

Temporal Variability in the Quality of Produced Water from Wells Tapping the Ozark Aquifer of Southeast Kansas

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Abstract

State and local agencies have become concerned that the available water supply from the Ozark aquifer in the Tri-state region of southeast Kansas, southwest Missouri, and northeastern Oklahoma may become unusable or require additional water treatment because of deteriorating quality resulting from overdevelopment. Many southwest Missouri and southeast Kansas water supplies withdraw water from a 30–60-mi (48–96-km)-wide transition zone in the Ozark aquifer that separates calcium, magnesium-bicarbonate ground water with low dissolved solids to the east from sodium-chloride brines to the west. Water-quality deterioration within the transition zone could potentially come about as a result of eastward migration or upward movement from deeper horizons of saline water. This study assessed variability in the quality of water produced from wells within the transition zone in southeast Kansas across a variety of time scales. Water samples were collected monthly from nine wells located in the transition zone over a two-year period and frequently during two 50+ hr chemical-quality pumping tests of Pittsburg well 8. The samples were analyzed for conductance and pH, and all major and selected minor dissolved inorganic constituents. Mixing curves of chloride versus bicarbonate/chloride ratio and chloride versus sodium/chloride ratio demonstrate that the produced water from Ozark aquifer wells is a mixture of low dissolved solids, calcium, magnesium-bicarbonate ground waters and sodium-chloride brines. Produced water from wells tapping sources in the Ozark and the overlying Springfield Plateau aquifers is a blend of waters from these sources, although the data suggest that the contribution from the Springfield is small relative to the Ozark aquifer. Fluctuations in the quality of the produced water during pumping most likely result from complex mixing of waters of differing quality from different parts of the Ozark aquifer within the well bore. This is borne out by bicarbonate/chloride ratio versus chloride concentration mixing curves and the dissolved constituent ratios indicative of bicarbonate and sodium in excess of that required to balance calcium + magnesium and chloride, respectively. Comparison of the 1979–1980 data with the 2006–08 data from this project indicates that the chloride concentration in some of the sampled supplies has increased. Based on extrapolation of the maximum estimated rate of chloride concentration increase, the earliest that water from Pittsburg wells 8 and 10 would exceed the recommended drinking water limit for chloride is estimated to be by the years 2045 and 2060, respectively, assuming continuation of the present rates of pumping.

Introduction

The Ozark aquifer is the single most important source of water in the Tri-state region of southeast Kansas, southwest Missouri, and northeast Oklahoma. Kansas water agencies and the Tri-State Coalition (a multi-state, nongovernmental organization consisting of water-related interest groups) are concerned that the available supply from the Ozark may become inadequate, rendered unusable, or require additional water treatment in the near future because of water-quality degradation. Many southeast Kansas and southwest Missouri water supplies withdraw water from wells that tap a 30–60-mi (48–96-km)-wide transition zone in the Ozark aquifer separating calcium-bicarbonate type ground waters with low dissolved solids to the east from sodium-chloride brines to the west (fig. 1).

Two earlier regional studies indicated significant short- and long-term changes in the chemical quality of

produced water from wells within or near the Ozark aquifer transition zone. Darr (1978) used 1966–1976 chloride data collected from public water supplies to infer the eastward movement of brackish water into Barton, Vernon, and Bates counties in southwestern Missouri. Macfarlane and Hathaway (1987) noted increases in the concentrations of sodium and chloride in the water produced from well 1 of the now defunct Crawford County RWD 7 between 1972 and 1980. Long-term pumping from the confined aquifer has significantly reduced and in some areas has reversed the hydraulic head gradient, which is generally from east to west across the water-quality transition zone in the Ozark aquifer. Development has produced coalesced cones of depression on the potentiometric surface within or near the transition zone in the Pittsburg, Kansas, and Miami, Oklahoma, areas (fig. 2; Macfarlane and Hathaway, 1987; Gillip et al., 2007). Macfarlane and Hathaway

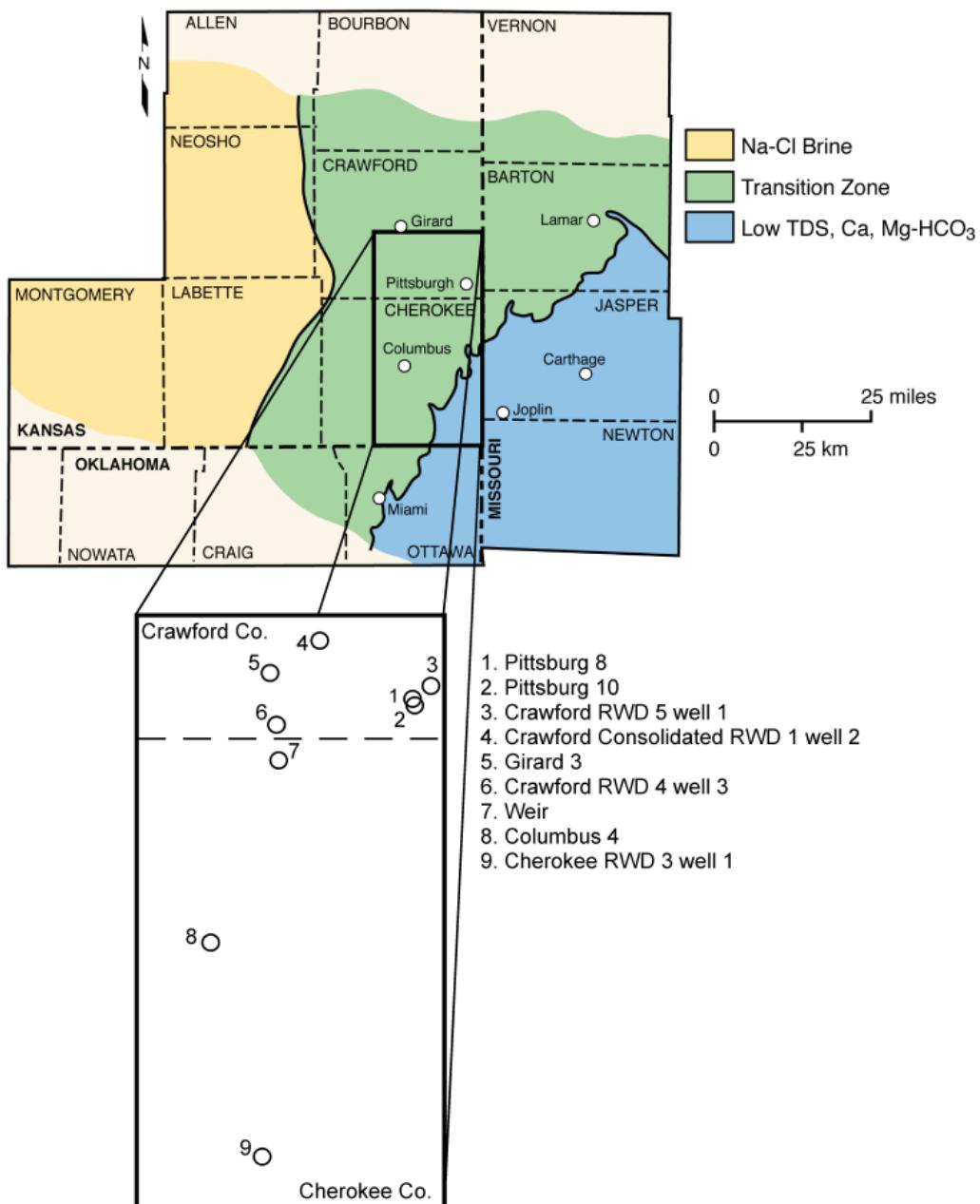


FIGURE 1—Location of the nine supply wells included in this project and Ozark aquifer water-quality provinces within the Tri-state region. The boundary separating the Na-Cl brine from the transition zone represents a chloride concentration of 2,500 mg/L, and the line separating the transition zone from the low TDS water is the Pennsylvanian–Mississippian boundary outcrop (Macfarlane and Hathaway, 1987).

(1987) suggested that hydraulic head gradient reversals and increases in the vertical hydraulic head gradient could potentially induce the reported increases in chloride.

To better understand the impact of pumping on water quality, a project was initiated in 2006 that focused on nine public supply wells that withdraw water from the transition zone within the Ozark aquifer in southeast Kansas (fig. 1; table 1). Historic water-quality data were available for six of the nine wells from regional surveys reported in Macfarlane and Hathaway (1987; table 2).

The objectives of the project were to 1) characterize the magnitude of fluctuations in the geochemistry of produced water from these wells based on samples collected monthly and repeatedly during the extended pumping of a single well, 2) assess long-term changes in the geochemistry of produced water from these wells since 1979–1980, and 3) use the results to better understand the causes of the short- and long-term changes in the geochemistry of the waters produced from these wells.

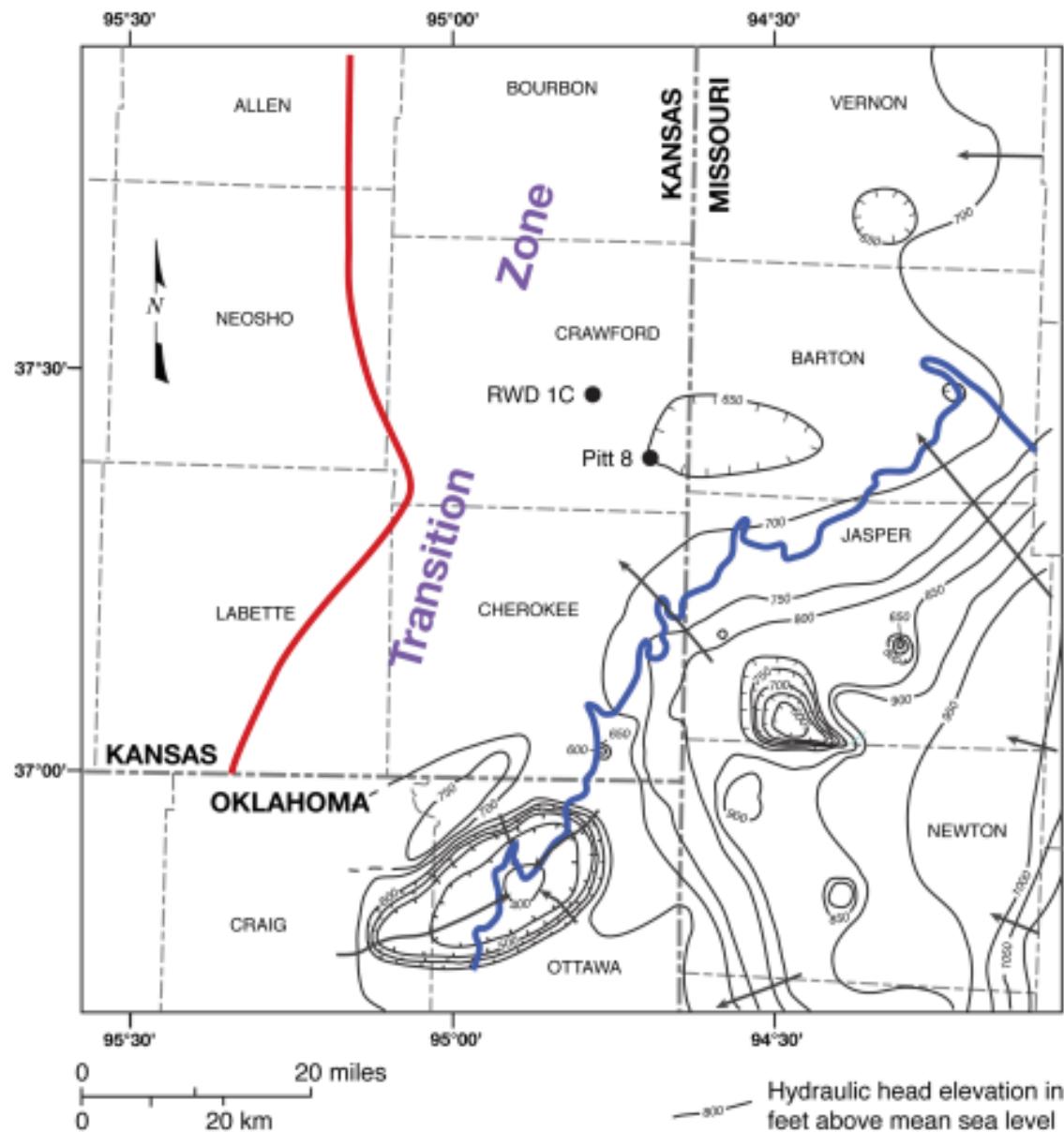


FIGURE 2—The 2006 Ozark aquifer potentiometric surface map of the Tri-state region with the water-quality transition zone in southeast Kansas and southwest Missouri. The heavy red and blue lines define the area of the saltwater to freshwater transition zone. The black dots labeled RWD 1C and Pittsburg 8 are the approximate locations of Crawford Consolidated RWD 1 well 2 and Pittsburg well 8, respectively. From Macfarlane and Hathaway (1987) and Gillip et al. (2007).

Regional Hydrogeology

The Tri-state region is located astride the boundary between the Ozark Dome in Missouri and the Cherokee basin in Kansas. The bedrock units generally dip westward at approximately 20 ft/mi (3.75 m/km; figs. 3–4; Macfarlane and Hathaway, 1987). The Ozark Plateau aquifer system in southeast Kansas and western Missouri consists of karstic and fractured Mississippian, Lower Ordovician, and Upper Cambrian carbonate rock units and has been subdivided into the Springfield Plateau, Ozark, and St. Francois regional aquifers (Jorgensen et al.,

1993; Macfarlane, 2000; table 3). The Springfield Plateau aquifer framework consists of Mississippian limestones and dolomitic limestone, whereas the Ozark consists primarily of Lower Ordovician and Upper Cambrian dolostones with quartzose sandstones most prominently developed within the Roubidoux Formation and at the base of the Gasconade Dolomite. Sandstones of the Roubidoux Formation rest on a regional unconformity developed at the top of the Gasconade Dolomite (Jorgensen et al., 1993). The rocks of the Roubidoux, Gasconade Dolomite, and

TABLE 1—Water-supply wells sampled in this project.

Well Name	PLS Location ¹	Well Depth (ft [m])	Ozark Aquifer Thickness Penetrated (ft [m])	Source(s) Tapped ²
Cherokee RWD 3 well 1	SWSWSE sec. 17, T. 34 S., R. 24 E.	1,050 (320)	530 (162)	O
Columbus 4	NENENW sec. 13, T. 32 S., R. 23 E.	1,785 (544)	747 (228)	S,O, SF
Crawford Cons. RWD 1 well 2	SESESE sec. 2, T. 30 S., R. 24 E.	1,013 (309)	348 (106)	O
Crawford RWD 4 well 3	NENENE sec. 16, T. 31 S., R. 24 E.	970 (296)	342 (104)	O
Crawford RWD 5 well 1	SESWSW sec. 23, T. 30 S., R. 25 E.	1,045 (319)	615 (187)	S, O
Girard 3	NESENE sec. 21, T. 30 S., R. 24 E.	1,165 (355)	445 (136)	O
Pittsburg 8	NENESE sec. 28, T. 30 S., R. 25 E.	1,050 (320)	550 (168)	O
Pittsburg 10	NESESE sec. 28, T. 30 S., R. 25 E.	1,052 (321)	550 (168)	O
Weir	SWSESW sec. 27, T. 31 S., R. 24 E.	920 (280)	300 (91)	P,S,O

¹Public Land Survey²Aquifers sourced by the supply wells: P = Pennsylvanian, S = Springfield Plateau, O = Ozark, and SF = St. Francois

TABLE 2—Chemical analyses of water samples collected in 1979–1980 from water-supply wells included in this project.

Well Name	Date Sampled	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
Pittsburg 10	4/18/79	577	65	27	48	5.0	0.79	325	68	38
	9/26/79	601	69	28	54	4.1	0.73	324	80	41
	5/15/80	446	62	31	55	4.6	0.85	326	81	41
Crawford RWD 5 well 1	4/18/79	468	42	19	58	3.6	0.51	265	21	58
	9/26/79	487	45	19	61	3.1	0.52	271	27	60
	5/14/80	365	46	22	62	3.8	0.56	275	26	58
Crawford Cons. RWD 1 well 2 (Formerly Crawford RWD 7 well 2)	10/7/80	625	71	32	111	8.9	1.37	341	87	135
Weir	4/19/79	546	60	27	43	6.0	0.95	318	53	37
	9/24/79	567	62	28	51	5.0	0.86	319	63	37
	5/12/80	417	58	32	50	5.7	1.01	319	65	38
Columbus 4	9/25/79	743	56	28	123	7.3	1.42	329	78	119
Cherokee RWD 3 well 1	4/19/79	594	44	20	115	5.5	1.07	189	28	191
	9/20/79	644	48	24	126	6.1	1.19	195	39	204
	5/13/80	544	46	24	122	6.4	1.20	195	38	200

Potosi formations are considered to be the most productive sources of water (Imes and Emmett, 1994). Most of the supply wells sampled in this project withdraw water from only the upper 600 ft (183 m) of the aquifer and do not extend below the Gasconade (table 1). Dissolution along fractures and bedding planes is the primary process by which secondary permeability has developed in the carbonate rocks, whereas sandstone-matrix permeability depends on the size, sorting, and degree of cementation of the grains (Imes and Emmett, 1994). As a result of these factors, the permeability of the Ozark aquifer is likely to vary over several orders of magnitude across its thickness (Doveton, 1986). Wells in southeast Kansas do not use the St. Francois aquifer as a source of water and as a result very little is known about it.

Ozark Plateaus aquifer system thickness ranges from 1,735 ft (529 m) in the Joplin, Missouri, area to 1,390 ft (424 m) at Parsons, Kansas (Macfarlane and Hathaway, 1987). The average thickness of the Ozark and Springfield Plateau aquifers is close to 1,000 ft (305 m) and 350 ft (114 m), respectively, within the study area (Imes and Emmett, 1994). The Springfield Plateau aquifer is unconfined across much of southwest Missouri and the southeast corner of Cherokee County, Kansas. Elsewhere, the Ozark Plateaus aquifer system is confined above by a sequence of Carboniferous (Pennsylvanian) shales and limestones and below by rocks of Precambrian age (fig. 4). One or more low-permeability units separate the Springfield Plateau from the Ozark aquifer in southern Crawford and Cherokee counties. Confining-layer thickness is generally less than

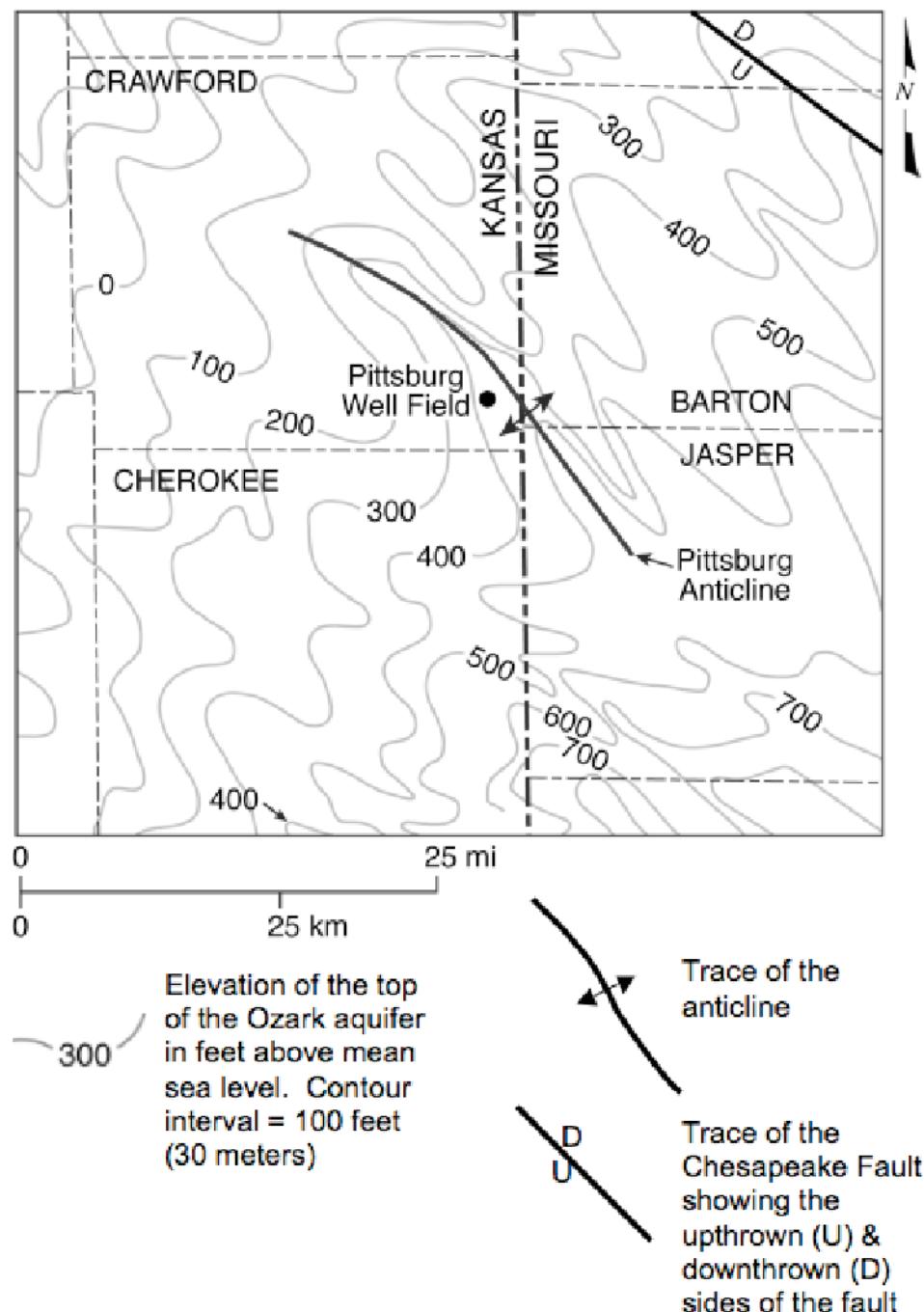


FIGURE 3—Contour map of the elevation of the top of the Ozark aquifer in parts of southeast Kansas and adjacent southwest Missouri showing the location of the Pittsburg well field on the crest of the Pittsburg anticline (from Macfarlane and Hathaway, 1987).

