USGS
science for a changing world

Borehole Geophysical, Water-Level, and Water-Quality Investigation of a Monitoring Well Completed in the St. Francois Aquifer in Oregon County, Missouri, 2005–08

Scientific Investigations Report 2010–5041

Borehole Geophysical, Water-Level, and Water-Quality Investigation of a Monitoring Well Completed in the St. Francois Aquifer in Oregon County, Missouri, 2005–08

By John G. Schumacher and Michael J. Kleeschulte

Scientific Investigations Report 2010–5041

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit http://www.usgs.gov or call 1-888-ASK-USGS

For an overview of USGS information products, including maps, imagery, and publications, visit http://www.usgs.gov/pubprod

To order this and other USGS information products, visit http://store.usgs.gov

Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
Volume		
gallon (gal)	3.785	liter (L)
Flow rate		
Foot per minute (ft/min)	0.3048	meter per minute (m/min)
foot per day (ft/d)	0.3048	meter per day (m/d)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Specific capacity		
gallon per minute per foot [(gal/min)/ft)]	0.2070	liter per second per meter [(L/s)/m]
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)

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

$$°F=(1.8×°C)+32$$

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

$$°C=(°F-32)/1.8$$

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

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83)."

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

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Borehole Geophysical, Water-Level, and Water-Quality Investigation of a Monitoring Well Completed in the St. Francois Aquifer in Oregon County, Missouri, 2005–08

By John G. Schumacher and Michael J. Kleeschulte

Abstract

A deep (more than 2,000 feet) monitoring well was installed in an area being explored for lead and zinc deposits within the Mark Twain National Forest in southern Missouri. The area is a mature karst terrain where rocks of the Ozark aquifer, a primary source of water for private and public supplies and major springs in the nearby Eleven Point National Wild and Scenic River and the Ozark National Scenic Riverways, are exposed at the surface. The potential lead deposits lie about 2,000 feet below the surface within a deeper aquifer, called the St. Francois aquifer. The two aquifers are separated by the St. Francois confining unit. The monitoring well was installed as part of a series of investigations to examine potentiometric head relations and water-quality differences between the two aquifers.

Results of borehole flowmeter measurements in the open borehole and water-level measurements from the completed monitoring well USGS-D1 indicate that a seasonal upward gradient exists between the St. Francois aquifer and the overlying Ozark aquifer from about September through February. The upward potentiometric heads across the St. Francois confining unit that separates the two aquifers averaged 13.40 feet. Large reversals in this upward gradient occurred during the late winter through summer (about February through August) when water levels in the Ozark aquifer were as much as 138.47 feet higher (average of 53.84 feet) than water levels in the St. Francois aquifer. Most of the fluctuation of potentiometric gradient is caused by precipitation and rapid recharge that cause large and rapid increases in water levels in the Ozark aquifer.

Analysis of water-quality samples collected from the St. Francois aquifer interval of the monitoring well indicated a sodium-chloride type water containing dissolved-solids concentrations as large as 1,300 milligrams per liter and large concentrations of sodium, chloride, sulfate, boron, and lithium. In contrast, water in the overlying Ozark aquifer interval of the monitoring well was a calcium-magnesium-bicarbonate type water containing less than 250 milligrams per liter dissolved solids and substantially smaller concentrations of major and trace elements.

Introduction

Good stewardship of our Nation's natural resources requires that the extraction and refining of minable ore deposits be conducted in harmony with the protection of the environment. This dilemma is faced by many land- and water-management agencies in mining areas of the Nation. As lead and zinc ore is mined, milled, and sent to the smelter, it leaves its footprint behind. These "footprints" can become remnants that may be environmentally detrimental to other natural resources. As ore reserves are depleted in one area, other deposits need to be found in previously unmined areas. The Viburnum Trend in southeastern Missouri (fig. 1) has been a world-class lead-zinc mining subdistrict since the 1960's. As ore reserves are being depleted in the Viburnum Trend, the search for additional lead and zinc reserves has focused on an area about 40 miles (mi) southwest where the potential reserves lie about 2,000 feet (ft) below the surface (fig. 1). This "exploration area" is within the Mark Twain National Forest and the watershed of the Eleven Point National Wild and Scenic River.

Description of the Study Area

The exploration area is in southeastern Missouri near the town of Winona, and lies between the Ozark National Scenic Riverways (ONSR) to the northeast and the Eleven Point National Wild and Scenic River to the south (fig. 1). The area is a region of mature karst terrain that has an extensive network of solution-enlarged fractures and bedding planes ranging from small channels to large conduits. The region is underlain by Ordovician and Upper Cambrian Series sedimentary rocks (Jefferson City Dolomite to the base of the Lamotte Sandstone) of the Ozark Plateaus aquifer system that overlie Precambrian granites and rhyolites that are exposed in the St. Francois Mountains to the northeast (fig. 1). The Ozark aquifer, which is more than 1,000 ft thick (fig. 2), comprises rocks from the Jefferson City Dolomite to the Potosi Dolomite and is exposed at the surface throughout most of southern Missouri (Imes and Emmett, 1994). In addition to having an extensive karst system, the Ozark aquifer is the primary source of water
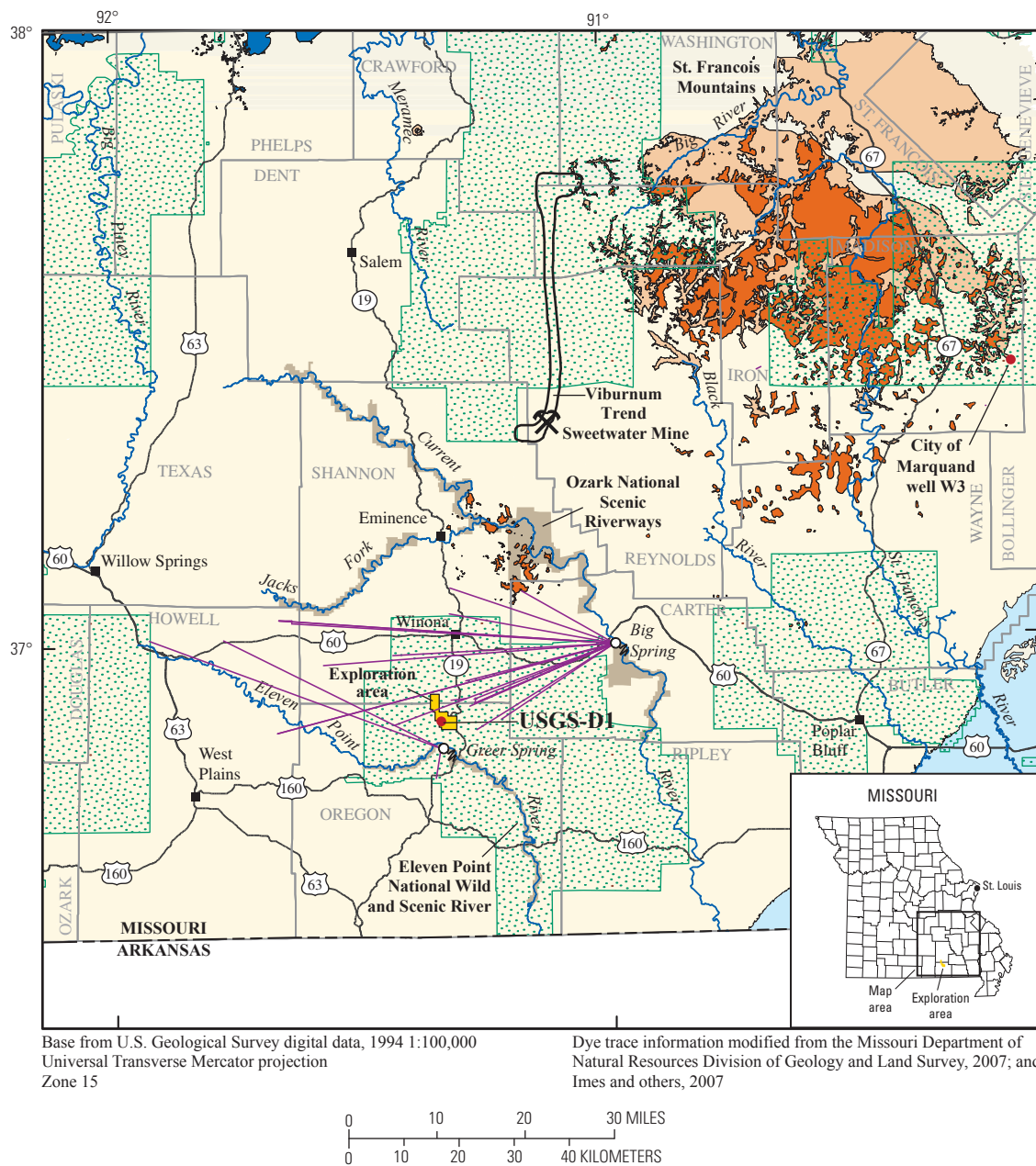
Figure 1.   Location of monitoring well USGS-D1, dye traces to Big Spring and Greer Spring, geohydrologic units, and physical features of south-central Missouri.

for private- and public-water supplies and major springs in southern Missouri (Miller and Vandike, 1997). Yields of water to wells generally is higher in the lower part of the Ozark aquifer with the Potosi Dolomite being the most productive and reliable water producing unit in the aquifer (fig. 2).

The two largest springs in Missouri are near the exploration area and developed within the Ozark aquifer: Big Spring (fig. 1), which has an annual mean discharge of 446 cubic feet per second (ft³/s), and Greer Spring, which has an annual

mean discharge of 343 ft³/s (U.S. Geological Survey, 2009). Discharge from these springs helps sustain flow in the Current River (Big Spring) and the Eleven Point River (Greer Spring). During low-flow conditions, Big Spring contributes more than 30 percent of the water to the Current River where its flow enters the river (Mugel and others, 2009). Dye-trace studies indicate that the exploration area probably lies within the recharge area for Big Spring and immediately north of the recharge area for Greer Spring (Imes and others, 2007).

System	Formation	Average approximate thickness, in feet	General lithology	General hydrologic properties	Geohydrologic unit
ORDOVICIAN	Jefferson City Dolomite	0 to 200	Crystalline cherty dolostone with abundant thin shale partings and occasional thin sandstone beds	Adequate for small domestic supply. Yields of 5 to 10 gallons per minute locally	OZARK AQUIFER
	Roubidoux Formation	0 to 200 (170 average)	Cherty, sandy dolostone. Middle 20 to 30 feet can be a clean sandstone	Normal yields of 15 to 50 gallons per minute	
	upper Gasconade Dolomite	40	Massively bedded, crystalline dolostone	Lower permeability than surrounding units	
	lower Gasconade Dolomite	250	Cherty dolostone with massive chert beds	Combined yields of upper and lower units range from 50 to 75 gallons per minute	
	Gunter Sandstone Member of Gasconade Dolomite	25 to 30	Sandstone or sandy dolostone	Normal yield of 40 to 50 gallons per minute, may exceed 200 gallons per minute in some locations	
CAMBRIAN	Eminence Dolomite	220	Crystalline dolostone with less than 5 percent chert and sand	Yields of 75 to 250 gallons per minute	
	Potosi Dolomite	200	Crystalline dolostone with abundant small solution cavities and quartz druse	Target zone of most high capacity wells. Yields of 200 to 1,000 gallons per minute	
	Derby-Doerun Dolomite	150	Generally fine-grained dolostone with shale and glauconite near base	Usually not a significant water source	ST. FRANCOIS CONFINING UNIT
	Davis Formation	180	Shale, siltstone, and fine-grained sandstone with interbedded limestone and dolostone	Not water bearing	
	Bonneterre Formation	350	Fine- to medium-grained dolostone with shale (False Davis unit) near top	Low yields of 5 to 15 gallons per minute	ST. FRANCOIS AQUIFER
	Lamotte Sandstone	100 to 300	Sandstone and sandy dolostone with arkose near base. Locally absent	Normal yields of 70 to 125 gallons per minute	
PRECAMBRIAN IGNEOUS ROCKS					BASEMENT CONFINING UNIT

NOTE: Nomenclature follows that of the Missouri Department of the Natural Resources Division of Geology and Land Survey

Thickness, stratigraphic information, and general hydrologic properties from Miller and Vandike,1997 and Imes and Emmett, 1994

Figure 2. Generalized geohydrologic units in south-central Missouri.

