Data on the hydraulic properties of the upper Ozark aquifer are scarce. The hydraulic conductivity of the combined upper and lower Ozark aquifer is estimated to range from greater than 1,000 ft/d to less than  $1.0 \times 10^{-2}$  ft/d (Imes and Emmet, 1994).

The Roubidoux Formation, Gasconade Dolomite, Eminence Dolomite, and Potosi Dolomite form aguifers of generally high yield (Harvey, 1980). Only the Roubidoux and Gunter Sandstone are commonly used in Arkansas and are grouped and discussed for the purposes of this report as the "lower Ozark aquifer." Where these units are exposed in Missouri, multiple studies have been conducted using dye traces and other approaches (Gott, 1975; Aley and Aley, 1987; Imes and Kleeschult, 1996). Results indicate a complex karst hydrologic system having long, interwoven flow paths that change drastically in terms of basin boundary extents and dominant flow paths with changing hydrologic condition (Mesko and Imes, 1995; Imes and Fredrick, 2002). Secondary porosity is provided by fractures, joints, bedding planes, vugs, dissolution conduits, and other karst features. This contributes to the high permeability values and the ability of the aquifer to convey great amounts of water. Secondary-porosity features are observed to decrease with depth (Lamonds, 1972). High yields at depth in the lower Ozark aquifer are attributed dominantly to porous sandstone layers, as reported for the Roubidoux Formation and Gunter Sandstone Member, rather than high hydraulic conductivity provided by karst features. Emerging data indicate the potential for localized karst-flow systems at depth within the Ozark aquifer (Brahana, 2011a). Though observations of paleokarst and solutional development are difficult to identify at depth, evidence provided by Palmer (2011) has shown that deep-seated dissolution has occurred within the Ozarks. Orndorff and others (2006) also provided evidence of karst development at depth in confined aguifers.

The lower Ozark aquifer is under confined conditions (Prior and others, 1999) and receives recharge from rainfall and streamflow interception in its outcrop areas in southern Missouri (Lamonds, 1972; Melton, 1976; MacDonald and others, 1977; Harvey, 1980; Prior and others, 1999). Harvey (1980) further detailed important recharge components and listed sinkholes, infiltration through conduits, and losing streams as the primary mechanisms of recharge. Some recharge occurs as leakage from the upper Ozark aquifer (Imes and Emmett, 1994; Adamski and others, 1995); however, the majority of recharge is attributed to lateral flow from the outcrop areas (Imes and Emmett, 1994; Adamski and others, 1995). The direction of groundwater flow generally follows the regional dip toward the south. Wells in Missouri intercept some of the groundwater in the lower Ozark aquifer before it reaches Arkansas (Prior and others, 1999).

Wells in the lower Ozark aquifer are among the most productive in the region (Lamonds, 1972); yields from the Roubidoux Formation range from less than 10 gal/min to about 600 gal/min (Caplan, 1960; Lamonds, 1972; Melton, 1976; MacDonald and others, 1977; Kilpatrick and Ludwig, 1990b; Prior and others, 1999). Yields from the Gunter Sandstone Member range from less than 100 gal/min to about 600 gal/min (Lamonds, 1972; Melton, 1976; MacDonald, 1977; Kilpatrick and Ludwig, 1990b; Imes and Emmett, 1994; Adamski and others, 1995; Renken, 1998; Prior and others, 1999; Czarnecki and others, 2014). Prior and others (1999) noted that wells were drilled to the deeper Gunter Sandstone Member only when yields from the Roubidoux Formation were insufficient. The wells often were dually completed, making it difficult to determine yields for the individual formations. Caplan (1960) reported that combined yields from the lower Ozark aquifer can be as much as 300 gal/min, although yields commonly are 50 gal/min or less. Melton (1976) noted that the distribution of well yields is not uniform, indicating that local lithologic differences and distribution of secondary porosity may affect well yields.

Data on the hydraulic properties of the Roubidoux Formation and the Gunter Sandstone Member in Arkansas are scarce. The hydraulic conductivity of the Ozark aquifer as a whole is estimated to range from more than  $1.0 \times 10^{-3}$  ft/s to less than 1.0×10<sup>-8</sup> ft/s (Imes and Emmet, 1994). Specific capacity values ranged from 0.1 to 3.8 (gal/min)/ft for the Roubidoux Formation, and several wells experienced no measurable drawdown while pumping. A single specific capacity of 0.1 (gal/min)/ft was reported from a well completed in the Gasconade Formation (Melton, 1976; MacDonald and others, 1977). Potentiometric surfaces of the lower Ozark aquifer are presented by Lamonds (1972), Melton (1976), MacDonald and others (1977), and Prior and others (1999) and generally show an overall southerly direction of flow following the regional deep of the formation constituting the aquifer.

## Water Levels

Water-level data for the Ozark aquifer are scarce. Where available, the data are very nonspecific in terms of the individual formation in which the well is completed, or if the well is completed in the lower Ozark aquifer compared to the upper Ozark aquifer. Most historical water levels were measured in open-hole wells, and the determination and assignment of the primary groundwater-yielding formation are difficult. This paucity of data results in (1) potentiometric maps that lack in detail, (2) a vertical distribution of head gradients that cannot be individually determined, and (3) an inability to understand groundwater flow in the aquifer, particularly at small, subregional scales.

The understanding of groundwater flow in the upper Ozark aquifer is derived from various reports and analysis of NWIS data performed for this report. Problems in understanding groundwater flow lies in the fact that the Ozark aquifer is not differentiated in most reports, although the dominantly unconfined upper Ozark aquifer has hydrologic characteristics vastly different from those of the deeper and confined lower Ozark aquifer. For the upper Ozark aquifer, precipitation provides direct recharge to the aquifer where exposed in Arkansas, and groundwater follows short (usually less than 10 mi), local flow paths that terminate near streams (Adamski and others, 1995). Therefore, recharge can be rapid and results in highly variable water levels with substantial seasonal changes. This also contributes to groundwater gradient reversals (Aley, 1988). The potentiometric surface of the combined (upper and lower Ozark aquifer undifferentiated) Ozark aquifer averages from about 700 to 1,000 ft of altitude (Adamski and others, 1995). The potentiometric surface generally is a subdued reflection of the topography where the upper Ozark aquifer crops out and is unconfined (Lamonds, 1972; Leidy and Morris, 1990b). Meta-analysis statistics conducted on data (altitude and water-level data from NWIS) compiled for this report from 1,081 wells showed that water levels closely correspond to land-surface altitudes with a correlation coefficient of 0.92. Groundwater-flow directions are lateral and outward from areas of high to low altitude. Small groundwater basins with short flow paths originating at higher altitudes and with discharge occurring at lower altitudes at streams and springs account for much of the overall groundwater-flow budget (Imes and Emmett, 1994; Adamski and others, 1995; Pugh, 1998, 2008b; Schrader, 2001a, 2005; Czarnecki and others, 2014).