20 ft (6.1 m) in these counties (Macfarlane and Hathaway, 1987).

Pre-development ground-water flow in both aquifers is generally in a northwesterly direction from southwest Missouri into the southeast Kansas study area (Macfarlane et al., 1981; Imes and Emmett, 1994). Recharge to the confined Ozark aquifer comes primarily from leakage moving downward from the Springfield Plateau aquifer across the confining layer (Imes and Emmett, 1994). Localized concentrations of high-yielding supply wells in

northeast Oklahoma, southwest Missouri, and southeast Kansas, including the Pittsburg area, have produced extensive cones of depression in the Ozark aquifer potentiometric surface (fig. 2; Macfarlane et al., 1981; Macfarlane and Hathaway, 1987; Gillip et al., 2007). Declines in the Ozark aquifer potentiometric surface since pre-development exceed 150 ft (45.7 m) at some locations in the Pittsburg area (Stramet, 1957; Macfarlane and Hathaway, 1987; Gillip et al., 2007).

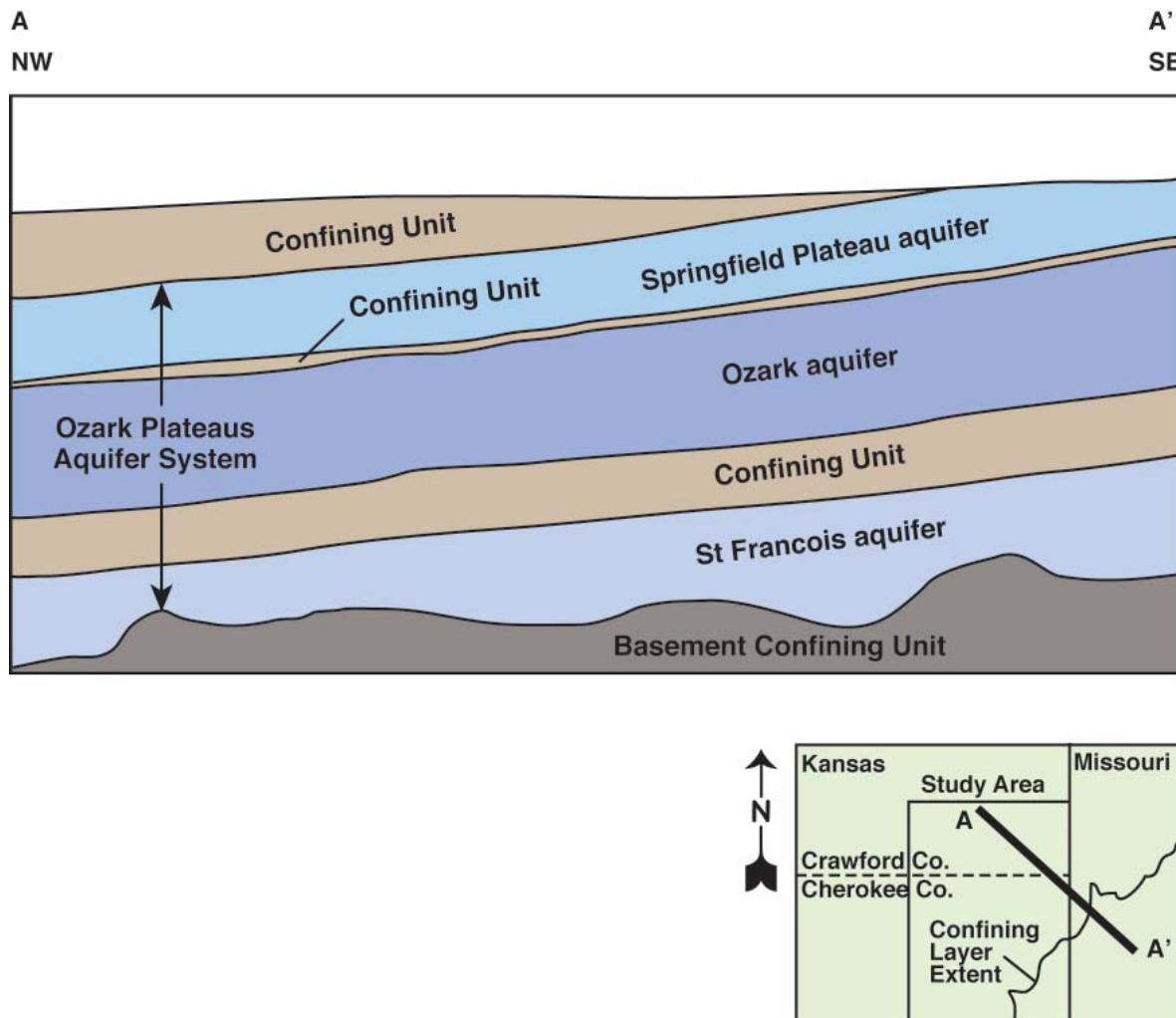


FIGURE 4—Schematic northwest to southeast cross section of the subsurface from southeast Kansas into southwestern Missouri generalized from Macfarlane and Hathaway (1987) showing the arrangement of aquifers and confining units in the Ozark Plateaus aquifer system based on well-log data. The freshwater-transition zone boundary is shown along the top of the figure.

Regional Water Quality

Where the Springfield Plateau aquifer is unconfined, ground-water quality in the underlying Ozark aquifer varies from calcium-bicarbonate to a mixed cation-bicarbonate type with a total dissolved solids (TDS) concentration of generally less than 500 mg/L (fig. 1; Macfarlane and Hathaway, 1987). Calcium/magnesium equivalent ratios in Ozark aquifer ground waters are typically 1–2, consistent with the predominantly dolomitic composition of the aquifer. Ratio values near 3 in water from wells located where the Springfield Plateau is the near-surface aquifer suggest leakage from the limestones of the overlying Springfield Plateau aquifer. The calcium/magnesium equivalent ratio range is from 0.66 to 4.00 with a median value of 1.19 in water from wells in areas of southwestern Missouri where the Springfield Plateau aquifer is overlain by Pennsylvanian strata (Darr, 1978). Water type in the

Springfield Plateau aquifer is generally calcium-bicarbonate with dissolved solids concentrations less than 1,000 mg/L where the aquifer is unconfined, but changes to a sodium-bicarbonate with dissolved solids concentrations ranging up to several thousand mg/L or more where the aquifer is confined by overlying Pennsylvanian strata (Macfarlane and Hathaway, 1987; Feder et al., 1969; Darr, 1978). Dissolved hydrogen sulfide levels are less than 0.2 mg/L.

To the west in the Cherokee basin of southeast Kansas and northeast Oklahoma, the Ozark Plateaus aquifer system is in the deep subsurface and isolated hydraulically from the near-surface sources of freshwater recharge. Here, the ground water in the Ozark aquifer is a sodium-chloride brine with a high TDS concentration that generally exceeds 10,000 mg/L (fig. 1). The brine environment is chemically reducing and the dissolved hydrogen sulfide concentration

ranges up to 100 mg/L where some of the brines are associated with oil fields (Macfarlane and Hathaway, 1987).

Within the transition zone that separates the saline from freshwater in the Ozark aquifer, the ground-water type changes laterally from calcium, magnesium-bicarbonate, and mixed cation-bicarbonate on the east to sodium-chloride on the west (fig. 1). Macfarlane and Hathaway (1987) noted that water samples from wells tapping the Ozark aquifer near the updip edge of the Pennsylvanian outcrop belt exhibited many of the geochemical changes associated with the transition from freshwater to brine. Hence, they set the freshwater-transition zone boundary in the Ozark aquifer to coincide with the updip edge of the Pennsylvanian outcrop belt. The brine/transition zone boundary shown in figs. 1 and 2 was set arbitrarily as the 10,000 mg/L TDS isocon, the limit that defines usable water in Kansas. Data are not available to determine the vertical variability in water quality from top to bottom within the Ozark aquifer in the transition zone. Based on a review of the data from the drilling of shallower Ozark wells, Macfarlane and Hathaway (1987) concluded that the

complexity of the aquifer framework and the regional and local structural fabric probably precludes a simple picture of increasingly saline water with depth within the transition zone.

Water pumped from wells completed in the Ozark aquifer transition zone contains measurable amounts of hydrogen sulfide ranging from trace amounts near the eastern side up to 40 mg/L near the western side, and sulfate concentrations from 110 mg/L near the eastern edge to 3 mg/L near the western edge. The simultaneous occurrence of these constituents in produced water indicates either that 1) a state of chemical equilibrium exists, 2) a very slow transition is occurring in the oxidation state of sulfur in the aquifer, or 3) pumping has produced a disequilibrium blend of waters from different parts of the aquifer (Macfarlane and Hathaway, 1987). Macfarlane et al. (1981) suggested that mixing different amounts of the water from the freshwater and brine sources could approximate the chemistries of water samples from the transition zone of the Ozark aquifer.

Methodology

Water samples were collected monthly from nine public water-supply wells located within the transition zone in Crawford and Cherokee counties in southeast Kansas (fig. 1; table 1). Newer wells tapping supplies in the Ozark Plateaus aquifer system are steel-cased through the Pennsylvanian to prevent fluids and natural gas from entering the well in the upper part of the boreholes. Below the casing and down to total depth, wells are completed as open boreholes from which water is produced. Five of the monitored wells tap supplies in the Ozark aquifer, and three tap supplies in both the Springfield Plateau and the Ozark aquifers (referred to in this paper as multi-aquifer wells). Of the three multi-aquifer wells, the older Weir city well potentially taps minor sources of water in the overlying Pennsylvanian rocks in addition to the Springfield Plateau and Ozark aquifers.

Water samples were collected in 500-mL polyethylene bottles after the well had been pumped for at least 15 minutes, or after the specific conductance and temperature had stabilized. If the well was running on arrival at the site, the water-supply operator was queried to obtain an estimate of how long the well had been pumping. Most of the time the well had been running for at least one hour prior to sampling. Some of the wells could not be sampled every month because of restrictions on the amount of water that could be pumped or mechanical problems.

Temperature, pH, and specific conductance were measured at the time of sampling. Samples were kept in an ice-chest after collection and later transferred to a refrigerator in the Analytical Services laboratory at the Kansas Geological Survey (KGS).

Water-quality pumping tests were conducted to assess changes in the chemistry of produced water over a single pumping period. Well 8 in the Pittsburg well field was selected for testing because it had been sampled monthly in the previous phase of this research. It is located on the western side of the regional cone of depression in the Ozark aquifer potentiometric surface (fig. 2) and structurally near the crest of the Pittsburg anticline (fig. 3; Macfarlane and Hathaway, 1987). Well 8 is cased through the overlying Springfield Plateau aquifer and was completed as an open borehole from the Jefferson City Dolomite into the upper part of the Gasconade Dolomite (table 3). Water is produced from the well by a turbine pump at the rate 1,875 gal/minute (118 L/second).

In 2008, tests were conducted in late June near the beginning of what is normally a period of high water demand and in early September just after the time of peak demand. The monitoring well hydrograph in fig. 5 shows that the elevation of the potentiometric surface is generally higher during low pumping-stress periods than it is during high pumping-stress conditions. The June test duration was 50.7 hours, during which 26 water samples were collected, and the September test duration was 51.8 hours, during which 28 samples were collected. The interval between samplings varied from 15 minutes to 8.8 hours in the June test and from 30 minutes to 3 hours in the September test.

Samples were refrigerated until processed in the KGS laboratory. Specific conductance and pH were measured after the samples had equilibrated to room temperature. Samples were then analyzed for calcium, magnesium, strontium, sodium, potassium, bicarbonate,

TABLE 3—Bedrock and hydrostratigraphic units in the study area modified from Jorgensen et al. (1993).

System/Subsystem		Series	Rock Unit	Hydrostratigraphic Unit	
Pennsylvanian	Middle Pennsylvanian		Marmaton Group Cherokee Group	confining unit	
Mississippian	Undifferentiated		Northview Shale Compton Limestone	Ozark Plateaus Aquifer System	Springfield Plateau aquifer
Ordovician	Lower Ordovician		Jefferson City Dolomite Roubidoux Formation Gasconade Dolomite		confining unit
Cambrian	Upper Cambrian		Eminence Dolomite Potosi Formation Derby and Doe Run Dolomites		Ozark aquifer
			Bonneterre Dolomite Lamotte Sandstone		confining unit
Precambrian	-		-		St. Francois aquifer
					confining unit

sulfate, and chloride. Anion analyses were performed using ion chromatography with a Dionex ICS-3000 and cation concentrations were measured using a Jarrel–Ash ICP. Prior to analysis, samples processed for the Dionex and the Jarrel–Ash were passed through 0.2-micron and 0.45-micron filters, respectively. Bicarbonate was determined using an automated titrimeter. Most of the analytical results are within 2% of electrical balance based on milliequivalent/liter (meq/L) values, and all of the analyses are within 5% of balance. TDS concentration was calculated by summing the major and minor constituent concentrations. In the TDS calculation, the bicarbonate concentration was multiplied by 49.17% to approximate the amount of carbonate that would be left in the residual solids after evaporating to dryness. The analytical results are in tables 4–15. Water-type classification is based on whether the percent meq/L contributions of individual dissolved cations and anions exceed 50% of the total meq/L concentration of cations or anions. Waters in which none of the constituent concentrations exceed 50% of the total cations or anions were classified as mixed.

Graphical displays of the concentration data were used to explore spatial and temporal relationships and develop mixing relationships between constituents and constituent ratios that represent the contributions of end-member ground waters of differing chemistry to the produced waters sampled in this project. The diamond-shaped field of the Piper diagram (Piper, 1944) was modified by rotation

of the coordinate axes 90° to allow for easier plotting and display of the monthly sample data from spreadsheets.

Mixing curves are useful for testing the hypothesis that a given water is a mixture of two end-member waters of differing chemistry based on their dissolved constituents. In the case of two end-member mixtures, the relationship between relative amounts and observed end-member concentrations and the mix in a water sample can be expressed as a mass balance equation (Hem, 1985):

$$C_1 V_1 + C_2 V_2 = C_3 (V_1 + V_2), \quad (1)$$

where C_1 and C_2 , and V_1 and V_2 , are the constituent concentrations and the volumes from sources 1 and 2, respectively, and C_3 and $(V_1 + V_2)$ are the constituent concentration and the volume of water produced at the well. In the case of relative contributions, the quantity $(V_1 + V_2)$ is equal to 1, and V_1 and V_2 are volume fractions.

Monthly pumpage data could not be obtained for most of the wells sampled because of the manner in which water withdrawals are tabulated by the water utilities. Some of the utilities rely on sources of both ground water from the Ozark Plateau aquifer system and surface water from Bone Creek Reservoir in Crawford County. Thus, it is difficult to quantify withdrawals from individual wells. However, on the basis of the types of pumps, the pumping rate, and frequency of use information, it is likely that Pittsburg 8 and Girard 3 are used more heavily than any of the other wells in this study.

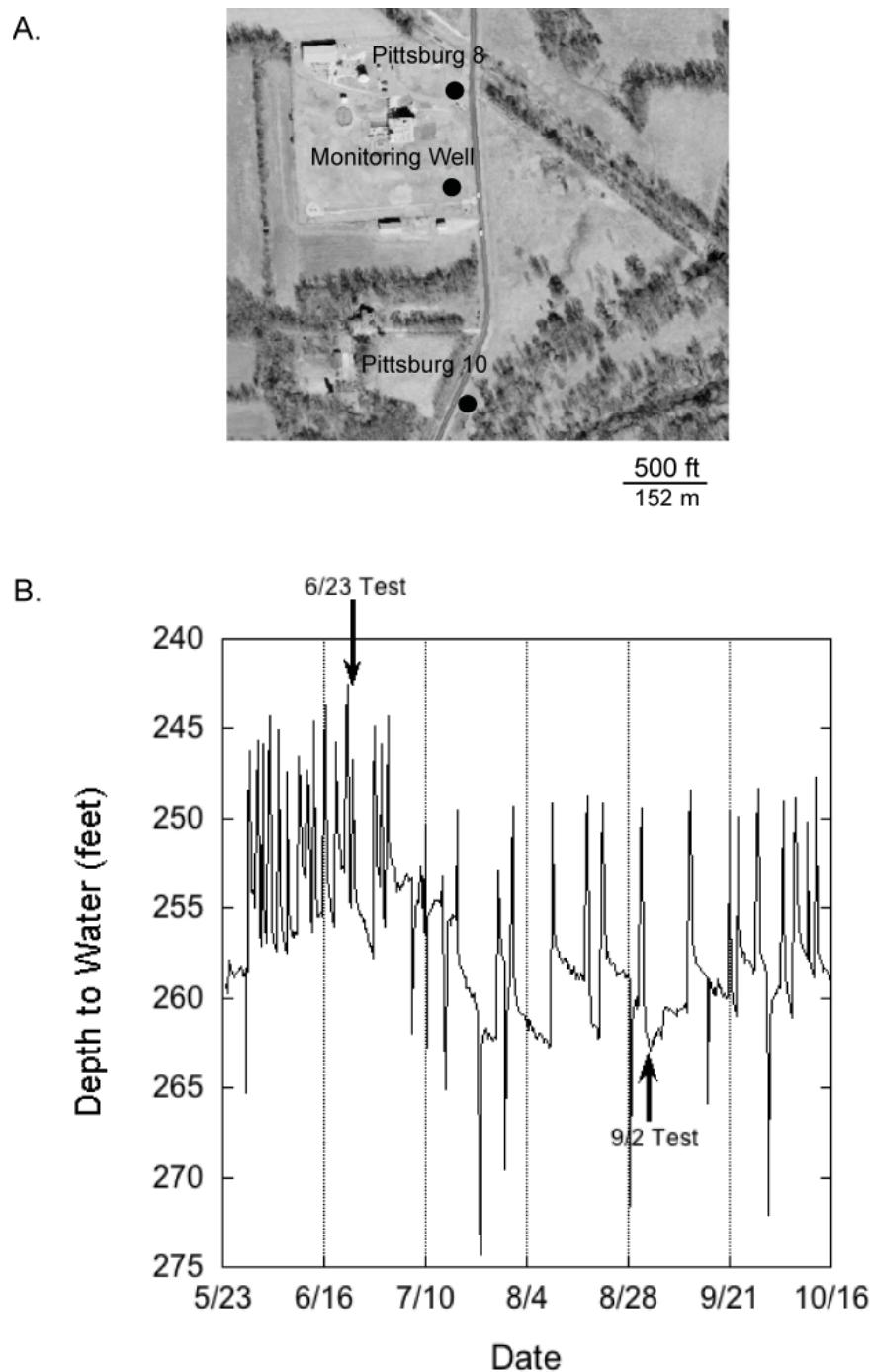


FIGURE 5—(A) Aerial photograph showing the location of the observation well (from which the hydrograph in B was generated) in relation to wells 8 and 10 in the city of Pittsburg, Kansas, field. (B) Hydrograph of the monitoring well completed in the Ozark aquifer in the Pittsburg well field showing depth to water from land surface. The arrows indicate the approximate start time of each chemical-quality pumping test.