Beneath the Ozark aquifer is a less permeable sequence composed primarily of dolostone, limestone, and shale known as the St. Francois confining unit (fig. 2). This confining unit separates the overlying Ozark aquifer from the deeper St. Francois aquifer (Imes and Emmett, 1994). The St. Francois confining unit consists of the Derby-Doerun Dolomite and the Davis Formation (fig. 2). Along the Viburnum Trend, the St. Francois confining unit is 230 to 280 ft thick, with a net shale thickness ranging from less than 25 to greater than 100 ft, and the thickness increases toward the west (Kleeschulte and Seeger, 2003).

The St. Francois aquifer lies beneath the St. Francois confining unit and consists of the Bonneterre Formation and underlying Lamotte Sandstone (fig. 2). The Bonneterre Formation primarily is a dolostone with variable quantities of shale in the upper part. The formation is the primary host rock for the lead and zinc mineralization in the Viburnum Trend and is the target unit in the exploration area (Kleeschulte and Seeger, 2003). The Lamotte Sandstone, which unconformably overlies the Precambrian igneous rocks, primarily is a clean quartzose sandstone that contains a basal arkosic conglomerate composed of weathered Precambrian igneous rocks. The thickness of the St. Francois aquifer can vary considerably because of the irregular surface of the underlying Precambrian rocks. In areas of southeastern Missouri near the St. Francois Mountains where the St. Francois aquifer is close to the land surface or crops out, the aquifer is the only source of groundwater available and yields adequate supplies of water for domestic and moderate capacity [100 to 200 gallons per minute (gal/min)] public-supply wells—with most of the yield originating from the Lamotte Sandstone (Miller and Vandike, 1997). Little is known about the quantity or quality of water in the aquifer outside of the St. Francois Mountains area because the overlying Ozark aquifer has sufficient quantity and quality of water for human use and few wells are drilled to the St. Francois aquifer.

Previous Investigations

Little information exists regarding the quantity and quality of water within the St. Francois aquifer and the degree of interconnectivity between the Ozark and St. Francois aquifers in the exploration area. The potential for lead-zinc mining in this environmentally sensitive karst area has concerned the U.S. Forest Service, the National Park Service, U.S. Department of the Interior Bureau of Land Management, and other land managers in regard to possible effects that mining may have on the water resources of the area. The concerns include the potential for mine dewatering in the St. Francois aquifer to cause water-level declines in the overlying Ozark aquifer and decreased spring flows in the area, and the effect that mine water pumped from the St. Francois aquifer will have on spring and stream water quality in the area.

To determine if mining in the exploration area potentially could affect groundwater levels and spring discharges in the overlying Ozark aquifer, the U.S. Geological Survey (USGS) conducted a series of geohydrologic investigations. The objectives of these investigations were to: (1) assess the permeability of the St. Francois confining unit (Kleeschulte and Seeger, 2003); (2) investigate the hydraulic characteristics, recharge area, and age of water discharged from Big Spring in the ONSR (Imes and others, 2007); and (3) install a monitoring well more than 2,000 ft deep (all depths in this report are feet below land surface) in the St. Francois aquifer within the exploration area to obtain potentiometric head and water-quality data from the Ozark and St. Francois aquifers.

Purpose and Scope

The purpose of this report is to describe methods used in the installation, borehole geophysical logging, and water-level measurement and water-quality sampling of a multi-port monitoring well (USGS-D1) installed in the exploration area and to present and interpret data collected during the installation, borehole geophysical logging, and sampling of the well. A focus of the study and this report is to examine the potentiometric head relations and water-quality differences between the St. Francois aquifer, where a potential lead-zinc ore body exists, and the overlying Ozark aquifer. Monitoring well USGS-D1 was installed during 2005, and data presented in this report were collected during 2005 through 2008. Borehole geophysical logs included caliper, natural gamma, and borehole flowmeter logs. A water-quality sample was collected from the Ozark aquifer during drilling of the well, and water-quality samples from the St. Francois aquifer were collected from the completed well during 2005 and 2006. Manual water-level measurements were collected beginning in 2005, and continuous water-level recorders were installed during 2006 and 2007 to further examine the potentiometric head relations between the St. Francois aquifer and overlying Ozark aquifer. To provide a framework for the interpretation of water-quality data from monitoring well USGS-D1, water-quality data for the Bonneterre Formation (St. Francois aquifer) were collected from several seeps in an active Viburnum Trend mine (Sweetwater Mine) about 40 mi northeast of monitoring well USGS-D1, and from a public-supply well about 80 mi to the northeast in Marquand that is completed in both the Ozark and St. Francois aquifers (fig. 1).

Methods and Approach

The following section discusses methods used for the installation and subsequent data collection from monitoring well USGS-D1. A summary of well installation and construction is presented, followed by a general discussion of borehole geophysical methods, water-level measurements, water-quality sampling, and analytical methods used. Except for water-quality data from mine seeps, all water-level and water-quality data are available online through the U.S. Geological Survey

National Water Information System at URL *http://waterdata. usgs.gov/nwis*. Unpublished water-quality data for mine seeps (L.R. Lee, U.S. Geological Survey, written commun., 2007) were collected as part of a U.S. Geological Survey Central Region Mineral Resources Center investigation on the economic and environmental characteristics of Ozark-region mineral deposits (URL *http://minerals.cr.usgs.gov/projects/ ozarks/index.html)*.

Monitoring Well Construction

Monitoring well USGS-D1 was installed using a combination of mud rotary and air-rotary methods. Mud-rotary drilling was attempted, but abandoned after substantial circulation loss between 200 and 300 ft deep, and the borehole was finished using air-rotary drilling. The target borehole depth was 2,250 ft; however, because large openings and caves were penetrated during drilling and considerable quantities of water were produced between 500 and 1,440 ft deep (estimated at more than 500 gal/min), two strings of steel casing set from 0 to 520 ft deep [12-inch (in.) inside diameter] and from 0 to 1,440 ft deep (7-in. inside diameter) were required to stabilize the borehole, the borehole diameter and depth were decreased (fig. 3). The borehole was air-rotary drilled to a final depth of 2,098 ft within the Bonneterre Formation. Immediately after drilling, caliper and natural gamma geophysical logs were run in the borehole, and a heat-pulse flowmeter was used to measure vertical groundwater flow in the borehole across the St. Francois confining unit.

Monitoring well USGS-D1 was constructed with three open ports to allow the collection of water-level and water-quality data from both the Ozark and St. Francois aquifers (fig. 3). A 2-1/2-in. inside diameter 80-ft long schedule 80 polyvinylchloride (PVC) screen was installed within the Bonneterre Formation from 2,018 to 2,098 ft deep (total depth of the borehole) and placed in a 118-ft thick silica-sand (WB10-20) filter pack in a 6-1/2-in. diameter borehole. The PVC riser was suspended from the 7-in. inside diameter secondary steel casing to minimize bowing of the long string of riser pipe and to facilitate installation of the 1-1/2 in. inside diameter galvanized tremie pipe used to place the filter pack and bentonite grout. Centralizers were placed at the bottom and top of the screen, and at 400-ft intervals along the PVC riser between the top of the screen and 560 ft. The screened and filter pack interval (1,980 to 2,098 ft deep) is designated port 3 (P3, USGS station ID 365117091215502) and is used for the collection of water samples and water-level measurements from the Bonneterre Formation of the St. Francois aquifer. To facilitate placement of a submersible sampling pump, the diameter of the PVC riser for P3 increases to a 3-1/2-in. inside diameter schedule 80 PVC riser above 560 ft (fig. 3). The annular space above the P3 filter pack partially was grouted, leaving an open interval designated as port 2 (P2, USGS ID 365117091215501) that extends from the top of the bentonite-grout annular seal at 1,698 ft to the base of a secondary

string of 7-in. diameter steel casing at 1,440 ft. P2 is open to the lower part of the Ozark aquifer (lower part of the Potosi Dolomite) and the upper part of the St. Francois confining unit (upper part of the Derby-Doerun Dolomite). P2 is accessed from the surface through the annulus between the 3-1/2-in. PVC riser of P3 and the 7-in. steel secondary casing (fig. 3). For the discussion in this report, data from P2 is attributed to the lower part of the Ozark aquifer (and not the St. Francois confining unit because of the low permeability of the confining unit) and data from P3 is attributed to the St. Francois aquifer. A second open annulus designated as port 1 (P1, USGS ID 365117091215503) extends from the top of the Portland cement annular seal for the 7-in. diameter steel secondary casing at 1,370 ft and the bottom of the 12-in. steel surface casing at 520 ft. P1 is open to the middle part of the Ozark aquifer (lower part of the Gasconade Dolomite, Eminence Dolomite, and the upper part of the Potosi Dolomite). P1 and P2 are adequate for water-level measurements, but their diameter is not sufficient for the collection of water samples.

Borehole Geophysical Methods

Geophysical logs were run in the monitoring well USGS-D1 borehole immediately after drilling was completed. The logs were run to determine the location and size of fractures, voids, or caves in the borehole and to assist in the determination of lithology and the potentiometric head across the St. Francois confining unit. Geophysical logs run at monitoring well USGS-D1 included caliper, natural gamma, and heat-pulse flowmeter logs.

The caliper log measures the diameter of the borehole using three spring-loaded mechanical "arms". The log provides a continuous record of the average borehole diameter. The arms ride along the side of the borehole as the caliper tool is pulled up the borehole. A sharp increase in the borehole diameter indicates the presence of a solution-enlarged fracture, bedding plane, or "void". Softer rocks, such as shale and mudstone, generally are eroded by the drilling process and can be recognized by an increase in borehole diameter and corresponding increase in natural gamma radiation. The caliper log was calibrated to within 0.1-in. immediately before use by using a 3-in. inside diameter PVC pipe and a 10.21-in. diameter calibration ring.