Much of the understanding of groundwater flow in the lower Ozark aquifer is derived from extrapolation of data from Missouri. Water levels in the Roubidoux Formation of the lower Ozark aguifer vary spatially and temporally and may vary by as much as 200 ft/yr. Variations in the resulting potentiometric surface reflect topographic relief, changes in pumping, and regional formation dip (Kilpatrick and Ludwig, 1990b). Water levels from the Gunter Sandstone of the lower Ozark aquifer vary spatially and temporally and vary by approximately 100 ft in a period of a few years (Edds and Remsing, 1986; Freiwald and Plafcan, 1987). Representative hydrographs showing water levels from wells completed in the upper and lower Ozark aguifers are shown in figure 114. The upper Ozark aquifer generally shows greater and more rapid water-level change than the lower Ozark aquifer because it is shallower and more exposed to direct infiltration of locally recharging precipitation. Water-level changes in the lower Ozark are more subdued and slower in response to precipitation. This lag time for the lower Ozark as compared with the upper Ozark aquifer results from the greater distance of the wells in Arkansas from the recharge area located to



Figure 114. Water levels in wells completed in the upper and lower Ozark aquifer of northern Arkansas.

the north in Missouri. Water levels in the Ozark aquifer are measured on a 3-year rotational basis; measurements were last made in 2010 in 56 wells and 5 springs by the USGS in collaboration with ANRC (Czarnecki and others, 2014). No continuous water-level monitoring sites are active for the Ozark aquifer.

Water levels in the lower Ozark aquifer generally rise to altitudes of approximately 400–1,000 ft and typically are within about 200 ft below land surface (Lamonds, 1972). Water-level altitudes for the lower Ozark aquifer show a much less well-defined relation with land surface than the upper Ozark aquifer or the Springfield Plateau aquifer. Water-level and elevation data compiled from 1,085 wells for this report show that water levels correspond poorly to land-surface altitudes with a correlation coefficient of 0.70, as compared to correlation coefficients of 0.92 and 0.98 for the upper Ozark and Springfield Plateau aquifers, respectively. This lack of correlation between water-level and land-surface altitudes for the lower Ozark aquifer is a reflection of the lesser control of topography, the less frequent occurrence of short, small-basin flow paths, and the predominance of long, regional flow paths.

Regional flow within the lower Ozark aquifer is to the south and southeast following the dip of the units toward the Arkansas River and Mississippi Alluvial Plain (Lamonds,

1972, Czarnecki and others, 2014). Evidence of upward leakage from the lower Ozark aguifer into the embayment aquifers is seen in water-budget and geochemical data (Mesko and Imes, 1995; also see the "Mississippi River Valley Alluvial Aquifer" section in this report). The paucity of well control points for the lower Ozark aquifer in northern Arkansas greatly limits the confidence and detail of groundwater-flow interpretation and any delineation of topographic and other local controls on water levels. Additional data are needed to better understand the flow system in the lower Ozark aquifer (Lamonds, 1972; Imes and Emmett, 1994; Czarnecki and others, 2014). Potentiometric surfaces generated for the undifferentiated Ozark aguifer using the relatively scarce available water-level data (fig. 115) have changed little through time (Pugh, 1998; Schrader, 2001a, 2005; Pugh, 2008b; Czarnecki and others, 2014). Therefore, more recent potentiometric surfaces (Czarnecki and others, 2014) resemble predevelopment surfaces constructed by Imes and Emmett (1994). The St. Francois confining unit, the lower confining unit for the Ozark aquifer, limits the downward flow of groundwater and hydrologically separates the Ozark aquifer from the St. Francois aquifer (Adamski and others, 1995).



Figure 115. Potentiometric surface of the Ozark aquifer in northern Arkansas, 2010.

Several studies have investigated long-term water-level trends within the Ozark aquifer to identify areas at risk for groundwater decline and to quantify the effect of water users converting from groundwater to surface-water sources (Pugh, 2008b; Czarnecki and others, 2014). The sparse and limited number of water levels greatly limits effective assessment and prediction of sustainable water levels for the Ozark aquifer. Nevertheless, declines had been noted in northwestern Arkansas (Benton, Carroll, and Washington Counties), which is an area of development and population growth (Czarnecki and others, 2014). Czarnecki and others (2014) reported recent decreases in the rate of water-level decline in some wells and increases in water levels for others. This positive news was related to the expansion of rural water-supply districts that have predominately converted to surface-water sources.

# Deductive Analysis and Projections of Groundwater Movement

Groundwater often receives less focus in terms of monitoring and management efforts than does surface water because it is less visible, hydrologic and geochemical changes typically occur more slowly, and it responds less quickly to external processes or boundary conditions. Furthermore, collecting information and developing an effective understanding of groundwater behavior is more challenging than for surface water. Digital simulation of groundwater has been an important tool for evaluating basic aquifer characteristics such as recharge rates, storage, permeability, flow rates, and flow paths. Groundwater-flow models are also important as a tool to predict aguifer responses to future conditions such as changes in pumping, land-development effects, and climatic effects. Although numerous localscale and regional investigations of groundwater have been conducted across the Ozarks, groundwater-flow models rarely have been used. Investigations that have developed groundwater-flow models specific to the Ozarks of Arkansas are Imes and Emmett (1994), Mesko and Imes (1995), and Czarnecki and others (2009).

A regional groundwater-flow model for the Ozarks was developed by Imes and Emmett (1994) as part of the USGS Central Midwest RASA to assess regional groundwater resources and to better understand hydraulic properties of the aquifer and groundwater flow. Simulation results indicated that the hydraulic conductivity of the Ozark aquifer is approximately 10 ft/d in the southern Ozarks of Arkansas and about 25 percent of precipitation occurring over the outcrop area of the Ozark aquifer infiltrated as recharge to the aquifer. Of that total, about 78 percent entered small-scale watersheds, flowing along short flow paths to quickly discharge into nearby streams and springs. The remainder (6 percent of precipitation) ended up in deeper, longer flow paths as regional groundwater flow. The pumping rates at that time (1990) were found to have little to no effect on the simulated regional water budget and potentiometric surfaces compared to simulated

predevelopment conditions. These results illustrate the great differences in the predominantly karst aquifers of the Ozarks and the granular aquifers of the Mississippi embayment. Results also highlighted the prevalence of small-scale watersheds and associated short groundwater flow paths in the surficial aquifers in the overall groundwater-flow budget.

Regional groundwater-flow simulations were conducted by Mesko and Imes (1995) linking simulations of two regional-scale models: the Ozark Plateaus Aquifer System model (Imes and Emmett, 1994) and the Mississippi embayment Aquifer System Model (Brahana and Mesko, 1988). Historical hydrogeological data in the Mesko and Imes study indicated the potential for groundwater to move from the Ozarks aquifer system to beneath the Fall Line or escarpment into the northern Mississippi embayment, ultimately to discharge to overlying embayment aquifers or directly to streams. The quantity of water simulated by the linked Ozark model moving from the Ozark Plateaus aquifer system under the Fall Line into the Mississippi embayment was 650-800 ft<sup>3</sup>/s more than the quantity simulated by the MERAS model. The most likely explanation for this difference was groundwater discharge to streams. Therefore, the results were initially interpreted as indicating that a considerable volume of groundwater might be discharging to embayment streams. To determine if these differences in simulated groundwater flow could be explained by discharge to base flow in streams, low-flow seepage measurements were made on the Black and Current Rivers and their major tributaries in 1987. The seepage data indicated that groundwater contributed about 1,000 ft<sup>3</sup>/s to the streams. These results were in precise agreement with model results confirming the scale and great importance of groundwater contribution to streamflow (Mesko and Imes, 1995).