Results

Monthly Sampling

The overall trend in the 2006–08 monthly samples from the Ozark and multi-aquifer wells collected during the study reflects spatial and temporal changes in water type across the Ozark transition zone described in Macfarlane and Hathaway (1987) from the 1979–1980 sampling events in the Tri-state region (tables 2, 4–13; fig. 6). Water samples from Pittsburg 8 and 10 and Crawford RWD 4 well 3 in the Ozark aquifer are a mixed cation-bicarbonate type with a TDS range of 478–551 mg/L. In contrast, water samples from the Cherokee County RWD 3 well 1 in the Ozark aquifer are a sodium-chloride type with a TDS range of 541–644 mg/L. In between these chemistries, water samples from Crawford Consolidated RWD 1 well 2 and Girard 3 fall into the mixed cation-mixed anion classification. TDS concentration ranges from 639–674 mg/L and 663–721 mg/L for the samples collected from Girard 3 and Crawford Consolidated RWD 1 well 2, respectively. The Crawford RWD 5 well 1 and the Weir city well are both multi-aquifer wells. Samples from Crawford RWD 5 well 1 are a mixed cation-bicarbonate type with a TDS range of 516–566 mg/L. Samples from the Weir city well are a mixed cation-bicarbonate type and range from more sodium rich to more calcium and magnesium rich with a TDS range of 396–497 mg/L. In contrast, the water type in the samples from another multi-aquifer well, Columbus 4, varies from a mixed cation-bicarbonate to a sodium-bicarbonate type with a TDS range of 466–617 mg/L. However, points on fig. 6 for the Columbus well 4 samples with higher bicarbonate and lower sulfate and chloride percentages fall within the ranges of bicarbonate

and sulfate and chloride percentages for the other two multi-aquifer wells.

Some of the monthly data sets exhibit linear trends on the modified Piper diagram in fig. 6, while others do not. Vertical trends in the data on fig. 6 for Pittsburg well 8, Crawford Consolidated RWD 1 well 2, and Crawford RWD 4 well 3 indicate that fluctuations in water quality could be primarily attributed to changes in the relative proportions of bicarbonate to sulfate + chloride concentrations in the water from one monthly sampling to the next. The linear trend in the data for Columbus well 4 indicates fluctuations in the relative proportions of both cations and anions, and the horizontal trend in the data for the Weir city well indicates primarily variations in the relative proportions of calcium + magnesium to sodium + potassium. Calcium/magnesium equivalent ratios of waters from all the monitored wells range from about 1.2 to 1.4.

Changes in Water Quality 1979–1980 to 2006–08

Six wells that were sampled for water quality in 1979–1980 (table 2) were included in the 2006–08 monthly sampling events (figs. 7–10). Comparison of the Crawford County water analyses from the 2006–08 events with those from 1979–1980 indicates significant changes in the quality and chloride concentrations of water produced by Pittsburg well 10 and Crawford Consolidated RWD No. 1 well 2. These wells are located within a regional cone of depression in the Ozark aquifer potentiometric surface (fig. 2; Macfarlane and Hathaway, 1987; Gillip et al., 2007).

TABLE 4—Water type and TDS concentration range for each of the nine wells sampled monthly from 2006–08.

Water Supply Well	Water Type	TDS Concentration Range (mg/L)	Number of Samples
Cherokee RWD 3 well 1	Sodium-chloride	541–644	20
Columbus well 4	Mixed cation-bicarbonate to sodium-bicarbonate	466–617	19
Crawford Consolidated RWD 1 well 2	Mixed cation-mixed anion	663–721	20
Crawford RWD 4 well 3	Mixed cation-bicarbonate	478–534	20
Crawford RWD 5 well 1	Mixed cation-bicarbonate	516–566	20
Girard 3	Mixed cation-mixed anion	639–674	20
Pittsburg 8	Mixed cation-bicarbonate	481–551	16
Pittsburg 10	Mixed cation-bicarbonate	516–545	3
Weir	Mixed cation-bicarbonate	396–497	18

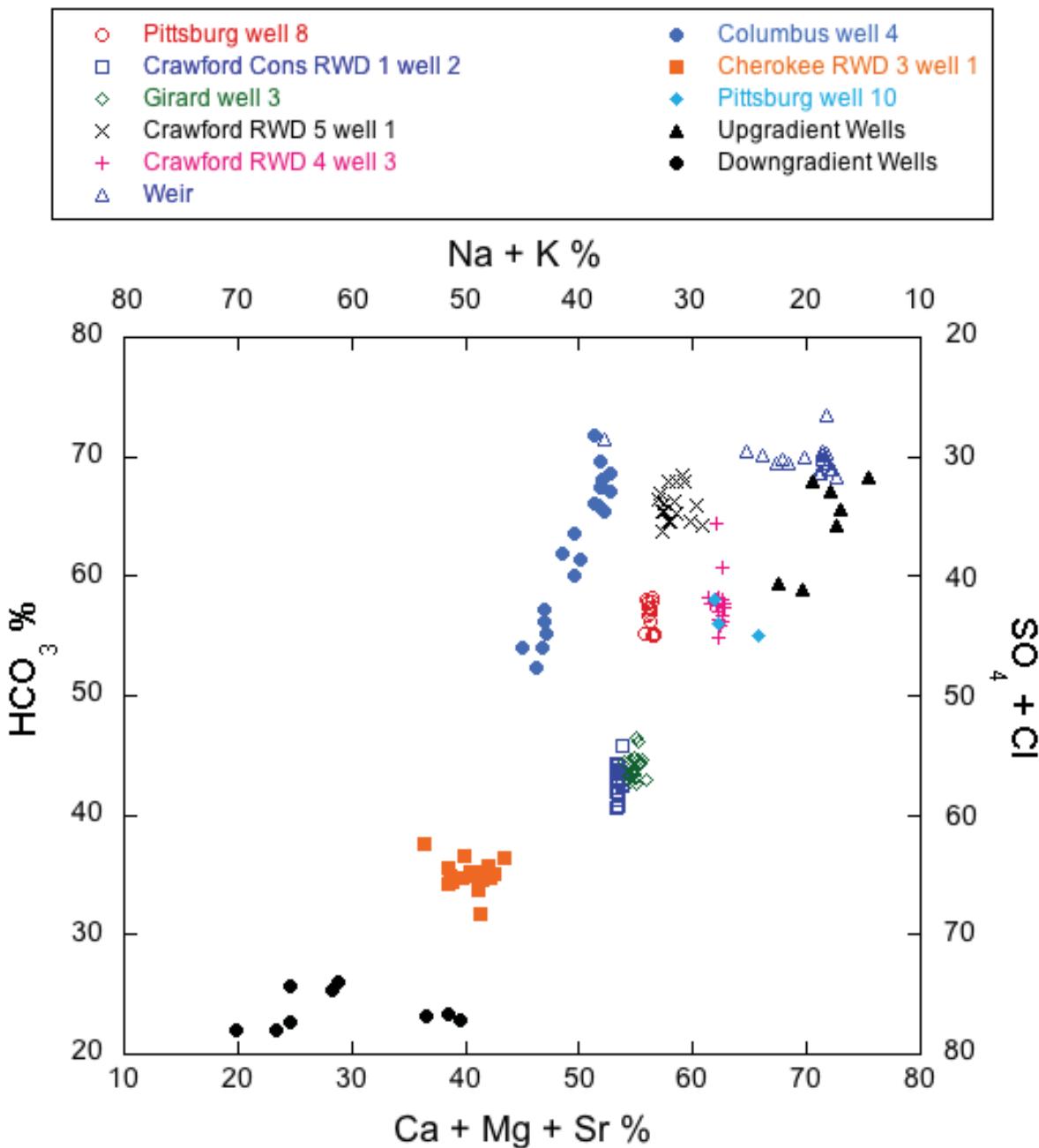


FIGURE 6—Plot of chemical data for the 2006–08 monthly series of water sampling events from the nine wells and for samples from downgradient wells with $>500 \text{ mg/L}$ chloride concentration and for upgradient and downgradient wells sampled in 1980 from Crawford and Cherokee counties on a modified Piper diagram. See Appendix 3 in Macfarlane and Hathaway (1987) for a complete tabulation of the sample analysis data from the upgradient and downgradient wells.

The analyses of water from the Crawford County Consolidated RWD No. 1 well 2 and Pittsburg well 10 (fig. 7) reveal slight changes in the relative amounts of calcium + magnesium + strontium and sodium + potassium but an increase in the relative amount of sulfate + chloride that is more pronounced. In all cases the chloride generally increased more than the sulfate concentration (fig. 9). The

average chloride concentration increased by about 50 mg/L from 1979–1980 to 2006–08 in water from both wells (from 40 to 90.7 mg/L for Pittsburg well 10 and 135 mg/L for a single sample from Crawford Consolidated RWD 1 well 2 in 1980 to 180 mg/L in 2006–08; fig. 9). However, this increase represented a doubling of chloride for the Pittsburg well but only about a 37% increase for the RWD

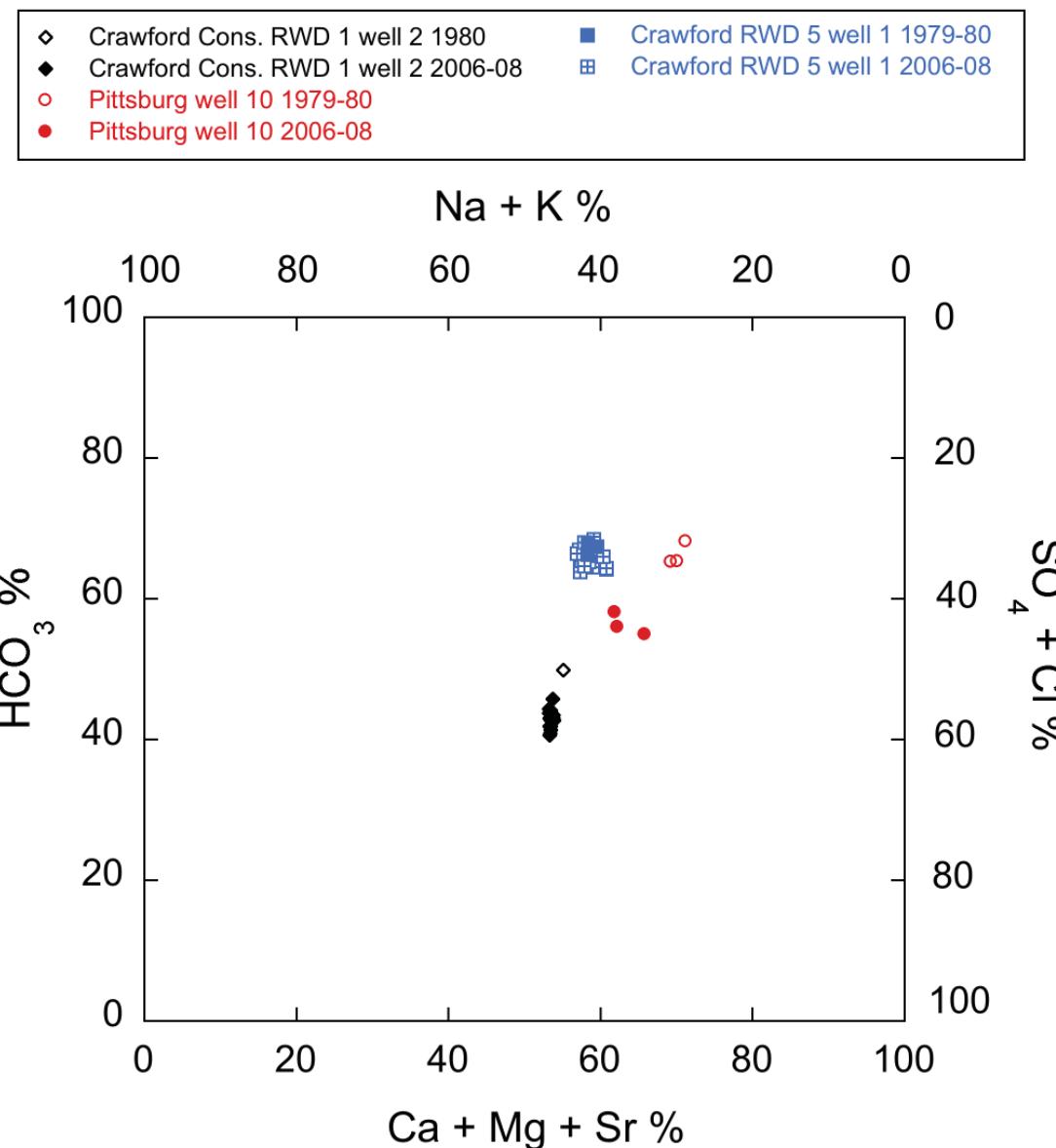


FIGURE 7—Plot of chemical data for the 1979–1980 and 2006–08 monthly series of water sampling events from Crawford County wells on a modified Piper diagram.

well. The average chloride increased for Crawford RWD 5 well 1 by about 11 mg/L from 1979–1980 to 2006–08 (from an average of 59 mg/L in 1979–1980 to 68 mg/L in 2006–08; fig. 9). The average sulfate concentration apparently did not change from 1979–1980 to 2006–08 for Crawford RWD 5 well 1 and Pittsburg well 10 (from an average of 76 mg/L in 1979–1980 to 78 mg/L in 2006–08 in Pittsburg well 10 and from 25 mg/L to 27 mg/L in Crawford RWD 5 well 1; fig. 9). Sulfate increased by 9 mg/L in water from Crawford Consolidated RWD 1 well 2 from 1980 to 2006–08 (from 87 mg/L in a single sample from 1980 to an average of 96 mg/L in samples from 2006–08; fig. 9).

TDS concentration remained unchanged but the range was narrower for the 2006–08 water samples than for the 1979–1980 samples from Pittsburg well 10 (from 446–601

mg/L in 1979–1980 to 516–545 mg/L in 2006–08; fig. 9). The TDS content increased from 365–487 mg/L in 1979–1980 to 516–566 mg/L in 2006–08 in water from Crawford RWD 5 well 1; (fig. 9). The average TDS concentration in water from Crawford Consolidated RWD 1 well 2 is almost 60 mg/L higher in the 2006–08 water samples than the single sample collected in 1980 (686 mg/L in 2006–08 and 625 mg/L in 1980 for the single sample; fig. 9).

In Cherokee County, the overall chemical quality of the water from the Weir city well and Cherokee RWD 3 well 1 apparently did not change significantly between 1979–1980 and 2006–08 (fig. 10). Assessment of change in the produced water from Columbus well 4 between 1979–1980 and 2006–08 is difficult because comparisons are being made between a single 1979–1980 analysis

TABLE 5—Chemical analyses of the monthly 2006–08 samples collected from Cherokee RWD 3 well 1.

Date Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
4/13/06	1081	7.60	590	44.4	21.9	136	7.5	1.32	220	39.6	211
5/15/06	1040	7.40	572	46.3	22.2	134	6.4	1.26	216	45.5	199
6/15/06	1010	7.45	559	45.9	22.3	130	6.2	1.21	212	43.2	195
7/13/06	1067	7.83	578	45.5	22.2	136	6.8	1.32	221	36.8	209
8/15/06	1140	8.00	592	44.1	21.8	142	8.3	1.38	224	42.7	210
9/19/06	1052	8.10	570	45.7	22.1	129	5.6	1.19	219	44.8	203
10/16/06	1021	7.52	562	46.8	22.5	133	6.0	1.31	209	40.0	198
11/21/06	1051	7.80	583	46.1	22.7	134	6.3	1.27	214	46.8	209
12/19/06	1011	8.00	564	46.5	22.6	129	5.8	1.19	213	42.9	200
1/26/07	1072	7.80	598	45.3	22.1	144	7.1	1.36	223	38.4	219
3/20/07	1137	7.90	618	46.0	22.5	149	6.7	1.30	239	47.2	217
4/1/07	1159	7.80	641	44.5	22.3	161	7.2	1.44	263	42.8	222
5/15/07	1163	7.95	644	47.2	22.8	152	7.3	1.50	243	47.5	235
6/1/07	1036	7.80	573	46.8	22.3	133	6.1	1.28	215	43.4	205
8/1/07	1031	7.34	558	47.8	22.8	129	6.0	1.24	210	44.5	193
10/1/07	1085	7.65	591	47.5	22.5	137	6.8	1.37	224	42.7	211
12/1/07	1145	7.90	545	49.5	23.4	129	6.0	1.23	211	31.9	189.
1/04/08	931	7.40	585	45.3	21.9	138	6.6	1.33	233	47.3	200
1/25/08	1015	7.41	571	46.8	22.7	131	6.1	1.25	222	41.9	201
2/28/08	1044	7.29	541	47.6	22.7	136	6.4	1.32	176	34.2	195

TABLE 6—Chemical analyses of the monthly 2006–08 samples collected from Columbus well 4.

Date Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
4/13/06	828	7.73	487	48.3	24.6	93.5	6.6	1.37	356	57.6	63.2
5/15/06	796	7.62	491	49.1	24.8	91.8	5.7	1.35	361	69.7	59.1
6/15/06	789	7.66	477	48.5	24.2	91.4	6.0	1.36	362	53.3	62.5
8/15/06	966	8.00	574	53.3	26.9	122	7.3	1.50	350	52.6	126
9/19/06	872	7.85	519	50.6	24.9	102	5.8	1.45	357	61.8	85.1
10/16/06	904	7.52	536	53.2	26.3	110	6.2	1.53	354	59.1	93.2
11/21/06	982	7.70	579	52.8	26.4	122	7.0	1.49	361	62.7	117
12/19/06	726	7.65	473	47.9	25.0	91.8	5.5	1.32	363	46.9	64.4
1/26/07	866	7.85	512	50.5	25.1	104	6.5	1.40	364	46.5	86.5
3/19/07	886	7.95	496	51.5	24.9	97	5.7	1.30	366	55.5	69.1
4/1/07	1037	7.80	594	54.8	27.0	127	6.6	1.59	356	54.5	136
6/1/07	815	7.70	470	50.1	24.9	91.0	5.2	1.38	362	47.0	61.4
8/1/07	980	7.20	573	53.6	25.7	121	7.0	1.54	361	66.3	108
10/1/07	1096	7.56	617	57.4	27.5	134	7.6	1.65	353	62.3	141
12/1/07	1102	7.58	612	55.0	27.2	137	7.0	1.59	364	54.6	140
1/04/08	787	7.45	530	52.0	25.4	111	6.8	1.48	362	54.7	88.8
1/25/08	776	7.62	466	48.7	24.6	94.4	5.7	1.37	374	39.3	56.0
2/28/08	806	7.42	469	50.8	24.8	94.9	6.2	1.44	359	43.0	59.4
5/15/08	829	7.75	484	51.6	25.3	93.3	5.4	1.41	361	55.1	62.3

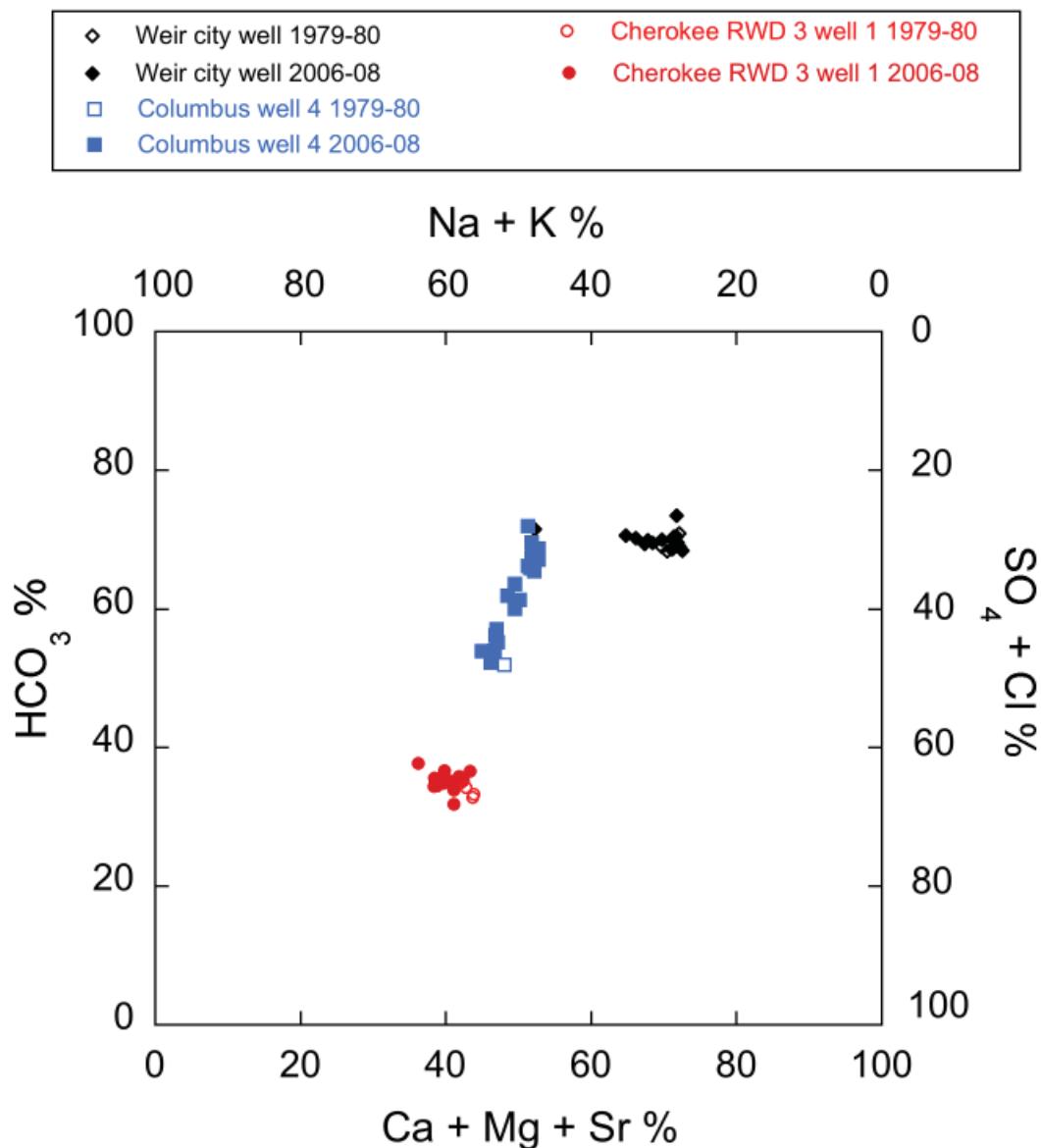


FIGURE 8—Plot of chemical data for the 1979–1980 and 2006–08 monthly series of water sampling events from Cherokee County wells on a modified Piper diagram.

and many 2006–08 analyses that exhibit wide month-to-month variability in dissolved constituent composition. However, based on the average chloride concentration in 2006–08 for water samples from Columbus well 4, the chloride apparently decreased from the 1979–1980 concentration level (from 119 mg/L for a single sample in 1979 to an average value of 88.3 mg/L in 2006–08; fig. 10). The change in the average chloride concentration in water from the Weir city well is within analytical error (from 37.3 mg/L in 1979–1980 to 38.5 mg/L in 2006–08; fig. 10). The average chloride concentration in water from Cherokee RWD 3 well 1 increased slightly from 198 mg/L in 1979–1980 to 206 mg/L in 2006–08 (about 4%; fig. 10). The largest change in the average sulfate concentration occurred in Columbus well 4 where it decreased about 30% from 78 mg/L in a single sample in 1979 to an average

concentration of 54.9 mg/L (fig. 10). The change in the average sulfate concentration in water from the Weir city well is within analytical error (from 60 mg/L in 1979–1980 to 61.4 mg/L in 2006–08; fig. 10). However, the average sulfate concentration in water from Cherokee RWD 3 well 1 increased from 35 mg/L in 1979–1980 to 42.2 mg/L in 2006–08 (about 20%; fig. 10).