The natural gamma log records the amount of gamma radiation (photons) emitted by the radioactive decay of naturally occurring radioisotopes in the bedrock. Most gamma radiation in natural materials is the result of the radioactive decay of uranium-238, thorium-232, their daughter products, and potassium-40 isotopes (Dresser Atlas Industries Inc., 1974). Clay minerals contain substantial quantities of potassium in their crystal lattice. Trace elements such as uranium also adsorb preferentially to clay minerals. As a result, an increase in natural gamma radiation generally indicates an increase in clay minerals, such as a shale or mudstone bed or clay-filled solution opening. Uranium and thorium also
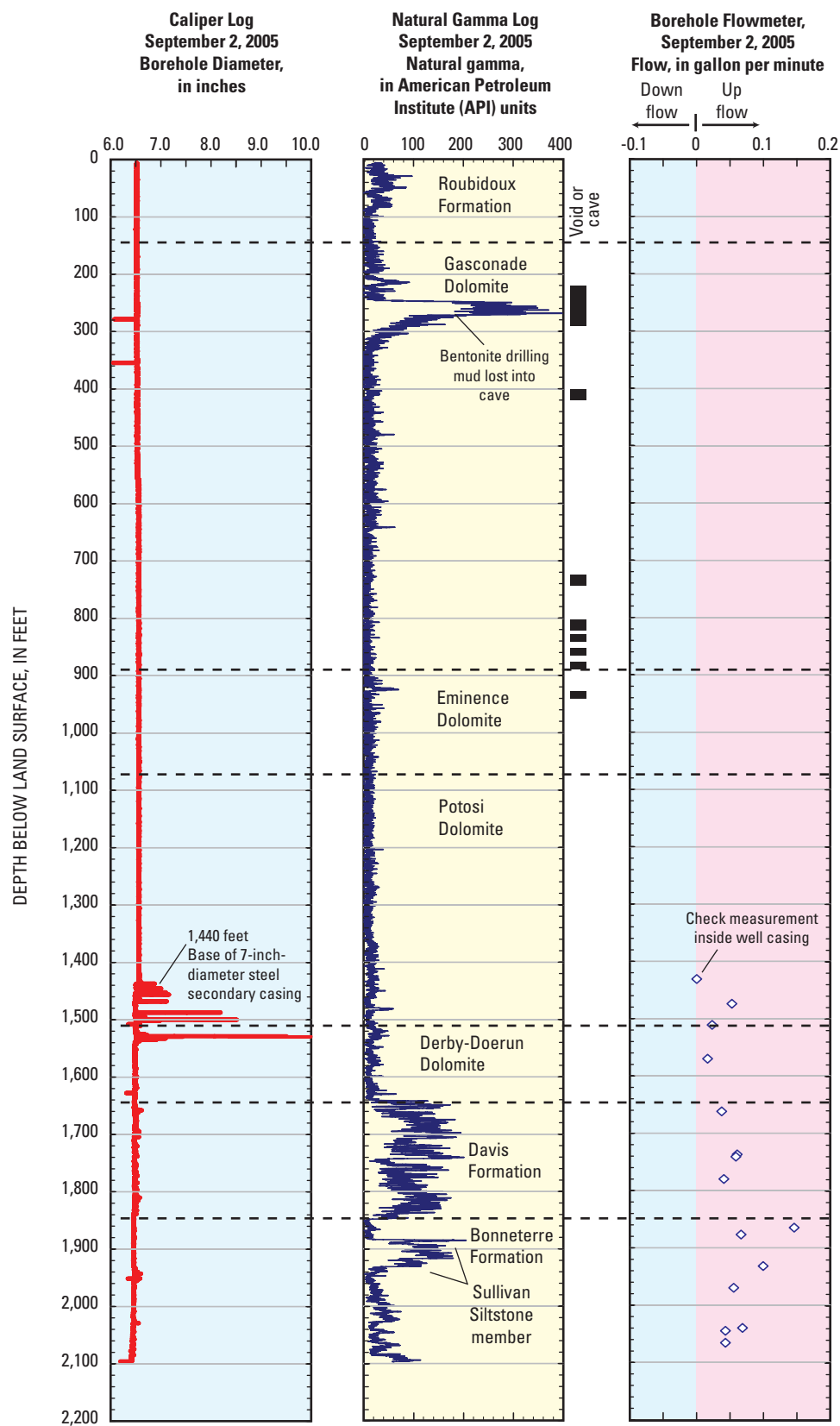
Figure 3.   Summary of well construction and data from borehole geophysical logs of monitoring well USGS-D1 near Winona, Missouri.
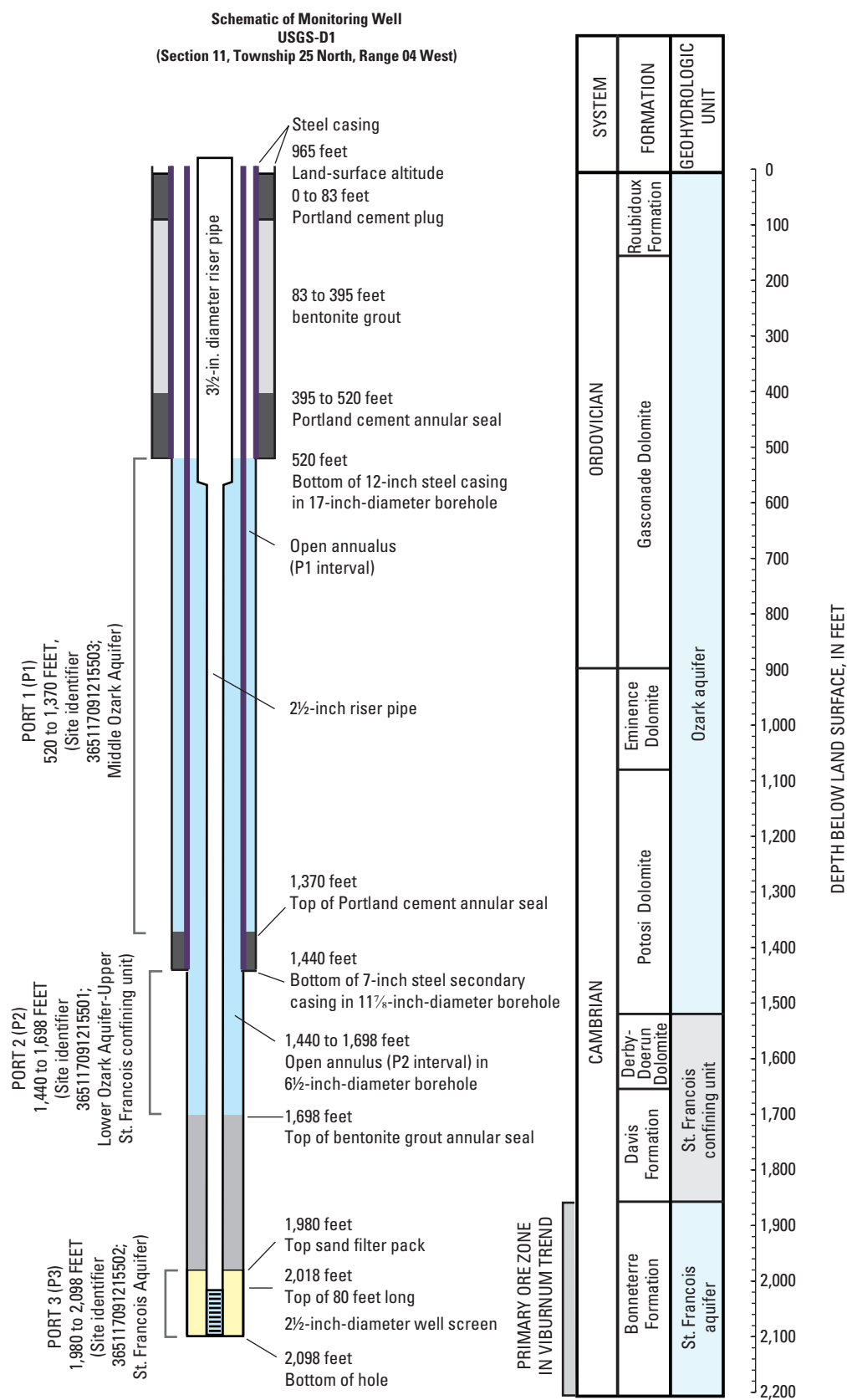
Figure 3. Summary of well construction and data from borehole geophysical logs of monitoring well USGS-D1 near Winona, Missouri.—Continued

may adsorb to iron oxides, and an increase in natural gamma could indicate the presence of iron oxides containing these trace elements. The natural gamma log can be used in dry or fluid-filled boreholes, and in cased or uncased wells. Well casing, however, decreases the gamma signal. Natural gamma logs commonly are used to help determine lithology and correlate geologic units between boreholes or wells (Keys, 1990). At monitoring well USGS-D1, the caliper and natural gamma logs were run simultaneously. These two logs were run upward from the bottom of the borehole at a logging rate of 15 feet per minute (ft/min) on September 2, 2005. One measure of the accuracy of logs is a comparison of depth readings from the logging unit at the beginning and end of the log run. The top of tools were zeroed to the land surface before lowering the tools down the borehole. The bottom of the borehole was reached at 2,098 ft, compared to an estimated 2,100 ft measured from the drill string. Upon return to the land surface after logging, the unit recorded a depth of 1.48 ft at the land surface, indicating a depth error of 1.48 ft in 2,098 ft or about 0.07 percent.

Vertical movement of water in a borehole is caused by the borehole intersecting geohydrologic units, zones, or fractures within units that have different potentiometric heads and permeabilities. The downward movement of water in a borehole indicates that shallower formations have higher potentiometric heads than deeper formations, whereas upward movement of water indicates higher potentiometric heads in deeper formations. The rate of water flow is related to the permeabilities of the various zones contributing and accepting water in the borehole. The direction and rate of vertical movement of water within the monitoring well borehole was measured using a heat-pulse flowmeter. A thorough discussion of the use of borehole-flowmeter measurements to detect higher permeability zones in a borehole is in Paillet (1998). The instrument functions by rapidly heating a small parcel of water using a metal mesh. High resolution thermisters are located above and below the metallic mesh and record the water temperature. The instrument has a flexible packer to seal the borehole between the instrument and the borehole wall to divert fluid flow in the borehole through the metallic mesh and past the thermisters. After the instrument is lowered to a specified depth, the direction and rate of fluid flow in the borehole is calculated when a temperature spike (heat pulse) is recorded by one of the thermisters. By convention, upward flow is recorded as a positive value and downward flow is recorded as a negative value. The heat-pulse flowmeter used at monitoring well USGS-D1 has a minimum operating range of about 0.01 gal/min in most boreholes (Conger, 1996) to a maximum of about 1.5 gal/min. Heat-pulse flowmeter measurements may be affected by a poor seal between the borehole wall and the instrument, especially if the borehole wall is rough or uneven If the seal between the instrument and the borehole wall is not complete, some water can bypass the instrument, resulting in measurements of flow that are less than the actual rate. Although the heat-pulse flowmeter is a calibrated probe, the data commonly are used as a relative indicator to identify

the direction of flow and water-producing or receiving zones within the borehole because the instrument is not easily calibrated in the field. At monitoring well USGS-D1, the factory calibration was used; however, a field check for "zero" flow was done by making several flow measurements inside the steel casing at 1,431 ft where no vertical flow should exist. These measurements indicated less than 0.03 gal/min of flow inside the casing.

Water-Level Measurements and Water-Quality Sampling

A primary objective for the installation of monitoring well USGS-D1 was to obtain water-level measurements from the Ozark and St. Francois aquifers to determine potentiometric head relations between these two aquifers. The potentiometric head is the altitude to which water would stand in a tightly cased well open to the aquifer. Potentiometric head relations between the St. Francois aquifer and overlying Ozark aquifer were determined by measuring depths to water in the Ozark aquifer (P1 and P2) and St. Francois aquifer (P3). Manual water-level measurements (depth to water) were made periodically in monitoring well USGS-D1. The depth to water was measured to the nearest 0.01 ft using a 400-ft long calibrated electric tape. Water-level measurements in each port were made from a common reference point at the top of the protective steel casing. The depth to water (water level) recorded was the average of three consecutive measurements. Submersible pressure transducers were installed in P2 and P3 during early 2007 and late 2006, respectively, and to provide continuous hourly water-level measurements. Because the pressure transducers used were non-vented and recorded the depth of water above the transducer relative to an absolute pressure, an additional pressure transducer suspended inside the top of the well casing was used as a barometer to correct for barometric changes by subtracting the output of the barometer from the submerged transducers as described in Freeman and others (2004). Data from the transducers were downloaded using a laptop computer at the time the periodic manual water-level measurements were made. The daily mean water level was computed from continuous hourly water-level measurements obtained from the pressure transducers.

Water-quality samples were collected from monitoring well USGS-D1 during 2005 and 2006 from the lower part of the Potosi Dolomite (Ozark aquifer) and from the Bonneterre Formation (St. Francois aquifer). All samples were collected according to established USGS protocols from the USGS National Field Manual (U.S. Geological Survey, 1997–2006). Samples were collected using a 3-in. diameter stainless steel submersible pump. The pump was suspended by 1-in. inside diameter threaded PVC riser pipe and powered using a portable generator. Because the unstable borehole required installation of a secondary steel casing and subsequent reduction of the borehole diameter, plans for a well screen in the lower part of the Potosi Dolomite (P2) were abandoned, and as

an alternative, water samples were collected from this inter-val during drilling. After the 7-in. diameter secondary steel casing was installed to 1,440 ft and cemented into place, the borehole was advanced to 1,520 ft, the drill tools removed, and a 3-in. submersible pumped installed to 540 ft deep. The borehole was pumped at 10 gal/min for 10 hours (hrs) before water-quality samples were collected from 1,500 ft deep using a discrete (point) sampler. Water samples from this interval were associated with the P2 interval in the completed monitor-ing well. After the well was completed, water samples from the Bonneterre Formation (P3) were collected by installing a dedicated 3-in. submersible pump in the P3 riser to 560 ft (point where the riser diameter reduced to 2-1/2 in.). The P3 interval yielded considerably less water than the P2 interval and required a PVC gate valve to reduce the pump discharge to less than 0.5 gal/min after the water level had been lowered to less than 40 ft above the pump. The small annulus between the pump and the P3 well casing (less than 1 in.) hampered the collection of water-level measurements, and only sporadic water-level measurements were made in P3 until the pump was removed in December 2006.

