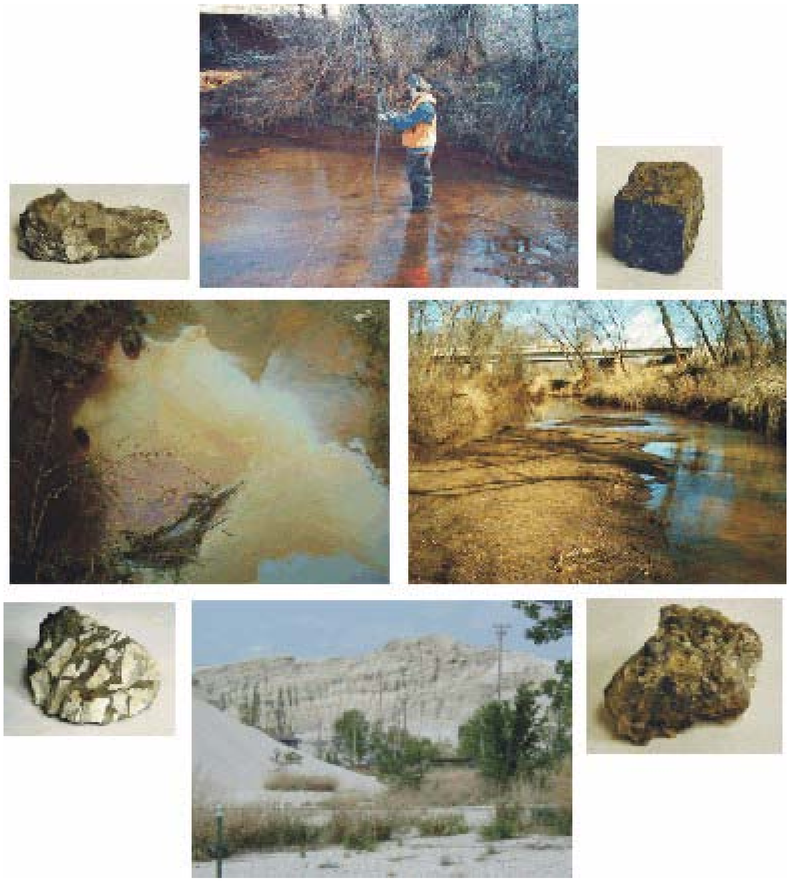
Prepared in cooperation with the
OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

Hydrology and Ground-Water Quality in the Mine Workings within the Picher Mining District, Northeastern Oklahoma, 2002–03

Scientific Investigations Report 2004–5043



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Cover: Photographs listed clockwise from top.

Photograph of USGS Personnel measuring streamflow at Tar Creek near Picher taken by Kelli DeHay, U. S. Geological Survey.

Photograph of galena, with fresh face (dark gray) and weathered edges (dark brown) taken by William Andrews, U.S. Geological Survey.

Photograph of Tar Creek near Commerce taken by Monica Allen, U.S. Geological Survey.

Photograph of sphalerite, galena, and quartz taken by William Andrews, U.S. Geological Survey.

Photograph of a mine tailings (chat) pile south of Picher, Oklahoma taken by William Andrews, U.S. Geological Survey.

Photograph of a breccia with white chert clasts in a matrix of dolomotized limestone taken by William Andrews, U.S. Geological Survey.

Photograph of metallic hydroxide film at Tar Creek near Picher taken by Kelli DeHay, U.S. Geological Survey.

Photograph of calcite crystals overgrown on dolomitic limestone taken by William Andrews, U.S. Geological Survey.

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U.S. Department of the Interior
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Conversion Factors and Datum

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ton, short (2,000 lb)	0.9072	megagram (Mg)

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

°F = (1.8 × °C) + 32

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

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

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

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

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Abstract

The Picher mining district of northeastern Ottawa County, Oklahoma, was a major site of mining for lead and zinc ores in the first half of the 20th century. The primary source of lead and zinc were sulfide minerals disseminated in the cherty limestones and dolomites of the Boone Formation of Mississippian age, which comprises the Boone aquifer. Ground water in the aquifer and seeping to surface water in the district has been contaminated by sulfate, iron, lead, zinc, and several other metals. The U.S. Geological Survey, in cooperation with the Oklahoma Department of Environmental Quality, investigated hydrology and ground-water quality in the mine workings in the mining district, as part of the process to aid water managers and planners in designing remediation measures that may restore the environmental quality of the district to pre-mining conditions.

Most ground-water levels underlying the mining district had similar altitudes, indicating a large degree of hydraulic connection in the mine workings and overlying aquifer materials. Recharge-age dates derived from concentrations of chlorofluorocarbons and other dissolved gases indicated that water in the Boone aquifer may flow slowly from the northeast and southeast portions of the mining district. However, recharge-age dates may have been affected by the types of sites sampled, with more recent recharge-age dates being associated with mineshafts, which are more prone to atmospheric interactions and surface runoff than the sampled airshafts.

Water levels in streams upstream from the confluence of Tar and Lytle Creeks were several feet higher than those in adjacent portions of the Boone aquifer, perhaps due to low-permeability streambed sediments and indicating the streams may be losing water to the aquifer in this area. From just upstream to downstream from the confluence of Tar and Lytle Creeks, surface-water elevations in these streams were less than those in the surrounding Boone aquifer, indicating that seepage from the aquifer to downstream portions of Tar Creek was much more likely.

Water properties and major-ion concentrations indicate that water in the mining area was very hard, with large concentrations of dissolved solids that increased from areas of presumed recharge toward areas with older ground water. Most of the ground-water samples, particularly those from the airshafts, had dissolved-oxygen concentrations less than 1.0 milligram per liter. Small concentrations of dissolved oxygen may have been introduced during the sampling process. The small dissolved-oxygen concentrations were associated with samples containing large iron concentrations that indicates possible anoxic conditions in much of the aquifer.

Ground water in the mining district was dominated by calcium, magnesium, and sulfate. Sodium concentrations tended to increase relative to calcium and magnesium concentrations. Ground-water samples collected in 2002-03 had large concentrations of many trace elements. Larger concentrations of metals and sulfate occurred in ground water with smaller pHs and dissolved-oxygen concentrations. Iron was the metal with the largest concentrations in the ground-water samples, occurring at concentrations up to 115,000 micrograms per liter. Cadmium, lead, manganese, zinc, and the other analyzed metals occurred in smaller concentrations in ground water than iron. However, larger cadmium concentrations appeared to be associated with sites that have small iron concentrations and more oxygenated waters. This is noteworthy because the small sulfate and iron concentrations in these waters could lead to conclusions that the waters are less contaminated than waters with large sulfate and iron concentrations.

Ground-water quality in the mining district was compared with subsets of samples collected in 1983-85 and in 2002. Concentrations of most mine-water indicators such as specific conductance, acidity, magnesium, sulfate, and trace elements concentrations decreased over that period. Calcium concentrations did not significantly change.

Mineral saturation indices indicated that the carbonate minerals aragonite, calcite and dolomite, that compose much of the Boone aquifer, were likely to dissolve at most sites. The sulfate minerals of lead (anglesite), barium (barite), cadmium, zinc (goslarite), calcium (gypsum), and iron (melanterite) were generally undersaturated in the ground-water samples, indicating likelihood for dissolution of those minerals and potential for those elements to dissolve into ground water. The clay mineral kaolinite, which is known to form as a hydrolysis product of feldspars at low temperatures, was oversaturated in most of the samples, indicating that it may precipitate out of local ground waters.

Lack of eh (redox) data makes it difficult to interpret the saturation state of the ferric oxyhydroxide minerals. It is likely that the ferric oxyhydroxide minerals could be dissolving, but precipitation is unlikely due to the lack of dissolved oxygen in the mine workings.

Introduction

The Picher mining district of northeastern Ottawa County, Oklahoma, (fig. 1) was the site of mining for lead and zinc ores from about 1900 until the mid-1970s (Christenson, 1995). From about 1900 to 1970, 1.7 million tons of lead and 8.8 million tons of zinc were produced in the district (State of Oklahoma, 2000). Lead and zinc ores were first discovered in the Picher mining district in 1901, with the main body of ore being discovered in 1912 (Playton and others, 1980). Those mining activities led to contamination of ground water and surface water by sulfate, iron, lead, zinc, and several other metals (Playton and others, 1980). The U.S. Geological Survey (USGS), in cooperation with the Oklahoma Department of Environmental Quality (ODEQ), investigated the hydrology and ground-water quality in the mine workings in the mining district from 2002-03 as part of the process to aid water managers and planners in designing remediation measures that may restore the environmental quality of the district to pre-mining conditions.

The primary sources of lead and zinc in the Picher mining district were sulfide minerals disseminated in the cherty limestones and dolomites of the Keokuk[1] and Reeds Spring Formations, otherwise known as the Boone Formation of Mississippian age (table 1, fig. 2). Sulfide minerals mined from the Boone Formation include sphalerite, galena, and the accessory minerals chalcopyrite, enargite, luzonite, marcasite, and pyrite (McKnight and Fischer, 1970). Exposure of these minerals to oxygenated water, such as when the mines were in operation or were filling with water, can create acidic solutions resulting in elevated concentrations of sulfate and metals in the ground water, surface water, and sediments.

The mining district is on the western flank of the Ozark uplift, with the units dipping westward at about 25 feet per mile to the axis of the Miami Trough, a syncline (McKnight and Fischer, 1970) located just west of Picher, Cardin, and Commerce, Oklahoma (fig. 1).

Although lead and zinc ores were known to occur in the district in the early 1900s, ore production in the district increased rapidly between 1915 and 1920 due largely to demand created by World War I (Playton and others, 1980). Mine production reached a peak by 1925 with an annual production of 387,000 tons of zinc and 101,000 tons of lead (McKnight and Fischer, 1970). The mines maintained moderate production levels until the 1950s when yields began to decline. Most of the large mining operations then abandoned the area, and only a small amount of ore was produced by mining of residual deposits until the mid-1970s (Christenson, 1995).

De-watering of the Boone Formation was necessary to mine the ores. After mining ceased in the mid-1970s, approximately 300 miles of underground mine tunnels filled with acidic, metals-rich ground water, which started to seep into Tar Creek and Lytle Creek through natural and man-made conduits (State of Oklahoma, 2000). In addition to water in mineshafts, approximately 165 million tons of metal- and sulfide-containing mine tailings (locally known as chat) were left by mining activities (State of Oklahoma, 2000). Some of the tailings have been removed from the area for use on gravel roads, road base, and as aggregate in concrete and asphalt (State of Oklahoma, 2000).

Several thousand people continue to live in the mining district and nearby areas, including members of eight Native American Tribes (State of Oklahoma, 2000). In 1993, Indian Health Service data indicated that 34 percent of Native American children in the area had blood-lead concentrations considered to be dangerous to human health (State of Oklahoma, 2000). Subsequent cleanup of contaminated soils by the U.S. Environmental Protection Agency and public education campaigns by state and local governments have led to a 50 percent reduction in elevated blood-lead concentrations in local children (State of Oklahoma, 2000).

The Boone Formation (table 1, fig. 2) comprises an important aquifer in the region and is the source of part of the baseflow to streams in the Picher mining district (Luza, 1986). Elevated trace-metal concentrations in ground water may seep to adjoining portions of the Boone aquifer, creeks, and streams in hydraulic connection with the aquifer, and to the underlying Roubidoux aquifer.

Purpose and Scope

This report describes the hydrology of the mine workings and the ground-water quality in 2002-03 in the Picher mining district. Water-level altitudes were measured 3-4 times at 20 ground-water sites in the mine workings and were continuously monitored for 12 months at two sites. Surface-water elevations also were measured at nine stream sites, with discharge measurements being made at two of the sites (figs. 1, 2). Ground-water samples from 16 mineshafts or airshafts completed in the mine workings in the Picher mining district were analyzed for water properties, dissolved trace elements, and chlorofluorocarbons (CFCs). Two of the mineshafts were sampled twice—in a shallow part of the water column and in a deep part of the water column.

Acknowledgments

Sincere thanks are extended to Ed Keheley, a local resident, who provided his time and assistance in locating sampling sites. Thanks also go to local landowners, James Thompson, Joel Thompson, Louanne Barrett, and Steve Turner, for their cooperation in obtaining water samples and water levels. John Dalgarn, with the Bureau of Indian Affairs, was helpful in pro-

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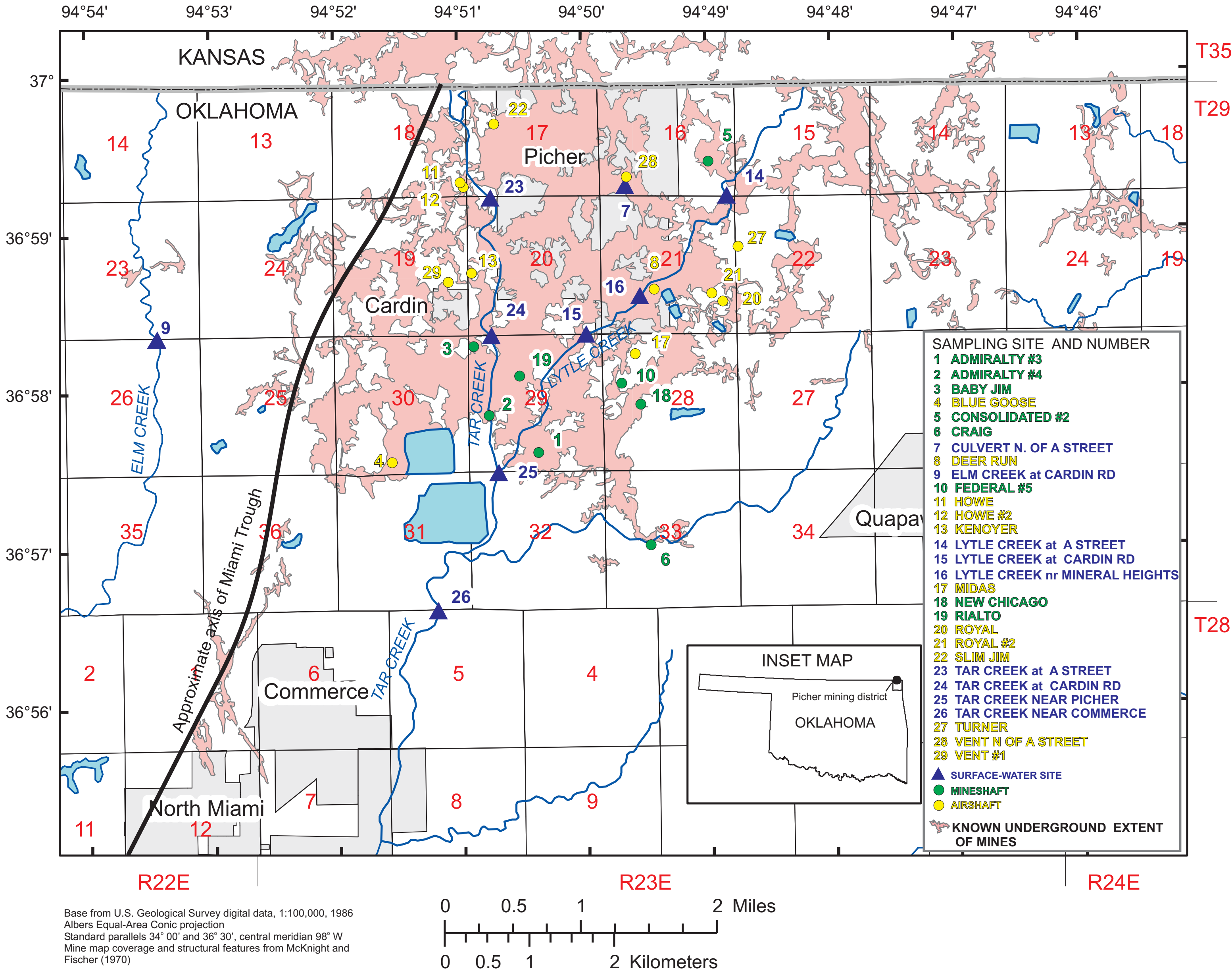
[1] Geologic names and stratigraphic ages in this report are accepted by the Oklahoma Geological Survey and are not necessarily the same as those used by the U.S. Geological Survey.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Mine map coverage and structural features from McKnight and Fischer (1970)

Figure 1. Location of sampling sites within the Picher mining district, Oklahoma, 2002–03.