Average TDS concentrations decreased in water from all Cherokee County wells, with the largest average decrease of about 30% in Columbus well 4 (from 743 mg/L in a single sample collected in 1979 to an average concentration of 524 mg/L in the 2006–08 samples; fig. 10). The average TDS concentration in water from the Weir city well decreased by about 16% between the 1979–1980 and 2006–08 series of sampling events (from 510 mg/L in 1979–1980 to 426 mg/L in 2006–08; fig. 10). A much

TABLE 7—Chemical analyses of the monthly 2006–08 samples collected from Crawford RWD 4 well 3.

Date Sampled	Sp. Con. (µS/cm)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
4/13/06	917	7.32	511	64.9	31.0	78.1	9.9	1.15	337	72.9	86.2
5/15/06	907	7.41	534	68.4	32.2	80.6	7.7	1.22	332	80.2	99.3
6/15/06	886	7.25	508	67.8	31.7	79.9	6.7	1.20	329	80.0	78.4
7/13/06	905	7.46	506	64.0	30.5	76.0	7.1	1.13	335	79.8	82.0
8/15/06	910	7.75	514	65.7	32.1	78.0	6.6	1.14	329	83.2	84.8
9/19/06	919	7.95	522	66.5	31.6	78.5	5.7	1.17	333	88.8	85.1
10/16/06	892	7.53	505	67.6	31.9	79.5	5.6	1.19	327	76.6	80.9
11/20/06	918	7.45	524	66.2	31.5	78.4	5.7	1.17	333	88.7	87.7
12/18/06	912	7.55	518	67.2	33.0	79.2	6.3	1.17	335	81.9	83.7
1/25/07	901	7.45	517	68.3	31.9	80.5	6.5	1.19	330	79.5	85.6
3/19/07	916	7.60	519	68.1	31.2	79.6	6.4	1.10	334	80.9	86.8
4/1/07	914	7.50	511	66.8	31.5	77.8	6.0	1.21	334	75.5	86.7
5/14/07	958	7.45	512	67.7	31.5	78.8	6.2	1.22	331	77.2	85.4
6/1/07	908	7.45	519	67.3	30.8	78.7	6.3	1.19	331	85.5	85.6
8/1/07	907	6.97	518	68.3	31.5	80.5	6.7	1.22	334	83.0	81.5
10/1/07	1319	7.26	517	68.2	31.4	80.4	6.6	1.21	337	79.4	83.1
12/1/07	925	7.21	504	71.2	33.6	83.2	6.7	1.26	336	60.8	81.4
1/4/08	773	7.13	515	68.0	29.7	80.1	6.5	1.18	334	83.6	80.4
1/25/08	875	7.16	513	67.8	31.0	80.1	6.5	1.20	331	77.8	84.5
2/27/08	893	6.82	478	67.9	31.5	80.4	6.7	1.21	337	58.9	64.7

TABLE 8—Chemical analyses of the monthly 2006–08 samples collected from Crawford RWD 5 well 1.

Date Sampled	Sp. Con. (µS/cm)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
4/13/06	680	7.62	545	46.9	21.0	66.7	4.3	0.64	291	26.7	69.7
5/15/06	665	7.54	531	47.1	20.8	63.7	4.3	0.63	287	32.1	65.0
6/15/06	660	7.40	538	46.9	21.0	65.5	4.0	0.64	290	26.1	73.4
7/13/06	680	7.70	516	48.4	21.3	59.7	3.8	0.62	275	29.4	67.3
8/15/06	651	7.90	520	47.1	21.2	61.0	4.2	0.61	279	27.9	68.5
9/19/06	709	7.95	538	47.0	20.7	64.2	3.4	0.63	293	32.0	67.1
10/16/06	662	7.42	523	49.4	21.5	61.1	3.2	0.63	279	31.3	66.8
11/20/06	692	7.60	556	48.0	21.6	69.3	3.9	0.66	296	30.8	74.7
12/18/06	682	7.80	540	46.4	21.0	66.9	4.0	0.64	295	29.2	66.3
1/25/07	684	7.65	544	47.0	21.7	68.5	4.0	0.64	296	18.6	77.2
3/19/07	691	7.80	541	47.1	20.9	66.8	4.1	0.60	293	31.4	66.8
4/1/07	675	7.60	525	49.0	21.9	62.3	3.6	0.64	286	22.4	69.0
5/14/07	705	7.75	535	48.4	21.2	67.6	3.9	0.67	285	31.1	67.6
6/1/07	694	8.00	541	49.2	21.6	70.7	4.0	0.69	296	19.2	70.6
8/1/07	685	7.16	546	48.0	21.1	69.6	4.2	0.68	297	31.1	64.2
10/1/07	686	7.45	566	48.9	22.4	65.9	3.9	0.64	319	29.5	65.6
12/1/07	692	7.51	534	49.7	21.7	69.3	4.1	0.68	293	22.5	63.4
1/4/08	579	7.22	525	48.0	20.9	65.7	3.8	0.65	285	29.1	62.9
1/25/08	654	7.28	527	48.5	21.4	65.8	3.8	0.66	292	22.9	63.4
2/27/08	660	7.10	522	48.4	21.3	64.0	4.0	0.64	290	22.8	60.9

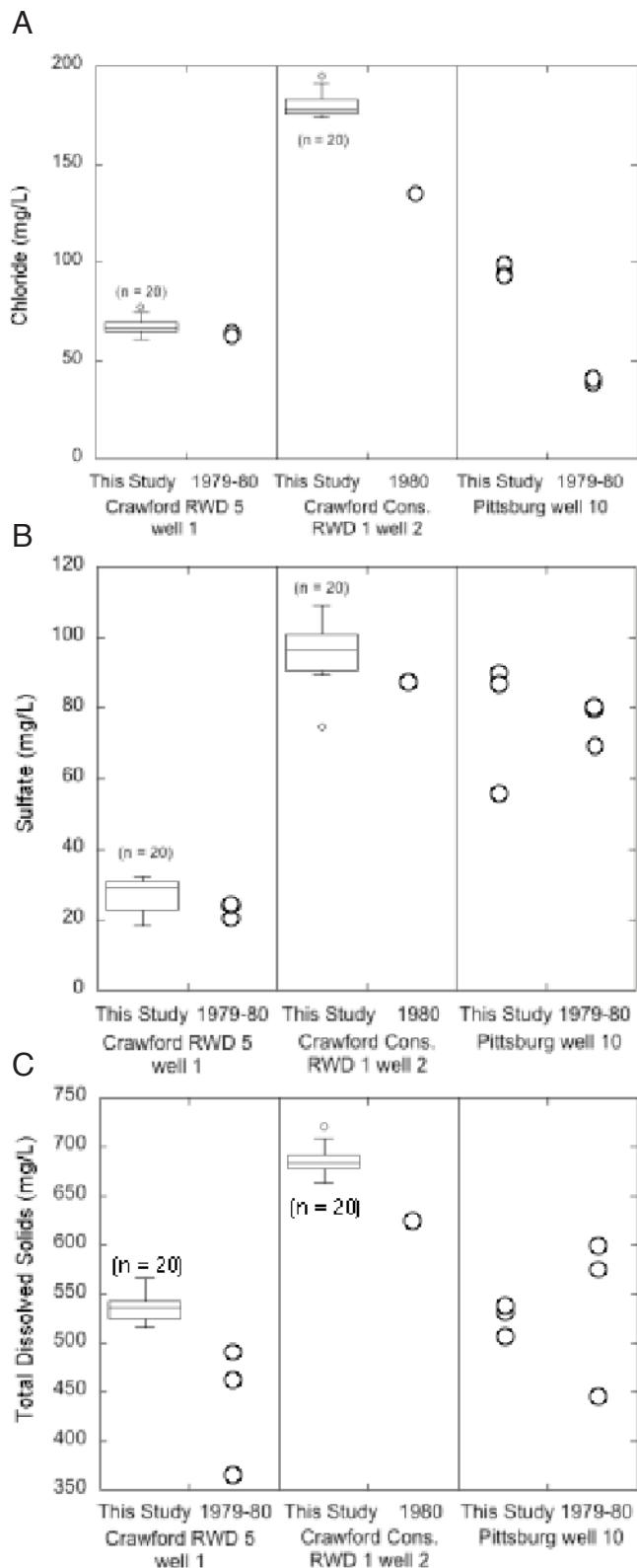


FIGURE 9—Box plot comparing the chloride, sulfate, and TDS concentrations of the 1979–1980 and 2006–08 water samples from wells in Crawford County.

smaller decrease in TDS concentration occurred in water from Cherokee RWD 3 well 1 from 594 mg/L in 1979–1980 to 582 mg/L from 2006–08 (fig. 10).

In general, the temporal chemical variations in water from individual wells represented on figs. 6–8 are smaller than the spatial chemical differences in water from the various wells. The grouping of all of the Ozark aquifer wells in southeast Kansas for which points are plotted on these figures is substantially different from the grouping of the sodium-bicarbonate type waters for wells in the Springfield Plateaus aquifer and of the sodium-chloride brines just to the west. Figure 6 includes points for waters from the Ozark Plateaus aquifer in Crawford and Cherokee counties that contained >500 mg/L when sampled during 1980; these points illustrate the trend towards lower bicarbonate and combined divalent cation (calcium, magnesium, and strontium) percentages and higher chloride and sulfate and monovalent cation (sodium and potassium) percentages. The points for these saline waters, Cherokee RWD 3 well 1, and Columbus 4 form a trend representing the mixing of ground water substantially affected by the Na-Cl type brine with freshwater of mixed cation-bicarbonate type. The group of points for the other wells in fig. 6 sampled in 2006–08 form a general trend of mixed cation-bicarbonate type waters with generally decreasing sodium and chloride concentrations that parallels the trend for the saline ground waters to Cherokee RWD 3 well 1 and Columbus well 4 freshwaters, but that is shifted to higher divalent cation percentages.

Chemical Quality Pumping Tests

Calcium, magnesium, sodium, and potassium concentrations decreased slowly with time in the June and September 2008 chemical-quality pumping tests for Pittsburg well 8 (fig. 11). In about the first 10 hours of both tests, the calcium/magnesium equivalent ratio fluctuated and then stabilized at approximately 1.34 until the end of the test. The bicarbonate concentration remained around $319 \text{ mg/L} \pm 6 \text{ mg/L}$ and $318 \text{ mg/L} \pm 2 \text{ mg/L}$ throughout the June and September tests, respectively. In the June test, the chloride and sulfate concentrations both generally decreased rapidly in the early part and then more gradually later in the test. In the September test, the chloride decreased during the first 10 hours of pumping and then leveled off at approximately 105 mg/L with some small fluctuation for the remainder of the test, while sulfate decreased slowly throughout the test. In both tests, the sulfate/chloride mass ratio trended towards lower values over time (fig. 12). In the June test, the sulfate/chloride ratio was in the range of 0.5 at the beginning of the test, but, in the September test, that ratio was somewhat less than 0.5 for most of the early part of that test. The bicarbonate/chloride mass ratio increased throughout the pumping period in the June test, but, in the September test, the ratio increased only during the first 10 hours and then

TABLE 9—Chemical analyses of the monthly 2006–08 samples collected from Crawford Consolidated RWD 1 well 2.

Date Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
4/13/06	1247	6.97	684	74.8	34.8	130	6.1	1.51	331	97.6	176
5/15/06	1247	7.06	686	76.1	35.2	128	7.4	1.48	323	99.9	178
6/15/06	1248	7.24	663	75.8	35.3	130	7.9	1.49	291	89.8	179
7/13/06	1233	7.31	689	75.3	35.2	129	7.5	1.48	334	91.1	184
8/15/06	1188	7.50	677	75.3	34.6	128	6.8	1.47	326	89.3	181
9/19/06	1229	7.50	688	74.3	34.8	127	6.7	1.46	325	106	177
10/16/06	1211	7.24	676	75.8	35.5	129	6.8	1.49	323	92.1	176
11/20/06	1250	7.30	679	74.0	34.5	127	6.9	1.45	326	96.5	178
12/18/06	1136	7.45	708	76.6	35.4	131	7.0	1.50	330	102	191
1/25/07	1223	7.30	682	75.6	34.6	130	7.4	1.45	324	90.5	183
3/19/07	1239	7.45	684	77.0	34.3	130	7.2	1.50	330	97.0	174
4/1/07	1255	7.20	721	77.0	35.3	131	7.1	1.54	334	109	195
5/14/07	1270	7.35	694	76.7	35.3	132	7.0	1.55	321	92.9	190
6/1/07	1137	7.35	680	77.6	35.1	132	7.1	1.56	328	89.4	176
8/1/07	1225	6.87	695	77.6	35.0	132	7.4	1.57	334	101	175
10/1/07	1245	6.93	681	74.6	34.1	125	7.0	1.49	327	97.8	180
12/1/07	1261	7.18	672	78.2	36.0	132	7.4	1.57	336	74.7	176
1/04/08	1055	7.09	676	77.6	35.6	133	7.5	1.56	294	101	175
1/25/08	1195	7.06	704	77.6	35.5	132	7.1	1.55	332	102	183
2/27/08	1221	6.60	690	77.8	35.4	133	7.5	1.56	335	95.9	174

TABLE 10—Chemical analyses of the monthly 2006–08 and other samples collected from Girard well 3.

Date Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
4/13/06	1157	7.34	639	71.0	33.0	113	7.4	1.33	323	90.0	153
5/15/06	1165	7.48	654	69.9	33.1	118	7.4	1.31	315	88.4	163
6/15/06	1112	7.30	674	72.9	32.9	113	7.3	1.36	314	99.0	153
7/13/06	1171	7.47	661	74.7	34.1	120	7.5	1.34	324	90.7	164
8/15/06	1108	7.65	656	72.3	33.2	115	7.2	1.33	313	98.9	155
9/19/06	1183	7.19	672	75.9	35.2	118	7.0	1.45	320	101	172
10/16/06	1144	7.62	651	74.4	33.9	118	6.3	1.35	313	95.2	155
11/20/06	1189	7.45	655	74.0	33.6	120	6.6	1.33	318	92.8	169
12/18/06	1145	7.65	656	75.4	34.9	121	7.0	1.38	320	97.2	179
1/25/07	1184	7.60	661	75.5	33.2	122	6.9	1.33	314	92.1	175
3/19/07	1181	7.80	673	75.7	33.1	120	6.8	1.30	320	95.6	165
4/1/07	1164	7.45	663	77.6	34.0	122	7.1	1.43	319	109	164
5/14/07	1221	7.60	639	75.3	34.1	123	6.5	1.39	309	90.2	168
6/1/07	1176	7.60	654	76.2	33.6	121	6.7	1.39	315	94.5	165
8/1/07	1162	6.95	654	76.1	34.1	122	7.0	1.43	320	96.9	160
10/1/07	1199	7.14	656	75.0	33.3	119	6.7	1.35	321	95.2	172
10/1/07	1204	7.20	639	76.5	34.3	124	6.9	1.39	322	96.5	174
10/1/07	1157	7.09	654	77.0	34.1	119	7.1	1.44	326	102	161
12/1/07	1203	7.33	674	78.9	35.2	124	7.0	1.43	321	68.9	164
1/04/08	991	7.30	661	76.4	34.0	120	7.0	1.40	319	99.3	159
1/25/08	1116	7.28	656	74.9	33.7	117	6.8	1.40	321	101	160
2/27/08	1164	6.97	672	76.1	33.7	123	7.0	1.39	321	94.7	161

TABLE 11—Chemical analyses of the monthly 2006–08 and other samples collected from Pittsburg well 8.

Date Sampled	Sp. Con. (µS/cm)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
4/13/06	875	7.41	499	57.4	26.1	87.4	5.2	0.95	318	50.1	97.5
5/15/06	911	7.43	517	61.4	27.9	90.7	6.6	0.97	315	56.1	107
6/15/06	857	7.42	495	58.3	26.5	88.9	5.3	0.95	316	45.8	103
7/13/06	897	7.47	509	59.1	26.9	88.8	6.1	0.95	322	47.0	111
8/15/06	854	7.80	503	58.5	27.2	90.0	5.5	0.94	311	42.3	115
9/19/06	913	7.75	516	59.2	27.0	88.9	4.6	0.95	319	57.9	109
11/20/06	965	7.15	551	64.6	30.5	98.0	5.7	1.02	318	61.6	122
12/18/06	907	7.75	514	59.3	27.5	90.3	5.0	0.95	319	46.4	117
1/25/07	894	7.60	512	59.2	26.9	91.4	5.1	0.95	316	49.6	112
3/19/07	900	7.60	515	59.7	26.5	89.1	5.2	0.90	319	55.2	110
3/20/07	883	7.95	498	59.0	26.2	88.5	4.9	0.90	319	47.2	103
3/20/07	882	7.80	506	58.6	26.0	87.7	5.0	0.90	318	54.4	106
4/1/07	889	7.50	484	56.1	25.7	85.0	4.7	0.93	319	38.6	106
5/14/07	904	7.60	494	58.7	26.2	88.1	4.9	0.96	315	42.6	107
10/1/07	955	7.72	542	74.8	32.0	78.1	6.0	1.07	335	82.2	92.4
12/1/07	991	7.24	535	65.6	29.9	92.6	5.2	1.01	319	49.2	125
12/1/07	958	7.26	519	63.5	28.9	92.4	5.2	1.01	319	44.7	116
12/1/07	933	7.31	510	62.0	28.4	91.3	5.1	0.99	320	42.9	112
12/1/07	918	7.31	506	62.6	28.2	92.6	5.2	1.00	319	41.0	108
12/1/07	903	7.35	498	61.1	27.6	91.6	5.3	0.99	320	38.9	104
1/25/08	754	7.17	503	59.4	26.0	89.8	5.2	0.97	314	53.2	103
1/25/08	858	7.31	500	58.7	26.0	88.5	4.9	0.96	319	48.0	106
2/27/08	873	7.13	481	57.8	26.0	87.7	5.1	0.95	321	37.5	97.2
2/27/08	874	7.17	495	57.9	26.3	88.3	5.2	0.96	323	45.3	101
2/27/08	875	7.21	493	58.3	26.6	89.2	5.2	0.97	321	44.8	98.9
2/27/08	875	7.13	506	58.8	26.7	89.9	5.2	0.98	322	53.2	102
2/27/08	872	7.16	495	58.6	26.5	89.4	5.1	0.97	322	45.5	99.4
2/27/08	875	7.18	502	60.2	27.3	91.8	5.3	1.00	322	45.5	102
2/27/08	874	7.16	488	57.5	26.2	88.0	5.2	0.96	318	45.0	98.3
2/28/08	869	7.16	495	58.7	26.5	89.7	5.3	0.98	320	45.7	100
2/28/08	874	7.16	498	59.0	26.7	90.3	5.3	0.98	321	45.5	101
2/28/08	873	7.20	494	58.2	26.4	88.9	5.2	0.97	322	45.4	99.5
2/28/08	873	7.18	499	59.3	26.8	91.0	5.3	0.99	321	45.2	101

TABLE 12—Chemical analyses of the monthly 2006–07 samples collected from Pittsburg well 10. Water from this well was sampled when Pittsburg well 8 was unavailable.