Sample intervals were purged before the collection of water samples. During purging, field measurements of specific conductance, temperature, pH, and dissolved oxygen were made in a flow-through chamber at 20- to 40-minute intervals until stable readings were obtained. Stable readings for field measurements were defined as readings that did not vary by more than the following amounts over three consecutive mea-surements: specific conductance (within 2 percent), tempera-ture [within 0.5 degrees Celsius (°C)], pH (within 0.2 standard pH units), and dissolved oxygen [within 0.5 milligrams per liter (mg/L)]. Specific conductance values were measured using a portable conductivity meter with temperature compen-sation designed to express readings in microsiemens per cen-timeter at 25 degrees Celsius (µS/cm). The pH was measured to the nearest 0.05 standard unit with a portable pH meter with temperature compensation. The meter was calibrated immediately before use using Natural Bureau of Standards (NBS) traceable buffers of pH 4.0, 7.0, and 10.0 at 25 °C. Water temperature was measured to the nearest 0.1 °C using the thermistor on the specific conductance meter. Dissolved oxygen was determined by a Rhodazine-D spectrophotometric method using vacuum ampules manufactured by CHEMetrics, Incorporated (White and others, 1990).

Once stable readings of field measurements were obtained, water samples were collected and processed in a mobile laboratory immediately after collection using meth-ods described by Wilde and others (1999) designed to mini-mize changes to the water-sample chemistry before analysis. Samples for analyses of dissolved major cations and anions, nutrients, trace elements, and carbon isotopes were filtered by placing a 0.45-µm (micrometer) nominal pore-sized dispos-able capsule filter directly at the pump discharge outlet (after reducing the pump discharge to 0.1 gal/min). These samples were placed in precleaned polyethylene bottles after the bottles had been field rinsed with filtered groundwater. Samples for

analyses of major cations and trace elements were placed in acid-washed polyethylene bottles and preserved to pH value less than 2.0 using concentrated ultrapure nitric acid. Samples for analyses of dissolved major anions were not preserved. Samples for analysis of nutrients were placed in amber poly-ethylene bottles and placed on ice for overnight shipment to the laboratory. Glass sample bottles for the analyses of carbon isotopes were filled from the bottom using a 0.25-in. diameter Teflon tube attached to the discharge end of the capsule filter and allowed to overflow for several minutes to avoid contact with the atmosphere before they were sealed with septum caps. Samples for analyses of oxygen isotopes were placed in glass bottles (bottom filled using the Teflon tubing) and sealed with a polyethylene "polyseal" cap after overfilling for several minutes. Additionally, an unfiltered, unpreserved sample was collected in a polyethylene bottle for determination of alkalin-ity (acid neutralizing capacity or ANC) onsite immediately after the collection of all samples. Sample bottles for alkalin-ity and isotopes were filled first followed by nutrients, major anions, and finally major cations and trace elements.

Analysis of water-quality samples for inorganic constitu-ents, nutrients, and total organic carbon were performed by the USGS National Water Quality Laboratory (NWQL) in Lake-wood, Colorado, according to methods described in Fishman (1993) or Garbarino and others (2006). Alkalinity and con-centrations of bicarbonate (HCO_3) and carbonate (CO_3) were determined onsite in the water-quality vehicle by incremental titration past the CO_3-HCO_3 and HCO_3-carbonic acid (H_2CO_3) inflection points using 0.1600 normal (N) sulfuric acid.

Analysis of oxygen isotopes were done at the USGS Stable Isotope Laboratory in Reston, Virginia (Epstein and Mayeda, 1953; Coplen, 1994), and analysis of carbon isotopes were done at the University of Waterloo in Ontario, Canada (Gleason and others, 1969). Analytical results for stable oxy-gen isotopes are presented as a ratio of the oxygen-18 (^{18}O) and oxygen-16 (^{16}O) relative to the isotopic ratio of a known standard and expressed in delta (δ) notation in per thousand parts or per mil (‰) of ^{18}O or $\delta^{18}O$. Analytical results for the stable isotopes of carbon are presented as a ratio of the car-bon-13 (^{13}C) and carbon-12 (^{12}C) relative to the isotopic ratio of a known standard and also expressed in per mil or $\delta^{13}C$. The reference standard for stable oxygen isotope ($^{18}O/^{16}O$) ratios is Vienna Standard Mean Ocean Water (VSMOW), and the Vienna Pee Dee Belemnite (VPDB) is the reference standard for stable carbon isotope ($^{13}C/^{12}C$) ratios. Concentrations of the radioactive carbon-14 (^{14}C) isotope are reported as a percent of modern carbon (pmC) referenced to an international standard known as "modern carbon" (mC) that is defined as 95 percent of the ^{14}C activity in 1950 of the National Bureau of Standards (NBS) oxalic acid standard.

Quality Assurance for Water-Level and Water-Quality Data

The manual water-level measurements periodically made in monitoring well USGS-D1 were used to verify the accuracy of the submersible pressure transducer measurements. The average absolute difference between the manual and submersible pressure transducer measurements was less than or equal to 0.09 ft and ranged from -0.16 to 0.18 ft (table 1). The differences were small as a percentage of the total depth of the measurements (within 0.05 percent) and generally within the accuracy of the transducers reported by the manufacturer of 0.066 ft (transducer used in P3) to 0.12 ft (transducer used in P2). The manual water-level measurements are considered the standard or "true" readings and the recorded pressure transducer data were adjusted to match the manual measurements made each time that the transducers were downloaded to correct for instrument drift. Because the transducers were initially set to match the manual measurements at the beginning of each recorded period, differences between the recorded and manual measurement made when each transducer was downloaded were prorated over the period of the record. For example, the pressure transducer was installed in P2 on February 12, 2007, and the transducer was set to match the manual water-level measurement of 319.66 ft below the land surface (table 1). On March 6, 2007, the transducer was downloaded and the difference of -0.11 ft between the ending recorded value of 292.90 ft and the manual measurement of 292.79 ft was prorated over the 22 days of record from -0.0050 ft on day 1 to -0.11 ft on day 22.

Adherence to established and published USGS protocols for the collection, processing, and analysis of water-quality samples was done to ensure that water-quality samples represented, as accurately as possible, the water quality of the sampled intervals of the aquifers. In addition, a quality assurance (replicate) sample was collected from the P2 interval of monitoring well USGS-D1 on August 30, 2005 while the well was being drilled (table 2). Immediately after the collection of the regular P2 sample at 0130, the replicate sample was collected using the same equipment and filter as the regular sample. The replicate sample was not analyzed for carbon isotopes. Because of concerns regarding stability of samples pumped from such a deep depth (such as sample warming and degassing) and time required to fill and process the large number of individual sample containers for each complete sample, a replicate sample rather than a duplicate water sample was collected.

Comparison of the regular and replicate sample results for constituents whose concentrations were not censored (less than) or estimated by the laboratory below the method reporting limit (Oblinger Childress, 1999), generally indicate that the relative percent difference (RPD) between concentrations of most major ions, nutrients, and trace elements in the regular and replicate samples generally were within 10 and often less than 5 percent (table 2). The RPD was calculated as the difference between the constituent concentration in the regular sample minus the concentration in the replicate sample divided by the average concentration in the regular and replicate sample. Although samples were not collected until purge parameters had stabilized, because the samples were replicate and collected 10 minutes apart, in addition to sample collection and analytical error, differences in concentrations also could be the result of subtle changes in water chemistry or small collodial particulates that could pass through the 0.45-μm pore-size filter used to filter the samples for dissolved major and trace constituents.

The RPD of potassium (K), nitrite as nitrogen (NO_2), and several trace elements such as boron (B), chromium (Cr), lead (Pb) selenium (Se), and thallium (Tl) in the regular and replicate samples were larger than 20 percent (table 2); however, concentrations of these constituents in one or both of the samples were near the reporting levels where analytical precision decreases. Several trace constituents had much larger RPDs that probably were not the result of lower analytical precision near the reporting levels including arsenic (As, 118 percent), iron (Fe, greater than -198 percent), manganese (Mn, -117 percent), and zinc (Zn, -147 percent). Concentrations of Fe [1,330 micrograms per liter (μg/L)], Mn (38 μg/L), and Zn (115 μg/L) in the replicate sample were larger than those in the regular sample (all less than 20 μg/L) and may indicate that small colloidal Fe-rich particles may have passed through the 0.45-μm pore-size filter used to filter the water samples for dissolved major and trace constituents. Trace elements such as Mn and Zn commonly are associated with Fe-rich particles (Hem, 1985).

Borehole Geophysical Logs

The caliper log indicated a generally smooth borehole wall between the bottom of the 7-in. secondary steel casing at 1,440 ft and the bottom of the borehole at 2,098 ft deep (fig. 3). Except for a 20-ft thick section immediately below the bottom of the casing from 1,440 to about 1,460 ft deep, and several short sections within the upper 60 ft of the Derby-Doerun Dolomite from 1,485 to 1,540 ft deep, the borehole diameter varied less than 0.25-in. from the 6.5-in. diameter bit used to drill the lower 660 ft of the borehole.

The generally small [less than about 100 American Petroleum Institute (API) units] natural gamma counts in the natural gamma log (fig. 3) reflected the predominant carbonate lithology of the bedrock. Natural gamma counts in dolostone generally are less than 100 API units (Dresser Atlas Industries Inc., 1974). The large spike in the natural gamma log between 200 and 300 ft deep is the result of more than 200 bags of bentonite drilling mud being lost into a large void or cave during drilling (fig. 3). The increase in gamma counts in the 1,640 to 1,845 ft deep interval corresponds to the shale-rich Davis Formation. A geologic log of drill cuttings confirmed the presence of substantial quantities of shale (up to 80 percent) with dolostone beginning at about 1,640 ft deep. The

Table 1. Quality-assurance data for continuous recording pressure transducers and manual water-level measurements at monitoring USGS-D1, 2005–08.

[ID, identifier; --, no data; all depths in feet below land surface unless noted otherwise]

Date	Time (hours)	Water level depth, in feet below land surface		Difference between manual measurement and submersible pressure transducer	
		Manual measurement	Submersible pressure transducer	Difference, in feet below land surface	Percent difference
P2 (lower part of the Ozark aquifer[1]; station ID 365117091215501)					
02/12/07	1115	319.66	--	--	--
03/06/07	1045	292.79	292.90	-.11	0.04
04/25/07	1215	326.93	326.83	.10	-.03
06/20/07	1025	351.60	351.50	.10	-.03
08/01/07	1015	373.54	373.53	.01	0
09/10/07	1105	383.71	383.59	.12	-.03
10/09/07	1015	391.17	391.20	-.03	.01
11/19/07	1045	398.00	--	--	
01/07/08	1020	389.63	389.63	0	0
03/11/08	1030	305.96	306.12	-.16	.05
05/28/08	1030	275.15	275.26	-.11	.04
07/25/08	1050	319.88	319.78	.10	-.03
10/01/08	1035	367.56	367.43	.13	-.04
Average absolute difference				.09	.03
P3 (St. Francois aquifer[2] ; station ID 365117091215502)					
12/18/06	1105	364.30	--	--	--
12/27/06	0956	366.24	366.24	0	0
01/31/07	1020	363.63	363.63	0	0
03/06/07	1030	363.26	363.29	-.03	.01
04/25/07	1145	367.26	367.35	-.09	.02
06/20/07	1000	367.33	367.38	-.05	.01
08/01/07	0945	370.31	370.13	.18	-.05
09/10/07	1055	373.05	373.14	-.09	.02
10/09/07	1030	374.31	374.34	-.03	.01
11/19/07	1015	376.38	376.38	0	0
01/07/08	1000	376.58	376.58	0	0
03/11/08	1005	372.56	372.38	.18	-.05
05/28/08	1005	362.20	362.33	-.13	.04
07/25/08	1040	365.05	365.06	-.01	0
10/01/08	1010	367.80	367.78	.02	-.01
Average absolute difference				.06	.02

[1]Sample interval open to the lower part of the Potosi Dolomite (lower Ozark aquifer) and the upper part of the Debry-Doerun Dolomite (St. Francois confining unit).