Availability of water has been a limiting factor for growth in the Ozarks; nevertheless, groundwater has historically been an important part of the resource base. Relatively minor attention and resources were focused on development of groundwater because of limited fiscal resources of the region and the regional groundwater system of the Ozarks is incredibly complex and challenging to characterize. As a result, an understanding of the Ozark Plateaus aquifer system is not at the same level as other important regional aquifers, and the available tools for assessing the system are insufficient to address evolving needs. Currently (2013), USGS is working on a regional assessment of groundwater availability of the Ozark Plateaus aquifer system as part of a USGS Groundwater Resources Program initiative (http://water.usgs.gov/ogw/ gwrp/activities/regional.html), whose objectives are to assess (1) growing demand and the role of groundwater as a resource for agricultural, industrial, and public-supply uses (Emmett and others, 1978; Dintelmann and others, 2006; Richards and Mugel, 2008; Richards, 2010), (2) regional climate variability and pumping affecting groundwater levels and groundwater and surface-water flow paths (Macfarlane and Hathaway, 1987; Imes and Emmett, 1994), (3) effects of the gradual shifting to greater dependence upon surface water in some

areas (Morgan, 2012) and, (4) potential effects on water use from shale-gas production (U.S. Environmental Protection Agency, 2010). Specific objectives related to the Ozark Plateaus aquifer system assessment include deductive analyses and projections of aquifer conditions using a newly developed groundwater flow model to (1) better understand groundwater movement in the Ozark Plateaus aquifer system, (2) quantify current water use and evaluate effectiveness of water-use monitoring approaches, (3) evaluate how groundwater and surface-water resources have changed over time, and (4) provide information to help project the systems response to future changes. The Ozark system model encompasses approximately 69,000 mi2 extending north to the Missouri River, south to the Arkansas River, west into Oklahoma and Kansas, and east to the Mississippi embayment. Groundwater use, groundwater levels, surface-water levels, streamflow, precipitation, temperature, land use, geophysical, and drillers' logs have been compiled to define hydrogeology and hydraulic properties of the system. These data were used to develop a conceptual model and ultimately can be used to construct a numerical model of the system.

# Water Use

There were 108 wells reported in the Ozark aquifer in 2010. Of those, 79 wells withdrew groundwater from the lower Ozark aquifer (comprised of the Roubidoux Formation and Gunter Member of the Gasconade Formation), and the remaining wells withdrew from the upper Ozark aquifer (fig. 116; Terrance W. Holland, U.S. Geological Survey, written commun., 2013). Primary use of the Ozark aquifer is for public supply; 76.45 Mgal/d was withdrawn for public supply in 2010. The high costs associated with drilling prevent smaller community-supply systems from using the more productive lower Ozark aquifer; although, some gas stations, campgrounds, mobile home parks, and resorts withdraw a small amount of groundwater in rural areas, but most others rely on wells in the upper Ozark aquifer.

The Roubidoux and Gunter units together compose the lower Ozark aquifer and account for the greatest yields and overall use in the Ozarks. Total reported use from the Roubidoux and Gunter in 2010 was 50.73 Mgal/d and 26.58 Mgal/d, respectively. Primary use of both units is public supply; 99.8 percent of use from the Roubidoux and 80.9 percent of use from the Gunter in 2010 was for public supply. Cherokee Village in Sharp County withdrew the most water from the lower Ozark aquifer in 2010 at 9.72 Mgal/d; all withdrawals were from wells listed as completed in the Roubidoux (Terrance W. Holland, U.S. Geological Survey, written commun., 2013). Decatur (Benton County) withdrew the most water from the Gunter Member in 2010 at 5.08 Mgal/d (Terrance W. Holland, U.S. Geological Survey, written commun., 2013). Other large users include the public supplies of Holiday Island (Carroll County), Corning (Clay County), and Mammoth Spring (Fulton County).

The Rubidoux and Gunter units were suggested as potential future groundwater supply sources in Randolph

and Lawrence Counties by Lamonds and others (1969). In Randolph County, one community tapped the Roubidoux in 1980 and the deeper Gunter in 2010; another community tapped the Roubidoux in 1978 (Lyle Godfrey, Arkansas Health Department, written commun., 2012). In Lawrence County, the Gunter was tapped in the late 1990s for public supply.

While groundwater use from the lower Ozark aquifer is substantial, and some wells have been drilled into the lower Ozark aquifer in recent years, use of the aquifer has decreased. Surface-water use has increased dramatically, and the vast majority of the population in northern Arkansas is served by surface water, especially in Benton and Washington Counties (see "Overview of Aquifers of Arkansas" section). Beaver Lake was developed in the 1960s by the U.S. Army Corps of Engineers primarily to provide water to the major cities in northwestern Arkansas: Fayetteville and Springdale (Washington County) and Rogers and Bentonville (Benton County) (Amy Wilson, Beaver Water District, written commun., 2012). Many other water districts have formed throughout northern Arkansas-Carroll-Boone Water District, Benton-Washington Regional Public Water Authority, and Madison County Regional Water District-to deliver surface water to smaller communities from Beaver Lake (Davis and Shephard, 2010). Bull Shoals, originally developed for hydroelectric generation and flood control, is currently (2013) providing water to many users in Marion County (U.S. Army Corps of Engineers, 2010). Thus, numerous wells in the lower Ozark aquifer have been abandoned.

Many communities have sought out surface water as a public-supply source because of quantity and quality issues with groundwater. Some municipalities have struggled to provide adequate supplies for growing demands with limited groundwater sources. Other areas tapping the lower Ozark aquifer have naturally occurring radon, radium, fluoride, and other undesirable constituents that have impaired use and increased treatment costs (Adamski, 1996). For some of these communities, like the Nail-Swain Water Association (Newton County), ADH issued Administrative Orders restricting groundwater use (U.S. Army Corps of Engineers, 2010). Development of an alternative water source for these areas is a top priority, and a project is underway to deliver water from Bull Shoals to multiple rural communities (U.S. Army Corps of Engineers, 2010; Ozark Mountain Regional Public Water Authority, 2013).

Irrigation use from the Ozark aquifers was estimated at approximately 20 Mgal/d in 2010 (Terrance W. Holland, U.S. Geological Survey, written commun., 2012). About 70 percent of irrigation water use is from the upper Ozark aquifer and occurs in counties in the aquifer's far eastern extent, where row crops like cotton, rice, and soybeans are commonly grown. Depth to water in most of these wells is approximately 100 ft. Agricultural use throughout the rest of the Ozark Plateaus is likely to be smaller in scale, mainly for growing fruit (Lamonds, 1972) that does not have the large water requirements of row crops. In addition, approximately 6 Mgal/d were withdrawn for two fish hatcheries in 2010 from the Gunter Member.



Domestic and livestock use are known to be underestimated for the Ozark aquifer. Domestic wells have been widely used since the 1880s (Purdue and Miser, 1916). Use has been reported in the shallower upper Ozark aquifer (Albin and others, 1967a; Lamonds and Stephens, 1969; Lamonds 1972; Kilpatrick and Ludwig, 1990b) but has often been poorly estimated—records have been spotty and estimation methods were inaccurate. Also, many wells fail to meet the 50,000 gal/d reporting requirement or are coregistered as a domestic well and therefore exempt from the water-use reporting program. For example, a well producing from the Ozark aquifer for livestock purposes, such as a chicken house or other animal operation, and also has a waterline to an adjacent house or garden for domestic purposes, would not have to report use as a coregistered well.