Date Sampled	Sp. Con. (µS/cm)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
10/16/06	873	7.23	516	59.2	27.0	88.9	4.6	0.95	319	57.9	109
6/1/07	910	7.40	537	75.0	32.3	73.3	5.6	0.99	327	90.3	88.9
8/1/07	934	6.96	545	75.2	32.4	78.4	6.0	1.07	333	86.3	90.8

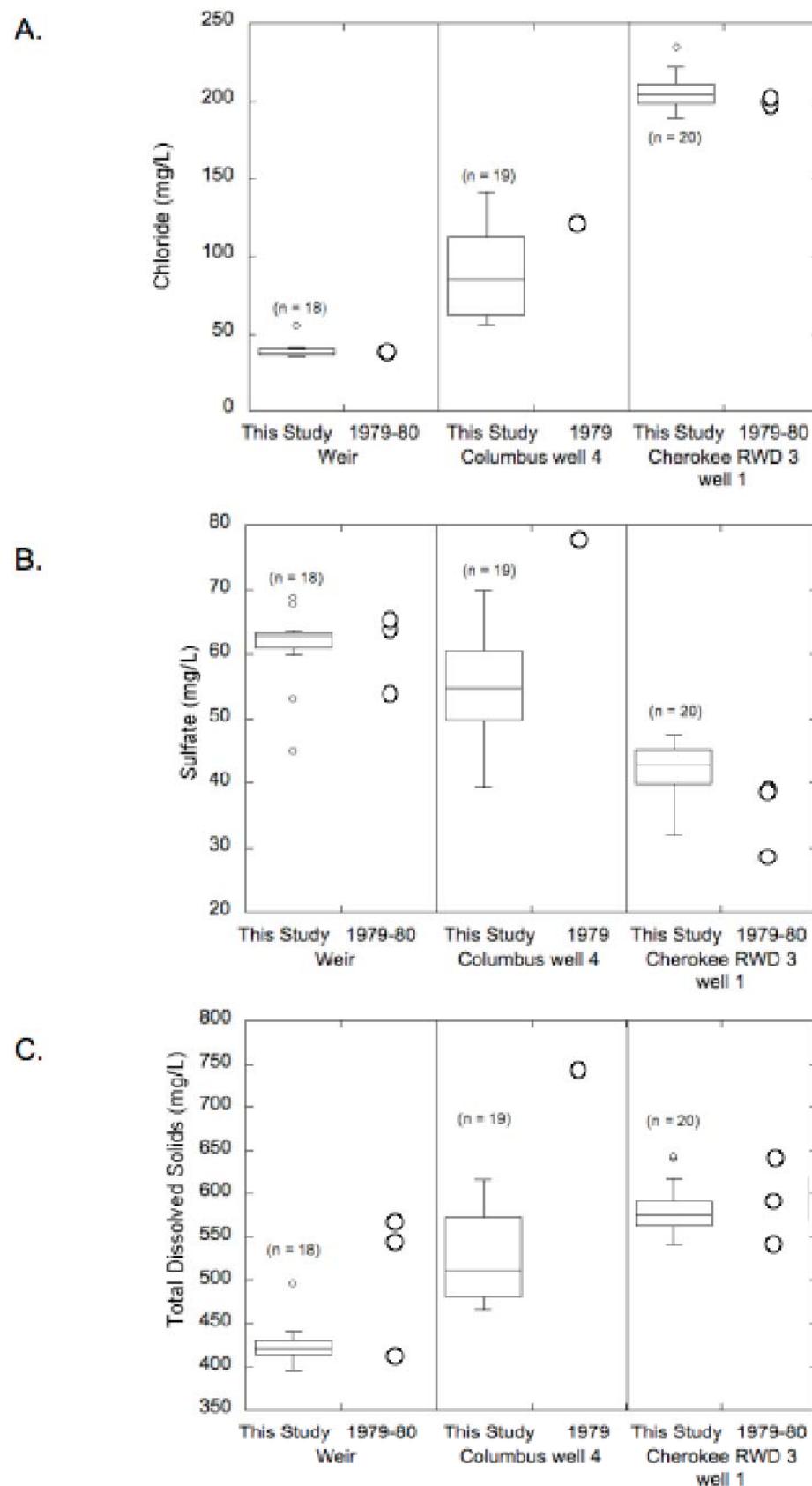


FIGURE 10—Box plot comparing the chloride, sulfate, and TDS concentrations of the 1979–1980 and 2006–08 water samples from wells in Cherokee County.

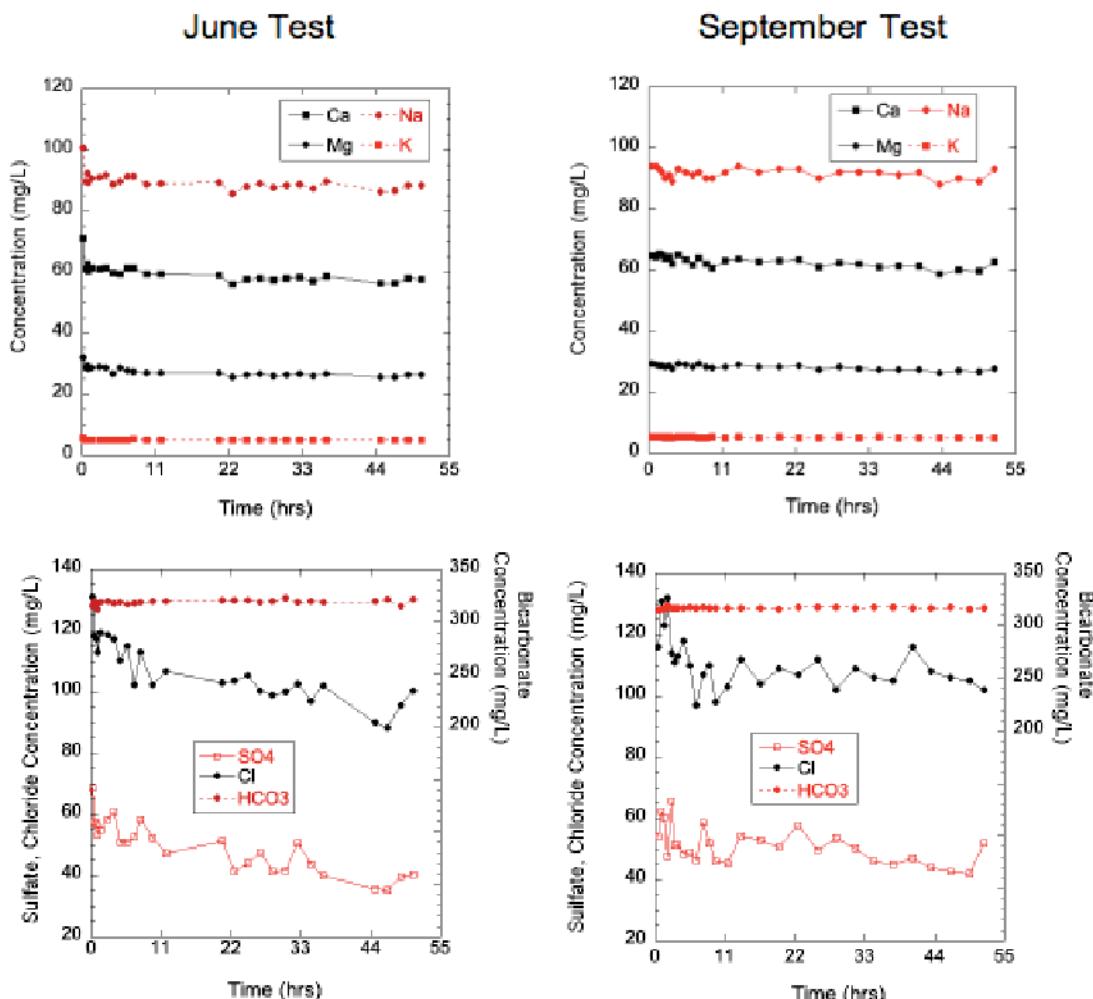


FIGURE 11—Temporal variations in the concentrations of selected major and minor constituents in water samples during the chemical-quality pumping tests of Pittsburg well 8 in June and September 2008.

was about 3 for remainder of the test (fig. 13). The TDS concentration decreased from 566 mg/L to 478 mg/L during the June test and from 543 mg/L to 484 mg/L during the September test.

The bicarbonate/(calcium + magnesium + strontium – sulfate) equivalent ratio is a measure of the amount of bicarbonate relative to that required to satisfy the calcium, magnesium, and strontium in the water that match up with carbonate mineral sources. The sulfate equivalent concentration is subtracted from the cation equivalent concentration to remove cation sources that match up with sulfate minerals. The (sodium + potassium)/chloride equivalent ratio is a measure of the amount of sodium + potassium relative to that required to satisfy the chloride equivalent concentration in the water. Because both ratios exceeded 1, they are defined as the excess bicarbonate and excess sodium + potassium ratios, respectively. In the June test, the lowest value of the excess bicarbonate ratio was near 1.1 in the very first sample but fluctuated between

about 1.2 and 1.3 for the remainder of the pumping period, while the excess sodium + potassium ratio varied but trended upward from 1.2 to around 1.4 to 1.5 (figs. 14 and 15). In the September test, the excess bicarbonate ratio fluctuated appreciably during the first 4 hours and then stabilized around 1.2. The excess sodium + potassium ratio also varied substantially in the first four hours of the test and then increased and fluctuated around a value of approximately 1.4 (fig. 15). The low excess bicarbonate and sodium indicated by the ratios suggest that a significant amount of sodium-bicarbonate water was not contributed from the Springfield Plateau aquifer to the Ozark aquifer while Pittsburg well 8 was pumping.

Mixing of Ground Waters from Differing Sources

Overall, the produced waters from the wells monitored in this project are mixtures of ground waters

TABLE 13—Chemical analyses of the monthly 2006–08 samples collected from the Weir city well.

Date Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
4/13/06	707	7.54	423	62.1	29.7	47.8	5.69	1.04	325	61.3	35.0
5/15/06	732	7.49	430	58.7	28.1	55.3	5.6	1.02	339	63.3	40.2
6/15/06	722	7.55	440	61.1	29.5	61.4	5.4	1.07	344	59.9	40.7
7/13/06	745	7.41	442	58.9	28.6	62.6	6.5	1.04	350	60.0	40.7
8/15/06	700	7.85	417	60.5	29.4	51.0	5.8	1.04	327	61.0	36.5
9/19/06	767	7.80	427	59.4	28.8	54.2	4.5	1.04	337	62.9	39.5
10/16/06	824	7.34	497	49.5	27.2	97.0	4.2	1.10	405	53.0	55.0
11/21/06	707	7.45	421	61.8	30.8	46.1	4.9	1.02	325	67.8	37.4
12/18/06	726	7.65	432	59.6	29.9	56.6	5.1	1.03	339	62.2	39.0
1/26/07	720	7.50	414	62.8	29.1	46.5	5.5	1.04	323	62.9	35.9
3/19/07	720	7.80	424	61.7	28.8	48.1	5.2	1.00	329	68.7	36.7
4/1/07	708	7.45	414	61.7	29.6	46.0	5.1	1.07	322	63.6	37.5
5/14/07	723	7.50	414	63.7	29.3	47.0	5.2	1.07	319	62.6	37.0
6/1/07	679	7.60	421	62.9	29.4	48.8	5.2	1.07	325	63.2	39.9
8/1/07	701	7.21	421	63.0	29.4	48.3	5.3	1.07	334	62.9	35.2
10/1/07	718	7.46	426	63.0	29.5	47.3	5.6	1.06	341	63.7	36.4
12/1/07	744	7.36	396	61.7	29.1	46.5	5.3	1.05	327	45.0	35.5
1/25/08	614	7.30	409	61.4	27.9	46.3	5.4	1.03	321	62.2	35.1

TABLE 14—Chemical analyses of samples collected during the June 2008 chemical-quality pumping test for Pittsburg 8.

Date/Time Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	T ($^{\circ}\text{C}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
6/23/2008 11:01:00	968	22.5	6.89	566	70.9	32.1	100.8	5.8	1.10	315	68.8	131
6/23/2008 11:16:00	938	22.1	6.99	519	60.9	28.6	89.7	4.9	0.97	320	57.6	119
6/23/2008 11:31:00	935	22.1	6.93	521	62.7	29.2	92.2	5.1	1.00	318	56.6	118
6/23/2008 11:46:00	931	22.1	6.99	505	60.5	28.3	89.4	5.0	0.97	312	53.4	113
6/23/2008 12:14:00	922	22.4	6.97	519	61.2	28.8	90.7	5.0	0.98	319	55.1	119
6/23/2008 13:21:00	917	23.0	6.95	522	61.1	28.9	91.0	5.1	0.99	320	58.3	118
6/23/2008 14:21:00	919	22.8	6.94	523	61.2	28.8	91.7	5.1	1.00	318	60.9	117
6/23/2008 15:21:00	914	22.8	6.96	500	59.6	26.6	88.8	5.0	0.95	319	50.9	110
6/23/2008 16:29:00	906	22.8	7.04	506	59.4	28.6	89.8	4.9	0.98	317	50.9	115
6/23/2008 17:29:00	902	22.8	7.05	499	61.5	27.8	91.3	5.0	0.98	318	52.8	103
6/23/2008 18:29:00	894	22.6	7.10	515	61.4	27.4	91.4	5.2	0.99	319	58.5	113
6/23/2008 20:29:00	896	22.2	7.00	494	59.4	27.0	88.8	5.1	0.96	320	52.3	103
6/23/2008 22:29:00	888	21.7	7.01	493	59.3	26.9	88.9	5.1	0.97	320	47.2	107
6/24/2008 7:19:00	878	20.7	7.02	494	59.0	27.0	89.5	5.1	0.97	321	51.4	103
6/24/2008 9:19:00	874	21.4	6.99	477	56.1	25.8	85.6	4.9	0.92	321	41.5	104
6/24/2008 11:19:00	873	22.1	7.07	486	57.8	26.4	88.0	5.0	0.95	321	43.9	105
6/24/2008 13:19:00	876	22.6	7.05	485	58.1	26.6	88.9	5.0	0.96	319	47.7	100
6/24/2008 15:19:00	876	22.2	6.89	475	57.3	26.1	87.7	4.9	0.95	320	41.5	99
6/24/2008 17:19:00	872	22.3	6.99	450	58.0	26.4	88.3	5.0	0.96	323	41.6	99.9
6/24/2008 19:19:00	871	21.9	6.93	490	58.3	26.6	88.8	5.1	0.97	319	50.6	103
6/24/2008 21:19:00	869	21.8	6.99	475	57.1	26.0	87.3	5.0	0.95	320	43.8	97.1
6/24/2008 23:19:00	863	21.8	6.97	480	58.7	26.6	89.6	5.1	0.98	319	39.9	102
6/25/2008 7:28:00	866	21.1	6.95	458	56.2	25.8	86.3	5.0	0.93	320	35.6	89.9
6/25/2008 9:28:00	865	21.5	6.94	457	56.5	25.8	86.8	5.0	0.94	322	35.3	88.2
6/25/2008 11:28:00	865	22.3	6.96	470	58.1	26.3	88.5	5.1	0.96	315	39.8	95.6
6/25/2008 13:28:00	871	22.4	7.04	478	57.6	26.3	88.4	5.0	0.96	322	40.2	101

TABLE 15—Chemical analyses of samples collected during the September 2008 chemical-quality pumping test for Pittsburg 8.

Date/Time Sampled	Sp. Con. ($\mu\text{S}/\text{cm}$)	T ($^{\circ}\text{C}$)	pH	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)
9/2/2008 9:40:00	975	22.0	7.2	520	64.7	29.2	94.0	5.3	1.04	315	53.9	116
9/2/2008 10:10:00	974	21.9	7.11	543	64.4	29.1	94.0	5.2	1.04	316	62.2	131
9/2/2008 10:40:00	972	22.0	7.32	533	65.5	28.6	93.0	5.3	1.01	316	60.4	123
9/2/2008 11:10:00	969	22.8	7.26	529	65.0	28.7	92.0	5.2	1.00	320	47.6	132
9/2/2008 11:40:00	970	23.3	7.17	524	63.6	28.5	90.0	5.1	0.98	317	65.7	114
9/2/2008 12:10:00	968	23.8	7.11	509	64.3	28.8	91.0	5.2	0.99	317	51.3	111
9/2/2008 12:40:00	928	23.6	7.09	505	62.0	27.7	89.0	5.0	0.96	317	51.2	113
9/2/2008 13:40:00	933	23.4	7.15	517	65.0	29.5	93.0	5.2	1.01	317	48.5	118
9/2/2008 14:40:00	961	23.5	7.17	507	63.5	29.0	92.0	5.2	0.99	318	49.0	110
9/2/2008 15:40:00	931	23.3	7.02	487	61.7	28.4	91.0	5.3	0.94	317	46.3	97
9/2/2008 16:40:00	956	23.3	7.11	514	64.0	29.2	92.0	5.1	1.01	318	58.6	107
9/2/2008 17:40:00	953	23.0	7.15	505	61.9	28.5	90.0	5.0	0.98	317	51.9	110
9/2/2008 18:40:00	950	22.4	7.18	485	60.6	28.1	90.0	5.3	0.92	317	46.0	98
9/2/2008 20:40:00	927	21.3	7.13	494	63.0	28.5	92.0	5.1	1.00	317	45.3	103
9/2/2008 22:40:00	945	21.3	7.14	516	63.8	28.9	94.0	5.2	1.02	317	54.3	112
9/3/2008 1:40:00	937		7.18	503	62.7	28.5	92.0	5.1	1.00	317	52.9	104
9/3/2008 4:40:00	928		7.24	506	63.1	28.3	93.0	5.2	1.01	316	50.8	109
9/3/2008 7:40:00	916	19.4	7.21	513	63.3	28.7	93.0	5.1	1.02	318	57.6	107
9/3/2008 10:40:00	926	20.6	7.27	503	61.1	27.5	90.0	5.0	0.99	318	49.6	112
9/3/2008 13:40:00	928	20.6	7.28	501	62.3	28.4	92.0	5.3	1.00	318	53.6	102
9/3/2008 16:40:00	918	20.3	7.27	503	61.9	27.6	92.0	5.1	1.00	317	50.3	109
9/3/2008 19:40:00	919	20.2	7.30	496	60.9	27.5	92.0	5.4	0.99	318	46.1	106
9/3/2008 22:40:00	913	20.1	7.29	493	61.3	27.2	91.0	5.1	0.99	318	45.1	105
9/4/2008 1:40:00	910		7.33	506	61.5	27.5	92.0	5.1	1.00	317	46.9	116
9/4/2008 4:40:00	913		7.34	487	58.8	26.2	88.0	4.9	0.95	317	44.0	108
9/4/2008 7:40:00	908	20.3	7.34	489	60.0	27.0	90.0	5.0	0.98	318	42.6	106
9/4/2008 10:40:00	910	20.1	7.28	484	59.6	26.8	89.0	5.0	0.97	316	42.0	105
9/4/2008 12:57:00	907	21.6	7.32	500	62.6	27.8	93.9	5.1	1.02	317	52.1	102

from 1) sodium-chloride brine and calcium, magnesium-bicarbonate freshwater sources in the Ozark aquifer (fig. 1); 2) the Ozark and Springfield Plateau aquifers in multi-aquifer wells; and 3) zones within the Ozark aquifer, each with its own ground-water chemistry (Macfarlane and Hathaway, 1987). Downward leakage from the overlying Springfield Plateau aquifer, though probably minor, may also mix with Ozark aquifer ground water in areas where the confining layer is fractured, thin, or absent. The relative amount contributed by each of these sources depends on well location within the transition zone, well construction, intensity and duration of pumping, and thickness and degree of fracturing of the confining layer separating the Ozark from the Springfield Plateau aquifer where it has not been eroded.