Table 1. Generalized stratigraphic column and water-yielding properties of Ordovician-age and younger units in Ottawa County, Oklahoma [modified from Christenson, 1995]

Geologic Systems	Geologic Units		Ranges of Thickness (feet)	Lithologies	Water-yielding properties
Pennsylvanian		Pennsylvanian units undivided	0-200	Shale, siltstone, sandstone, limestone, and thin coal seams	Wells generally yield less than 1 gallon per second
Mississippian		Mississippian units, undivided	0-100	Limestone, shale, siltstone, and sandstone	Wells generally yield less than 1/2 gallon per second.
	Boone aquifer	Boone Formation	250-350	Chert, and fine- to coarse-grained gray, light gray, and bluish limestone	Wells generally yield less than 0.5 gallon per second, with local yields as much as 15 gallons per second
		Northview Shale and Compton Limestone	0-30	Greenish-black or dull-blue shale, and gray, nodular, shaley limestone	Do not yield significant quantities of water
Devonian and Mississippian		Chattanooga Shale	0-30	Black, carbonaceous, fissile shale	Does not yield significant quantities of water
Ordovician	Roubidoux aquifer	Cotter Dolomite and Swan Creek Sandstone	110-550	Buff to brown cherty dolomite with sandy and clayey zones	Wells generally yield less than 0.5 gallons per second, but locally yield up to 7 gallons per second
		Jefferson City Dolomite	200-420	Buff, gray, and brown cherty dolomite	Well yields unknown
		Roubidoux Formation	65-250	Light-colored, cherty dolomite with 2 or 3 layers of sandstone, each 15-20 feet thick	Principal aquifer in Ottawa County. Wells yield 1.6 to ~160 gallons per second
		Gasconade Dolomite and Gunter Sandstone Member	25-325	Light-colored cherty dolomite; Gunter Sandstone Member is sandstone or sandy dolomite at the base.	Gasconade Dolomite does not yield substantial quantities of water. Gunter Sandstone Member can yield a few gallons per second.

USGS personnel measuring streamflow at Tar Creek near Commerce, Oklahoma, (note iron hydroxide staining of streambed)

USGS personnel measuring streamflow at Tar Creek near Picher, Oklahoma, (note iron hydroxide staining of streambed sediments and streambank vegetation)

Metallic hydroxide film on Tar Creek at Douthat, Oklahoma

Tar Creek at Highway 69

Mine tailings (chat) pile south of Picher, Oklahoma

Boulder of cherty dolomite from the Boone Formation

Figure 2. Photographs taken in the Picher mining district of Oklahoma, 2002. Top and middle photographs taken by Monica Allen and Kelli DeHay, U.S. Geological Survey. Bottom photographs taken by William Andrews, U.S. Geological Survey.

viding access to sites on Indian trust land. The authors also thank numerous individuals within the USGS for their assistance in various phases of the study. Special thanks are extended to Monica Allen, USGS, for her help with the data collection.

Methods

Ground-water altitudes and surface-water elevations were collected within the Picher mining district in 2002-03. Ground-water-quality samples were collected at many of the ground-water sites. Statistical summaries were calculated for the water-quality constituents collected at these sites, and the water-quality constituents were compared to constituents collected from ground water in the mine workings in 1983-85.

Field Methods

Ground-Water Altitudes, Surface-Water Elevations and Streamflow

Ground-water altitudes were measured at 20 ground-water sites completed in the Boone aquifer, and nine surface-water elevations were measured in the Picher mining district (fig. 1). Ground-water altitudes and surface-water elevations were measured four times from September 2002 to March 2003 at most sites. Ground-water altitudes and surface-water elevations were not measured at all sites during the first two water-level-measurement trips because some sites were located during the course of the study. Depths to the water table were measured using a steel tape to mark the distance from the water surfaces to fixed tape-down points. Ground-water ltitudes and surface-water elevations of the tape-down points at each site were established through optical surveying from benchmarks of known altitude and by differentially corrected dual-frequency global-positioning system surveys.

Two of the ground-water sites, the Blue Goose and the Slim Jim (fig. 1), were instrumented with pressure transducers and data-collection platforms to collect continuous water levels from October 2002 to October 2003.

Streamflow was measured at Tar Creek near Picher (USGS Station number 07185088) and Tar Creek near Commerce (USGS Station number 07185090) from September 2002 to March 2003 (fig. 1). The streamflow measurements coincided with the ground-water level measurements and were done according to methods described in Rantz and others (1982).

Water-Quality Methods

Sixteen ground-water sites, composed of nine airshafts and seven mineshafts in the Picher mining district, were sampled once from October 2002 to January 2003 using methods described in the USGS Water-Quality Field Manual (Wilde and Radtke,1998). Ground water was sampled using a Grundfos submersible pump and Teflon-lined polyethylene tubing. The sampling sites were purged until field parameters were stable as described in Wilde and Radtke (1998). A multi-parameter probe was used to measure the field water properties using a flow-through chamber. Specific conductance, pH, water temperature, and dissolved-oxygen concentrations were measured at each site. The multi-parameter probe was calibrated at the beginning of each day, using methods described in Wilde and Radtke (1998).

Sampling sites were completed within the Boone aquifer and were located based on records and reports of the USGS and Oklahoma Water Resources Board. Site information also was obtained from Picher residents who were knowledgeable of the area.

Water-quality samples were collected between 55 and 80 feet below land surface at most of the sites. The samples were collected closer to the water table rather than in the mine workings that are typically located around 150 to 200 feet below land surface. Samples were collected at shallower depths to determine the general quality of water in the mining area, rather than focusing on water quality in the mine workings. Two of the 16 ground-water sites (Admiralty #3 and Consolidated #2) were sampled both in the upper part of the water column (around 60 feet below land surface (bls)) and in the deeper part of the water column (around 200 feet bls).

Ground-water samples were analyzed for specific conductance, pH, water temperature, dissolved oxygen, and alkalinity in the field, and for major ions and trace elements at the USGS National Water Quality Laboratory in Lakewood, Colorado (tables 2 and 3). The laboratory reporting levels (LRL) are listed for the major ions and trace elements (table 3). Laboratory reporting levels control false negative error. The probability of falsely reporting a non-detection for a sample that contained an analyte at a concentration equal to or greater than the LRL is predicted to be less than or equal to 1 percent (Childress and others, 1999). Samples to be analyzed for those constituents were filtered using a 0.45-micrometer pore-size capsule filter prior to decanting into sample bottles.

Concentrations of dissolved CFCs and other dissolved gases (nitrogen, oxygen, methane, and carbon dioxide) in water from selected sites were measured at the USGS CFC Laboratory in Reston, Virginia, to estimate recharge-age dates based on historic atmospheric concentrations of CFCs (table 2).

Data-Analyses Methods

Summary statistics were calculated for the water-quality constituents from water samples collected from the mining area in 2002-03 using the program S-Plus 2000 (MathSoft, Inc., 1999). Comparisons were shown for selected water properties and constituents thought to be the primary indicators of mine water for this system, including specific conductance, pH, calcium, magnesium, sulfate, iron, lead, manganese, and zinc.

Water-quality constituents from water samples collected from the mine workings in 1983-85 were compared to those collected in 2002 using the Wilcoxon rank-sum test, also

Table 2. Laboratory analyses methods for analyzed water-quality constituents

[USGS, U.S. Geological Survey; --, no lab code]

Constituent or constituent group	USGS schedule or lab code	Analysis method	Method reference
Major ions	2750	Induction coupled plasma	Fishman and Friedman (1989), Fishman (1993), and American Public Health Association (1998)
Trace elements	2703	Induction coupled plasma mass spectrometry	Faires (1993), McLain (1993), Jones and Garbarino (1999), and Fishman and Friedman (1989)
Chlorofluorocarbons and dissolved gases	--	Gas chromatograph and electron capture	Busenberg and Plummer (1991)

Table 3. Water-quality constituents analyzed in ground-water samples collected from 16 sites within the Picher mining district, Oklahoma, 2002-03

[USGS, U.S. Geological Survey; SC, analytical schedule code]

Constituent	Laboratory reporting level	Constituent	Laboratory reporting level
Major ions, USGS SC2750, in milligrams per liter (* denotes units in micrograms per liter)			
Dissolved solids	10.0	Chloride	0.20
Calcium	0.012	Fluoride	0.17
Magnesium	0.008	Bromide	0.016
Sodium	0.09	Iron*	10.0
Potassium	0.11	Silica	0.13
Sulfate	0.18		
Trace elements, USGS SC2703, in micrograms per liter			
Aluminum	1.6	Lead	0.08
Antimony	0.02	Manganese	0.18
Arsenic	1.9	Molybdenum	0.33
Barium	0.2	Nickel	0.06
Beryllium	0.06	Selenium	2.6
Cadmium	0.037	Silver	0.20
Chromium	0.8	Uranium	0.018
Cobalt	0.015	Zinc	1.0
Copper	0.23		

known as the Mann-Whitney test (MathSoft Inc., 1999; Helsel and Hirsch, 1992). Statistical tests and comparisons were calculated for water properties and constituents designated as indicators of mine water. Those properties and constituents included: specific conductance, pH, alkalinity, calcium, magnesium, sulfate, aluminum, cadmium, copper, iron, lead, manganese, nickel and zinc. Because most of the sixteen sites sampled in 2002-03 were sampled at shallower depths than in previous studies, the results are not directly comparable to most previous studies in which water was collected at deeper depths. To compare the 2002-03 water samples to the samples collected in 1983-85 the 2002-03 samples were regrouped using only samples with specific conductance greater than 2,000 microsiemens per centimeter (µS/cm) and combined with 14 water-quality samples collected from abandoned mineshafts in 2002 (DeHay, 2003). The resultant data were only from 2002.

The Wilcoxon rank-sum test was used because it is a nonparametric test, which does not require normally distributed data. The Wilcoxon rank-sum test is done on ranked data instead of the actual constituent concentrations. The Wilcoxon rank-sum test has two hypotheses. The null hypotheses was that the concentrations of chemical constituents in the water samples from the mine workings were the same in 1983-85 and 2002. The alternative hypothesis was that the concentrations in water samples taken from the mine workings in 1983-85 and 2002 were significantly different, meaning the 2002 concentrations were either greater or lesser than concentrations in samples from 1983-85. The null hypothesis was rejected if the p-value of the test was less than or equal to 0.05.

CFC samples were collected from 18 sites to determine the time of recharge for water in the mines; however some of the samples were damaged during shipping so only data for 14 sites is available. CFCs are synthetic volatile organic compounds that have been used in refrigerants and aerosols since the 1930's. Ground-water age can be dated by measuring concentrations of CFC-11, CFC-12, and CFC-113 and relating their measured concentrations back to known historical concentrations (Plummer and Friedman, 1999). Dissolved gases (nitrogen and argon) were also collected to help estimate the recharge temperature which is needed to determine the recharge age. The accuracy of the determined recharge age depends on how perfectly the CFCs are transported in water and how the CFCs are affected by chemical processes (Plummer and Friedman, 1999). Microbial degradation and sorption onto organic or mineral surfaces can affect CFC concentrations in the ground water (Plummer and Friedman, 1999). Other factors that can affect the recharge age determination are uncertainties in recharge elevation and temperature, and mixing of younger and older waters (Plummer and Friedman, 1999).

To determine the geographic distribution of ground-water altitudes, surface-water elevations and water-quality constituents, a series of maps of those parameters were drawn. To investigate the general chemistry of the ground-water system and minerals that may be dissolved by or precipitated from the ground water, water-quality data were input to the PHREEQC mineral saturation and equilibrium model, using the default PHREEQC mineral equilibrium data base (Parkhurst and Appelo, 1999).

Quality-Assurance Samples

Quality-assurance samples were collected and analyzed to identify the degree of accuracy, precision, and bias of environmental samples. Quality-assurance samples for this study consisted of an equipment blank and three environmental replicate samples.

Equipment Blank

An equipment blank was collected to verify any water-quality effects of the sampling equipment, composed of a stainless steel and Teflon Grundfos RediFlo-2 pump and 300 feet of Teflon-lined polyethylene tubing. and the cleaning procedures used to prepare the pump for sampling. Water-quality data from that sample indicated that the sampling equipment was unlikely to have had a substantive effect on the detection of analyzed water-quality constituents (appendix 2).

Replicates

Replicate quality-control samples are used to evaluate variability in water-quality data due to analytical or sample collection procedures. Replicate samples were collected sequentially, following the collection of environmental samples, and were analyzed for concentrations of major ions and trace elements. Precision is used as a measure of variability of analytical sampling and procedures. Precision can be calculated as the relative percent difference (RPD) between the replicate and the environmental samples, as follows:

$$RPD = [|C_1 - C_2| / ((C_1 + C_2) / 2)]*100$$

where C_1 is the concentration of the environmental sample and C_2 is the concentration of the replicate sample.

If the estimated concentration of a constituent in a sample pair was less than the minimum reporting level, then the RPD was not calculated. Most of the RPD values were less than 2 percent (appendix 2). Most of the larger RPD values were associated with samples having small constituent concentrations [trace elements less than 0.5 micrograms per liter (µg/L)] (appendix 2). However, some of the samples of dissolved solids, potassium, aluminum, barium, copper and zinc had concentrations greater than 0.5 µg/L and RPD values greater than 2 percent. The results of the replicate samples indicate that the constituent concentrations were reproducible in environmental samples and were not likely to be substantially skewed by analytical or sampling procedures.

Hydrology

Hydrology of the Picher mining district is described using ground-water altitudes and surface-water elevations, precipitation, and daily streamflows. Recharge-age dating of ground-water samples is used to evaluate differences in ground-water flow.

Ground-Water Altitudes and Surface-Water Elevations

Ground-water altitudes and surface-water elevations were measured at 29 sites in the Picher mining district: 20 ground-water sites and 9 surface-water sites. The ground-water sites were abandoned mineshafts and air shafts completed in the Boone aquifer. Ground- and surface-water levels were collected synoptically four times during a 6-month period—on September 24, 2002, December 16, 2002, and January 22, 2003, and March 10, 2003. The water-level map for March 2003 (fig. 3) indicates that the water table in much of the mining district was relatively flat at about 800 feet. The relatively flat topography (except for chat piles), the fractured and karstic nature of the Boone aquifer, and especially the large interconnected voids created by the mine workings may all have contributed to a hydraulic gradient that was so small that it was within the range of measurement error. In addition, the concrete collars on many of the mineshafts sampled may have been subject to subsidence or shifting that could contribute to measurement error.

Surface-water elevations decreased by an average of about 9 feet per mile on Tar Creek and an average of about 7 feet per mile along Lytle Creek as the streams flowed southward (fig. 3). Along the upstream portions of Tar and Lytle Creeks, the surface-water elevations were several feet higher than those of surrounding ground-water altitudes. The sediments in this area appear to be saturated sediments or water is collecting over local low-permeability shales of Pennsylvanian age overlying the Boone aquifer (table 1, fig. 3). Surface water in this area may be contributing to ground-water in the mine workings. In mineshafts near that area, ground water was observed to cascade down the walls of the mineshafts. In the area of the confluence of the streams, surface-water elevations were lower than the ground-water altitudes, and the mine water is discharging to the streams in that area. The area around Douthat Bridge and southward is where the mine discharges first began flowing in the 1970s (State of Oklahoma, 2000).