[2]Sample interval within the Bonneterre Formation.

Table 2.   Values of selected physical properties and concentrations of chemical constituents in the regular and replicate sample from monitoring well USGS-D1, August 30, 2005.

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; $CaCO_3$, calcium carbonate; N, nitrogen; P, phosphorus; µg/L, microgram per liter; <, less than; >, greater than; --, no data; E, estimated value; all concentrations dissolved unless noted otherwise]

Property or chemical constituent	Unit	Reporting level	P2[1], regular sample collected at 0130	P2[1], replicate sample collected at 0140	Relative percent difference (RPD)[2]
Dissolved oxygen	mg/L	0.1	0.6	0.6	0
pH, units	standard units	--	7.5	7.5	0
Specific conductance	µS/cm	5	420	420	0
Water temperature	°C	--	15.2	15.2	0
Hardness	mg/L	1	240	240	0
Calcium	mg/L	.044	49	47.8	2.5
Magnesium	mg/L	.02	29.7	29.8	-.3
Potassium	mg/L	.008	.9	1.5	-50
Sodium	mg/L	.1	1.5	1.5	0
Alkalinity as $CaCO_3$	mg/L	1	208	208	0
Bicarbonate	mg/L	1	257	257	0
Carbonate	mg/L	1	<1	<1	--
Chloride	mg/L	.12	1.38	1.44	-4.3
Sulfate	mg/L	.18	15.3	15.2	.7
Fluoride	mg/L	.08	<.1	<.1	--
Silica	mg/L	.058	10.2	9.7	4.7
Dissolved solids (TDS), total	mg/L	10	234	235	-.4
Ammonia as N	mg/L	.02	<.04	<.04	--
Nitrate plus nitrite as N	mg/L	.04	<.06	<.06	--
Nitrite as N	mg/L	.002	<.008	E.004	>66.7
Orthophosphate as P	mg/L	.02	<.02	<.02	--
Phosphorus as P	mg/L	.04	<.04	<.04	--
Organic carbon, total	mg/L	.6	--	.9	--
Organic carbon, dissolved	mg/L	.4	--	.5	--
Antimony	µg/L	.054	2.4	2.5	-4.1
Arsenic	µg/L	.044	3.5	.9	118
Barium	µg/L	.6	14	15	-6.9
Beryllium	µg/L	.2	<.2	<.2	--
Boron	µg/L	2	8	E6.4	22.2
Cadmium	µg/L	.02	0.1	.1	0
Chromium	µg/L	.12	E.03	<.04	>- 28.6
Cobalt	µg/L	.01	1.3	1.3	0
Copper	µg/L	1	E.4	.4	0
Iron	µg/L	6	<6	1,330	> -198
Lead	µg/L	.03	.12	<.08	> 40
Lithium	µg/L	.06	<2	<2	--
Manganese	µg/L	.26	10	38	-117
Molybdenum	µg/L	.028	5.4	7	-25.8
Nickel	µg/L	.12	7	6.9	1.4
Selenium	µg/L	.04	6.1	<.08	195
Strontium	µg/L	.4	33	39	-16.7
Thallium	µg/L	.02	.06	0.11	-58.8
Vanadium	µg/L	.8	<2	<2	--
Zinc	µg/L	2.8	17.4	115	-147

[1]Sample interval open to the lower part of the Potosi Dolomite (lower Ozark aquifer) and the upper part of the Derbry-Doerun Dolomite (St. Francois confining unit).

[2]Calculated as the difference between the regular minus the replicate sample result divided by the average of the regular and replicate result expressed as percent.

natural gamma counts abruptly decrease below 1,845 ft deep at the top of the Bonneterre Formation. The Sullivan Siltstone member of the Bonneterre Formation (about 1,880 to 1,930 ft deep) has a substantially larger gamma signature than the rest of the Bonneterre Formation. The geologic log identified the Sullivan Siltstone member as a dark gray, medium-to fine-grained siltstone.

Borehole-flow measurements made in the lower part of monitoring well USGS-D1 indicate an upward flow of water from the Bonneterre Formation that exits the borehole in the Derby-Doerun Dolomite and lower part of the Potosi Dolomite (fig. 3). Borehole-flow measurements were made under ambient (non-pumping) conditions on September 3, 2005, about 20 hours after the drill rods had been removed. Measurements were made in the open borehole within the lower Potosi Dolomite, Derby-Doerun Dolomite, Davis Formation, and Bonneterre Formation at 14 depths ranging from 1,474 to 2,065 ft deep (fig. 3). At the time the flow measurements were made, the borehole was open from 1,440 to 2,098 ft, and the static water level in the borehole was 406.4 ft below the top of the protective steel casing. The borehole-flow measurements were all positive values, indicating upward flow at rates ranging from an estimated 0.02 to 0.15 gal/min with an average upward flow of 0.06 gal/min (table 3). The upward flow in

the borehole indicates that at the time of the borehole-flow measurements, the potentiometric head in the St. Francois aquifer was higher than the potentiometric head in the overlying St. Francois confining unit and the lower part of the Ozark aquifer.

Water-Level Measurements

Water-level measurements from the completed monitoring well indicate a complex relation between the potentiometric head in the Ozark aquifer and potentiometric head in the upper part of the St. Francois aquifer at monitoring well USGS-D1. Considerable variability in the potentiometric head within the Ozark aquifer (P1 and P2) may be in response to precipitation (fig. 4). The water level in the lower part of the Ozark aquifer (P2) fluctuated more than 170 ft with the pressure transducer recording large increases during February through about May followed by a period of generally decreasing water level from about June through January. The largest water level increases generally occurred during or after periods of higher weekly rainfall recorded at a weather station in West Plains, Missouri (National Oceanic and Atmospheric

Table 3.   Summary of borehole flowmeter measurements in monitoring well USGS-D1, September 3, 2005.

[E, estimated value; <, less than; n/a, not applicable; all measurments made using a heat-pulse flowmeter]

Depth below land surface, in feet	Borehole flow, in gallons per minute	Flow direction	Geologic unit	Geohydrologic unit
1,431	E<.01	none	Inside steel casing	n/a
1,474	.05	up	Potosi Dolomite	Ozark aquifer
1,511	E.02	up	Debry-Doerun Dolomite	St. Francois confining unit
1,570	E.02	up	Debry-Doerun Dolomite	St. Francois confining unit
1,662	.04	up	Davis Formation	St. Francois confining unit
1,737	.06	up	Davis Formation	St. Francois confining unit
1,741	.06	up	Davis Formation	St. Francois confining unit
1,780	.04	up	Davis Formation	St. Francois confining unit
1,865	.15	up	Bonneterre Formation	St. Francois aquifer
1,877	.07	up	Bonneterre Formation	St. Francois aquifer
1,932	.10	up	Bonneterre Formation	St. Francois aquifer
1,970	.06	up	Bonneterre Formation	St. Francois aquifer
2,040	.07	up	Bonneterre Formation	St. Francois aquifer
2,045	.04	up	Bonneterre Formation	St. Francois aquifer
2,065	.04	up	Bonneterre Formation	St. Francois aquifer
Average upward flow	.06			

Administration, 2009). For example, between February and April 2008, the water level in P2 increased more than 170 ft after several weeks of higher precipitation. After peaking during April 2008, the water level in P2 gradually decreased through December 2008, when data collection ended. The correlation between the water level increase in P2 and precipitation is not exact, possibly because the water level in monitoring well USGS-D1 may be responding to local precipitation events that may not necessarily be reflected in the precipitation record at the West Plains weather station about 40 mi southwest of monitoring well USGS-D1. Although manual water-level measurements made during 2005 and 2006 before the pressure transducers were installed also indicate considerable variability in water level, the measurements were not of sufficient density to discern the complexity of the seasonal pattern observed in the pressure transducer data (fig. 4). The large and rapid response of water level in P2 to weekly precipitation is consistent with observations made by Miller and Vandike (1997) in an unused municipal well in West Plains, Missouri.

The unused municipal well at West Plains has been used as an observation well by the Missouri Department of Natural Resources (MDNR) since the 1950s. Although the well has 800 ft of pressure-grouted casing, water levels in the well can increase as much as 200 ft within a few hours after a major precipitation event. The large and rapid increases in water levels in the West Plains observation well were attributed by Miller and Vandike (1997) to be caused by hydraulic pressure head increases in the shallow zones of the aquifer being rapidly transmitted to deeper zones as a result of the intense karst development in the aquifer. This mechanism probably is the cause of the rapid and large increases in water levels observed in P2 (fig. 4).

A comparison of manual water-level measurements indicates that, with one exception, water levels in the middle Ozark aquifer (P1) were about 0.3 ft higher than those in the lower Ozark aquifer (P2) indicating a generally downward gradient within the Ozark aquifer (table 4). On December 6, 2006, the water level in P2 (273.90 ft) was slightly higher

EXPLANATION

Port P1—Station identifier 365117091215503; middle Ozark aquifer (lower part of the Gasconade Dolomite, Eminence Dolomite, and upper part of the Potosi Dolomite)

Port P2—Station identifier 365117091215501; lower part of the Ozark aquifer (lower part of the Potosi Dolomite) and upper part of the St. Francois confining unit (upper part of the Derby-Doerun Dolomite)

Port P3—Station identifier 365117091215502; St. Francois aquifer (Bonneterre Formation)

Pressure transucer

—— Port P2
—— Port P3

Manual measurement

○ Port P1
■ Port P2
▲ Port P3

Figure 4.   Water levels in the Ozark aquifer and St. Francois aquifer in monitoring well USGS-D1 near Winona, Missouri, and weekly precipitation recorded at West Plains, Missouri, September 1, 2005, through December 31, 2008.

Table 4. Manual water-level measurements in monitoring well USGS-D1, September 14, 2005, through October 1, 2008.

[--, no data; ID, identifier; all values in feet below land surface]

Date	P1[1]	P2[2]	P3[3]
09/14/2005	--	--	382.36
10/14/2005	--	--	383.67
11/02/2005	412.80	413.14	384.16
11/03/2005	--	413.09	--
11/04/2005	--	413.05	--
12/01/2005	--	302.03	359.32
01/11/2006	--	393.25	382.52
01/19/2006	--	383.71	380.28
03/29/2006	--	--	360.22
04/12/2006	--	--	367.62
12/06/2006	274.01	273.90	362.75
12/18/2006	299.70	300.30	364.30
12/27/2006	315.05	315.45	366.24
01/31/2007	291.74	292.28	363.63
02/12/2007	--	319.66	--
03/06/2007	292.34	292.79	363.26
04/25/2007	326.52	326.93	367.26
06/20/2007	351.34	351.60	367.33
08/01/2007	373.37	373.54	370.31
09/10/2007	383.55	383.71	373.05
10/09/2007	391.04	391.17	374.31
11/19/2007	397.78	398.00	376.38
01/07/2008	389.45	389.63	376.58
03/11/2008	305.65	305.96	372.56
05/28/2008	274.50	275.15	362.20
07/25/2008	319.20	319.88	365.05
10/01/2008	367.19	367.56	367.80

[1]Station ID 365117091215503, sample interval open to the middle part of the Ozark aquifer (lower part of the Gasconade Dolomite, Eminence Dolomite, and upper part of the Potosi Dolomite).