Produced water type generally becomes increasingly more sodium and chloride rich with increasing distance down the hydraulic gradient from the eastern, fresh-

transition zone boundary (fig. 1). This relationship is most clearly illustrated in the plots of chloride versus the bicarbonate/chloride ratio and chloride versus the (sodium + potassium)/chloride ratio for the wells sampled in this project (figs. 16 and 17). Both plots show two outer mixing lines that bound regions where points plot for published and unpublished analyses of Ozark aquifer water samples collected in 1979–1980 from the Tri-state region (Macfarlane and Hathaway, 1987). Points for saline waters (with chloride concentration >500 mg/L) collected in 1980 from downgradient wells in the Ozark Plateau aquifer in Crawford and Cherokee counties and from low-chloride upgradient wells in southwestern Missouri are also plotted in figs. 16 and 17. The dashed line in fig. 16 represents a mixing curve fitted to the water-chemistry data from the upgradient and downgradient end members. This mixing curve plots within the region defined by the two bounding curves, and with the exception of Cherokee

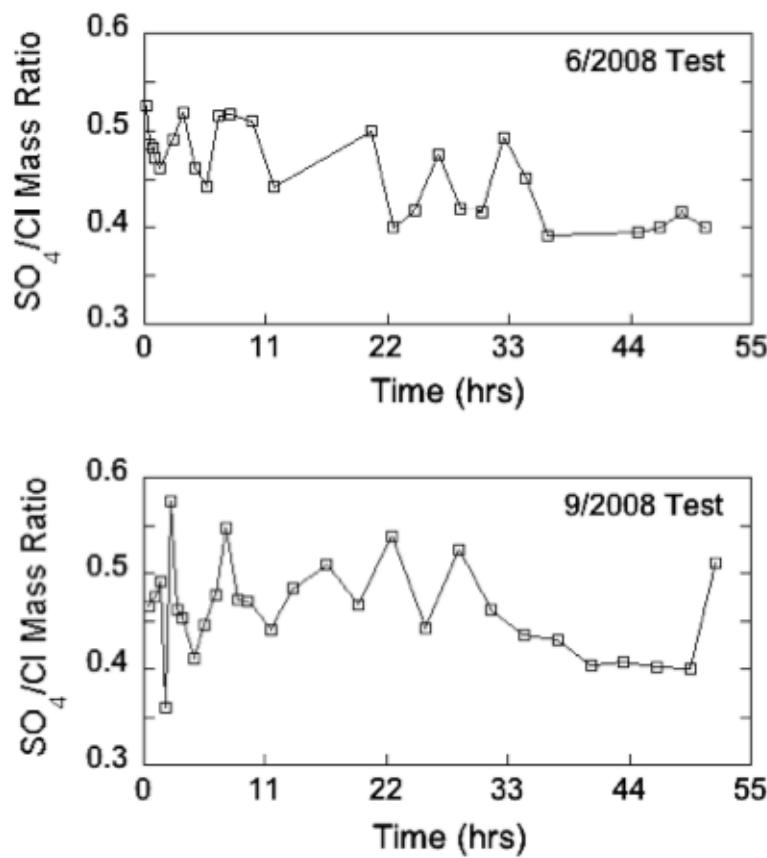


FIGURE 12 (left)—Temporal variations in the SO_4/Cl mass ratio in water samples during the chemical-quality pumping tests of Pittsburg well 8 in June and September 2008.

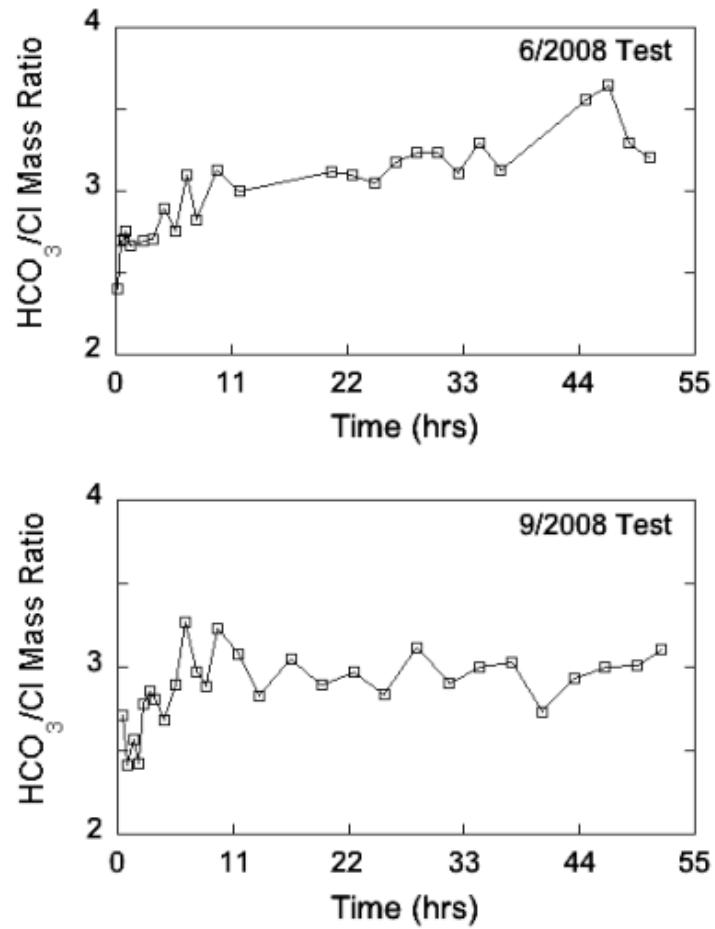


FIGURE 13 (right)—Temporal variations in the HCO_3/Cl mass ratio in water samples during the chemical-quality pumping tests of Pittsburg well 8 in June and September 2008.

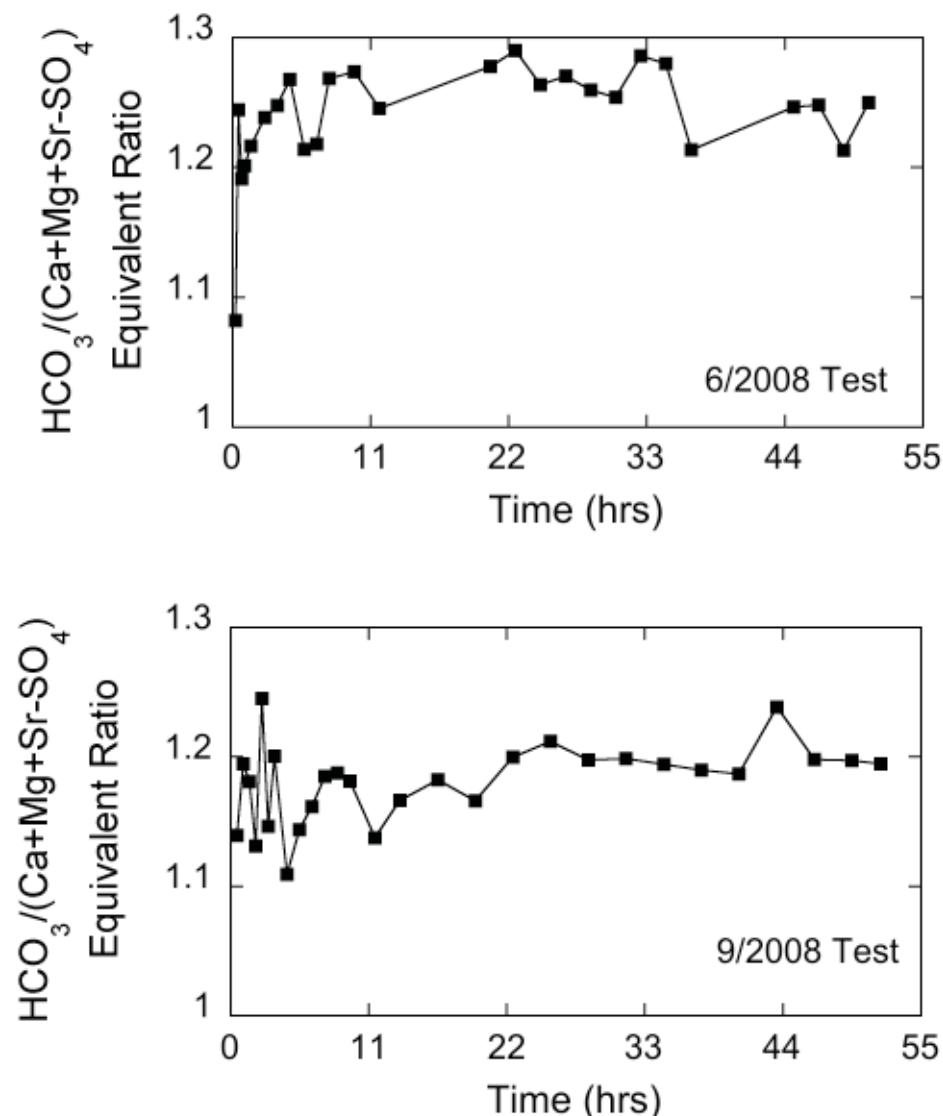


FIGURE 14—Temporal variations in the bicarbonate/(calcium + magnesium + strontium – sulfate ratio) in water samples during the chemical-quality pumping tests of Pittsburg well 8 in June and September 2008.

RWD 3 well 1, points for all the Ozark well samples fall along it. A decrease in the bicarbonate to chloride ratio with an increase in the chloride concentration from the Crawford RWD 4 well 3 and Pittsburg well 10 to Girard well 3 and Crawford Consolidated Rural Water District 1 well 2 demonstrates a progressive westward change in water type across southeastern Crawford County. The data from multi-aquifer wells plot very close to or directly on the dashed mixing curve line, which suggests that the relative contribution of water from the Springfield Plateau aquifer to these wells is minor. In fig. 17, the (sodium + potassium)/chloride equivalent ratio approaches 1 as the chloride concentration increases to 200 mg/L. However, for reasons discussed later in this section, many of the monthly data sets do not plot parallel to the bounding mixing curves for the 1979–1980 data.

Addition of the historic data from the 1979–1980 period to the chloride versus bicarbonate/ratio plot

of fig. 16 provides a means of evaluating changes in water chemistry over time in the context of the mixing of water within the Ozark aquifer transition zone (fig. 18). Differences among the sets of data collected from this project and the historic data indicate that the most significant changes in Ozark aquifer chemistry occurred in the waters produced from Pittsburg 10 and Crawford Consolidated RWD 1 well 2, with little if any change in the water pumped by Cherokee RWD 3 well 1 (fig. 18). For the Crawford RWD 5 well 1 multi-aquifer well, a slight shift in the monthly data toward higher chloride relative to the historic data suggests only a minor change in water quality with respect to chloride and bicarbonate. The quality of the produced water from the other multi-aquifer wells does not appear to have changed significantly between the two sampling periods.

Within the transition zone, the sulfate/chloride ratio generally decreases with increasing chloride

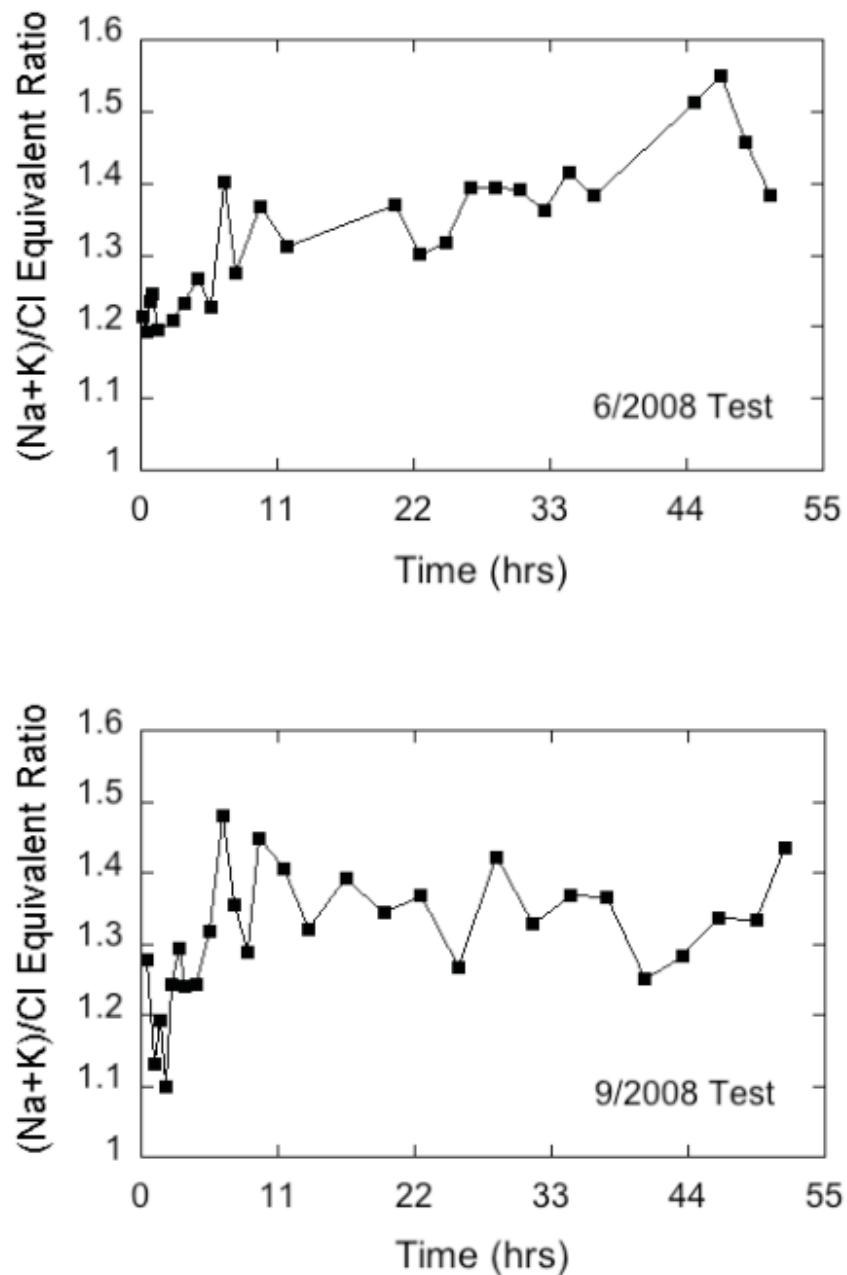


FIGURE 15—Temporal variations in the (sodium + potassium)/chloride ratio in water samples during the chemical-quality pumping tests of Pittsburg well 8 in June and September 2008.

concentration (fig. 19) as mixing with sodium-chloride type water increases down the hydraulic gradient towards the Cherokee basin brines. In addition, the sulfate concentration generally decreases as hydrogen sulfide concentration increases (Macfarlane and Hathaway, 1987). This relationship is thought to reflect a lateral change within the Ozark aquifer toward more chemically reducing conditions. Although, in aggregate, the monthly sample data generally follow a pattern of decreasing sulfate/chloride ratio with increasing chloride concentration, only the Weir city well and Columbus well 4 monthly data had a substantial change in chloride concentration that followed the overall trend of points in fig. 19.

Data from the water-quality pumping tests also suggest that zones of differing water quality within the aquifer contribute water to a pumping well at different rates throughout a single pumping period. It is also possible that the quality of water produced by individual zones may change without a change in the relative amount contributed to the well during pumping. Figure 20 is a plot of the bicarbonate/chloride ratio versus chloride concentration for the samples from both pumping tests plotted with the same mixing curve as the dashed line on fig. 16. The plot shows an excellent fit between the data and the chloride-bicarbonate mixing curve. The trend of the plotted pumping test chloride and the (sodium + potassium)/chloride ratio

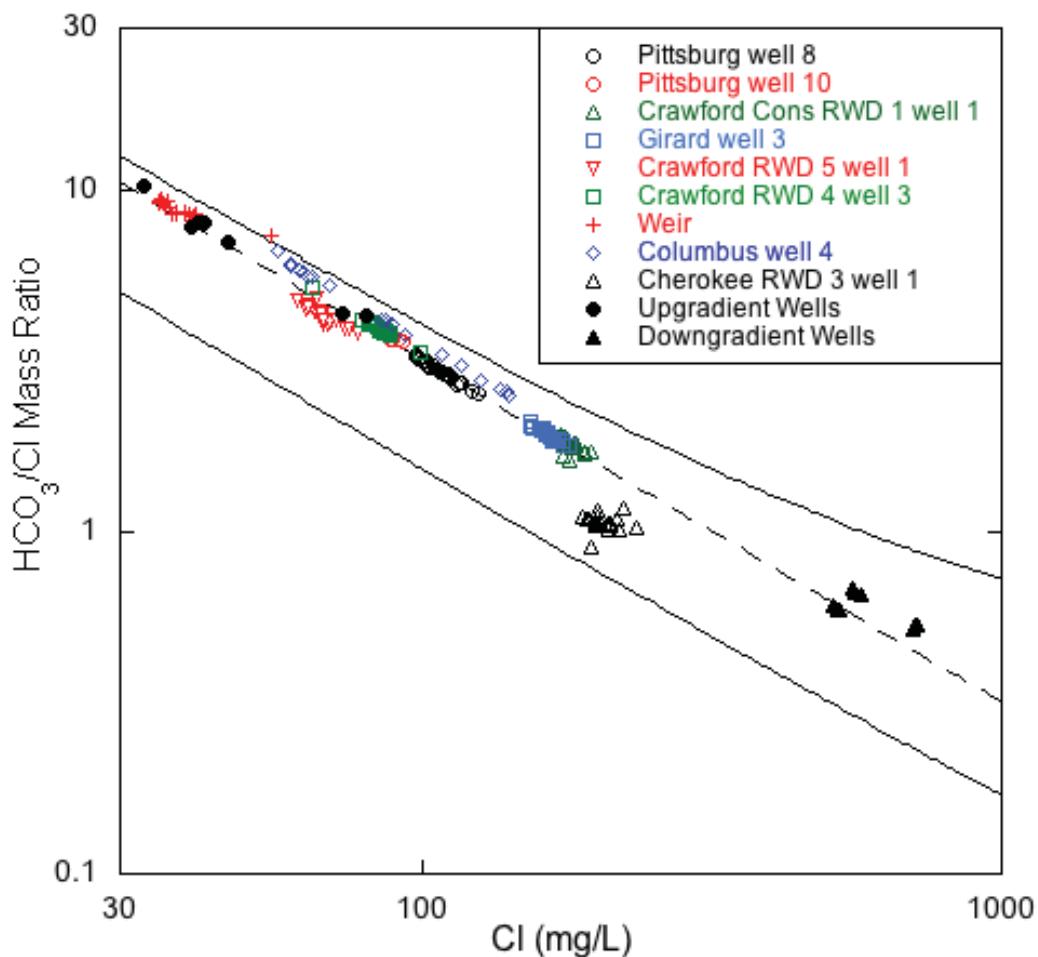


FIGURE 16—Chloride concentration versus bicarbonate/chloride ratio for the monthly samples of 2006–08 and for samples from upgradient and downgradient wells sampled in 1979–1980 from Crawford and Cherokee counties and adjacent southwestern Missouri. The solid lines are curves that describe the mixing curves that bound where points would plot for the 1979–1980 sample data for the Tri-state region and the dashed line is a mixing curve based on a low-chloride end member for the freshest waters from the 2006–08 monthly data and a high-chloride end member for the middle of the group of the saline waters. The curves describe the mixing of various proportions of waters from the low TDS concentration, calcium, magnesium-bicarbonate province and the high TDS, sodium-chloride sources.

values follows well the trend of the monthly data for Pittsburg 8 and many of the other supplies sampled, but not as well as the overall trend of the data from the 1979–1980 samplings (fig. 21). The ranges of the bicarbonate to chloride and sodium + potassium to chloride ratios and the chloride concentration values are greater for the samples from the pumping tests than for the Pittsburg well 8 monthly samples. The differences in trend between the regional 1979–1980 data sets and the monthly data and the high degree of variability of the sodium + potassium/chloride ratios over the pumping period are both consistent with time varying amounts of these constituents being contributed to the open borehole from different zones each with its own water chemistry.

Springfield Plateau aquifer wells located above the Ozark aquifer transition zone in southeast Kansas and

southwest Missouri produce sodium-bicarbonate type water (Darr, 1978; Macfarlane and Hathaway, 1987). Macfarlane and Hathaway (1987) noted that water samples from some of the multi-aquifer wells within the bounds of the Ozark aquifer transition zone contained bicarbonate in excess of that required to satisfy the equivalent carbonate contribution of calcium, magnesium, and strontium in the sample. The excess bicarbonate ratio is about the same for both the Ozark and multi-aquifer wells, but the excess sodium + potassium ratios are generally higher for the multi-aquifer wells. Excess sodium + potassium values range from about 1.5 to almost 3 in samples from the multi-aquifer wells and 1 to about 1.5 for samples from the Ozark wells. The lower values for the Ozark well samples suggest that leakage across the confining unit is at most minor.