Commercial groundwater use of the Ozark aquifer was estimated at 0.1 Mgal/d in 2010 (Terrance W. Holland, U.S. Geological Survey, written commun., 2013). Most use in the Ozarks is seasonal for recreational activities including resorts, parks, campgrounds, and golf courses. Commercial use is also suspected to be underreported because many wells may not meet the 50,000 gal/d reporting requirement. No industrial use was recorded for the Ozark aquifer in 2010, but previous industrial users have included concrete companies. In 1985, 1.53 Mgal/d was reported for commercial use (Kilpatrick and Ludwig, 1990a).

# Water Quality

The Ozark aquifer, together with the Springfield Plateau aquifer, is one of the major aquifers of the Ozark Plateaus. Similar to the Springfield Plateau aquifer, the Ozark is a karst aquifer within carbonate rocks described in previous sections. Additionally, agriculture in the form of beef and dairy cattle, swine, and poultry operations is the predominant land use in this region of steep topography and thin soils (Adamski, 1997). There is a high degree of connectivity between the surface and groundwater, expressed in the occurrence of sinkholes, solution fractures, caves, losing streams, large springs, and other karst features. This leads to nutrients, bacteria, and other surface-derived contaminants that are associated with the agricultural activities as posing the greatest threat to groundwater quality in the Ozark aquifer, particularly that of the upper Ozark aquifer (Peterson and others, 2000). The karst geology is well developed with the upland areas of the Salem Plateau estimated to have 1 to 10 sinkholes per 100 mi<sup>2</sup> (Harvey, 1980). Spring discharges that exceed 100 ft<sup>3</sup>/s are common (Imes and Smith, 1990). The surface extents of the Ozark aquifer and the Springfield Plateau aquifer in northern Arkansas are mapped at the highest groundwater vulnerability index in the State (Arkansas Soil and Water Conservation Commission, 1991).

There are 16 formations that constitute the upper Ozark aquifer (table 5), which dominantly are represented by dolostones composed of or containing a high percentage of dolomite. Water-quality data in USGS NWIS commonly are reported by the well-completion depth and formation penetrated by the driller. Water-quality data in USGS NWIS from the upper part of the Ozark aquifer are reported from 7 of the 16 upper Ozark formations: Fernvale Limestone, Everton Formation, Joachim Dolomite, St. Peter Sandstone, Cotter Dolomite, Jefferson City Dolomite, and Powell Dolomite. Well depths in the upper Ozark aquifer ranged from 19 to 1,210 ft, although 71 percent of the wells were less than 500 ft deep. By comparison, well depths for the lower Ozark aquifer in Arkansas ranged from 506 to 3,534 ft, with 45 of 62 wells (73 percent) being more than 1,000 ft. The following sections discuss water quality of the Ozark aquifer. Historical publications often do not separate the shallow upper Ozark aquifer from the lower Ozark aquifer, especially with respect to regional studies. The following discussion will focus on the upper and lower Ozark aquifers separately where the data are available and meaningful differences exist in geochemistry and water quality.

## General Geochemistry and Water Type

Groundwater from the carbonate rocks constituting the Ozark aquifer is of a hard to very hard, calcium-magnesiumbicarbonate type (Albin and others, 1967a; Lamonds and others, 1969; Lamonds, 1972; MacDonald and others, 1977; Harvey, 1980; Kilpatrick and Ludwig, 1990b; Leidy and Morris, 1990b; Imes and Emmett, 1994; Adamski and others, 1995; Prior and others, 1999; Kresse and Fazio, 2004). Pure dolomite minerals contain an equal number of calcium and magnesium ions. Dissolution of the dominant dolomite mineralogy in the Ozark aquifer produces a groundwater reflective of this rock chemistry and has approximately equal equivalent concentrations of calcium and magnesium. Some spatial variation is imparted by variable mineralogy and lithology and from formation to formation. Kresse and Fazio (2004) compared calcium/magnesium ratios in groundwater from individual formations of the upper Ozark aquifer and noted slightly higher median, mean, and maximum calcium/ magnesium ratios in the combined St. Peter Sandstone and Everton Formation exposures compared to the Powell, Cotter, and Jefferson City Dolomites. Calcite cement in the lower part of the St. Peter Sandstone was noted as influencing the higher ratio. Calcium-magnesium ratios exceeding 1.0 for the upper Ozark aquifer, where exposed, probably are influenced by occurrence of limestone or calcite cement in various formations of the Ozark aquifer.

Data compiled for this report generally support the dominant calcium-magnesium water type for groundwater from the Ozark aquifer and reflect the dominant dolomitic geochemistry of rocks constituting the Ozark aquifer. The upper Ozark aquifer had calcium/magnesium equivalent ratios ranging from 0.5 to 32.5 with a median of 1.2. The lower Ozark aquifer had ratios ranging from 0.4 to 26.2 with a median of 1.1. All but the maximum ratio of 26.2 in the lower Ozark aquifer were less than 2.0 and demonstrate the narrow range of low ratios nearing the 1:1 ratio of pure dolomite. Conversely, 24 of 123 of the calcium/magnesium ratios for the upper Ozark aquifer exceeded 2.0. These 24 sites reflected ratios typical of that from the Springfield Plateau aquifer. Comparison of calcium/magnesium ratios from the upper Ozark aquifer to surface geology revealed that the higher ratios occurred in samples from wells located in outcrop areas of the Springfield Plateau aquifer (Boone Formation; fig. 117). By comparison, in areas where the Ozark aquifer is exposed (Fernvale Limestone through Jefferson County Dolomite; fig. 117), calcium/magnesium ratios are near 1.0 (fig. 117). Groundwater in the upper Ozark aquifer exhibiting higher calcium/magnesium ratios similar to those of the Springfield Plateau aquifer may be explained by (1) incorrect aquifer designation indicating that these wells are actually completed in the Springfield Plateau aquifer, (2) open-hole completions where wells penetrate rocks of the Ozark and Springfield Plateau aquifers, or (3) leakage from the Springfield Plateau aquifer down into the upper Ozark aquifer where the Chattanooga Shale confining layer is incompetent or absent. Harvey (1980) noted higher calcium/magnesium ratios for the Ozark aquifer on the Springfield Plateau and attributed slow leakage of water from overlying limestone formations to the increased ratios. Kresse (1991) compared calciummagnesium ratios in groundwater from the Springfield Plateau and Ozark aquifers in Searcy County. Some wells that were cased and receiving groundwater only from the upper Ozark aquifer had ratios similar to that of the Springfield Plateau aquifer. Because the Chattanooga Shale was absent in Searcy County, Kresse (1991) attributed leakage from the overlying Springfield Plateau aquifer as the source of the higher ratios.

Values of pH ranged from 4.8 to 8.7 with a median of 7.3 in the upper Ozark aquifer (table 44). Values ranged from 6.7 to 8.4 with a median of 7.7 in the lower Ozark aquifer (table 45). For both aquifers, pH showed no trend with increasing well depth or dissolved solids. For the upper aquifer,  $R^2$  values for relations of pH to well depth and dissolved-solids concentrations were 0.0003 and 0.0135 (fig. 118*A*, *B*), respectively, and were 0.0031 and 0.0687, respectively, in the lower aquifer (fig. 118*C*, *D*). Thus, median pH values and relations of pH to well depth and dissolved solids are similar in the less geochemically evolved groundwater for the upper Ozark aquifer compared to that in the more geochemically evolved groundwater for the lower Ozark aquifer. This suggests that infiltrating, low-pH rainwater (average of 4.7 standard units; Kresse and Fazio, 2002) is rapidly buffered by carbonate minerals in the overlying regolith and unsaturated bedrock prior to reaching the aquifer. This interpretation is supported by additional work conducted by Pollock and others (2011) who observed well-buffered regolith and cave drip water in the unsaturated zone above a cave in the upper Ozark aquifer.