The continuous water-level recorders installed in the Blue Goose and Slim Jim mineshafts (fig. 1) indicated that the aquifer near those mineshafts was recharged relatively rapidly, responding closely to precipitation events both in time and in magnitude (fig. 4). Greater evapotranspiration during the spring and summer may have diminished the magnitude of ground-water-level rises in response to storm events (fig. 4).

Surface-water runoff closely corresponded to precipitation, with mean daily streamflows at the Neosho River near Commerce gage ranging from 20 cubic feet per second at the end of a dry period in late August 2003, to about 20,000 cubic feet per second during rainy periods in March, April, and May 2003 (US Geological Survey, 2003; fig. 4). The Neosho River near Commerce gage is not shown on fig. 1, but is located 4.5 miles west of Commerce, Oklahoma, and 4 miles upstream from the confluence of Elm Creek with the Neosho River.

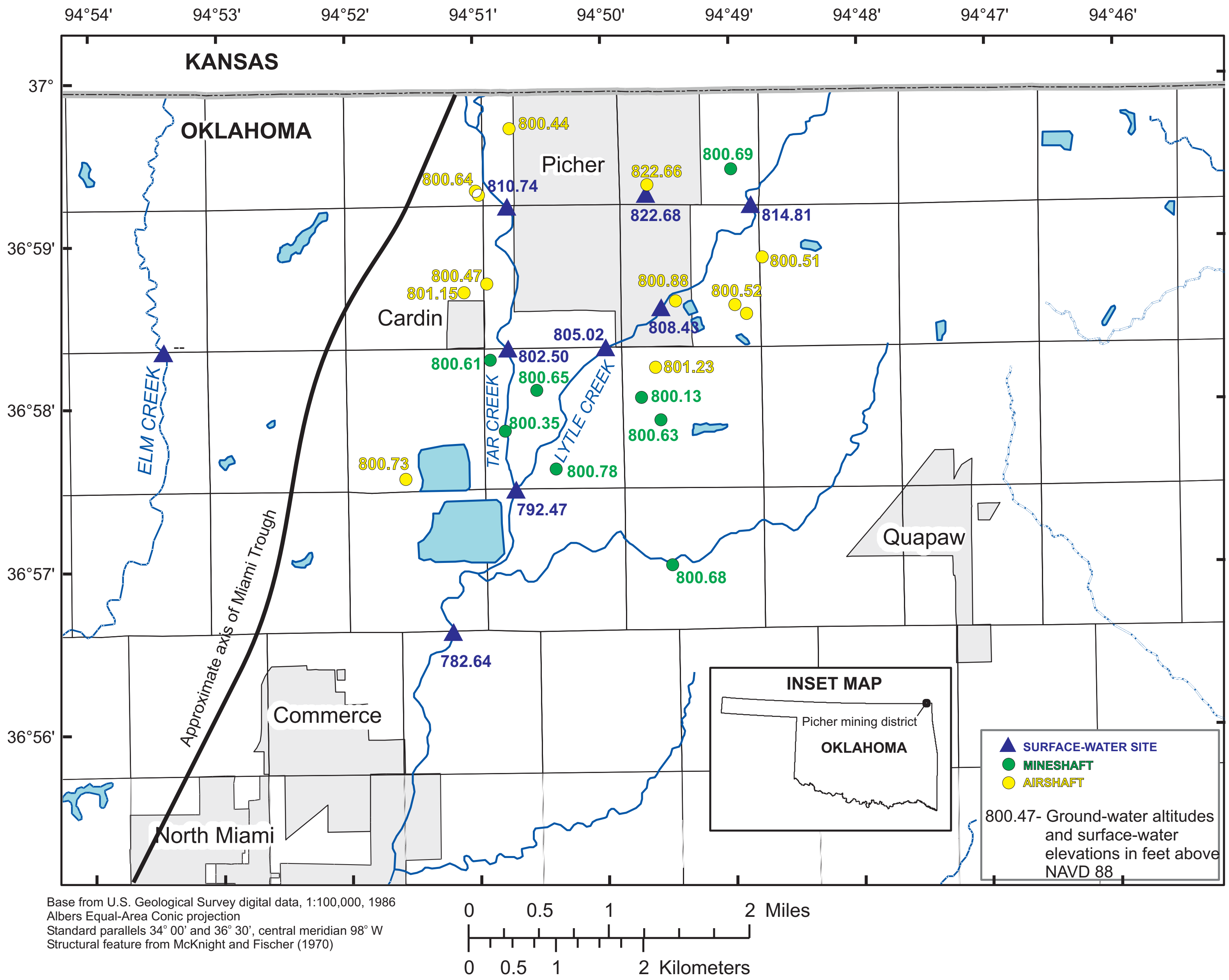
Recharge-Age Dating Using Chlorofluorocarbons and Other Dissolved Gases

As mentioned in the previous section, the water table in the mining district is relatively flat, at approximately 800 feet above NAVD 88, giving little indication of ground-water flow directions through most of the district. Recharge-age dates from CFC concentrations and dissolved gases may provide some indication of ground-water flow or recharge (appendix 3). The CFC data was difficult to interpret. The laboratory likes three duplicate samples from each well to estimate the time of recharge. Some of the samples were damaged during shipment so three samples for each well were not available. Also, CFCs are degraded under reducing conditions and the dissolved gas data indicates the water in the mine workings was highly reducing because of lack of oxygen in the samples and the presence of methane (J. Castile, U.S. Geological Survey, written. commun., 2003). The estimated recharge-age data for each sample was based mainly on CFC-113 and CFC-12 concentrations. CFC-11 is the least stable under reducing conditions (J. Castile, U.S. Geological Survey, written. commun., 2003).

Based on the available CFC data, the water samples with the youngest recharge-age dates were located in the southeastern and northern part of the mining district (fig. 5), indicating that those areas may have received more recent recharge to the Boone aquifer. Water samples with older recharge-age dates occurred toward the Miami Trough to the west (fig. 5) that could indicate that flow is much faster through the central part of the mines and is slower at the western and eastern edges so recharge rates are slower. An alternative explanation for the distribution of recharge-age dates is the relation of those dates to the type of ground-water sites sampled. Mineshafts, which had larger openings flush with the ground surface, tended to have more recent recharge-age dates than water samples from the airshafts, which had 8-12 inch openings in pipes a foot or more above the land surface. The morphology of mineshafts may be more conducive to ground water interaction with the atmosphere and runoff of recent rainfall.

Ground-Water Quality

In this section, ground-water quality of the mine workings is described using results from samples collected at 16 sites in 2002-03 (appendix 1). These data are later regrouped and compared to ground-water quality data collected in 1983-85 to eval-



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 3. Ground-water altitudes and surface-water elevations within the Picher mining district, Oklahoma, March 2003.

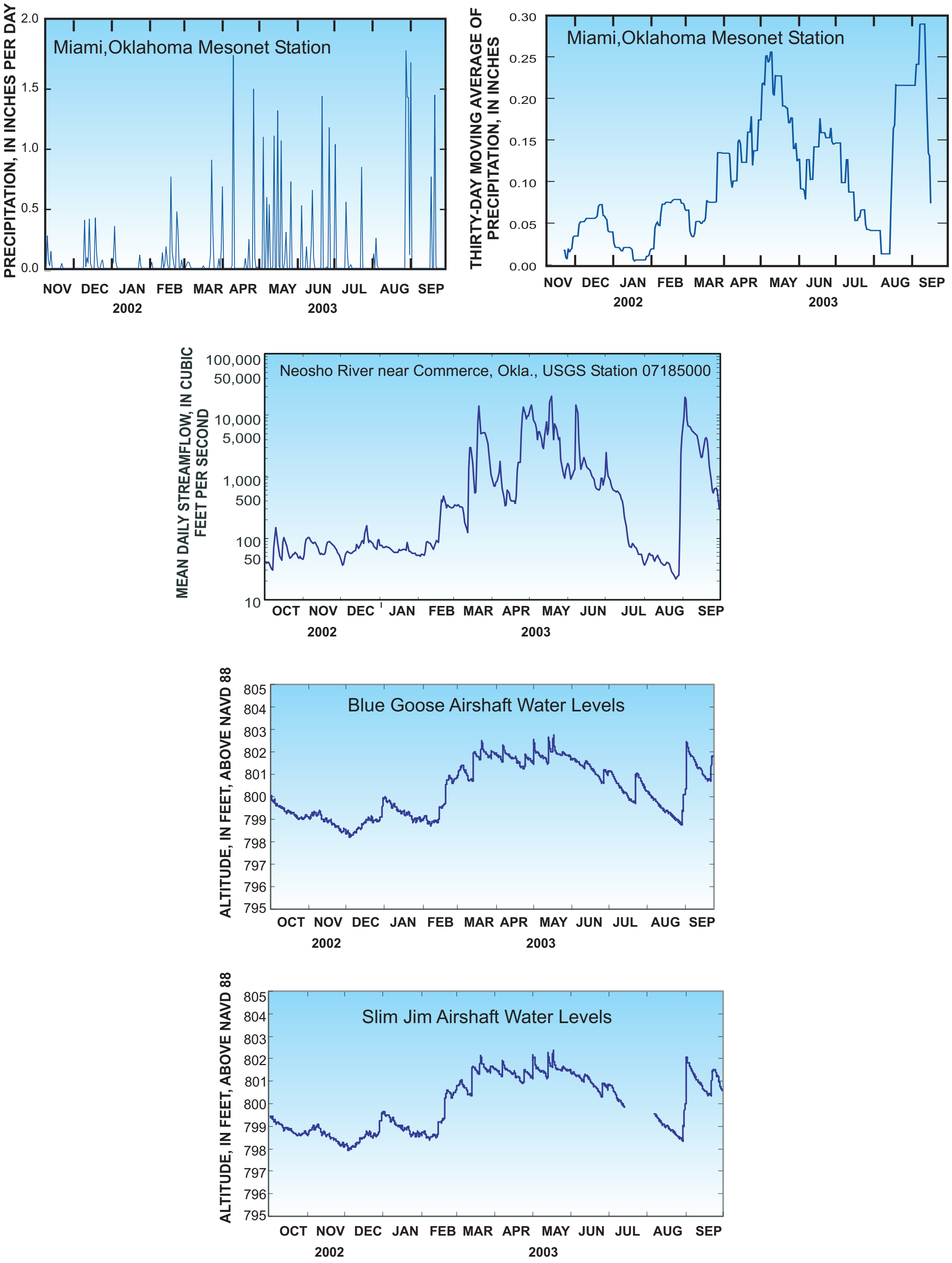
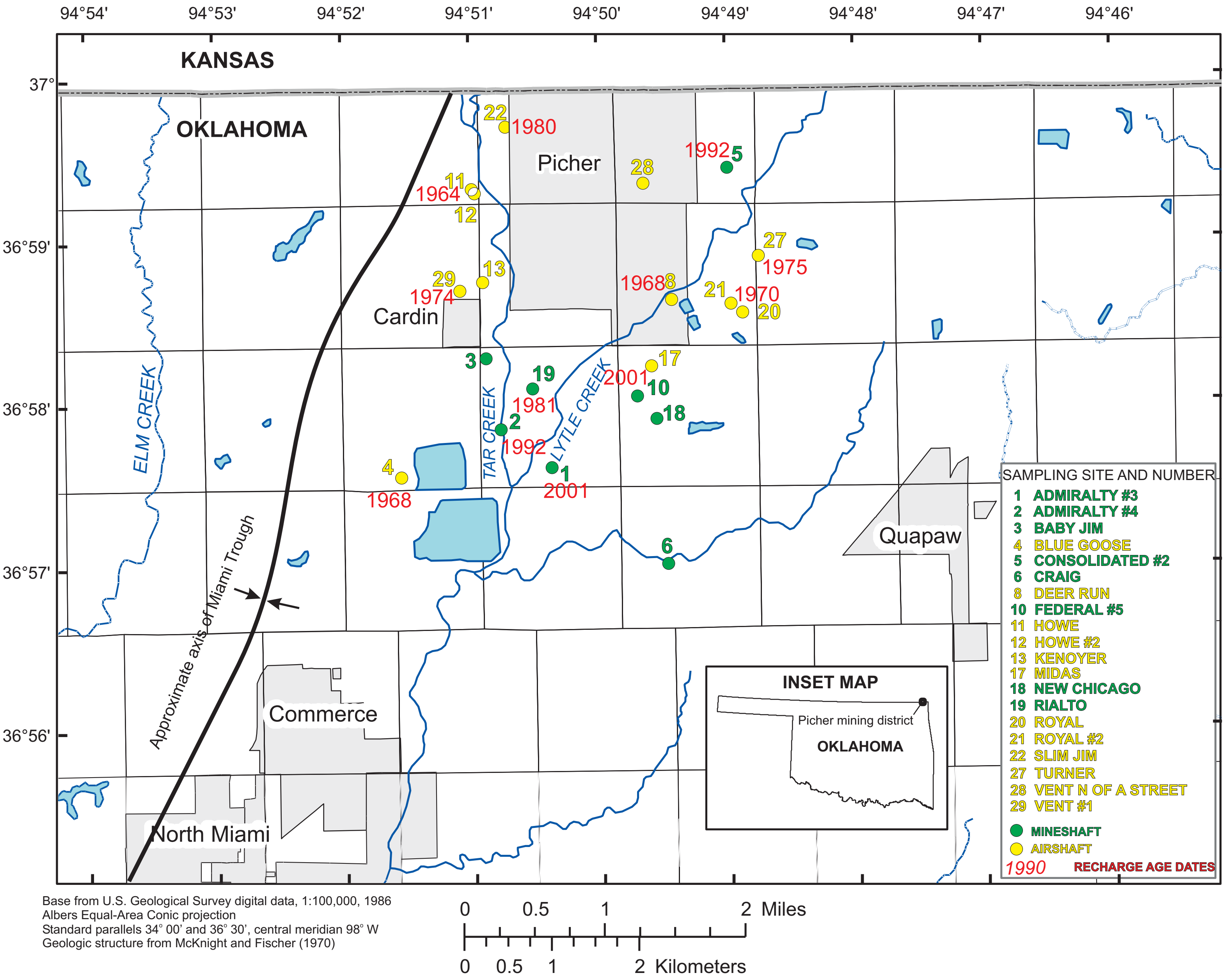


Figure 4. Daily precipitation and 30-day moving average of precipitation at the Miami, Oklahoma, Mesonet station, mean daily flows at Neosho River at Commerce, Oklahoma, and continuous water-levels at the Blue Goose and Slim Jim air-shafts within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Geologic structure from McKnight and Fischer (1970)

Figure 5. Recharge-age dates of ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

uate changes over time. When maps of water-quality data are presented, only data for samples collected from the shallow part of the mine workings are used (depths of 55-80 feet)

Ground-Water Quality of the Mine Workings in the Picher Mining District, 2002-03

Specific conductances in the mine workings in the Picher mining district were relatively large ranging from 463 to 2,860 µS/cm, with a median concentration of 1,560 µS/cm (table 4; appendix 1). Specific conductance is related to the concentration of dissolved constituents in the water. The large specific conductance values indicate relatively large dissolved-solids concentration (fig. 6).

Water-sample pHs were generally slightly acidic, with only 25 percent of the samples having neutral or alkaline pH (greater than 7.0) (table 4). The median pH value was 6.7, ranging from 6.0 to 7.9. There was no particular pattern relating pH and recharge-age dates in the water samples (fig. 7), so pH must be due to local factors such as dissolution of carbonate minerals and buffering capacity of carbonate minerals in the aquifer matrix.

All water samples contained at least small concentrations of dissolved oxygen (table 4), ranging from 0.3 to 8.2 mg/L. However, in samples where dissolved oxygen was less than 1.0 mg/L, the oxygen could have been introduced during the sampling process and the dissolved-oxygen concentration in the aquifer may have been less. The low dissolved oxygen concentrations were associated with samples containing high dissolved iron concentration that indicates possible anoxic conditions in much of the aquifer. While sampling the sites with dissolved oxygen less than 1.0 mg/L, hydrogen sulfide odors were noted to emanate from the water. Four of the sixteen ground-water sites had dissolved oxygen concentrations greater than 1.0 mg/L (fig. 8). As with recharge age-dates and dissolved-solids concentration, dissolved oxygen in the ground-water locally may be affected by greater exposure to the atmosphere and greater recharge from surface runoff through open mineshafts.