[2]Station ID 365117091215501, sample interval open to the lower part of the Ozark aquifer (lower part of the Potosi Dolomite) and the upper part of St. Francois confining unit (upper part of the Derby-Doerun Dolomite).

[3]Station ID 365117091215502, sample interval within the Bonneterre Formation.

(0.11 ft) than the water level in P1 (table 4). This slight difference is within 0.1 percent (about 0.27 ft) of the depth measured and could be the result of measurement error or indicate short-term responses to recent rainfall (fig. 4).

Water levels in the St. Francois aquifer (P3) were less variable than water levels in the overlying Ozark aquifer, and fluctuated less than 30 ft during the study period (fig. 4).

Overall, water-level fluctuations in P3 were a subdued response to those in P2 or P1. Sharp increases in the P2 water level were mimicked by much smaller water level increases in P3. For example, the large 170 ft water level increase in P2 during February through April 2008 was followed by a similar, but smaller (less than 20 ft) water level increase in P3 that peaked in April 2008 (fig. 4). The similar, but subdued response in P3 water level to water-level changes in P2, was unexpected and may indicate a small degree of connection between the Ozark and St. Francois aquifers. This connection may be the result of faulty well construction, such as a poor well seal or leaking well casing that will be discussed in more detail in the water-quality section.

An important finding from the water-level data from monitoring well USGS-D1 is that, at times, the potentiometric head in the St. Francois aquifer is higher than that in the overlying Ozark aquifer, indicating periods of an upward gradient across the St. Francois confining unit. This condition existed at the time the borehole flowmeter log was run in September 2005. The continuous water-level data from the pressure transducers indicate that the upward gradient between P3 and P2 occurred on 288 of the 688 days (about 42 percent) for which continuous data are available. The magnitude of the upward potentiometric head across the St. Francois confining unit (maximum of 22.84 ft; average of 13.40 ft) was much smaller than the magnitude of the downward potentiometric heads (maximum of 138.47 ft; average of 53.84 ft). Based on nearly 2 years of continuous water-level data, an upward gradient existed across the Ozark confining unit from late summer through late winter (about September to February) with an abrupt transition to a downward gradient from late winter through late summer (about February through August). The abrupt change from upward to downward gradients in about February is mostly the result of large increases in water levels in the Ozark aquifer in response to precipitation (fig. 4) and rapid recharge.

Although P3 is open to more than 100 ft of the Bonneterre Formation of the St. Francois aquifer, this interval yielded only small quantities of water. The quantity of water that could be pumped from the P3 interval during purging before the collection of water-quality samples was small and averaged only about 0.4 gal/min with drawdowns of 94 to 111 ft—resulting in an estimated specific capacity of about 0.004 gallons per minute per foot of drawdown (gal/min/ft). The P3 interval could be only minimally stressed to avoid drawing the water level down to the pump because the diameter of the riser pipe decreased from 3-1/2 to 2-1/2-in. at 560 ft, limiting the depth to which the 3-in. diameter sampling pump could be installed. The estimated small specific capacity of the P3 interval is consistent with small vertical hydraulic conductivity measurements of the Bonneterre Formation in the Viburnum Trend of less than 10^{-10} foot per day (ft/day) reported by Kleeschulte and Seeger (2003) and published data indicating limited yield of water to wells open to the Bonneterre Formation in southern Missouri (Miller and Vandike, 1997).

Water Quality

Analyses of water samples collected from monitoring well USGS-D1 indicated substantial differences between the water quality in the upper part of the St. Francois aquifer and the overlying Ozark aquifer. Water samples from the St. Francois aquifer [Bonneterre Formation (P3)] contained larger specific conductance values and concentrations of the major ions sodium (Na), K, chloride (Cl), and sulfate (SO_4) and trace elements such as B and lithium (Li), as compared to the water sample collected during August 2005 from the Ozark aquifer [lower part of the Potosi Dolomite (P2)] during drilling (table 5). The initial P3 sample (November 4, 2005) contained 1,300 mg/L of dissolved solids and was a Na-Cl type water that plots near the Na plus K- SO_4 plus Cl vertex on the tri-linear diagram (fig. 5). In contrast, background Ozark aquifer water samples and the P2 sample generally contained less than 250 mg/L dissolved solids, are calcium (Ca) plus magnesium (Mg)- HCO_3 type water and generally contained less than 5 milligrams per liter Na and Cl and less than 10 µg/L of B (Imes and Emmett, 1994; Imes and others, 1996; Miller and Vandike, 1997). The concentrations of Na (450 mg/L), Cl (469 mg/L), sulfate (214 mg/L) B (1,980 µg/L), and Li (261 µg/L) in the initial P3 sample were about 10 to 300 times larger than those in the P2 sample (table 5). However, concentrations of Ca (9.5 mg/L) and Mg (8.6 mg/L) in the initial P3 sample were unusually low and may reflect the exchange of these cations for Na from the Na-bentonite used as the annular seal. Data for subsequent P3 samples plot along a line trending between the P2 sample and the initial P3 sample (fig. 5), indicating that P3 samples collected during 2006 probably were a mixture of water from the two aquifers possibly caused by a faulty well seal or casing leak. The geochemical code PHREEQC (Parkhurst and Appelo, 1999) was used to evaluate the mixing of water from the P2 and P3 intervals assuming that the November 2005 P3 sample represents a St. Francois aquifer (Bonneterre Formation) end member mixing with an Ozark aquifer water represented by the August 2005 P2 sample. Results of simple mixing and allowing for exchange of Ca and Mg for Na on the bentonite used as the annular seal indicated that the water quality of the P3 samples collected during 2006 can be approximated by mixing from 1 percent (April 2006 sample) to 43 percent (October 2006 sample) of St. Francois aquifer water (November 2005 P3 sample) with water from the lower part of the Ozark aquifer (P2 sample). The mixing scenarios support the hypothesis of a faulty well construction, allowing mixing of water from the Ozark and St. Francois aquifers. Based on the continuous water-level data collected during 2007 and 2008 (fig. 4), downward flow of water from the Potosi Dolomite probably was occurring when the April and May 2006 samples were collected, causing a leftward shift in plotting position on figure 5. Upward flow of water from the Bonneterre Formation probably was occurring during the fall of 2006, resulting in a shift to the right of the October 2006 sample (fig. 5). As previously discussed, a leak caused by faulty well construction also may be the cause of the subdued response of water levels in P3 to changes in water levels in P2 (fig. 4).

The magnitude of the apparent leakage of water between the P2 and P3 zones suggested by the shift in plotting position of the P3 water samples on figure 5 and similar, but subdued response, of continuous water-level measurements in P3 to water level changes in P2 (fig. 4) probably is small and nearly undetectable. According to the mixing model, the leftward shift in plotting position from the November 2005 P3 sample to the April 2006 (1 percent P3 water) sample represents a downward flux of nearly 750 gallons (gal) of P2 water (volume of water in the well pipe, filter pack, and volume of water removed during purging). Assuming that this water moved steadily downward during the 160 days between the collection of the two samples and mixed completely within the well pipe and filter pack (degree of mixing would depend upon where the leak occurred), an estimated 5 gal of leakage occurred each day or about 0.003 gal/min. This rate is nearly an order of magnitude smaller than what could be measured with the heat-pulse flowmeter. This estimated leakage rate likely is a maximum value because it is unlikely that complete mixing occurs, especially within the filter pack. The rate of leakage is dependant upon the differential head between the P2 and P3 intervals and is expected to vary with time.

Despite an apparent well-construction problem or casing leak that is allowing mixing of water from the Ozark and St. Francois aquifers and possible Ca-Mg:Na exchange on bentonite grout, sample results indicated that water within the Bonneterre Formation at this location is a Na-Cl type water with large specific conductance values and large concentrations of dissolved solids, Na, Cl, SO_4, B, and Li (table 5). The large concentrations of Na, Cl, SO_4 and other ions in P3 samples (excluding the April 2006 sample) are unusual because water in the St. Francois aquifer in most of southern Missouri typically has low dissolved solids concentration and is a Ca-Mg-HCO_3 type water (Miller and Vandike, 1997). However, except where the St. Francois aquifer is exposed near the St. Francois Mountains in southeastern Missouri (fig. 1), few wells penetrate the St. Francois aquifer because of the adequate yields of potable water from the overlying Ozark aquifer. Consequently, relatively little is known about the variability of water quality within the St. Francois aquifer in much of southern Missouri.

Two other occurrences of unusual water quality within the St. Francois aquifer are the City of Marquand well W3 on the southeast flank of the St. Francois Mountains and several mine seeps from the Sweetwater Mine in the southern part of the Viburnum Trend (fig. 3). Marquand well W3 is a flowing well more than 1,000 ft deep and open to both the Ozark and St. Francois aquifers. A May 2003 water sample collected at the surface by the MDNR (presumably a mixture of water from the Ozark and St. Francois aquifers) had large (about 250 mg/L) concentrations of Na, Cl, and SO_4. Because of the large Cl and SO_4 concentrations, the city never put the well into production (Ken Duzan, Missouri Department of Natural

Table 5. Selected water-quality data from monitoring well USGS-D1, City of Marquand well W3, and mine seeps from the Sweetwater Mine in the Viburnum Trend.

[μS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; CaCO₃, calcium carbonate; ID, identifier; rep, replicate sample; N, nitrogen; P, phosphorus; μg/L, microgram per liter; <, less than; --, no data; E, estimated value, all concentrations dissolved unless noted otherwise]

Date	Time	Specific conductance (μS/cm)	Water temperature (°C)	pH (units)	Dissolved oxygen (mg/L)	Hardness (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Alkalinity as CaCO₃ (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)
P2[1], USGS-D1 (lower part of the Ozark aquifer[2]; station ID 36511709121555501)													
8/30/2005	0130	420	15.2	7.5	0.6	240	49	29.7	.9	1.5	208	257	0
8/30/2005 (rep)	0140	420	15.2	7.5	.6	240	47.8	29.8	1.5	1.5	208	257	<1
8/30/2005	0440	--	--	--	--	--	--	--	--	--	--	--	--
P3, USGS-D1 (St. Francois aquifer[3]; station ID 36511709121555502)													
11/4/2005	1200	2,410	22.8	8.4	1.0	59	9.5	8.6	4.8	450	221	255	4
4/13/2006	0800	457	20	7.4	<1.0	220	41.9	27.4	1.0	12	220	268	<1
5/11/2006	1440	768	20	7.9	--	150	28.2	19.4	1.9	108	204	251	<1
10/12/2006	1515	1,320	22.2	8.0	.4	92	17.8	11.5	3	220	212	257	<1
City of Marquand well W3 (Ozark aquifer and St. Francois aquifer; station ID 3725550910101101)													
12/12/2006[4]	1730	5,950	14.4	7.9	--	460	119	37.5	9.9	1,030	216	260	--
12/12/2006[5]	1757	2,690	14.4	7.7	--	230	53.8	22.5	5.7	460	277	336	--
Viburnum Trend Sweetwater Mine seeps (St. Francois aquifer)[6]													
12/11/2002 (S1)	--	6,040	18.3	7.7	--	--	416	7.6	5.4	960	--	72	--
12/11/2002 (S2)	--	1,653	18.8	8.1	--	--	48.0	13.0	3.3	220	--	211	--
12/11/2002 (S3)	--	463	18.0	7.5	--	--	38.0	20.0	1.3	18	--	274	--