No strong spatial trend was noted for the distribution of dissolved solids in the lower Ozark aquifer. However, a general trend of increasing dissolved solids was observed moving from the south toward the northeast, especially in the eastern extent. The greatest frequency of dissolved solids greater than 300 mg/L occurred in the exposed sections of the Powell, Cotter, and Jefferson City Dolomites as compared to the St. Peter and Everton Formations (not shown in fig. 117). Bicarbonate exhibited strong positive correlations with dissolved-solids concentrations for the upper (fig. 118E) and the lower (fig. 118F) Ozark aquifers, with R<sup>2</sup> values of 0.9235 and 0.7387, respectively. The spatial distribution of bicarbonate was similar to that of dissolved solids with higher concentrations observed to the northeast. Kresse and Fazio (2004) noted lower mean, median, and maximum bicarbonate and dissolved-solids concentrations in groundwater from the St. Peter and Everton Formations compared to other formations of the upper Ozark aquifer. There is insufficient evidence to discern if these differences are attributable to the solubility of carbonate minerals between the formations or if the higher concentrations are an artifact of longer residence time and greater rock/ water interaction in the Powell, Cotter, and Jefferson City Dolomites along longer flow paths.



Figure 117. Spatial distribution of selected chemical constituents in groundwater from the Ozark aquifer in northern Arkansas.

**Table 44.** Descriptive statistics for selected chemical constituents in groundwater from the upper Ozark aquifer in northern Arkansas. [mg/L, milligrams per liter; μg/L, micrograms per liter; μS/cm, microsiemens per centimeter at 25 degrees Celsius]

Constituent	Minimum	Median	Maximum	Standard deviation	Number of wells
Calcium (mg/L)	4.4	63	140	21.13	132
Magnesium (mg/L)	0.8	28	71	14.49	132
Sodium (mg/L)	0.7	2.4	696	61.95	129
Potassium (mg/L)	0.1	1.1	22	2.76	127
Bicarbonate (mg/L)	2.0	313	1,720	169.02	104
Chloride (mg/L)	0.3	4.1	105	12.27	133
Sulfate (mg/L)	0.4	8.8	138	20.40	133
Silica (mg/L)	0.13	9.9	20	2.56	117
Nitrate (mg/L as nitrogen)	0.01	0.62	7.2	1.26	124
Dissolved solids (mg/L)	52	285	1,735	154.64	132
Iron (µg/L)	0.05	5.2	1,600	252.26	112
Manganese (µg/L)	0.13	0.13	40	6.86	123
Arsenic (µg/L)	0.03	0.03	6.96	1.12	73
Hardness (mg/L as calcium carbonate)	20	243	520	101.88	84
Specific conductance (µS/cm)	89	518	2,840	250.98	130
pH (standard units)	4.8	7.3	8.7	0.45	133

**Table 45.** Descriptive statistics for selected chemical constituents in groundwater from the lower Ozark aquifer in northern Arkansas.  $[mg/L, milligrams per liter; \mug/L, micrograms per liter; \muS/cm, microsiemens per centimeter at 25 degrees Celsius]$ 

Constituent or characteristic	Minimum	Median	Maximum	Standard deviation	Number of wells
Calcium (mg/L)	11	45	91	16.95	55
Magnesium (mg/L)	0.07	23	83	13.95	55
Sodium (mg/L)	0.73	2.3	100	29.66	40
Potassium (mg/L)	0.4	1.7	6.1	1.45	27
Bicarbonate (mg/L)	22	270	548	102.16	31
Chloride (mg/L)	1.0	4.0	113	19.08	63
Sulfate (mg/L)	0.4	12	49	10.42	59
Silica (mg/L)	1.7	9.4	14.4	2.54	23
Nitrate (mg/L as nitrogen)	0.01	0.18	29	5.79	48
Dissolved solids (mg/L)	93	276	431	75.85	59
Iron (µg/L)	0.05	30	3,600	667.73	29
Manganese (µg/L)	0.13	10	7,000	1,181.78	35
Arsenic (µg/L)	0.03	0.03	4.5	1.43	12
Hardness (mg/L as calcium carbonate)	50.9	200	400	80.71	51
Specific conductance (µS/cm)	10	459	1,640	231.36	39
pH (standard units)	6.7	7.7	8.4	0.44	43



**Figure 118.** Relation of pH to *A*, well depth and *B*, dissolved solids in the upper Ozark aquifer and to *C*, well depth and *D*, dissolved solids in the lower Ozark aquifer; and relation of bicarbonate to dissolved solids in *E*, the upper Ozark aquifer and *F*, the lower Ozark aquifer.

## Nitrate

Nitrate concentrations in 124 samples from the upper Ozark aquifer ranged from 0.01 to 7.2 mg/L with a median of 0.62 mg/L (table 44). For purposes of this section, "elevated" concentrations of nitrate (expressed as nitrogen) refer to concentrations exceeding 0.4 mg/L, which is considered a background concentration for nitrate in relatively undisturbed areas of the Ozarks (see "Springfield Plateau Aquifer" section). For the lower Ozark aquifer, nitrate concentrations in 48 samples ranged from 0.01 to 29 mg/L with a median of 0.18 mg/L (table 45). Two wells in the lower Ozark aquifer had concentrations of 28 and 29 mg/L, which was far above the maximum concentration in the upper Ozark aquifer. However, the median of 0.18 mg/L reflects the overall lower nitrate concentrations in the lower Ozark aquifer compared to that of the upper Ozark aquifer (median of 0.62 mg/L).

The two very high nitrate concentrations in a deep, confined aquifer pose questions on the transport of nitrate to such depths. Prior and others (1999) noted that problems in the ability to retrieve samples representing groundwater only from the Roubidoux or Gunter geologic units (lower Ozark aquifer) were related directly to depth of the casing. Casing for domestic wells in the Ozark Plateaus typically is advanced only through 1-3 ft of bedrock (effectively casing off unconsolidated regolith material) with the remainder of the well being an open-hole completion. For deeper publicsupply wells, the casing is advanced through parts of the upper, shallow formations to a depth determined by drillers and water suppliers, and the remainder is left as an open-hole completion. Although the ADH recommends casing entirely through overlying, shallow exposed formations, no legally binding regulation has been enacted that requires such casing. Because overlying formations are not fully cased, or perhaps the casing has become compromised during completion or deteriorated over time, there is increased opportunity for influx of surface-derived contaminants into the deeper confined formations of the lower aquifer. No relation was found between well depth and nitrate concentrations for the lower or upper Ozark aquifers. Several nitrate concentrations that exceeded 1.0 mg/L occurred throughout a range of 500-3,500 ft in the lower Ozark aquifer. One well with a depth of 3,420 ft had a concentration of 3.4 mg/L, although most concentrations were less than 1.0 mg/L. These elevated nitrate concentrations may be ascribed to the increased vulnerability of karst aquifers to surface-derived contaminants and to the lack of adequate well casing regardless of well depth.