About half of the alkalinities in the ground-water samples exceeded 200 mg/L as calcium carbonate (table 4), which is consistent with the dissolution of carbonate minerals in the mine workings. Calcium and magnesium concentrations were relatively large (table 4), which is consistent with the large alkalinities and not unusual in an aquifer containing slightly acidic water and abundant calcite and dolomite. Calcium concentrations ranged from 79.7 to 581 mg/L, and magnesium concentrations ranged from 6.01 to 123 mg/L. The cationic ratios were dominated by calcium, with magnesium as a secondary constituent (fig. 9).

Sodium (fig. 10) and potassium were relatively minor cationic constituents of the water samples. There were, however, several sites that had from 20 to 50 percent of total cations that were sodium plus potassium (fig. 9). Ground water can become more enriched in sodium and potassium due to gradual dissolution of silicate minerals with increased residence time and contact with aquifer materials (Kharaka and Hanor, 2003).

Sulfate was the dominant anion in most of the samples and calcium was the dominant cation, meaning that most samples were in the $CaSO_4$ (gypsum/anhydrite) portion of the piper diagram (fig. 9). Sulfate concentrations ranged from 85.8 to 1,750 mg/L. Sulfate concentration exceeded the U.S. Environmental Protection Agency (USEPA) secondary drinking-water standard of 250 mg/L (USEPA,2004) in most of the samples (table 4, fig. 11). Sulfate concentration may have been related to local oxidation of sulfide minerals or dissolution of gypsum formed when the mines were open and exposed to oxygen (McKnight and Fischer, 1970). Although ground water was probably anoxic over much of the sampled area, the abundant iron in the aquifer may act as a sink that takes up much of the dissolved oxygen and forms iron oxyhydroxide minerals (Hem, 1992). Chloride occurred in relatively small concentrations in ground-water samples collected in the mining district except for the Blue Goose airshaft (table 4, fig. 9).

Dissolved trace elements were dominated by iron, manganese, and zinc (fig. 12). Approximately two-thirds of the iron concentrations, nine-tenths of the manganese concentrations, and one-third of the zinc concentrations exceeded USEPA secondary drinking-water standards for those trace elements (fig. 12, U.S. Environmental Protection Agency, 2004). Secondary standards for those trace elements were established to prevent taste or staining problems from water, rather than any possible deleterious health effects from consumption of water with elevated concentrations of those trace elements.

Substantial portions of the samples exceeded the USEPA Chronic Criterion Concentrations for protection of aquatic life for concentrations of cadmium, nickel, and zinc (USEPA, 2004; fig. 12). The greatest concentrations of trace elements, except cadmium, were associated with water samples having pH of 6.5 or less and dissolved oxygen concentration less than 1.0 mg/L (fig. 13), which are conditions favorable to dissolution of iron and manganese oxides and hydroxides (Elder, 1988, p. 11-16). The sum of dissolved trace elements concentration tended to be greatest at sites that produced water samples with lesser pHs and dissolved oxygen concentrations (fig. 13).

Four of the water samples contained arsenic concentrations ranging from 27 to 51 µg/L (appendix 1) that exceeded the proposed USEPA drinking-water standard of 10 µg/L (U.S. Environmental Protection Agency, 2004). Two of the samples exceeding the USEPA drinking-water standard were collected from the deeper part of the aquifer and are not shown on figure 14. Arsenic was generally not detected at concentrations greater than the reporting limit of two at most of the sampling sites (fig. 14). The large arsenic concentrations seem to be associated with large iron concentrations (fig. 15) suggesting the source of arsenic may be dissolution of iron-containing sulfide or oxyhydroxide minerals.

Cadmium is a metal occurring in trace concentrations in the ore-bearing units of the mining district. Consumption of drinking water containing small concentrations of cadmium may cause damage of renal tubes in kidneys and greater rates of

Table 4. Summary statistics of water properties, major ions, and dissolved trace elements for ground-water samples collected in the Picher mining district, Oklahoma, 2002-03

[µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; LRL, laboratory reporting level; --, no statistic calculated; ---- , no censored data for this constituent; <, less than;]

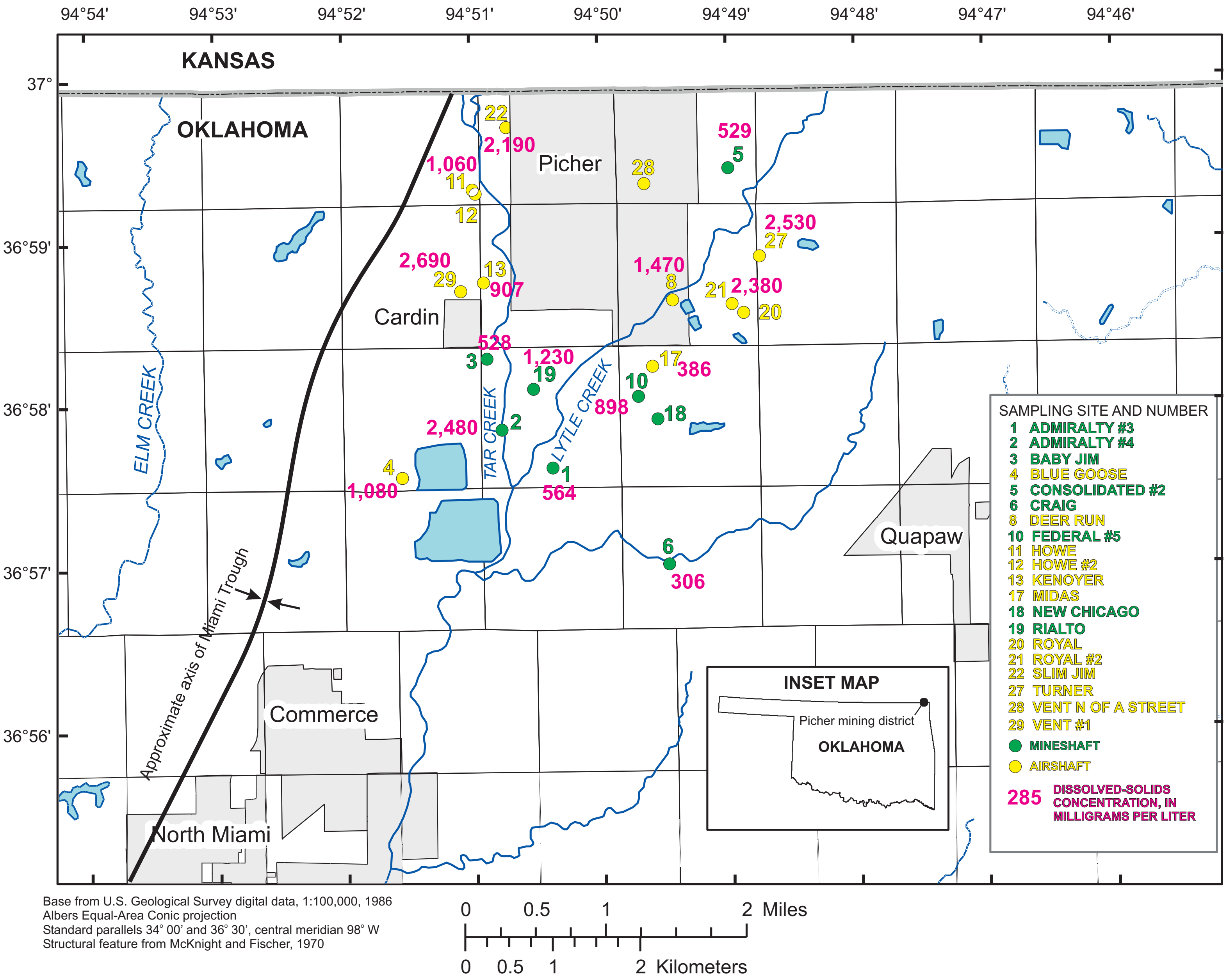
Constituents and physical properties	Statistics method[1]	Number of samples	LRL	Minimum	Percentiles			Maximum
					25	50	75	
Specific conductance (µS/cm at 25°C)	1	18	----	463	858	1,560	2,510	2,860
pH, field (standard units)	1	18	----	6.0	6.5	6.7	7.0	7.9
Water temperature (°C)	1	18	----	15.6	16.0	16.2	17.1	18.0
Dissolved oxygen (mg/L)	1	17	----	0.3	0.3	0.7	0.9	8.2
Hardness, total (mg/L as $CaCO_3$)	1	18	----	220	415	670	1600	1,800
Alkalinity, lab (mg/L as $CaCO_3$)	1	18	1	64	152	197	265	362
Dissolved solids (mg/L)	1	18	10	306	608	1,155	2,455	2,870
Calcium (mg/L)	1	18	0.012	79.7	130	172	454	581
Magnesium (mg/L)	1	18	0.008	6.01	19.7	45.2	88.4	123
Sodium (mg/L)	1	18	0.09	3.06	11.8	40.2	59.3	326
Potassium (mg/L)	1	18	0.11	0.72	2.14	4.34	6.94	14.6
Sulfate (mg/L)	1	18	0.18	85.8	313	630	1,488	1,750
Chloride (mg/L)	1	18	0.20	0.67	1.94	7.42	18.28	147
Fluoride (mg/L)	1	18	0.17	<0.17	0.22	0.38	1.44	3.32
Bromide (mg/L)	2	18	0.016	<0.02	0.03	0.06	0.11	0.47
Silica (mg/L)	1	18	0.13	6.72	9.18	12.4	13.4	21.8
Aluminum (µg/L)	2	18	1.6	<2	<2	<2	15	267
Antimony (µg/L)	3	18	0.3	<0.30	--	--	--	<0.60

Table 4. Summary statistics of water properties, major ions, and dissolved trace elements for ground-water samples collected in the Picher mining district, Oklahoma, 2002-03—Continued

[µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; LRL, laboratory reporting level; --, no statistic calculated; ---- , no censored data for this constit-

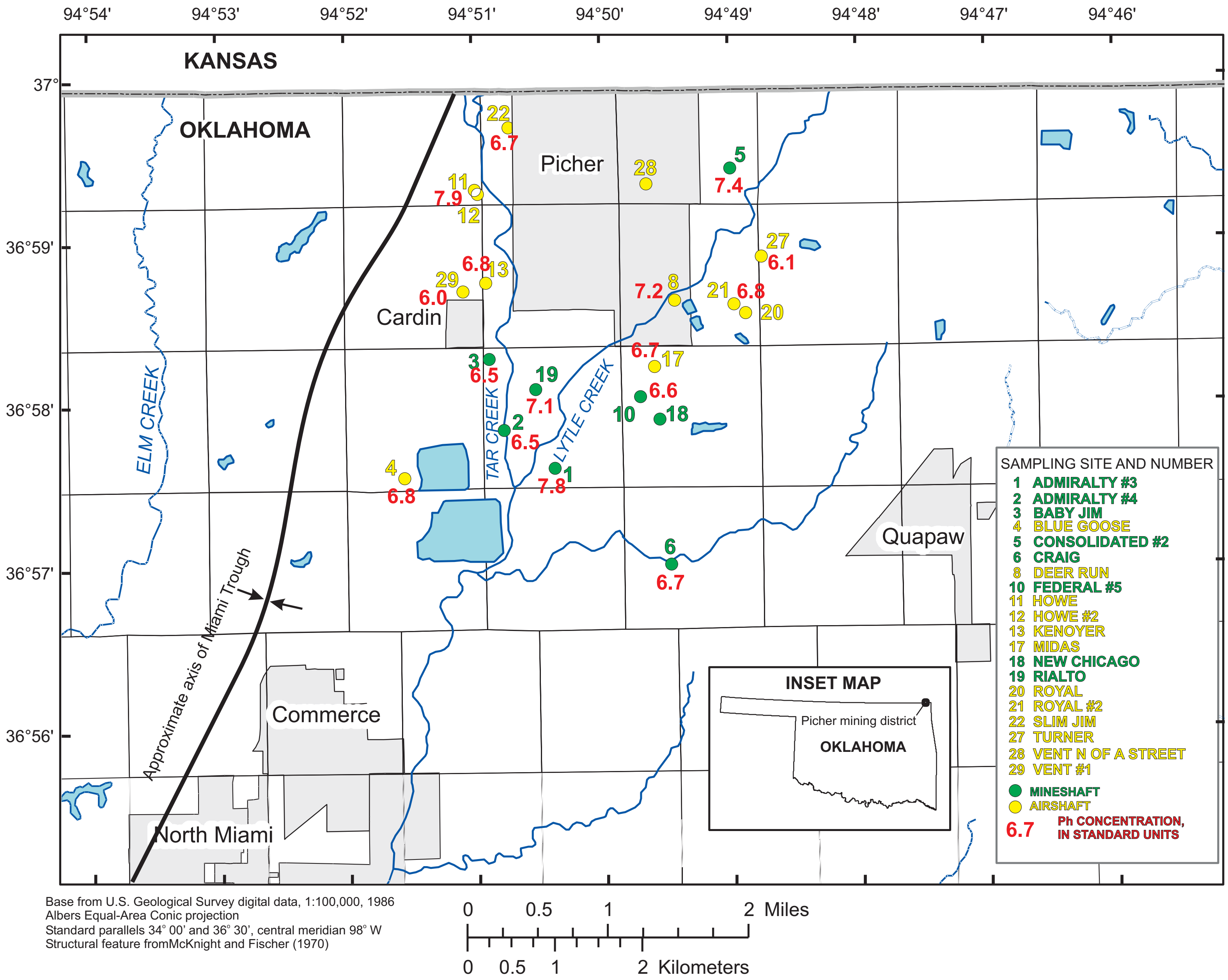
Constituents and physical properties	Statistics method[1]	Number of samples	LRL	Minimum	Percentiles			Maximum
					25	50	75	
Arsenic (µg/L)	2	18	1.9	<2	<2	<2	9.75	51
Barium (µg/L)	1	18	0.05	6	10.8	22.5	34.5	58
Beryllium (µg/L)	2	18	0.06	<0.06	<0.06	<0.06	0.14	0.3
Cadmium (µg/L)	1	18	0.037	<0.04	<0.04	0.34	2.32	113
Chromium (µg/L)	3	18	0.80	<0.80	--	--	--	<0.80
Cobalt (µg/L)	1	18	0.015	0.21	0.48	2.48	32.2	74.2
Copper (µg/L)	1	18	0.23	0.90	2.12	2.40	3.75	8.4
Iron (µg/L)	2	18	10	<10	<10	3,350	39,900	115,000
Lead (µg/L)	2	18	0.08	<0.08	<0.08	0.14	0.75	16.9
Manganese (µg/L)	1	18	0.18	0.6	186	622	1,565	4,680
Molybdenum (µg/L)	2	18	0.33	<0.33	<0.33	0.60	2.0	3.7
Nickel (µg/L)	1	18	1.0	3.55	11.6	22.4	163	633
Selenium (µg/L)	2	18	2.6	<3	<3	3	--	3
Silver (µg/L)	3	18	0.2	<0.2	--	--	--	<0.2
Zinc (µg/L)	1	18	1	2	978	2,080	5,482	20,100
Uranium (µg/L)	1	18	0.018	0.13	0.22	0.44	1.34	10.3

[1] Statistical Method 1. ordinary percentile calculation; 2.censored data present, (Helsel and Hirsch, 1992), 3. no calculation, more than 80 percent of the data were censored.