Date	Time	Chloride (mg/L)	Sulfate (mg/L)	Fluoride (mg/L)	Silica (mg/L)	Dissolved solids, total sum (mg/L)	Ammonia as N (mg/L)	Nitrate plus nitrite as N (mg/L)	Nitrite as N (mg/L)	Ortho-phosphate as P (mg/L)	Phosphorus as P (mg/L)	Organic carbon, total (mg/L)	Organic carbon, dissolved (mg/L)
P2[1]: USGS-D1 (lower part of the Ozark aquifer[2]; station ID 36511709121555501)													
8/30/2005	0130	1.38	15.3	<0.1	10.2	234	<0.04	<0.06	<0.008	<0.02	<0.04	--	--
8/30/2005 (rep)	0140	1.44	15.2	<.1	9.7	235	<.04	<.06	E.004	<.02	<.04	0.9	0.5
8/30/2005	0440	--	--	--	--	--	--	--	--	--	--	--	--
P3, USGS-D1 (St. Francois aquifer[3]; station ID 36511709121555502)													
11/4/2005	1200	469	214	7.7	6.5	1,300	<.04	<.06	<.008	<.09	<.04	1.7	--
4/13/2006	0800	7.32	23.5	.3	7.4	258	<.04	<.06	.013	<.02	<.04	1	--
5/11/2006	1440	82.8	53.2	2.1	7.4	430	--	--	--	--	--	--	--
10/12/2006	1515	202	103	4.6	7.6	701	.03	<.06	<.002	E.004	<.04	1.2	--
City of Marquand well W3 (Ozark aquifer and St. Francois aquifer; station ID 3725550910101101)													
12/12/2006[4]	1730	1,480	727	3.5	8.0	3,540	.17	<.06	<.002	E.005	<.04	--	--
12/12/2006[5]	1757	585	294	2.4	7.9	1,600	.13	<.06	E.001	E.006	<.04	--	--
Viburnum Trend Sweetwater Mine seeps (St. Francois aquifer)[6]													
12/11/2002 (S1)	--	1,400	1,100	3.5	4.9	--	--	1.8	--	--	--	--	--
12/11/2002 (S2)	--	270	200	2.8	4.5	--	--	.3	--	--	--	--	--
12/11/2002 (S3)	--	11	44	1.9	3.8	--	--	.08	--	--	--	--	--

Table 5. Selected water-quality data from monitoring well USGS-D1, City of Marquand well W3, and mine seeps from the Sweetwater Mine in the Viburnum Trend.—Continued

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; CaCO₃, calcium carbonate; ID, identifier; rep, replicate sample; N, nitrogen; P, phosphorus; µg/L, microgram per liter; <, less than;--, no data; E, estimated value, all concentrations dissolved unless noted otherwise]

Date	Time	Antimony (µg/L)	Arsenic (µg/L)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)
P2[1], USGS-D1 (lower part of the Ozark aquifer[2]; station ID 365117091215501)													
8/30/2005	0130	2.4	3.5	14	<0.2	8	0.1	E0.03	1.3	E0.4	<6	0.12	<2
8/30/2005 (rep)	0140	2.5	.9	15	<.2	E6.4	.1	<.04	1.3	.4	1,330	<.08	<2
8/30/2005	0440	--	--	--	--	--	--	--	--	--	--	--	--
P3, USGS-D1 (St. Francois aquifer[3]; station ID 365117091215502)													
11/4/2005	1200	.5	.4	11	<.2	1,980	E.02	1.2	.2	<40	E3	E.04	261
4/13/2006	0800	<.20	.1	28	<.2	45	E.02	.4	.2	E.3	5,020	1.51	6
5/11/2006	1440	<.20	.2	30	<.2	462	<.04	.3	.2	E.3	2,450	<.08	66
10/12/2006	1515	<.06	.4	26	<.2	1,100	<.04	2	.1	<40	782	.74	151
City of Marquand well W3 (Ozark aquifer and St. Francois aquifer; station ID 372555090101101)													
12/12/2006[4]	1730	E.2	1.3	12	<.6	1,140	.2	E.2	.4	<1.2	29	<.36	614
12/12/2006[5]	1757	<.12	.5	13	<.6	674	.1	E.2	E.04	<.80	1,100	<.24	249
Viburnum Trend Sweetwater Mine seeps (St. Francois aquifer)[6]													
12/11/2002 (S1)	--	--	7.2	43	--	--	.05	--	1.43	1	150	.5	1,090
12/11/2002 (S2)	--	--	4.5	25	--	--	.02	--	.6	.5	50	2.6	191
12/11/2002 (S3)	--	--	1	9	--	--	.33	--	4.82	11	50	27.5	11

Date	Time	Manganese (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	Carbon-14, percent modern	Carbon-14, percent modern error	Carbon 13/12 ratio (per mil)	Oxygen 18/16 ratio (per mil)
P2[1], USGS-D1 (lower part of the Ozark aquifer[2]; station ID 365117091215501)													
8/30/2005	0130	10	5.4	7	6.1	33	.06	<2	17.4	--	--	--	--
8/30/2005 (rep)	0140	38	7	6.9	<.08	39	.11	<2	115	36.78	0.25	-12.5	-6.36
8/30/2005	0440	--	--	--	--	--	--	--	--	37.02	.24	-12.4	--
P3, USGS-D1 (St. Francois aquifer[3]; station ID 365117091215502)													
11/4/2005	1200	65	6.8	.9	0.14	201	E.02	2	97.5	--	--	--	--
4/13/2006	0800	125	5.4	3.8	<.08	56	<.04	<2	17.2	--	--	-12.26	-6.36
5/11/2006	1440	50	3.4	1.2	--	135	<.04	<2	68	--	--	--	-6.38
10/12/2006	1515	20	1.9	.2	--	191	<.04	<.6	48.1	19.2	.13	-8.96	-6.6
City of Marquand well W3 (Ozark aquifer and St. Francois aquifer; station ID 372555090101101)													
12/12/2006[4]	1730	90	30.4	2	--	3,560	<.12	<2	25.4	--	--	--	--
12/12/2006[5]	1757	47	9.5	.2	--	1,230	<.08	<2	1,330	--	--	--	--
Viburnum Trend Sweetwater Mine seeps (St. Francois aquifer) 6													
12/11/2002 (S1)	--	179	72	8.2	--	6,320	.3	--	2	--	--	--	--
12/11/2002 (S2)	--	4.8	19	1.9	--	988	.1	--	2	--	--	--	--
12/11/2002 (S3)	--	4.2	2.9	12.9	--	109	.1	--	31	--	--	--	--

[1] Point sample collected from 1,500 feet deep during drilling. Borehole open from 1,440 to 1,520 feet and purged 10 hours at 10 gallons per minute before sampling.

[2] Sample interval open to the lower part of the Potosi Dolomite (Ozark aquifer) and the upper part of the Debry-Doerun Dolomite (St. Francois confining unit).

[3] Sample interval within the Bonneterre Formation.

[4] Point sample collected at 950 feet deep from the St. Francois aquifer part of the well. Water flowing from well about 2 gallons per minute.

[5] Sample collected from water flowing from wellhead at the land surface.

[6] Data from, U.S. Geological Survey Central Region Mineral Resources Center (L.R. Lee, U.S. Geological Survey, written commun., 2007).
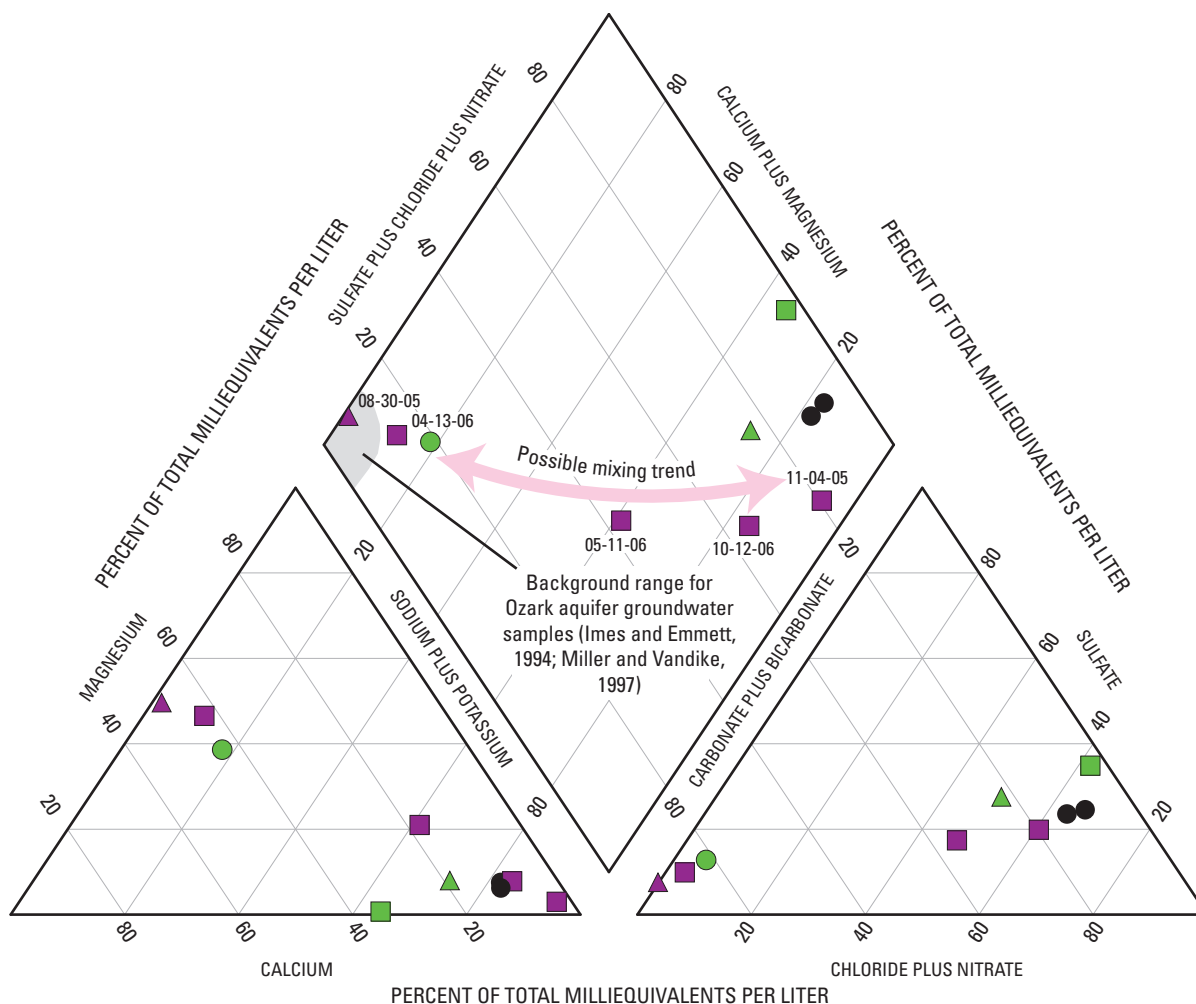
Figure 5. Trilinear diagram of major constituents in water samples from monitoring well USGS-D1, City of Marquand well W3, and mine seeps from the Sweetwater Mine in the Viburnum Trend.

Resources, Public-Drinking Water Program, written commun., 2007). A December 2006 point sample collected by the USGS from 950 ft deep (within the St. Francois aquifer) had even larger concentrations of Na, Cl, and SO_4 (table 5) than the May 2003 MDNR sample, indicating a large dissolved solids concentration and Na-Cl type water in the St. Francois aquifer beneath Marquand. Similar to samples from P3 of monitoring well USGS-D1, water samples from Marquand well W3 were

a Na-Cl type water and also contained large concentrations of B (674 and 1,140 µg/L) and Li (249 and 614 µg/L; table 5).

Several water samples collected from seeps emerging from the Bonneterre Formation in the Sweetwater Mine on the southern end of the Viburnum Trend (fig. 1) also contained large concentrations of Na, Cl, SO_4, and Li (B was not analyzed in these samples). Mine seeps S1 and S2 contained the largest concentrations of Na (960 and 220 mg/L), Cl (1,400

and 270 mg/L), Li (1,090 and 191 µg/L) and other constituents (table 5) and are near a fault within the mine known as the Sweetwater Fault (Walker, 1993). The water chemistry of these seeps may be indicative of relict formation water or mineralizing brines within the St. Francois aquifer that migrated along this fault (L.R. Lee, written commun., 2007). The unusual water quality in the Marquand W3 samples and P3 sample also may be of similar origin.