Numerous studies have discussed the occurrence of elevated nitrate in groundwater from karst aquifers of the Ozark Plateaus, and several have noted lower overall concentrations in the Ozark aquifer compared to the Springfield Plateau aquifer (Leidy and Morris, 1990b; Smith and Steele, 1990; Steele and McCalister, 1990, Adamski, 1997; Huetter and others, 1997; Kresse and others, 2011). These studies were conducted in northwestern Arkansas, which is dominated by exposures of the Boone Formation that constitutes the Springfield Plateau aquifer. A common hypothesis within these studies was that the lower concentrations in the Ozark aquifer were because of the protection afforded by overlying formations of the Springfield Plateau aquifer and the Ozark aquifer confining unit (Chattanooga Shale). Median nitrate concentrations from the upper (table 44) and lower (table 45) Ozark aquifers were 0.62 and 0.18 mg/L, respectively, compared to 1.8 mg/L from the Springfield Plateau (table 43).

To investigate confinement as the dominant control on lower nitrate concentrations, Kresse and others (2011) compared nitrate data from two separate studies. One study (Adamski, 1997) was in northwestern Arkansas where the Ozark aquifer is confined by overlying Mississippian-age formations. The other study (Kresse and Fazio, 2004) was conducted in northeastern Arkansas where the aquifer is unconfined, exposed at the surface, and more vulnerable to contamination. Kresse and Fazio (2004) sampled groundwater from the upper Ozark aquifer in northeastern Arkansas and reported median nitrate concentrations in springs of 0.47 mg/L and median concentrations in wells of 0.63 mg/L. These data compared closely to median concentrations from springs (0.40 mg/L) and wells (0.60 mg/L) in the confined upper Ozark aquifer sampled in northwestern Arkansas (Adamski, 1997). Because median nitrate concentrations for the Ozark are similar in areas whether confined or exposed, Kresse and others (2011) hypothesized that other factors must influence the lower vulnerability of the Ozark aquifer to surface-derived contaminants.

A positive correlation between nitrate concentrations and agricultural land use in northwestern Arkansas for groundwater collected dominantly from the Springfield Plateau aquifer (see "Springfield Plateau Aquifer" section) was shown by Adamski (1997) and Kresse and others (2011). One plausible explanation for the lower nitrate concentrations in the Ozark aquifer is lower agricultural land use in the northeastern part of the Ozark Plateaus, where the Ozark aquifer is exposed at the surface. Kresse and others (2011) determined percent agricultural land use in the upper Ozark aquifer in northeastern Arkansas using data from Kresse and Fazio (2004) and plotted nitrate concentrations and 10 percent increments of increasing agricultural land use to investigate the effects of increasing agricultural land use on nitrate concentrations (fig. 119A). The results were compared to that of Kresse and others (2011) for well and spring nitrate concentrations in northwestern Arkansas (fig. 119B). Mean nitrate concentrations for the upper Ozark aquifer were much lower for all categories of percent agricultural land use compared to data taken from the Springfield Plateau aquifer in northwestern Arkansas. The overall mean nitrate concentration of 0.73 mg/L for data from the upper Ozark aquifer in northeastern Arkansas was exceeded for most agricultural land-use categories greater than 30–40 percent (fig. 119A), and all mean nitrate concentrations for agricultural land use below 30 percent were less than about 0.3 mg/L. Conversely, the mean nitrate concentrations for agricultural land use below



EXPLANATION

7 Number of samples

**Figure 119.** Nitrate concentrations and agricultural land use for groundwater from *A*, the Ozark aquifer in northeastern Arkansas and *B*, from the Springfield Plateau aquifer in northwestern Arkansas.

30 percent for the Springfield Plateau aquifer in northwestern Arkansas were all greater than 1.0 mg/L (upward to 1.9 mg/L) (fig. 119B). The highest mean nitrate concentrations for the upper Ozark aquifer (fig. 119A) occurred at percent agricultural land use between 50-60 percent (mean nitrate concentration of 1.2) and 60 to 70 percent (mean nitrate concentration of 1.3 mg/L). By comparison, the mean nitrate concentrations at these categories, 50-60 percent and 60-70 percent, for the Springfield Plateau aquifer data were 2.8 and 3.2 mg/L, respectively (fig. 119B). Therefore, nitrate concentrations are much lower in the upper Ozark aquifer than in the Springfield Plateau aquifer for similar increases in agricultural land use. This finding indicates that the upper Ozark aquifer, even where exposed at the surface, is less vulnerable to contamination than the Springfield Plateau aquifer, regardless of the percent agricultural land use. The soils overlying the upper Ozark aquifer, or the geologic units of the shallow part of the aquifer itself, may have physical characteristics (lower permeability soils, thicker regolith, less fracturing and dissolution of rocks, fewer bedding planes, and other factors) favoring a lower vulnerability to influx of surface-derived contaminants than the soils overlying the Springfield Plateau aquifer.

A general trend of a higher density of elevated nitrate concentrations was observed in the eastern part of the upper Ozark aquifer, where it is exposed, compared to areas where the upper Ozark aquifer is overlain by the Chattanooga Shale and the Springfield Plateau aquifer (fig. 117). Therefore, some protection is afforded where it is confined by overlying formations of the Springfield Plateau aquifer and the Ozark confining unit. An important protection and management conclusion based on these data is that sufficient casing for isolating groundwater from the more vulnerable Springfield Plateau aquifer should prevent influx of surface-derived contaminants into the upper Ozark aquifer in this area of the Ozark Plateaus. No spatial trend was noted for nitrate concentrations in the lower Ozark aquifer. The fact that elevated nitrate concentrations occur in the confined, lower Ozark aquifer at well depths exceeding 1,000 ft suggests inadequate casing in these wells. The casing of all overlying formations when drilling wells for public supply could prevent contamination of the lower Ozark aquifer.

## Pesticides

The occurrence of pesticides in groundwater from the Ozark Plateaus in Arkansas, Kansas, Missouri, and Oklahoma was investigated by Adamski (1997). Pesticides were detected in 14 of 63 (22 percent) of the samples from the Ozark aquifer (the upper and lower Ozark aquifer were not differentiated). Many of the sampling sites were located in northwestern Arkansas. Pesticides were detected at a lower rate in the Ozark aquifer compared to the Springfield Plateau aquifer, demonstrating the reduced vulnerability of the Ozark aquifer to surface-derived contaminants. The most commonly detected pesticides were tebuthiuron; atrazine; prometon; desethylatrazine, a metabolite of atrazine; and simazine. These compounds are herbicides that are commonly used on pastures and noncrop areas.

## Radium

Radium in groundwater was analyzed as part of the Ozarks National Water Quality Assessment study (Adamski and others, 1995). The combined radium-226 and radium-228 activity ranged from 5.1 to 13.9 picocuries per liter (pCi/L) in 18 water samples from public-supply wells in Missouri in 1983 and ranged from 4.9 to 12.8 pCi/L in samples from several public-supply wells in northern Arkansas in 1987–89. Depths of these wells ranged from 250 to more than 1,700 ft below land surface. Only one well in Arkansas had levels above the Federal MCL of 5 pCi/L.