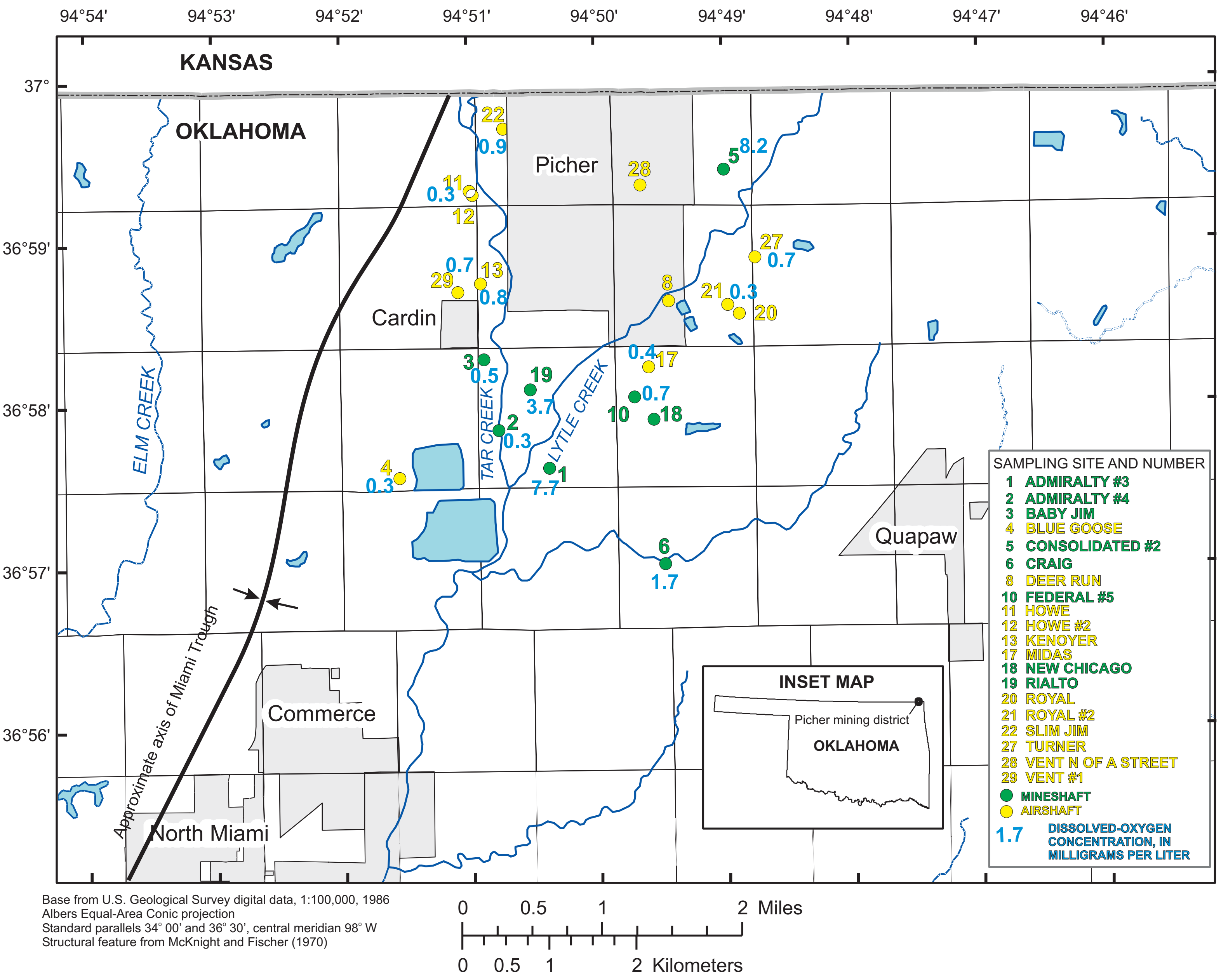
Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer, 1970

Figure 6. Dissolved-solids concentrations in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature fromMcKnight and Fischer (1970)

Figure 7. pH in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



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Structural feature from McKnight and Fischer (1970)

Figure 8. Dissolved-oxygen concentrations in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

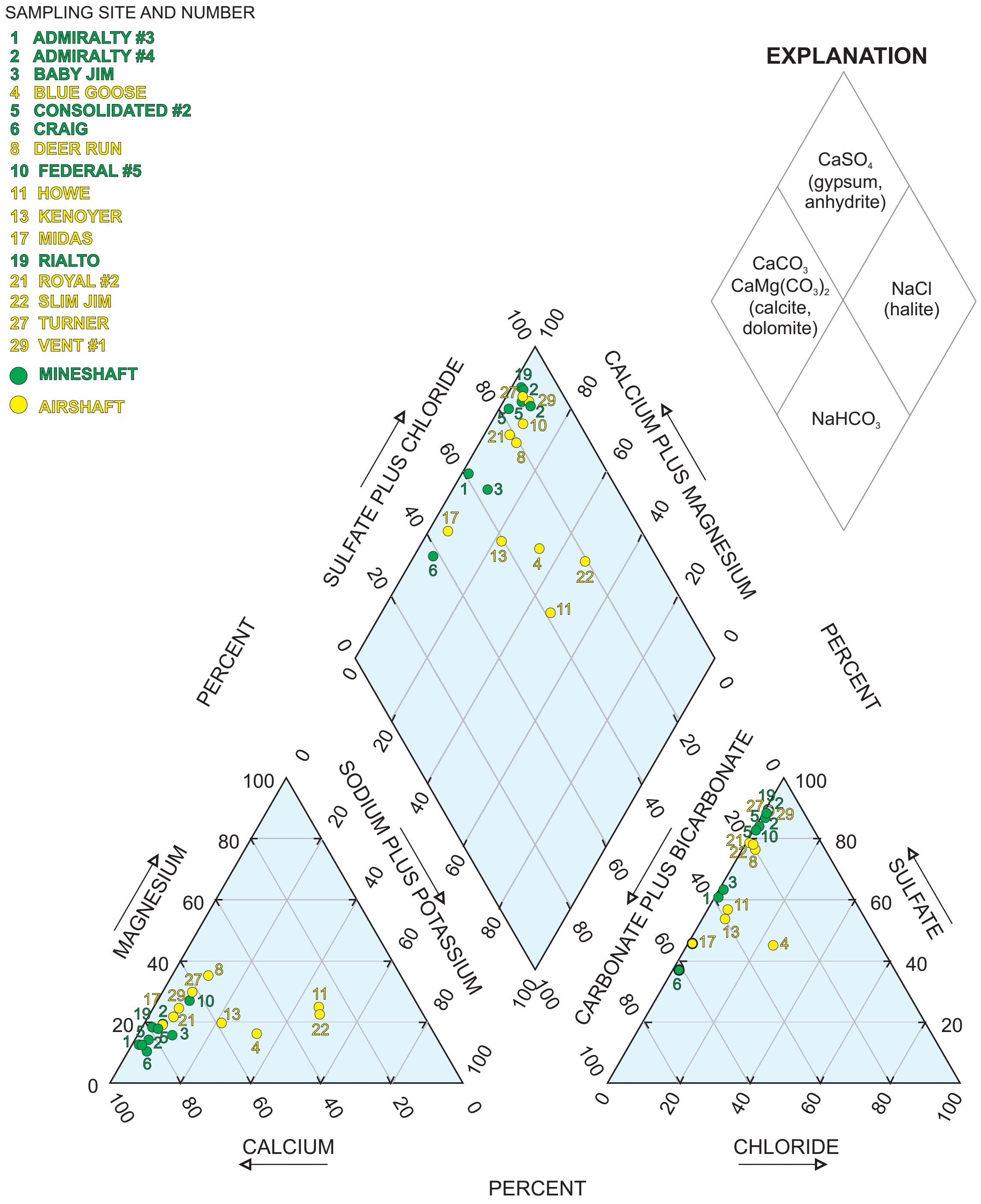
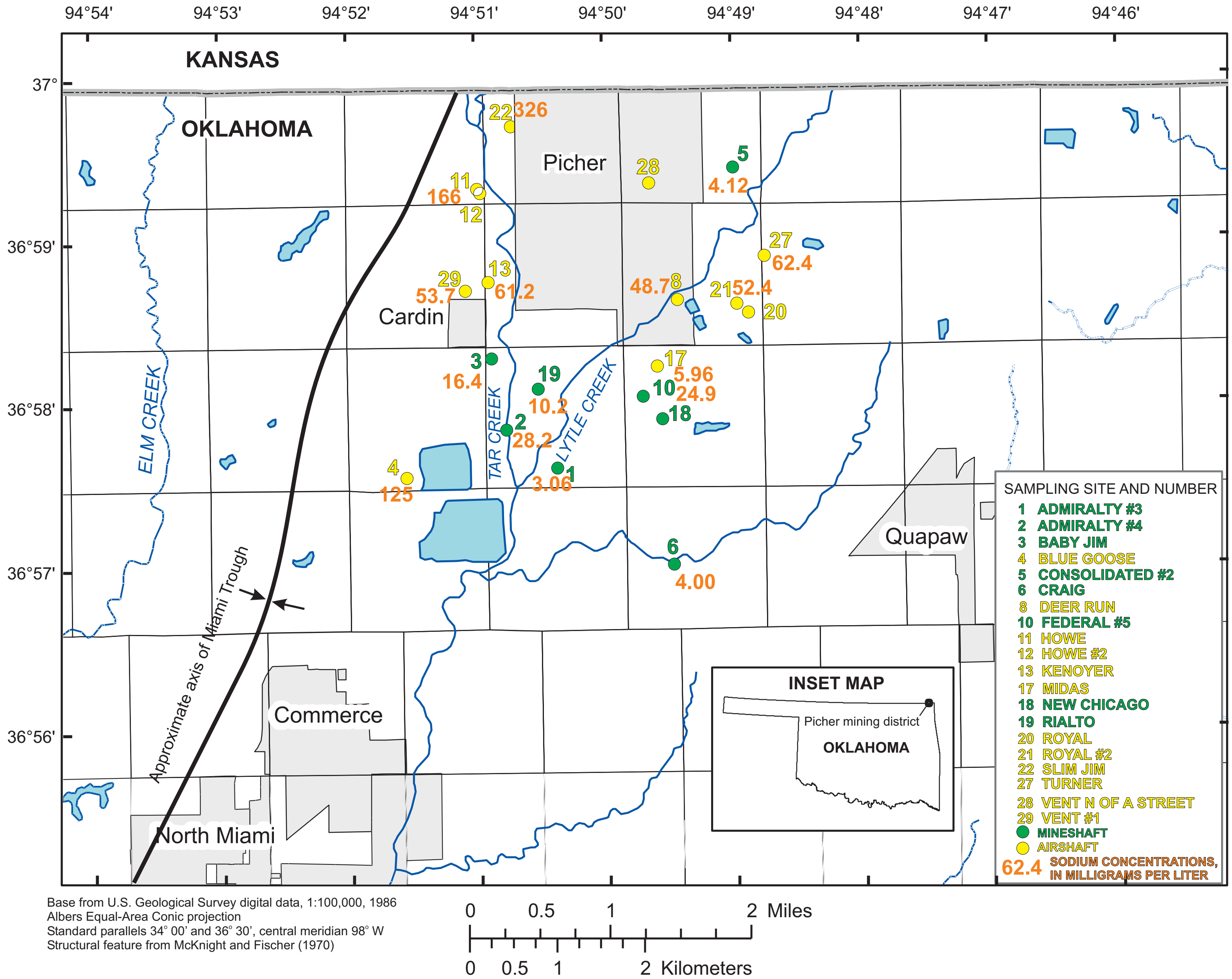
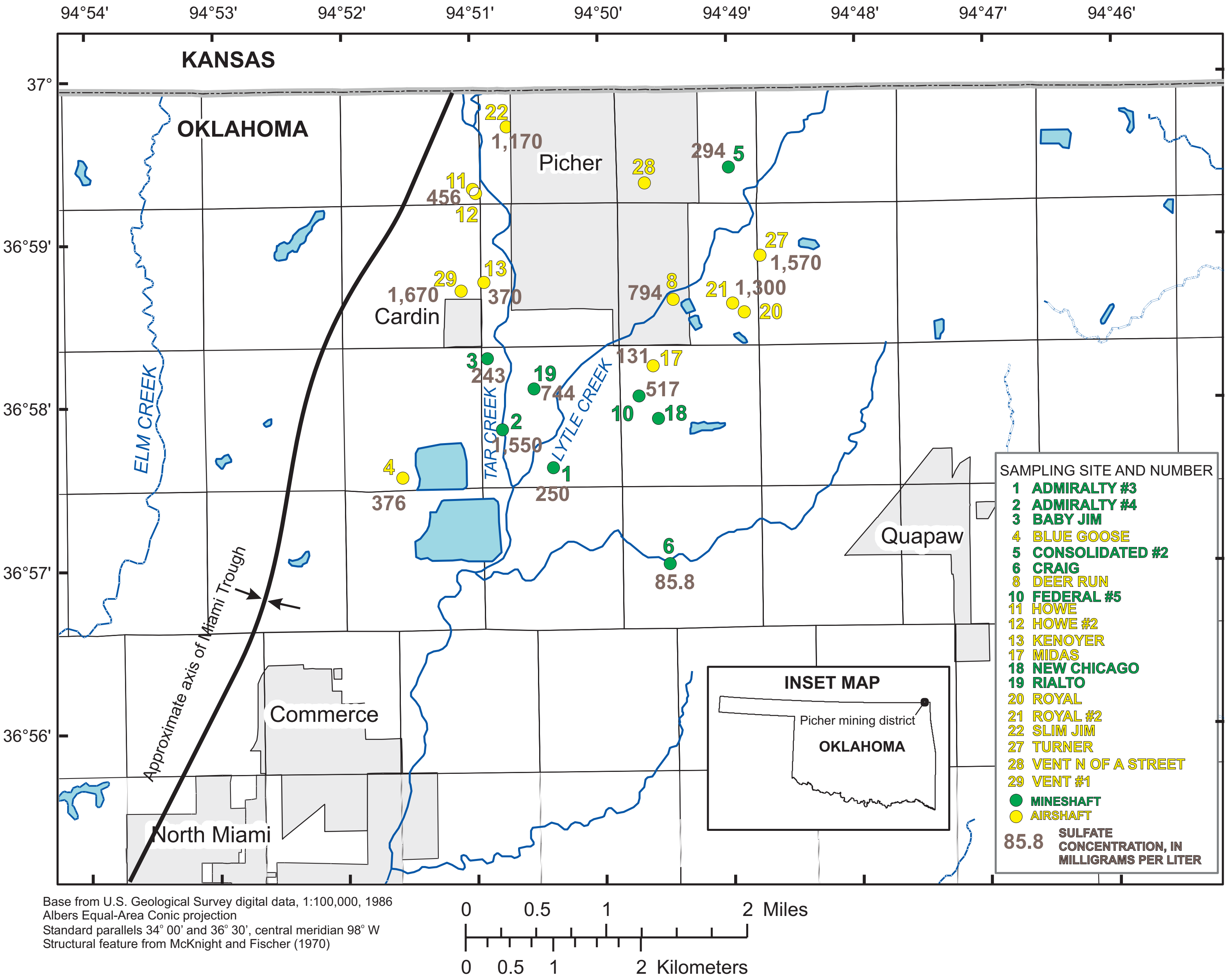


Figure 9. Major-ion composition in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 10. Sodium concentrations in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 11. Sulfate concentration in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