Isotopes of carbon in groundwater can provide insight in understanding the evolution of groundwater chemistry, flow paths, and interpretation of groundwater age (Clark and Fritz, 1997). Carbon generally enters the groundwater system as carbon dioxide (CO_2) dissolved in precipitation or as dissolved CO_2 gas produced from the decomposition of organic matter in the soil zone (Fritz and Fontes,1980). This carbon subsequently is transported through the unsaturated zone to the water table where, in the case of the Ozark aquifer, it is diluted (enriched) by exchange and dissolution of the carbonate minerals in the unsaturated zone and the aquifer matrix. In temperate climate regions, such as Missouri, the $\delta^{13}C$ value of the soil zone/unsaturated zone CO_2 gas is about -25 ‰ (Fritz and Fontes, 1980). Carbonate rocks (dolostone and limestone) in the Ozark aquifer have $\delta^{13}C$ values of about 0 ‰ (Clark and Fritz, 1997).

Water samples from springs and wells in the Ozark aquifer of southern Missouri generally plot along a line of carbonic acid weathering (dissolution) of dolomite (Imes and others, 1996; 2007) according to the equation:

$$Ca, Mg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (1)$$
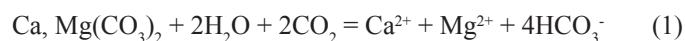
In the above equation, carbon is equally derived from CO_2 gas and dissolution of carbonate minerals, which yields an estimated $\delta^{13}C$ of the bicarbonate in water of about -12.5 ‰. The $\delta^{13}C$ values of the two P2 samples (-12.5 and -12.4; table 5) are consistent with the dissolution of carbonate minerals by carbonic acid. The October 2006 P3 sample had a $\delta^{13}C$ value of -8.96 ‰, which is heavier than the value predicted by equation 1. The heavier $\delta^{13}C$ value in the P3 sample may indicate that water in the Bonneterre Formation is much older, allowing for enrichment in ^{13}C by isotopic exchange between aqueous dissolved inorganic carbon (DIC) and carbonate minerals in the aquifer matrix. The $\delta^{13}C$ value in the April 2006 P3 sample (-12.26 ‰) was nearly identical to the P2 $\delta^{13}C$ values and is consistent with the mixing model derived from the major ion data indicating that the April 2006 P3 sample actually is mostly P2 water. Overall the $\delta^{13}C$ values in samples from P2 (-12.5 and -12.4 ‰) were depleted as compared to $\delta^{13}C$ values (-6.78 to -9.41) reported for samples from Ozark aquifer wells in southwestern Missouri and southeastern Missouri (Pope and others, 2009).

The DIC ^{14}C activity in the October 2006 P3 sample (19.2 pmC) was smaller than the DIC ^{14}C in the P2 sample (about 37 pmC; table 5), indicating that the DIC in the St. Francois aquifer (P3 sample) probably is older than the DIC in the overlying Ozark aquifer (P2 sample). Using the simple

"leaky casing" mixing model derived from the major constituent data, the estimated DIC ^{14}C activity for the St. Francois aquifer at P3 is about 2 pmC, indicating that the water potentially is thousands to tens of thousands of years old. However, because ^{14}C is likely lost by isotopic exchange or dissolution of "dead" carbon (millions of years old) in aquifer carbonate minerals (Maloszewski and Zuber, 1991), this estimated value and the laboratory reported DIC ^{14}C values in table 5 may be too small and not provide reliable estimates of actual ages of water in the samples. Perhaps coincidentally, the estimated DIC ^{14}C activity value in P3 of about 2 pmC, is similar to values reported by for the confined Ozark aquifer in southwestern Missouri and southeastern Kansas (Pope and others, 2009). The pmC values in Ozark aquifer water samples from southwestern Missouri and southeastern Kansas samples were determined by Pope and others (2009) to be unreliable because of exchange with dead carbon in the aquifer matrix.

Summary and Conclusions

A deep (more than 2,000 feet deep) monitoring well (USGS-D1) was installed within an area being explored for lead and zinc deposits within the Mark Twain National Forest in southern Missouri. The area is a mature karst terrain where rocks of the Ozark aquifer, a primary source of water for private and public-supplies and major springs in the nearby Eleven Point National Wild and Scenic River and the Ozark National Scenic Riverways, are exposed at the surface. The potential lead deposits lie about 2,000 feet below the surface within a deeper aquifer, called the St. Francois aquifer. The two aquifers are separated by the St. Francois confining unit. The deep monitoring well was installed as part of a series of investigations to determine the degree of connection between the two aquifers, specifically to examine potentiometric head relations and water-quality differences between the St. Francois aquifer, where a potential lead-zinc ore body exists, and the overlying Ozark aquifer.

Results of borehole flowmeter measurements in the open borehole and water-level measurements from the completed monitoring well USGS-D1 indicate that a seasonal upward gradient exists between the St. Francois aquifer and the overlying Ozark aquifer from about September through February. The upward potentiometric heads across the St. Francois confining unit that separates the two aquifers averaged 13.40 feet with a maximum value of 22.84 feet. Large reversals in this upward gradient occurred during late winter through summer (about February through August) when water levels in the Ozark aquifer were as much as 138.47 feet higher (average of 53.84 feet) than water levels in the St. Francois aquifer. Most the fluctuation of potentiometric gradient is driven by precipitation and rapid recharge causing large and rapid increases in water levels in the Ozark aquifer.

Analysis of water-quality samples collected from monitoring well USGS-D1 indicated that the water within the

upper part of the St. Francois aquifer in the exploration area is a sodium-chloride type water containing dissolved solids concentrations as large as 1,300 milligrams per liter and large concentrations of sodium and chloride (equal to or greater than 450 milligrams per liter), sulfate (more than 200 milligrams per liter), and the trace elements boron and lithium (more than 1,900 and 200 micrograms per liter). In contrast, water in the overlying Ozark aquifer is a calcium-magnesium-bicarbonate type water that contains dissolved solids concentrations less than 250 milligrams per liter), less than 5 milligrams per liter sodium and chloride, and less than 10 micrograms per liter of boron and lithium. Outside of the St. Francois Mountains area, few wells in southern Missouri penetrate the St. Francois aquifer and relatively little known about the quality of water in the aquifer. The small quantity of previously available data indicate that water in the St. Francois aquifer has low dissolved solids concentration and is calcium-magnesium-bicarbonate type water. However, analysis of water-quality samples collected from monitoring well USGS-D1, the city of Marquand well W3, and several seeps within the Sweetwater Mine in the Viburnum Trend indicated the presence of local areas of the St. Francois aquifer that have a sodium-chloride type water with concentrations of sodium, chloride, and sulfate exceeding several hundred milligrams per liter and concentrations of the trace elements boron and lithium exceeding several hundred micrograms per liter.

References Cited

Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrology: New York, Lewis Publishers, 328 p.

Conger, R.W., 1996, Borehole geophysical logging for water-resource investigations in Pennsylvania: U.S. Geological Survey Fact Sheet 218–85, p. 4

Coplen, T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances: Pure and Applied Chemistry, v. 66, p. 273–276.

Dresser Atlas Industries Inc., 1974, Log review 1: Dresser Atlas Division, USA, 128 p.

Epstein, S., and Mayeda, T., 1953, Variation of O-18 content of water from natural sources: Geochimica Cosmochimica Acta, v. 4, p. 213–224.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Freeman, L.A., Carpenter, M.C., Rosenberry, D.O., Rousseau, J.P., Unger, R., and McLean, J.S., 2004, Use of submersible pressure transducers in water-resources investigations: U.S. Geological Survey Techniques of Water-Resource Investigations, book 8, chapter A3, accessed May 2008 at URL *http://pubs.usgs.gov/twri/twri8a3/.*

Fritz, P., and Fontes, J.C., eds., 1980, Handbook of environmental isotope geochemistry: Elsevier Scientific Publishing Company, New York, New York, 543 p.

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap.1, 88 p.

Gleason, J.D., Friedman, I., and Hanshaw, B.B., 1969, Extraction of dissolved carbonate species from natural water for carbon-isotope analysis: U.S. Geological Survey Professional Paper 650–D, p. D248–D250.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 3rd ed., 263 p.

Imes, J.L., and Emmett, L.F., 1994, Geohydrology of the Ozark Plateaus aquifer system in parts of Missouri, Arkansas, Oklahoma, and Kansas: U.S. Geological Survey Professional Paper 1414–D, 127 p.

Imes, J.L., Schumacher, J.G., and Kleeschulte, M.J., 1996, Geohydrologic and water-quality Assessment of the Fort Leonard Wood Military Reservation, Missouri, 1994–95: U.S. Geological Survey Water-Resources Investigations Report 96–4270, 134 p.

Imes, J.L., Plummer, L.N., Kleeschulte, M.J., and Schumacher, J.G., 2007, Recharge area, base-flow and quick-flow discharge rates and ages, and general water quality of Big Spring in Carter County, Missouri, 2000–04: U.S. Geological Survey Scientific Investigations Report 2007–5049, 80 p.

Keys, W.S., 1990, Borehole geophysics applied to groundwater investigations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 2, chap. E2, 150 p.

Kleeschulte, M.J., and Seeger, C.M., 2003, Stratigraphy and vertical hydraulic conductivity of the St. Francois confining unit in the Viburnum Trend and evaluation of the unit in the Viburnum Trend and exploration areas, southeastern Missouri: U.S. Geological Survey Water-Resources Investigations Report 03–4329, 57 p.

Maloszewski, P., and Zuber, A., 1991, Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers: Water Resources Research, v. 27, p. 1,937–1,945.

Miller, D.E., and Vandike, J.E., 1997, Groundwater resources of Missouri—Missouri State Water Plan Series: Rolla, Missouri Department of Natural Resources, Division of Geology and Land Survey, v. 2, 210 p.

Missouri Department of Natural Resources, Division of Geology and Land Survey, 2007, Missouri environmental geology atlas: Rolla, Division of Geology and Land Survey, CD-ROM.

Mugel, D.N., Richards, J.M., Schumacher, J.G., 2009, Geohydrologic investigations and landscape characteristics of areas contributing water to springs, the Current River, and Jacks Fork, Ozark National Scenic Riverways, Missouri: U.S. Geological Survey Scientific Investigations Report 2009–5138, 80 p.

National Oceanic and Atmospheric Administration, 2009, National Climate Data Center, accessed January 15, 2009, at URL *http://www.ncdc.noaa.gov/oa/climate/stationlocator. htm.*

Oblinger Childress, C.J., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p.

Paillet, F.L., 1998, Flow modeling and permeability estimates using borehole logs in heterogeneous fractured formations: Water Resources Research, v. 34, no. 5, p. 997–1,010.

Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (Version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99–4259, 312 p.

Pope, L.M., Mehl, H.E., and Coiner, R.L., 2009, Quality characteristics of groundwater in the Ozark aquifer of northwestern Arkansas, southeastern Kansas, southwestern Missouri, and northeastern Oklahoma, 2006–07: U.S. Geological Survey Scientific Investigations Report 2009–5093, 60 p.

U.S. Geological Survey, variously dated 1997 through 2006, National field manual for the collection of water quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1–A9, various pagination, accessed January 2008 at: URL *http://pubs. water.usgs.gov/twri9A.*

U.S. Geological Survey, 2009, Surface-water data for Missouri: accessed March 2009 at URL *http://waterdata.usgs. gov/mo/nwis/sw.*

Walker, Wayne, 1993, Geology of the Sweetwater Mine, Viburnum Trend, southeast Missouri *in* Childress, Andrew ed., The Viburnum Trend, a second look: Guidebook of the 40th annual meeting, September 24 to 25, 1993, p. 44–64.

White, A.F., Peterson, M.L., and Solbau, R.D., 1990, Measurement and interpretation of low levels of dissolved oxygen in groundwater: Ground Water, v. 28, no. 4, p. 584–590.

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., 1999 Collection of water samples: U.S. Geological Survey Techniques of Water-Resource Investigations, book 9, chap. A4, updated version available at URL *http://pubs. water.usgs.gov/twri9A4/.*