Sampling of public-water systems by the ADH revealed a systemic radium problem in the lower Ozark aquifer. Three systems in Newton County, three in Searcy County, three in Boone County, and one each in Marion and Carroll Counties have had at least one well with historical violations for the combined radium MCL of 5 pCi/L. Contamination above the MCL of 5 pCi/L for these public-supply wells presently is attributed to an association with early Paleozoic shales within the lower Ozark aguifer. The contamination has resulted in abandonment of wells and selection of alternate sources of drinking water for most of these systems. The Ozark Mountain Regional Public Water Association is constructing a surface intake on Bull Shoals Lake in eastern Newton County to replace many of the public-water suppliers using groundwater from the Ozark aquifer (Darcia Routh, Arkansas Department of Health, written commun., 2013).

## Iron

Iron concentrations generally are low in groundwater from the Ozark aquifer throughout the Ozark Plateaus. Iron concentrations ranged from 0.05 to 1,600  $\mu$ g/L with a median of 5.2  $\mu$ g/L (fig. 120; table 44) in the upper Ozark aquifer and from 0.05 to 3,600  $\mu$ g/L with a median of 30  $\mu$ g/L in the lower Ozark aquifer (fig. 121; table 45). Only 4 of 112 samples from the upper Ozark aquifer exceeded the Federal secondary drinking-water regulation of 300  $\mu$ g/L, and 4 of 29 samples from the lower Ozark aquifer exceeded this limit.



Figure 120. Interquartile range of selected chemical constituents in groundwater from the upper Ozark aquifer in northern Arkansas.



Figure 121. Interquartile range of selected chemical constituents in groundwater from the lower Ozark aquifer in northern Arkansas.

## Sulfate

Sulfate concentrations generally are low in the Ozark aquifer and were below the Federal secondary drinkingwater regulation of 250 mg/L in all samples from the upper and lower Ozark aguifer. Whereas the maximum sulfate concentration in 59 samples from the lower Ozark aquifer was 49 mg/L, the upper Ozark aquifer had a maximum of 138 mg/L, and 6 of 133 samples were greater than 50 mg/L (table 44). Sulfate concentrations generally were below 10 mg/L in areas where formations composing the upper Ozark aquifer (Fernvale Limestone through Jefferson City Dolomite; fig. 117) are exposed and greater than 20 mg/L (upward to 138 mg/L) where the upper Ozark aquifer is overlain by younger formations (fig. 117). Shale formations typically have groundwater with elevated sulfate concentrations relative to overlying and underlying aquifers (Kresse and Hays, 2009). Leakage through the overlying Chattanooga Shale that serves as the Ozark aquifer confining unit may be contributing sulfate to the upper Ozark aquifer in this area.

#### Chloride

Chloride concentrations generally are low throughout the Ozark aquifer. Concentrations ranged from 0.3 to 105 mg/L with a median of 4.1 mg/L in the upper Ozark aquifer (fig. 120; table 44) and ranged from 1.0 to 113 mg/L with a median of 4.0 mg/L in the lower Ozark aquifer (fig. 121; table 45). Various reports have commented on potential higher salinity groundwater in the lower Ozark aquifer, where it dips steeply south of the Springfield-Salem Plateaus toward the Arkansas River. Lamonds (1972) stated that groundwater in the southern extent of the lower Ozark aquifer was assumed to be highly mineralized but did not provide spatial information on salinity gradients or saltwater-freshwater transition zones. MacDonald and others (1977) stated that chloride increases with the regional gradient toward the Arkoma Basin and calculated salinity concentrations ranging from 2,000 to 3,000 mg/L using formation density and induction-electric logs. Imes and Emmett (1994) stated that the lower Ozark aquifer was saline only in the region between the Boston Mountains and the Arkansas River. Prior and others (1999) stated that most wells advanced into the lower Ozark aquifer in the Boston Mountains were reported to contain brine and hypothesized that deeper wells in the extreme southern Ozark Plateaus probably would encounter increased water salinity. A general spatial trend was noted for increases in chloride to the south (fig. 117). Wells with the highest chloride concentrations, which are located near the southern boundary of the Springfield Plateau (Boone Formation), may represent an approximate southern boundary of usable fresh groundwater in the lower Ozark aquifer. No spatial trends were apparent for chloride concentrations in the upper Ozark aquifer.

In summary, the Ozark aquifer comprises carbonate formations that have weathered to form a karst terrain, which increases vulnerability to surface-derived contaminants. Because agriculture in the form of dairy and beef cattle, poultry, and swine operations is the dominant land use in the Ozark Plateaus, nutrients, bacteria, and pesticides pose the greatest threat to groundwater quality. Elevated nitrate concentrations were noted in groundwater from the upper and lower Ozark aquifer, in spite of the fact that the lower Ozark aquifer is confined and well depths generally are more than 1,000 ft. The thin soils and karst features associated with the Ozark aquifer coupled with insufficient casing appear to facilitate the transport of agricultural contaminants to the upper and lower Ozark aquifers. An important protection and management conclusion based on these data is that sufficient casing for isolating groundwater from the more vulnerable Springfield Plateau aquifer may prevent influx of surfacederived contaminants into the upper Ozark aquifer in this area of the Ozark Plateaus.

# Summary

Aquifers in Arkansas that currently serve or have served as important sources of water supply were described with respect to existing State and Federal groundwater protection and management programs, geology, hydrologic characteristics, water use, water levels, deductive analyses, and projections of aquifer conditions using groundwater models, and water quality for 16 aquifers. State and Federal protection and management programs were described according to regulatory oversight, management strategies, and ambient groundwater-monitoring programs that currently are in place for assessing and protecting groundwater resources throughout the State. Information was compiled and summarized from about 550 historical and recent publications that describe the hydrology and geochemistry of each of the aquifers. Additionally, more than 8,000 sites with groundwater-quality data were obtained from the U.S. Geological Survey National Water Information System and the Arkansas Department of Environmental Quality databases and entered into a spatial database to investigate distribution and trends in groundwater chemical constituents for each of the aquifers.

The 16 aquifers of the State are divided into two major physiographic regions: the Coastal Plain of eastern Arkansas and the Interior Highlands of western Arkansas. Aquifers in the Coastal Plain comprise Cenozoic-age strata consisting primarily of Cretaceous, Tertiary, and Quaternary sands, gravels, silts, and clays, with groundwater primarily produced from coarse-grained sands and gravels within these aquifers. Except for isolated areas of Quaternary alluvial deposits that serve as valuable sources of groundwater supply, aquifers of the Interior Highlands predominantly consist of fractured sandstone, shale, chert, and carbonate rocks. These rocks are well indurated and primary porosity is low. Secondary porosity is created by weathering, fracturing, and dissolution, resulting in relatively low storage and low well yields from aquifers of the Interior Plains. Groundwater in the Coastal Plain of Arkansas represents one of the most valuable natural resources in the State, driving the economic engines of agriculture, while also supplying abundant water for commercial, industrial, and public-water supply. In terms of age from youngest to oldest, the aquifers of the Coastal Plain include: Quaternary alluvial aquifers including the Mississippi River Valley alluvial aquifer, the Jackson Group, and the Cockfield, Sparta, Cane River, Carrizo, Wilcox, Nacatoch, Ozan, Tokio, and Trinity aquifers.