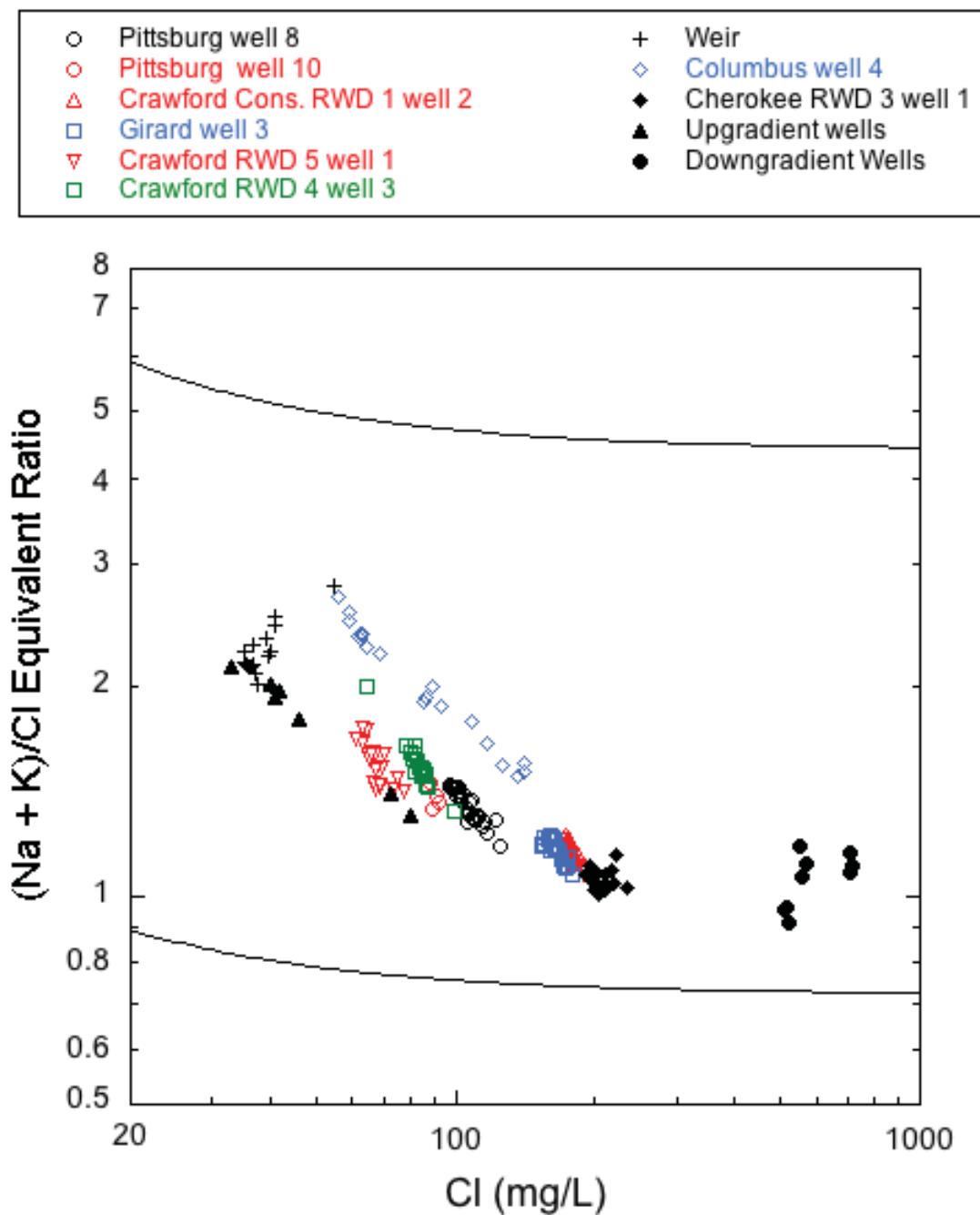


FIGURE 17—Chloride concentration versus sodium/chloride ratio values for the monthly samples of 2006–08 and for samples from upgradient and downgradient wells sampled in 1979–1980 from Crawford and Cherokee counties and adjacent southwestern Missouri. The solid lines are curves that describe the mixing curves that bound where points would plot for the 1979–1980 sample data for the Tri-State region. The curves describe the mixing in various proportions of waters from the low TDS concentration, calcium, magnesium-bicarbonate province and the high TDS, sodium-chloride province.

Discussion

The vertical variation in water quality in any well within the transition zone ultimately depends on the amount of mixing that has occurred over long periods between the inflowing low TDS freshwater from recharge areas in southwest Missouri and the resident sodium-chloride

brines to the west in the Cherokee basin (Macfarlane and Hathaway, 1987). The plots in figs. 11–15 for the Pittsburg well 8 pumping tests imply that waters of differing quality are contributed from different parts of the aquifer at different rates to the well during pumping. Changes in the

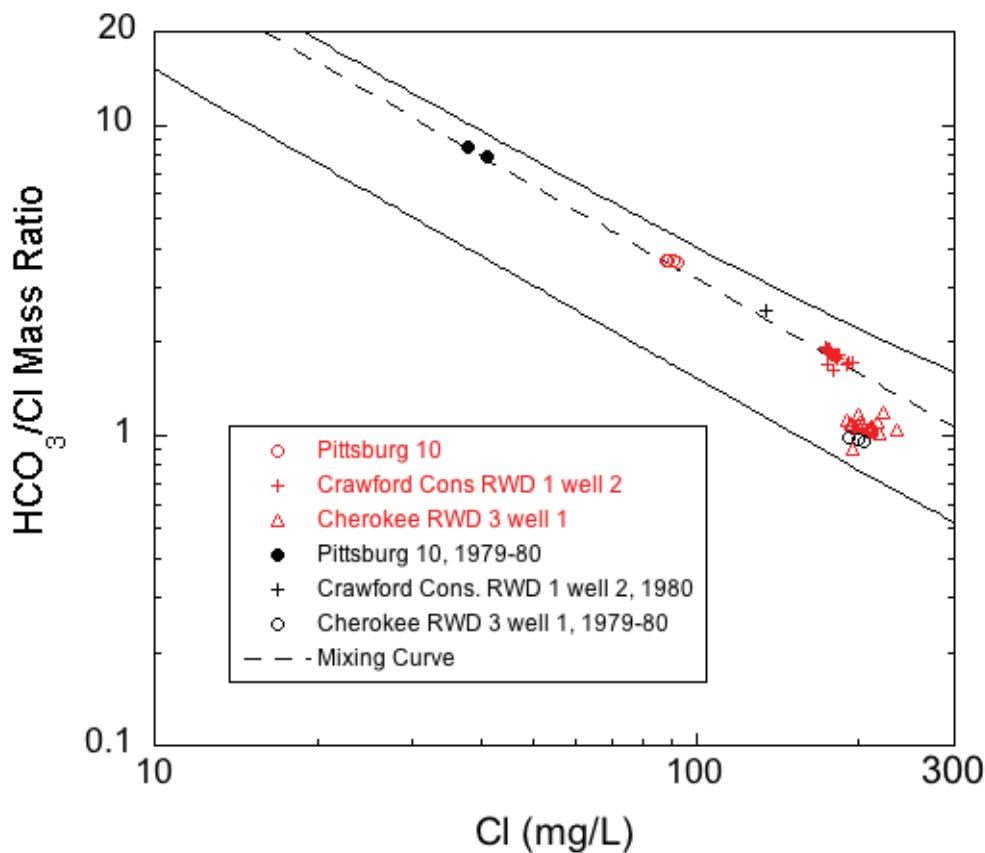


FIGURE 18—Comparison of the 1979–1980 and 2006–08 chloride and bicarbonate/chloride ratios in samples from Pittsburg well 10, Crawford Consolidated RWD 1 well 2, and Crawford RWD 5 well 1.

constituent concentrations as pumping progressed during the tests indicate that the amounts contributed from each source within the aquifer change with time. In particular, the excellent fit of the data points from both tests with the mixing curve on a bicarbonate to chloride ratio versus chloride plot clearly indicates changes in the mixing of water from fresh and more saline end-members within the open borehole of the well.

This interpretation is supported by U.S. Geological Survey data from August 2007 flowmeter measurements and sampling of produced water collected at various depths within the open borehole section from the Pittsburg well 10 after it had been pumped for one week (figs. 1, 22A1, 22A2; Pope et al., 2009). The depth and construction of well 8 are nearly identical to those of well 10, which is located approximately 1,400 ft (427 m) to the south. The pump in well 10 is situated in the cased portion of the borehole, 350 ft (107 m) below the well top. A well-bore flowmeter survey of Pittsburg well 10 revealed that 77% of the flow into the open borehole was contributed by two thin zones from 837 ft to 857 ft (255 m to 261 m) in the lower part of the Roubidoux Formation (Zone 2) and from 977 ft to 997 ft (298 m to 304 m) in the middle of the Gasconade Dolomite (Zone 3; fig. 22A1). More of the total flow

came from Zone 2 (about 46%) than Zone 3 (about 31%). Because of the close proximity, similar construction, and depth of the wells, it is reasonable to conclude that the open borehole section of well 8 also penetrates Zones 1 through 4. Chloride concentration and the bicarbonate to chloride ratio for six water samples collected within the borehole from 487 to 1,030 ft below the top of well 10 after a week of pumping ranged from 54 mg/L to 110 mg/L and 2.73 to 5.37, respectively (fig. 22A2).

The chloride concentration entering from each of the four zones in the open borehole of well 10 was estimated using a rearranged form of equation 1, the flowmeter data (fig. 22A1), and chloride concentrations of water sampled from various levels within the well (fig. 22A2). In the calculation, it is assumed that the flow entering the open borehole from each of the zones moves upward toward the pump and mixes with water below the zone. Equation 1 can be expressed as

$$C_1 f_1 + C_2 f_2 = C_3 (f_1 + f_2), \quad (2)$$

where f_1 is the fractional amount of water in relation to the total at the top of the zone with a chloride concentration of C_1 that is moving upward from below the zone in question,

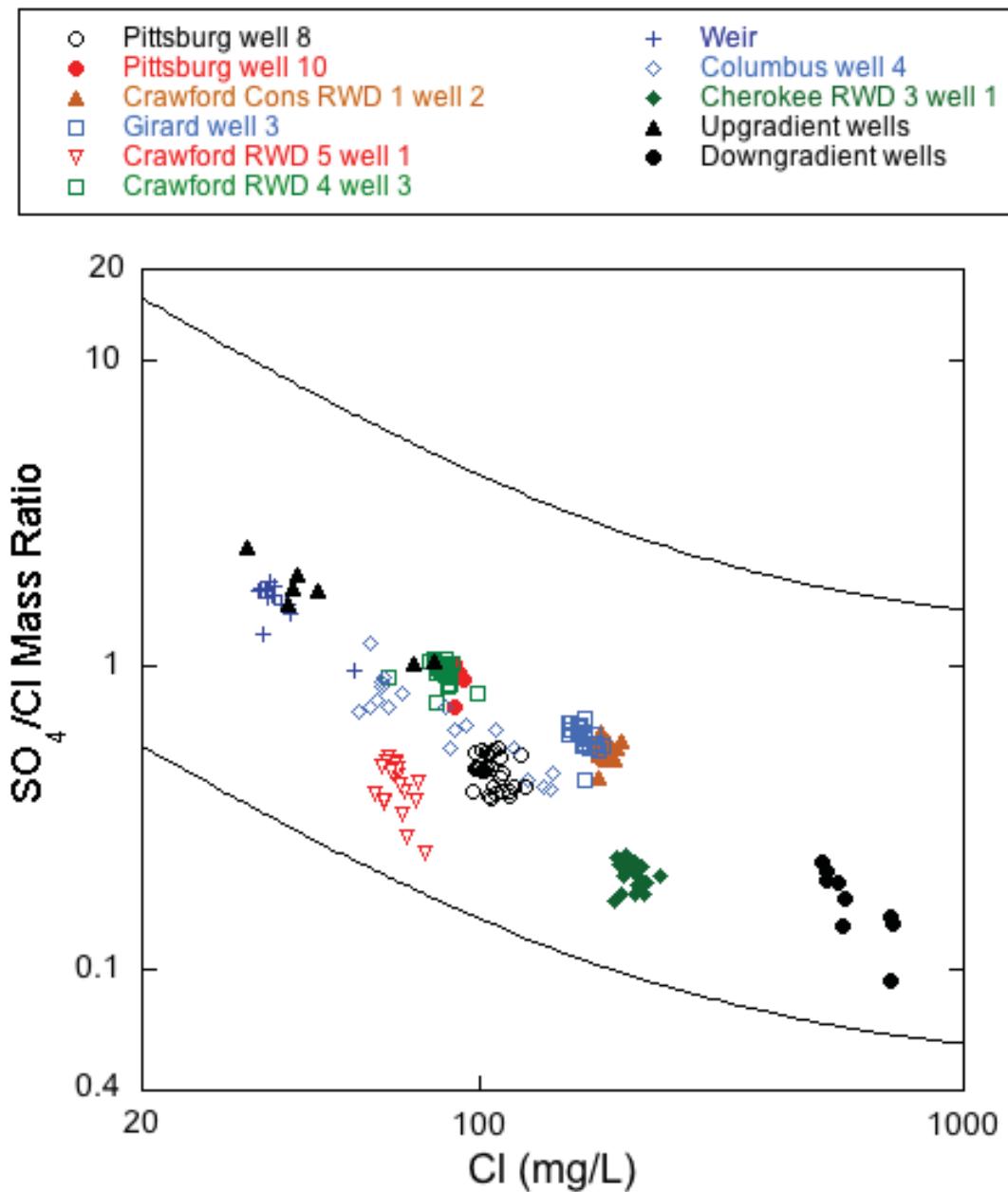


FIGURE 19—Chloride concentration versus sulfate/chloride ratio for the monthly samples of 2006–08 and for samples from upgradient and downgradient wells sampled in 1979–1980 from Crawford and Cherokee counties and adjacent southwestern Missouri. The solid lines are curves that describe the mixing curves that bound where points would plot for the 1979–1980 sample data for the Tri-state region. The curves describe the mixing of various proportions of water of low TDS concentration and calcium, magnesium-bicarbonate type with water of low to moderate sulfate and high TDS concentration and sodium-chloride type with very low sulfate.

f_2 is the fractional amount of water in relation to the total at the top of the zone with a chloride concentration of C_2 that is moving into the well from the zone, and C_3 is the concentration of the mix at the top of the zone. With two end-member mixing, $f_1 + f_2$ are equal to 1 and

$$f_2 = 1 - f_1. \quad (3)$$

Substitution of equation 3 into equation 2 and solving for C_2 produces

$$C_2 = (C_3 - C_1 f_1) / (1 - f_1). \quad (4)$$

The profile in fig. 22A3 combines the calculated chloride concentrations of water entering the well in each zone with the chloride concentrations of the samples collected between the zones. The calculation was performed starting at the top of zone 3 and moving upward. The plot shows that the chloride concentration does not change monotonically with depth from zone to zone but rather decreases from 77 mg/L to 60 mg/L from Zone 1 to Zone 2,

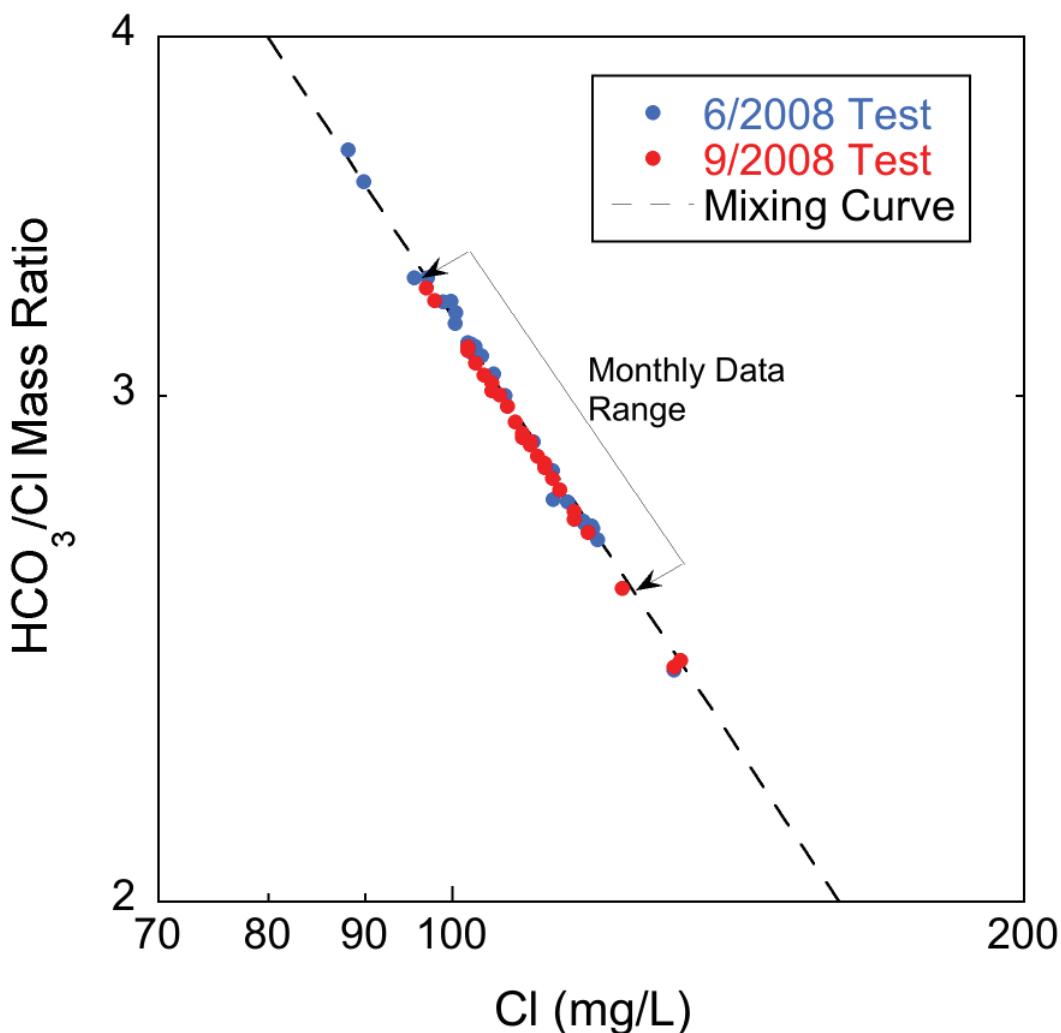


FIGURE 20—Chloride concentration versus bicarbonate/chloride ratio for the samples from the June and September 2008 water-quality pumping tests of Pittsburg well 8. The dashed line is the same mixing curve as on fig. 16 that fits the monthly datasets for the nine project wells.

increases from 60 mg/L to 122 mg/L from Zone 2 to Zone 3, and decreases from 122 mg/L to 54 mg/L from Zone 3 to Zone 4. These changes occur over a vertical interval of about 300 ft (91 m) in the upper part of the Ozark aquifer. The lowest chloride concentration and highest bicarbonate to chloride ratio occurred in water collected near the bottom of the well, indicating that saline water is not entering the deepest zone of the well at the well location. However, it is important to note that for the most productive zones, Zone 2 produced lower chloride water than Zone 3.

The well-head sample collected after a week of pumping Pittsburg well 10 plots close to the mixing curve in fig. 22B and follows the trend of decreasing chloride concentration and increasing bicarbonate to chloride ratio with increasing length of the pumping period established in the June and September 2008 pumping tests of Pittsburg well 8 (figs. 11 and 13). The close overlap of the

range of data for Pittsburg wells 8 and 10 shown on fig. 22B suggests that the temporal changes in the chloride concentration and bicarbonate to chloride ratio observed in both well 8 tests could have resulted from changes in the relative volumes of water contributed to the well by different zones over time. Changes in the quality of water produced from different depth zones over time, as well as a combination of both processes could also be explanations. It is unclear which of these scenarios accounts for the general decrease in the chloride concentration of the water produced at the wellhead (fig. 11). The substantially different water quality and flow rate for different depth zones in the aquifer suggest that some of the variability in the chloride and bicarbonate concentrations occurring during both pumping tests could have resulted from small variations in the pumping rate.