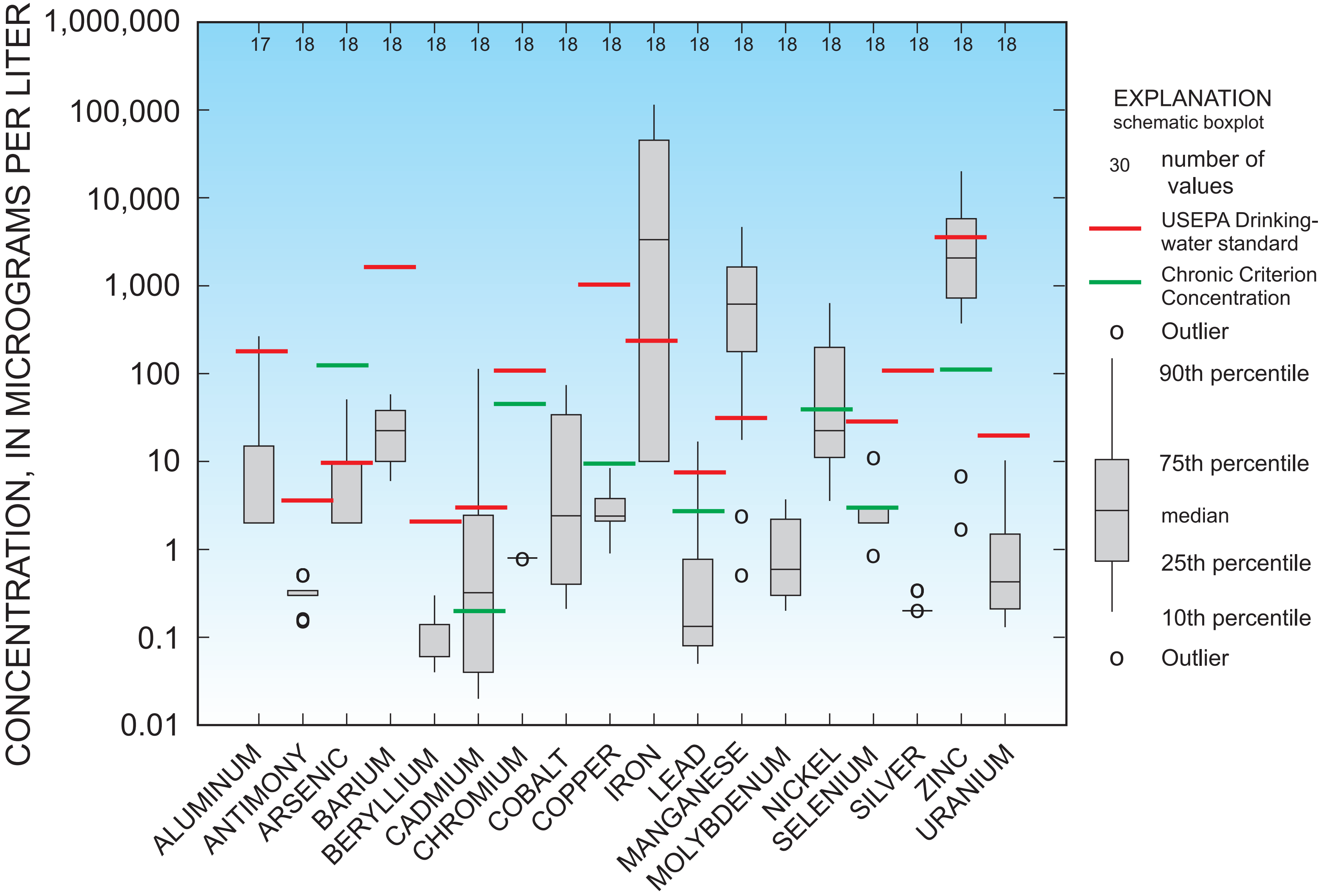


Figure 12. Concentrations of dissolved trace elements in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

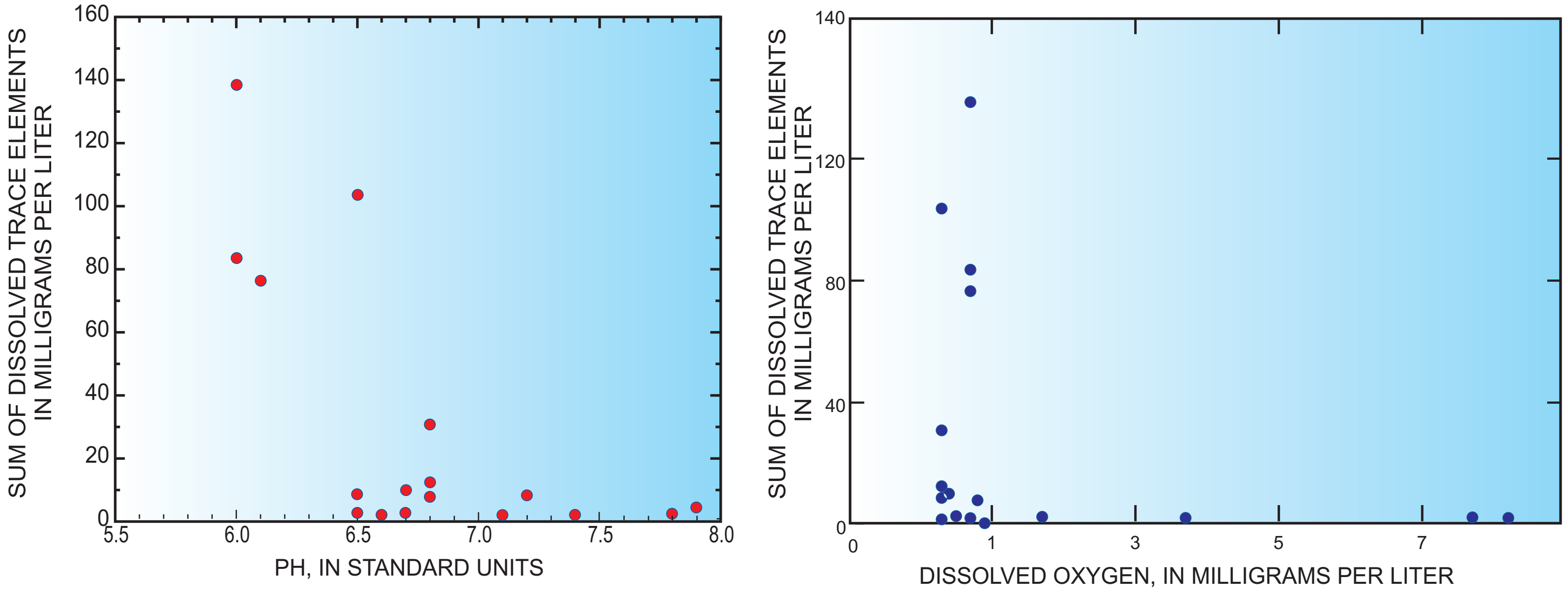
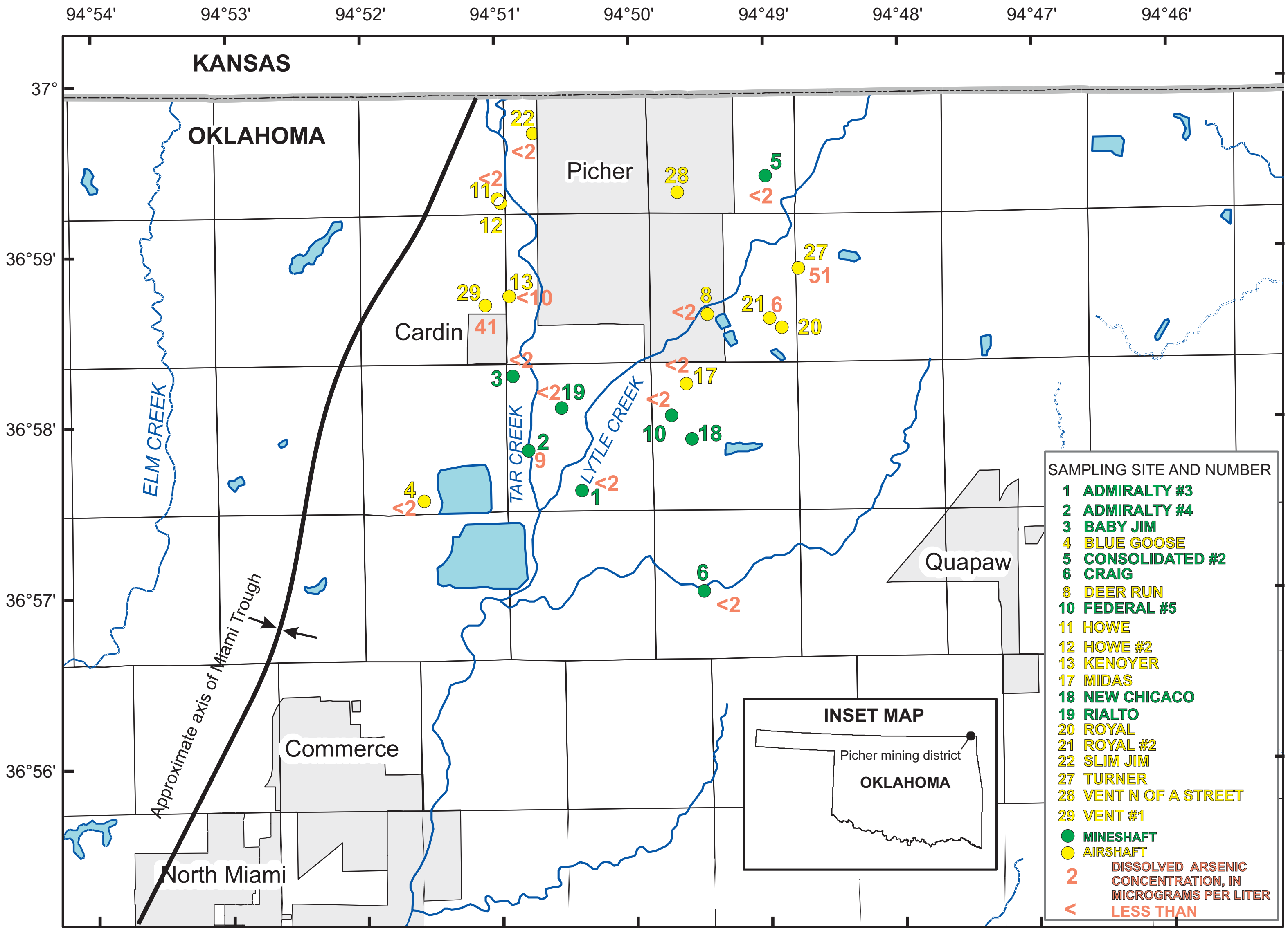


Figure 13. Sum of dissolved trace elements concentration, in relation to pH and dissolved oxygen in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 14. Arsenic concentrations in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

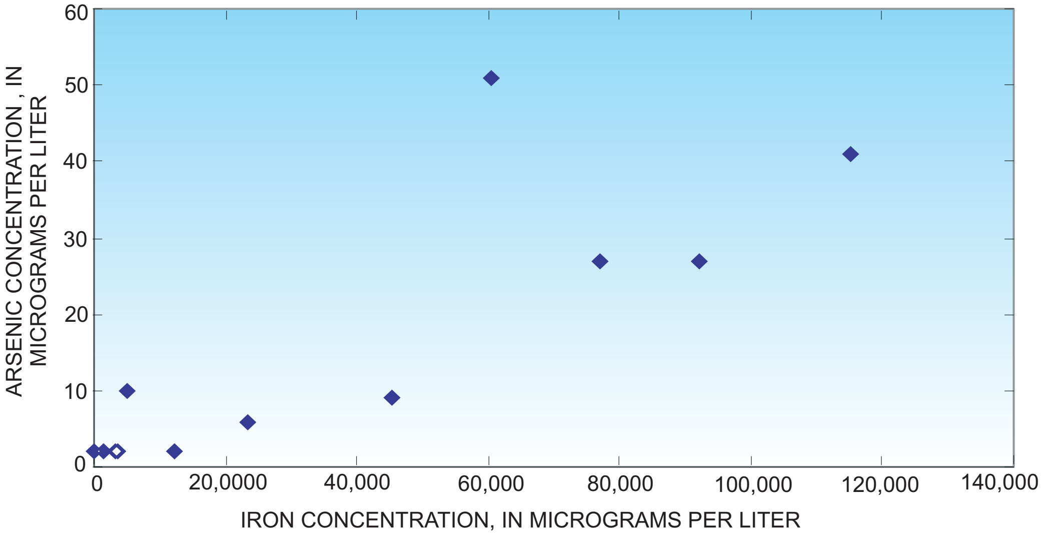


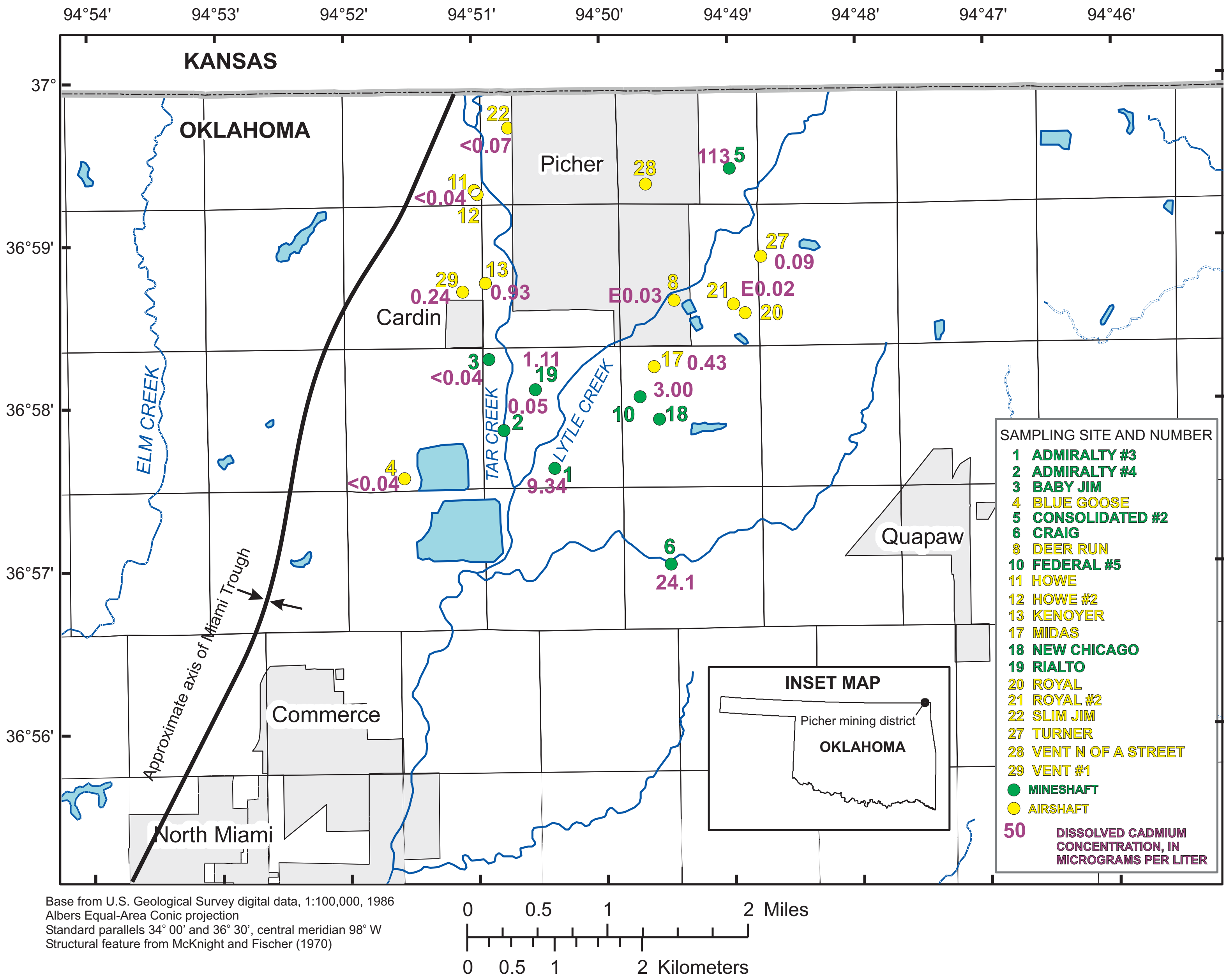
Figure 15. Relation between dissolved arsenic concentrations and dissolved iron concentrations in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

osteoporosis, may cause birth defects, and may be carcinogenic (Jarup and others, 1998; Reesal and others, 1987). The USEPA established a maximum contaminant level for cadmium in drinking water of 5 µg/L (U.S. Environmental Protection Agency, 2004). Cadmium concentration was generally less than 1 µg/L, with the exceptions of the Consolidated#2 mineshaft in the northeast part of the mining district and the Admiralty#3, Craig, and Federal#5 mineshafts in the southern part of the district (fig. 16). Larger cadmium concentrations appear to be associated with sites that have small iron concentrations and more oxygenated waters. This is noteworthy because since the small sulfate and iron concentrations in the waters could lead to conclusions that the waters are less contaminated than waters with large sulfate and iron concentrations.