The Mississippi River Valley alluvial aquifer is the most important aquifer in terms of total groundwater used in Arkansas. Arkansas ranks fourth nationally in groundwater use, and 94 percent of all groundwater used in Arkansas is from the Mississippi River Valley alluvial aquifer. Wateruse rates continue to increase for this aquifer; rates in 2010 from the aquifer were approximately 7,400 million gallons per day (Mgal/d). Intensive use has led to (1) severe water-level declines resulting in deep cones of depression in the potentiometric surface, (2) rates of pumping that exceed recharge and are unsustainable in many areas, and (3) designation of critical groundwater area status for the aquifer in several areas of eastern Arkansas. These conditions have led to development of alternate water supplies, including construction of major surface-water diversions and the drilling of deeper wells into the Sparta aquifer to supplement irrigation water demands. Water quality generally is good throughout the aquifer. However, elevated iron concentrations in most areas preclude use of the aquifer for public-supply, commercial, and industrial purposes without treatment. Elevated salinity additionally occurs in different areas of eastern Arkansas, resulting from upwelling of high-salinity water from underlying formations or evapotranspiration in clay-rich backswamp areas.

The Jackson Group in south-central Arkansas is formally designated as a regional confining unit, though serving as a locally important aquifer for domestic and farm supply for six counties up through the 1990s. Low well yields and poor water quality, in addition to wider availability of public-supply sources, have resulted in no known use from the aquifer at the time of this report.

The Cockfield is a principal aquifer in southeastern Arkansas and had a reported use of approximately 19 Mgal/d in 2010. This aguifer serves dominantly as source of domestic supply but has been used for small public-supply systems. It has been increasingly used over the years as a public supply and more recently for irrigation. Groundwater in the outcrop area has low pH and dissolved solids, elevated nitrate and iron concentrations, and is a calcium-bicarbonate water type. Groundwater downdip from the outcrop area is affected by cation exchange and transitions to a sodium-bicarbonate water type. Compared to the outcrop area, groundwater downdip has higher pH and increasing dissolved solids and lower nitrate and iron with more strongly reducing conditions further along the flow path. An area of elevated salinity occurs in Chicot County with chloride concentrations as high as 1,800 mg/L that results from upwelling of saline water from great

depths. Elevated sulfate concentrations in the central part of the aquifer were attributed to leakage of high-sulfate groundwater from the Jackson Group.

The Sparta aquifer is the second most important aquifer in Arkansas in terms of volume of use and provided approximately 196 Mgal/d of water in 2010. The aquifer was used in the past dominantly as a source of public and industrial supply, although irrigation use has increased over the years in response to critically declining water levels in the Mississippi River Valley alluvial aquifer. Pumping rates that exceed recharge rates have resulted in severe waterlevel declines and the formation of eight separate cones of depression in the potentiometric surface. Groundwater from the Sparta aquifer generally is of very high quality; however, isolated areas contain slightly elevated chloride concentrations resulting from upwelling of high-salinity water from underlying formations. Changes in geochemistry result from a transitioning of calcium-bicarbonate to a sodium-bicarbonate water type along the flow path. There also are concomitant increases in dissolved solids, decreases in iron, and decreases in nitrate with changes in redox conditions along the flow path.

The other aquifers of the Coastal Plain, the Cane River, Carrizo, Wilcox, Nacatoch, Ozan, Tokio, and Trinity aquifers, generally are used as important local sources of domestic, industrial, and public supply. In terms of reported water use, the Wilcox is recognized as the most important of these aquifers with a reported water use in 2010 of approximately 37 Mgal/d. All other aquifers have reported uses of less than 4 Mgal/d each. Use of groundwater from the Cane River, Carrizo, Tokio, and Trinity aguifers is solely in and near the respective outcrop areas in southeastern Arkansas. These aquifers all exhibit increasing salinity at various distances downdip from the outcrop areas that renders the groundwater unusable for most purposes. Water use for the Nacatoch and Wilcox aquifers also is restricted to areas in and near to the outcrop area with salinity increasing in the downdip direction in southwestern Arkansas. However, there is a higher percentage of sand in these aquifers in the northeastern part of the State that results in high quality water and in greater use of the aquifers in this region. Increasing sand percentages also occur for the Cane River and Carrizo Formations in the northeastern part of the State. However, these sands cannot be distinguished from and are included as part of the Sparta aquifer in this region. An increase in salinity downdip from the outcrop area for all of these aquifers in southwestern Arkansas was attributed to possible residual salinity from original marine depositional environments. In southwestern Arkansas, all of these aquifers had groundwater with low pH, high iron, and were of a calcium-bicarbonate water type in and near the outcrop area. The groundwater transitions to a sodium-bicarbonate water type with increasing dissolved solids, pH, and salinity, as well as lower iron and nitrate concentrations in the downdip direction of flow.

The Interior Highlands of northern and western Arkansas has less reported groundwater use than other areas of the State. This is the result of a combination of factors including (1) prevalent and increasing use of surface water, (2) less intensive agricultural uses, (3) lower population and industry densities, (4) less potential yield of the resource, and (5) lack of detailed reporting. The overall lower well yields from aquifers of the Interior Highlands result in domestic supply as the dominant use, with minor industrial, public, and commercial-supply use. When large volumes are required for public and industrial supply with a growing population, surface water supplies the majority of these water needs. However, surface water is not available for large expanses of the rugged and remote Interior Highlands, so locally available groundwater is a critical, though small-scale water resource. The aquifers of the Interior Highlands generally occur in shallow, fractured, well-indurated, structurally modified bedrock compared to the relatively flat-lying, unconsolidated sediments of the Coastal Plain.

Spatial trends in groundwater geochemistry of the Interior Highlands differ greatly from trends noted for aquifers of the Coastal Plain. In the Coastal Plain, the prevalence of long regional flow paths resulted in regionally predictable and mappable geochemical changes. In the Interior Highlands, groundwater moves along short, topographically controlled flow paths (from hilltops to valleys) within small watersheds. Consequently, dense data coverage from numerous wells would be required to effectively characterize these small groundwater basins and to define small-scale geochemical changes along any given flow path. Dominant changes in geochemistry for the Ouachita aquifer and the Western Interior Plains confining system were attributed to (1) rock type, (2) residence time along individual flow paths, and (3) resultant rock/water interaction and changes in redox zonation. Generally, groundwater evolves along flow paths from a calcium- to a sodium-bicarbonate water type, with increasing reducing conditions that result in denitrification, elevated iron and manganese, and ultimately to production of methane in the more geochemically evolved and strongest reducing conditions.

In the Ozark and Springfield Plateau aquifers, rapid influx of surface-derived contaminants such as nitrogen, coupled with little to no attenuation processes, is attributed to the karst landscape developed on Mississippian- and Ordovician-age carbonate rocks. Agriculture in the form of beef and dairy cattle, swine, and poultry operations is the predominant land use in this region of steep topography and thin soils. There is a high degree of connectivity between the surface water and groundwater, expressed in the occurrence of sinkholes, solution fractures, caves, losing streams, large springs, and other karst features. This kart-derived interconnection leads to nutrients, bacteria, and other surface-derived contaminants associated with agricultural activities posing the greatest threat to groundwater quality in the Ozark aquifer. A direct correlation was noted for increasing nitrate concentrations with increasing percentage of agricultural land use for the Springfield Plateau and Ozark aquifers. Additionally, areas with a higher density of karst features were shown to have higher nitrate concentrations than areas with less karst features. Even in areas of similar agricultural land use, the presence of karst features was shown to account for approximately 12 percent of the variation between nitrate concentrations (12 percent greater in areas with dense karst features) for increasing agricultural land use.