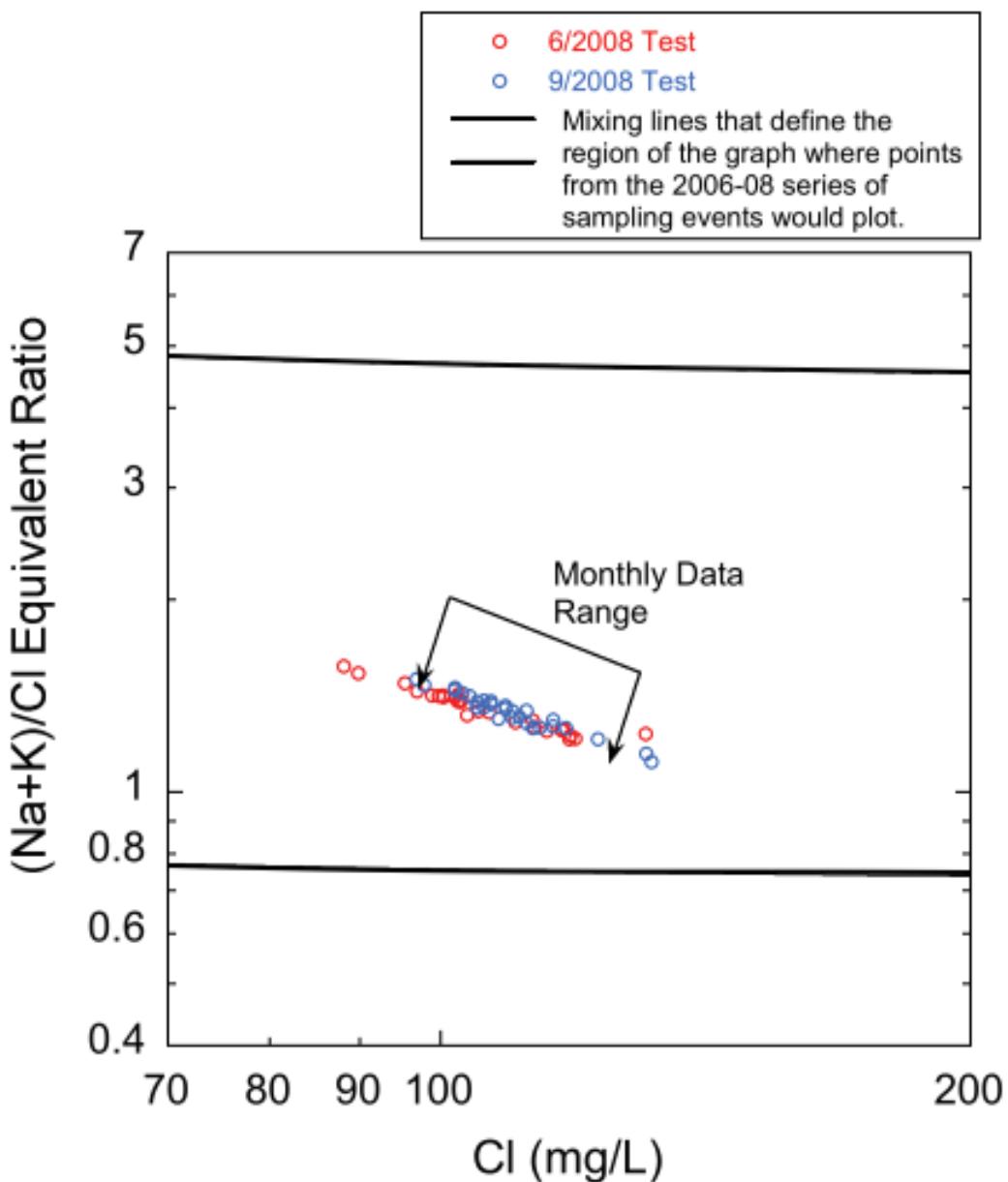


FIGURE 21—Chloride concentration versus sodium + potassium/chloride ratio values for the samples from the June and September pumping tests for Pittsburg well 8. The solid lines are mixing curves that bound the region where the points would plot for the data from the 1979–1980 sampling events.

After a week of pumping well 10, more of the flow entering the open borehole came from Roubidoux Formation sandstones in Zone 2 than from the equally thick Zone 3 in the dolostones of the Gasconade dolomite (fig. 22A1). This difference in flow rates suggests that the transmissivity of Zone 2 is higher than that of Zone 3. Most of the flow from Zone 3 is from secondary permeability features within the Gasconade Dolomite. Data are not available from well 10 to assess the degree of vertical fracturing or carbonate rock dissolution in this interval of the well. However, the Pittsburg well field is located near

the crest of the Pittsburg anticline (fig. 3) and fracture sets developed on and parallel to the crest of the structure would be extensional in origin, presumably with wider apertures than sets developed on the flanks or in the adjacent synclines. The higher chloride concentration in water discharging from Zone 3 suggests that these more open fractures could tap sources of higher chloride water that could exist in the lower part of the Ozark and St. Francois aquifers. However, vertical profiles of hydraulic head in the open borehole section of well 10 were not collected prior to and following pumping to lend support for this hypothesis.

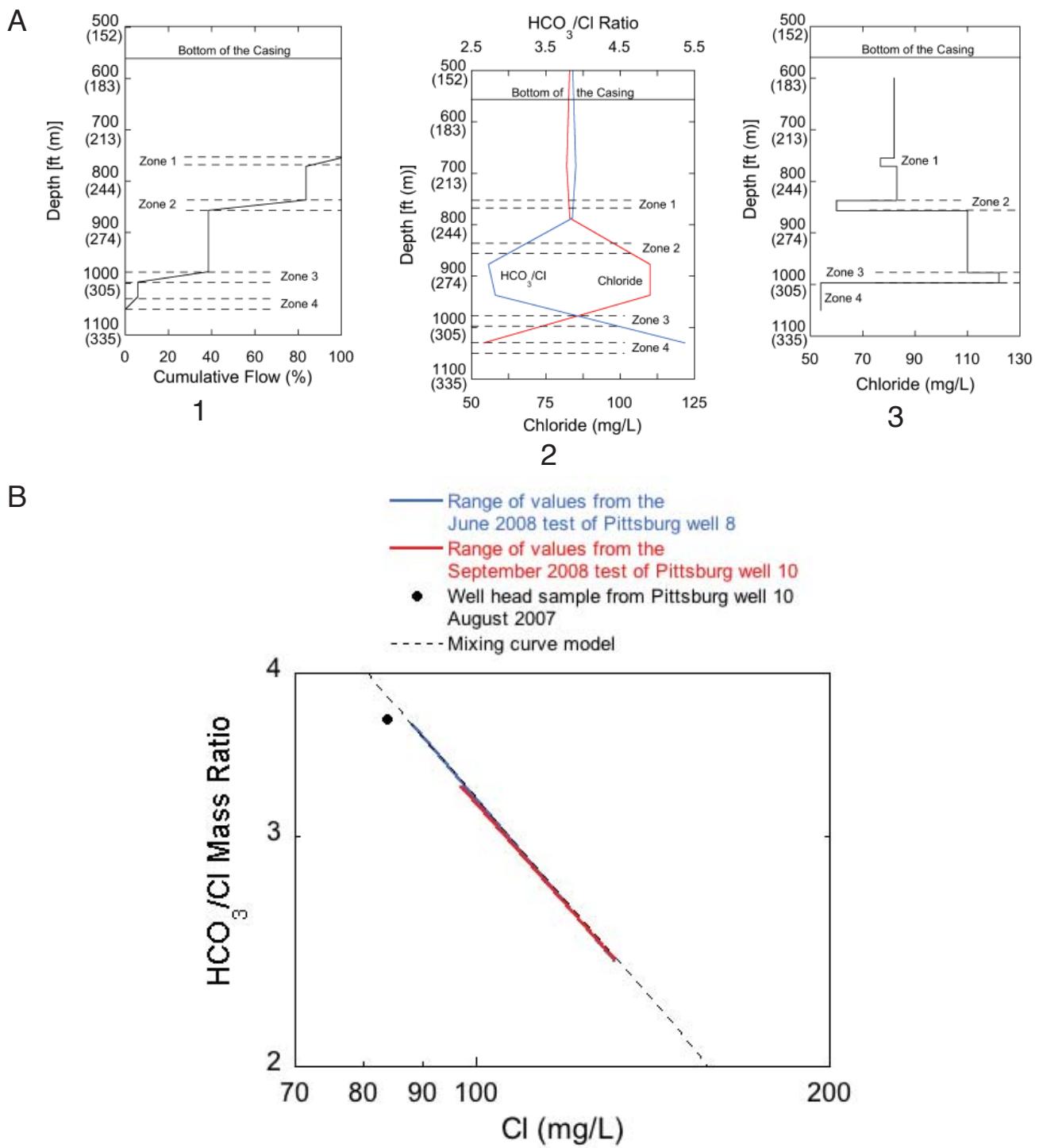


FIGURE 22—(A) Cumulative flow (A1), chloride concentration and bicarbonate to chloride ratio (A2), and calculated zonal chloride concentration (A3) versus depth in Pittsburg well 10; and (B) chloride concentration and bicarbonate to chloride ratio range for samples from the June and September 2008 pumping tests of Pittsburg well 8 in comparison to the wellhead sample collected from Pittsburg well 10. All samples were collected after one week of continuous pumping. Pittsburg well 10 data are from Pope et al. (2009).

Drawdown from individual pumping events could induce 1) lateral flow of lower chloride water through the Roubidoux Formation sandstones from the shallow part of the aquifer and 2) upward flow of higher chloride water from deeper transmissive intervals within the Gasconade

Dolomite into the well and the adjacent sandstones. The June test was conducted prior to the annual period of high pumping stress, and hydraulic head in the aquifer was higher in the well field (fig. 5) and presumably in both Zones 2 and 3. Prior to this test, the hydraulic head in Zone

3 could have been higher than in Zone 2, which would have allowed higher chloride water to move into this upper zone. When the pump for well 8 was turned on, water from all of the zones would start to flow into the well. In the early part of the pumping period, the higher chloride water from Zone 3 and the part of Zone 2 affected by Zone 3 water would have entered the well resulting in the observed higher chloride concentration (fig. 11). Continued pumping would have gradually flushed the higher chloride water from Zone 2, resulting in a gradual decline in the chloride concentration with time. Turning off the well could potentially have allowed water from deeper zones to continue to flow slowly upwards into the well from Zone 3 into Zone 2 during recovery. Prior to the September well 8 pumping test, higher pumping stress lowered the hydraulic head in the Ozark aquifer in the Pittsburg area generally as indicated by the lower water levels in the monitoring well (fig. 5). This could have increased the vertical hydraulic head gradients within the Ozark aquifer and consequently, the potential for upward flow from deeper flow zones during pumping. The early drawdown in the September well 8 test could have initially induced more flow into the well from Zone 2 than from Zone 3 causing the chloride in the produced water in the early part of the pumping period to decrease (fig. 11). As pumping progressed, the flow from Zone 2 could have slowed sufficiently relative to Zone 3 because of further increases in the vertical hydraulic head gradient so that the continued decline in the chloride concentration of the produced water over time would have eventually ceased (fig. 11). Alternatively, vertical head gradients could have induced leakage of water from Zone 3 to Zone 2 within the aquifer resulting in a decreasing rate of decline in the chloride concentration.

Long-term change in the quality of produced water is occurring very slowly and over many cycles of pumping and recovery and high and low stress periods at Pittsburg well 10 and Crawford Consolidated RWD 1 well 2 as indicated by the datasets from this project, the 1979–1980 sampling events, and from Darr (1978). Because of the limited sampling that was done in 1979–1980, the amount of change in the bicarbonate and chloride concentrations over the last 25 years is difficult to gauge (fig. 18). However, if the variability in the monthly data from Pittsburg well 8 is similar to that of Pittsburg 10, the apparent change in produced water quality from Pittsburg well 10 from 1979–1980 to 2006–08 is much greater than the monthly variability (fig. 16). The chloride concentration versus bicarbonate/chloride mixing plot in fig. 16 shows that the long-term change in quality of the produced water from Pittsburg well 8 follows the mixing curve from lower chloride to higher chloride values. Assuming that the water quality in Pittsburg well 10 has evolved over time in a manner similar to that of Pittsburg well 8, then the general decrease in chloride concentration and an increase in the bicarbonate/chloride ratio during both pumping tests appears opposite to the long-term trend. Higher levels of

pumping during certain times of the year cause a general lowering of the hydraulic head within the Ozark aquifer and the Pittsburg area wells to produce higher chloride water after extended pumping such as indicated by fig. 18.

Upward migration of saline water from the lower part of the Ozark and St. Francois aquifers is a much simpler explanation of the increased salinity in the Pittsburg area wells than eastward migration of more saline water into the area. The observed decrease in the chloride concentration with extended pumping in the well 8 pumping tests is difficult to explain if it is assumed that saline water is moving into the area from the west. In that scenario, the chloride concentration in the produced water during a single pumping period should be relatively constant or possibly increase with time. However, data are currently lacking to evaluate the potential for upward movement of more saline water into the upper part of the Ozark aquifer from deeper zones.

Macfarlane and Hathaway (1987) and Imes and Emmett (1994) speculated that downward leakage from the Springfield Plateau aquifer was a major source of recharge to the Ozark aquifer in the Tri-state region. This is not evident in the results of the Pittsburg 8 chemical-quality pumping tests (figs. 14–15). Ground waters from the Springfield Plateau aquifer in southeast Kansas are a sodium-bicarbonate type (Macfarlane and Hathaway, 1987). A Springfield Plateau aquifer well located 1 mi (1.3 km) northeast of Pittsburg 8 was sampled twice in 1979–1980. The average excess sodium + potassium and bicarbonate ratios from the two samplings are 15.3 and 21.7, respectively. In the June pumping test, the excess sodium + potassium ratio rose to approximately 1.5 with some fluctuation throughout the pumping period. In the September test, the ratio rose early and then remained relatively constant at approximately 1.35 throughout the remainder of the pumping period. In both tests, the excess bicarbonate ratio remained relatively constant with values below 1.25. The low excess bicarbonate and sodium + potassium ratios from the June and September tests suggest that pumping-induced recharge from leakage is either negligible or, if small, is masked by cation exchange and carbonate equilibria that alter the water chemistry.

The chloride concentration for the three monthly samples collected from Pittsburg well 10 during 2006 to 2007 ranged from 88.9 to 109 mg/L. The chloride concentration range for three samples obtained from the same well during 1979–1980 was 38–41 mg/L. If the minimum and maximum differences in chloride concentration between the two sampling periods are divided by the time between the periods, the rate of chloride increase ranges from 1.8 to 2.6 mg/L/yr. The minimum and maximum chloride concentrations observed for the two pumping tests of Pittsburg well 8 during 2008 were 88.2 and 132 mg/L, respectively. If the chloride content of Pittsburg well 8 during 1979–1980 was about the same as for Pittsburg well 10 (around 40 mg/L), then the

rate of chloride increase for Pittsburg well 8 ranges from 1.7 to 3.2 mg/L/yr. Based on the value and the date of the maximum chloride concentration observed for each of the two wells and the maximum rate of chloride increase, and assuming that the increase rate remains linear with time, the chloride level would not exceed the recommended drinking water limit of 250 mg/L until approximately 37 years (the year 2045) for Pittsburg well 8 and 54 years (the year 2060) for Pittsburg well 10.

The range in increase rate estimates indicate that the data from the monthly sampling and pumping tests of Pittsburg well 8 have important ramifications for designing a water-quality monitoring protocol to determine long-term

changes in water quality. For this well, the greater ranges of chloride concentration for the pumping test samples than for the monthly samples underscores the need to factor short-term variability in produced water chemistry into the frequency of sampling, the timing of sampling relative to pump start-up and possibly to seasonal water use, and the analysis of the resulting data for trend. The monthly sampling results for many of the other wells sampled in this project exhibit trends indicating changes in the relative proportions of the cations, anions, or both (fig. 6). Longer-term pumping tests of these other wells could reveal results similar to those found for Pittsburg well 8.

Conclusions

The results of this study reflect the lateral variability in the chemical quality of the water within the Ozark aquifer transition zone described in Macfarlane and Hathaway (1987) and provide documentation of the effects of pumping on produced-water quality. The chemical character of water produced from the Ozark aquifer ranges from mixed cation-bicarbonate type for Pittsburg wells 8 and 10 and Crawford RWD 4 well 3 to a sodium-chloride type for Cherokee RWD 3 well 1 and other wells yielding even higher chloride concentration. As a group, water from the multi-aquifer wells with a chloride content less than 80 mg/L (Weir city well, Crawford RWD 5 well 1, and about half of the Columbus well 4 samples) had a higher bicarbonate percentage and a lower sulfate and chloride percentage of total anions than water only from the Ozark aquifer. However, the much lower sodium and potassium percentage and higher calcium and magnesium percentage of total cations for the multi-aquifer wells than for samples from the Springfield Plateau aquifer suggest that the contribution of water from the Springfield Plateau aquifer is minor relative to the contribution produced from the Ozark aquifer. With the exception of Columbus well 4 and the Weir city well, variability in the chemistry of the monthly samples collected during 2006–08 was small for each site relative to the range among the sample sites.

Data for the chemical-quality pumping tests indicate that different zones within the Ozark aquifer produce waters of differing chemistries at variable rates to Pittsburg well 8 as it pumps. The general decrease in TDS and chloride concentrations relative to bicarbonate concentration indicates mixing of a relatively greater amount of ground water of low TDS concentration and of calcium, magnesium-bicarbonate type than of sodium-chloride type. Differences in the manner in which the bicarbonate/chloride ratio changed over time between the June and September tests suggest that vertical head gradients, both under pumping and nonpumping conditions, play an important role in the temporal pattern of changes in salinity during these pumping tests. Variability in the water chemistry of the monthly samples from most of the sites

seems to be primarily related to the range in water quality within the Ozark aquifer. This may also be the main cause of changes observed in the water quality for the Columbus 4 and Weir city wells.

The results of this study compared with the results of the 1979–1980 sampling of Macfarlane and Hathaway (1987) indicate that Pittsburg well 10 and Crawford Consolidated RWD 1 well 2 have experienced long-term increases in chloride. Changes for the other sites from 1979–1980 to 2006–08 were either small or insignificant. Chloride concentration increase in water from wells in the Pittsburg area most likely has resulted from pumping stress associated with the higher density of high-yielding supply wells in southeastern Crawford County and the adjacent area of Missouri. It is possible that the changes in quality are influenced by local upconing of higher chloride, higher TDS, transition-zone water from deeper zones within the Ozark or the St. Francois aquifers. If the long-term increases in chloride concentration are linear with time, the earliest dates that Pittsburg wells 8 and 10 would produce water greater than the recommended drinking water limit of 250 mg/L are the years 2045 and 2060, respectively.

The variability in the chemical data from monthly sampling and the Pittsburg well 8 pump tests indicates that detection of long-term water-quality changes in the produced water from the wells within the transition zone will be difficult unless its variability over shorter time scales is factored into the analysis. To be successful, 1) water sampling events over the entire network and at individual well sites need to be more frequent to assess decadal changes and monthly variability and 2) the changes in water chemistry that occur under different levels of pumping stress during a single extended pumping event need to be considered in the analysis of trend. However, for these recommendations to more fully contribute to our understanding of the Ozark Plateaus aquifer system as a whole, attention needs also to focus on gathering vertical hydraulic-head profiles and water-quality pumping tests like those conducted in Pittsburg well 10 in existing and future wells. Data from these tests are a requisite for

fully assessing the mechanisms that cause water-quality degradation in individual, open borehole wells.

Acknowledgments

This work was made possible by grant funds from the U.S. Geological Survey managed by the Kansas Water Resources Research Institute at Kansas State University, Manhattan, Kansas. The author wishes to acknowledge the assistance of Ed Reboulet with the fieldwork for this project and Rudy Ghijsen, Elizabeth Petroske, and Mike Magnuson of the KGS Analytical Services Laboratory for their careful analysis of the water samples collected for this project. The author also wishes to express appreciation to the operators of the water supplies that were sampled in this project. The author especially wishes to express his appreciation to Steve Gillis, City of Pittsburg, for his

assistance that enabled the KGS to conduct the pumping tests on Pittsburg well 8. While working on this project, the author benefited from discussions with Walt Aucott, Mike Pope, and John Czarnecki of the U.S. Geological Survey on the work they were conducting on the Ozark aquifer in the Tri-state region. Margaret Townsend, Jim Butler, and Don Whittemore of the Kansas Geological Survey; Jim Vandyke of the Division of Geology and Land Survey, Missouri Department of Natural Resources; John Schumacher, Supervisory Hydrologist of the U.S. Geological Survey's Missouri Water Science Center; and Ralph Davis, professor and chair of the Department of Geosciences, University of Arkansas–Fayetteville, critically edited and reviewed the manuscript and provided helpful suggestions that solidified the ideas expressed in the manuscript and strengthened its overall message.

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