Iron was the metal that occurred in the largest concentrations in the ground-water samples compared to other trace elements (table 4). The largest iron concentrations occurred at the Royal#2, Turner, and Vent#1 airshafts, and the Admiralty#4 mineshaft in which ground-water samples had relatively low pH and small dissolved oxygen concentrations (figs. 7, 8, and 17). Iron concentrations had a similar distribution in the samples as sulfate, indicating possible relation to oxidation and dissolution of the iron-sulfide minerals marcasite and pyrite.

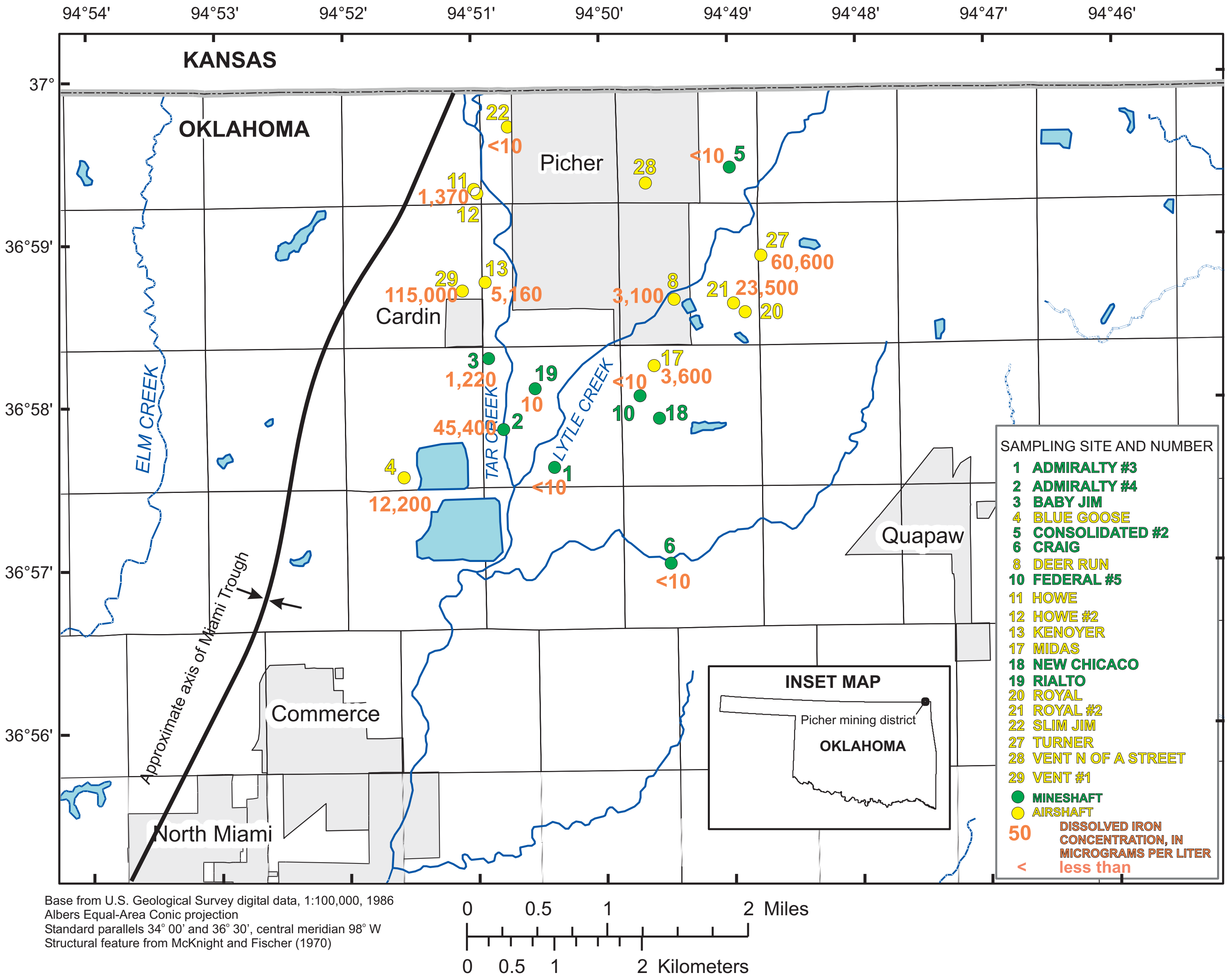
The occurrence and distribution of lead merits concern, not only because of its known occurrence in the rocks composing the Boone Formation, but also because of the known deleterious health effects of consumption of even small concentrations of lead through water or other media. Lead is widely known as a neurotoxin, capable of causing learning disorders, memory lapses, irritability, fatigue, dizziness, depression, peripheral neuropathy (lead palsy) and also has been linked to kidney damage, hearing loss, impotence, and increased incidence of miscarriage, and is a possible carcinogen (Canadian Centre for Occupational Health and Safety, 1998; Agency for Toxic Substances and Disease Registry, 1999b, and U.S. Environmental Protection Agency, 2003). Most of the ground-water samples had detectable concentrations of lead (fig. 18; appendix 1). Only one sample, from the Admiralty#3 mineshaft, exceeded the USEPA Treatment Technique level of 15 µg/L (USEPA, 2004), which can only occur in 10 percent of water samples from a public-water supply before corrective action must be taken (U.S. Environmental Protection Agency, 2004).

Manganese is commonly associated with iron and, similar to iron, tends to occur in greater concentrations in water under reducing conditions. In oxidizing conditions, manganese tends to form low-solubility oxides and hydroxides, limiting concentrations in water. Although manganese is not regarded as being as toxic or hazardous as cadmium or lead, long-term consumption of water or food with large concentrations of manganese has been associated with a condition known as manganism, the symptoms of which are mental and emotional disturbances and slow, clumsy body movements (Agency for Toxic Substances



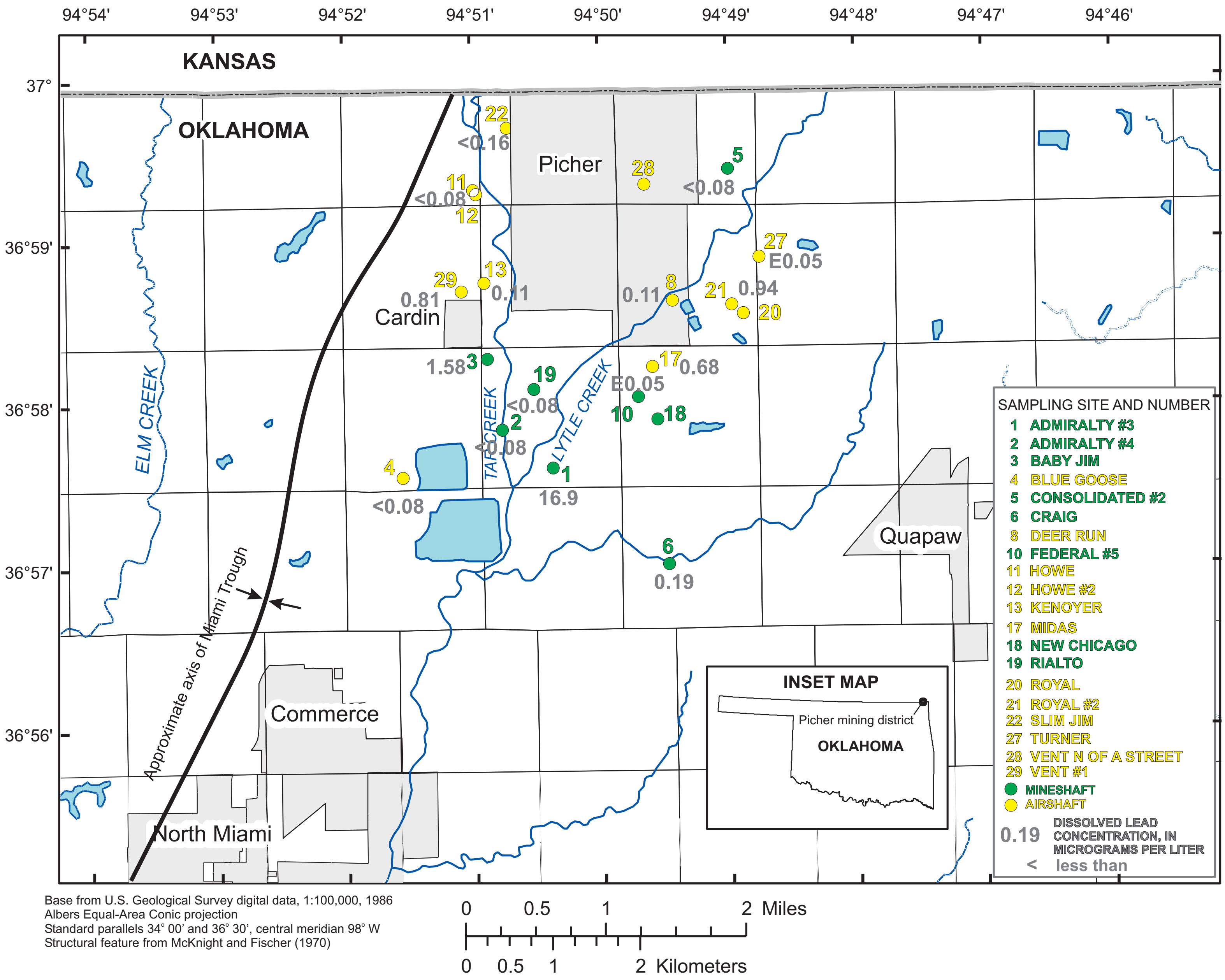
Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 16. Cadmium concentrations in ground-water samples collected within the Picher mining district, Oklahoma 2002–03.



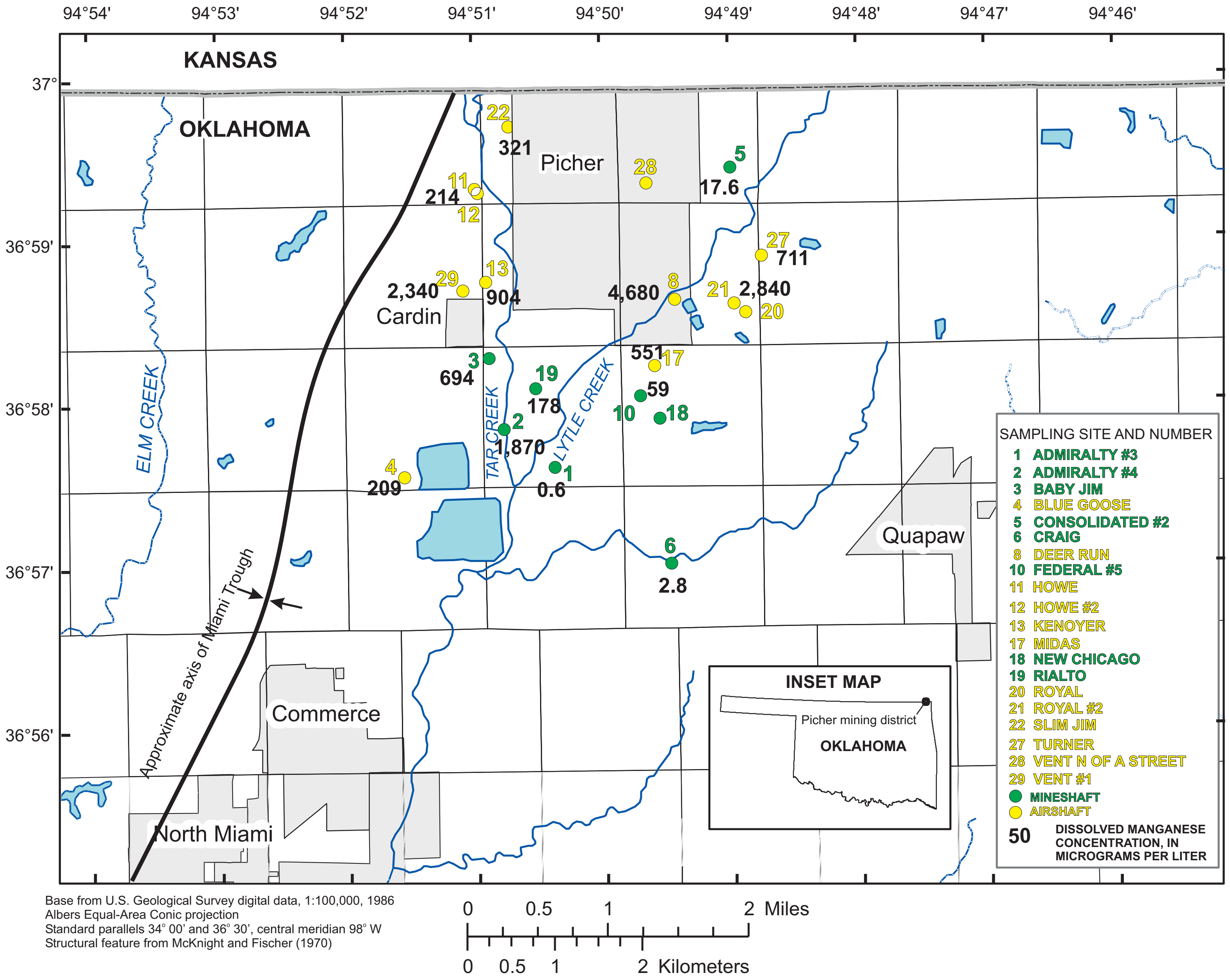
Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 17. Iron concentration in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 18. Lead concentration in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 19. Manganese concentration in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

and Disease Registry, 1995). Manganese concentrations were associated with areas with lesser pH (figs. 7 and 19).

Zinc, like manganese, is commonly considered to be a dietary supplement rather than a toxic element. However, at elevated concentrations, short-term intake of zinc has been associated with stomach cramps, nausea and vomiting, and debilitated immune systems (Agency for Toxic Substances and Disease Registry, 2003). Long-term ingestion of zinc at large concentrations (100-150 milligrams per day) has been associated with anemia, pancreas damage, and decreased levels of high-density lipoprotein (HDL) cholesterol (Agency for Toxic Substances and Disease Registry, 2003). Water from the Vent#1 airshaft had the greatest zinc concentration (20,100 µg/L or 20.1 mg/L). Similar to manganese, the largest zinc concentrations were associated with sites with the most acidic pHs and the lowest dissolved oxygen concentrations (figs. 7, 8, and 20).

Ground-Water-Quality Changes from 1983-85 to 2002

Because most of the 16 sites sampled in 2002-03 were sampled at shallower depths than in previous studies and were potentially influenced by water from other zones, those water-quality data may not be directly comparable to data from previous studies in which samples were collected in the mine workings. The USGS collected water from the mine workings within the Picher mining district in 1983-85 (Parkhurst, 1987). The sites sampled in 1983-85 were mineshafts and airshafts located near to those sampled in 2002-03. To compare the 2002-03 data with data collected in 1983-85, a subset of 21 samples was selected—7 samples from this study and 14 samples collected from abandoned mineshafts in 2002 (Appendix 4; DeHay, 2003) (which will be referred to as 2002 in this section).

The water-quality samples from the abandoned mineshafts indicated water within the mine workings typically had a specific conductance greater than 2,000 µS/cm. So for this comparison, 21 water-quality samples collected in 2002 with a specific conductance greater than 2,000 µS/cm were selected to compare to data from the mine workings in 1983-85. Water-quality data from ground-water samples collected in 1983-85 were included in the comparison, except data from two sites sampled in Kansas (Parkhurst, 1987), which were outside of the study area of this report.

Water-quality data from the 35 samples collected in 1983-85 were compared to water-quality data from 21 samples collected in 2002 using the Wilcoxon rank-sum test (Helsel and Hirsch, 1992), which can produce a p-value as a measure of the probability of similarity of data groups. Lesser p-values indicate less likelihood of the null hypothesis being significant. For this report a p-value of less than 0.05 means that constituent concentrations in samples collected in 2002 were different than in those 1983-85, at a confidence level greater than 95 percent.

The Wilcoxon rank-sum test indicated that the concentrations of most mine-water indicator constituents were greater in 1983-85 samples than in 2002 samples, except for pH values that were greater in the 2002 samples and calcium concentrations that did not change significantly (figs. 21 and 22). Arsenic concentrations were not available for the 1983-85 data so they could not be compared.

Specific conductance in 2002 samples were less than in 1983-85 samples, indicating decreases in dissolved mineral constituents with time in local ground water. The median value of specific conductance was 3,820 µS/cm in 1983-85 and 2,630 µS/cm in 2002 within the mine workings (fig. 21).

The pH has significantly ($p<0.0001$) increased in the mine workings since 1983-85. Median pH values were slightly acidic (less than 7.0) both in 1983-85 and in 2002, with the median value of pH in the 1983-85 data set being 5.7 and the median value in the 2002 data set being 6.1 (fig. 21). However, in the 1983-85 data set, there were more outliers having pH concentrations less than 4.8 compared to the 2002 data. In the 2002 data set the range of concentrations tended to be smaller and closer to neutral (fig. 21). The increase in pH since 1983-85 is probably due to reduction in sulfide oxidation indicated by a significant reduction in dissolved iron and zinc along with the continued dissolution of carbonate minerals.

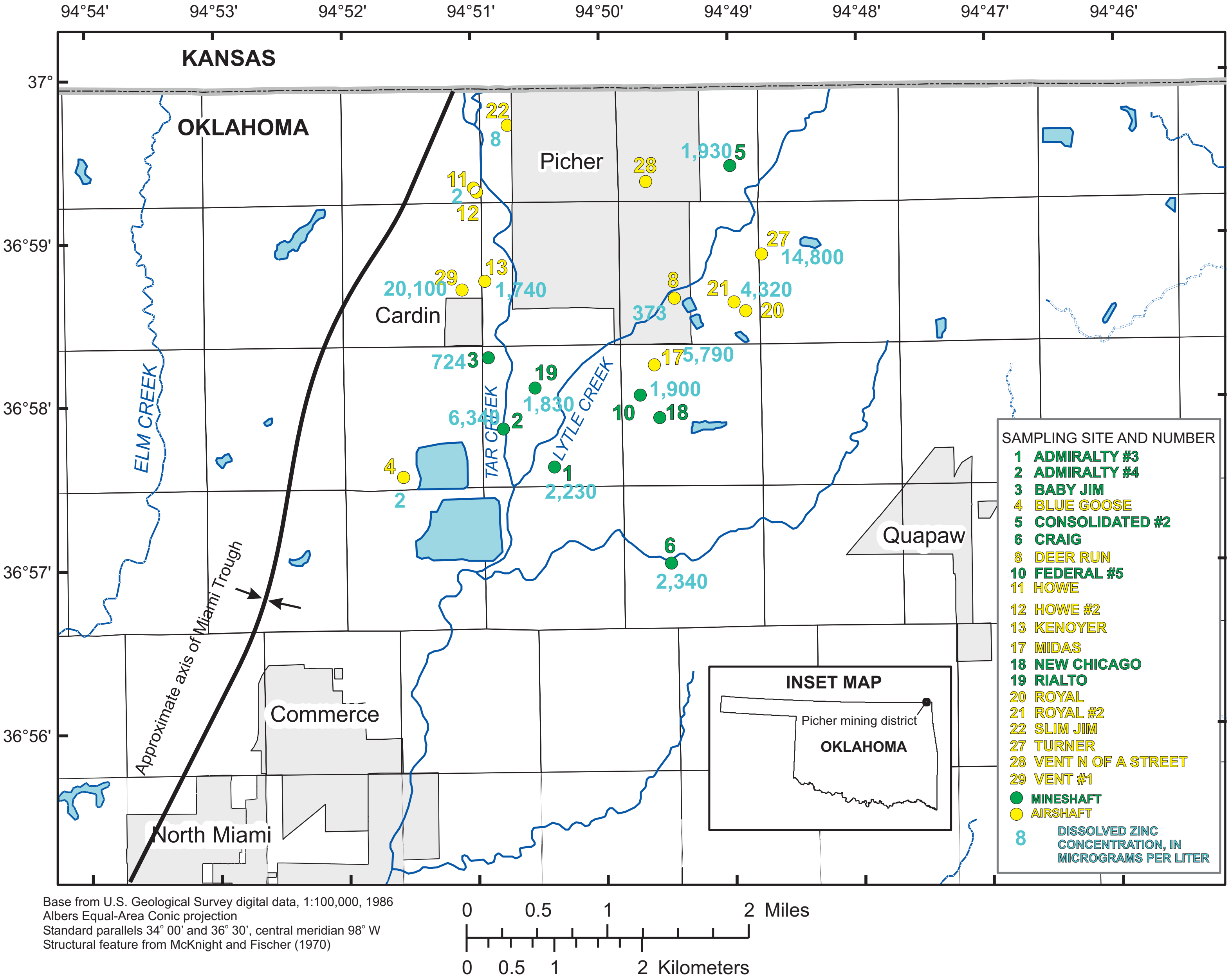
Alkalinities were greater in the 1983-85 samples than in the 2002 samples (fig. 21). The alkalinity analyses in 1983-85 were done with unfiltered samples, whereas, the alkalinity titrations in 2002 were done with filtered samples. The unfiltered samples could contain more colloids (microscopic particles) of calcium carbonate that may have caused greater alkalinities in the 1983-85 samples.

The Wilcoxon rank-sum test indicated that calcium concentrations were not significantly different between the 1983-85 and 2002 data sets (fig. 21). Magnesium concentrations were greater in the 1983-85 data set than in the 2002 data set (fig. 21). The median value of magnesium concentrations in 1983-85 was 203 mg/L and was 59.7 mg/L in 2002 (fig. 21). The significant decrease in magnesium concentrations over time may be due to decreasing dolomite dissolution as water in the mines became less acidic and corrosive to carbonate minerals such as dolomite. Calcium concentrations in local ground water may not have changed to the same extent as magnesium due to the presence of other potential sources of calcium [such as gypsum ($CaSO_4*H_2O$), calcite ($CaCO_3$)] to local ground water.

Sulfate concentrations decreased between 1983-85 and 2002 in the mine workings. The median concentration of sulfate in 1983-85 was 2,700 mg/L and in 2002 was 1,470 mg/L (fig. 21).

Concentrations of metals also decreased between 1983-85 and 2002, perhaps due to decreased dissolution rates of metallic sulfide minerals as waters in the mine workings became less acidic. Cadmium and lead are two metals of concern in ground water in the mining district due to the health risks (Agency for Toxic Substances and Disease Registry, 1999a, 1999b; Canadian Centre for Occupational Health and Safety, 1998; Jarup and others, 1998; and Reesal and others, 1987).

Cadmium concentrations significantly decreased from a median 10 µg/L in 1983-85 to 0.6 µg/L in 2002. Unlike the 1983-85 data, greater cadmium concentrations appeared to be associated with waters that have less sulfate (fig. 23). Cadmium



Base from U.S. Geological Survey digital data, 1:100,000, 1986
Albers Equal-Area Conic projection
Standard parallels 34° 00' and 36° 30', central meridian 98° W
Structural feature from McKnight and Fischer (1970)

Figure 20. Zinc concentration in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

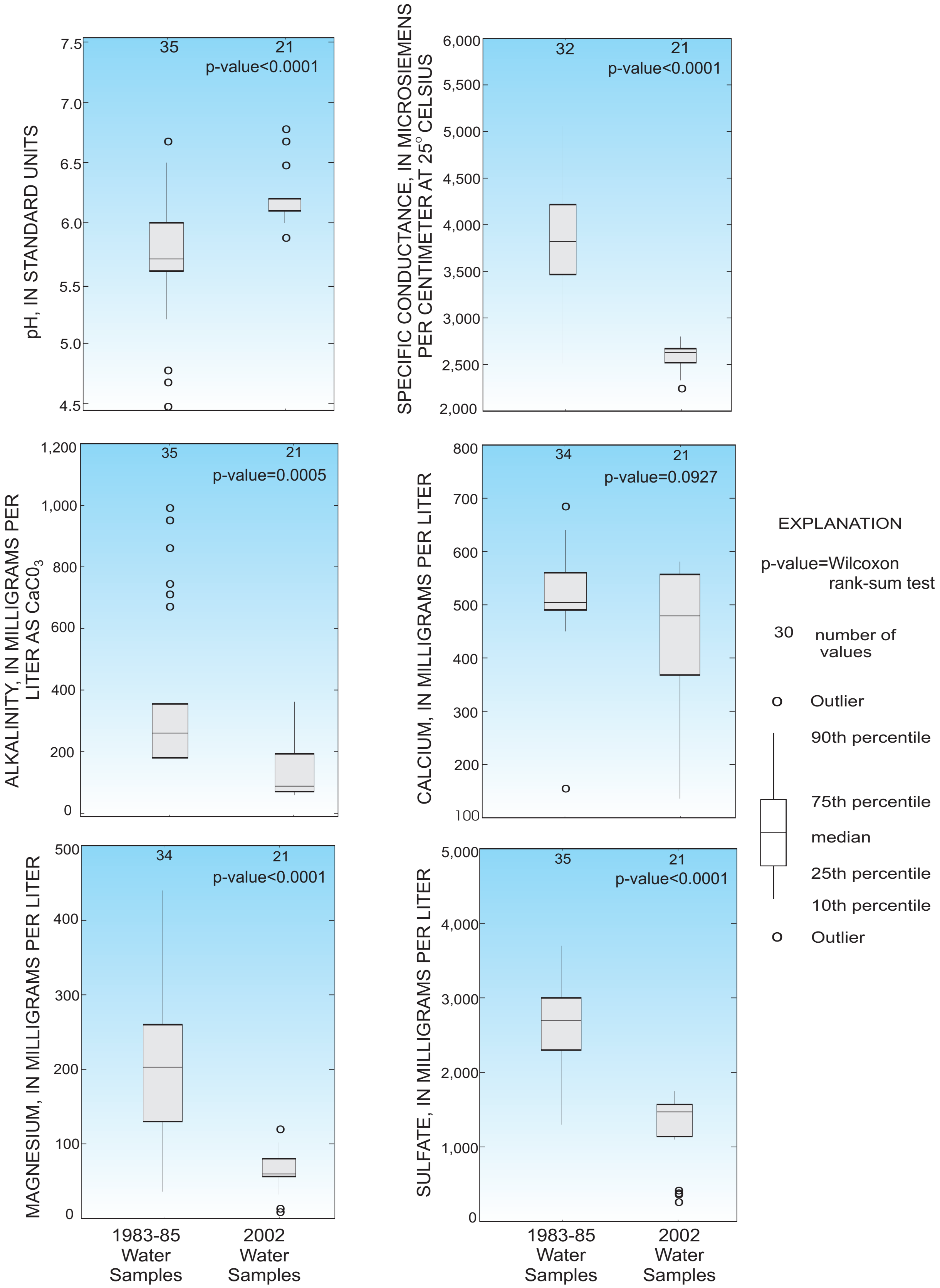


Figure 21. Selected water-quality concentrations from ground-water samples collected within the Picher mining district, Oklahoma, 1983–85 and 2002.

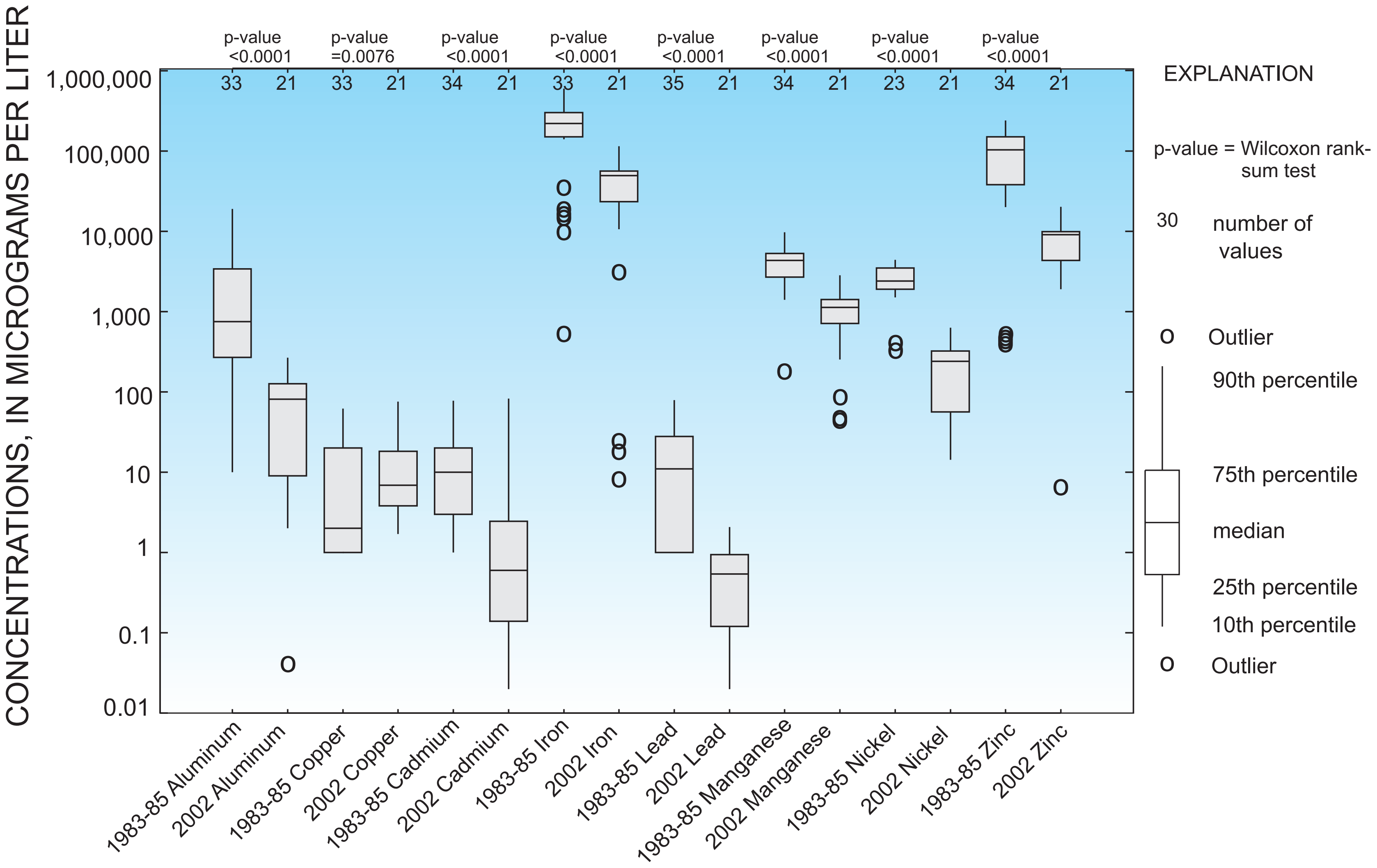


Figure 22. Concentrations of dissolved trace elements in water samples collected within the Picher mining district, Oklahoma, 1983–85 and 2002.

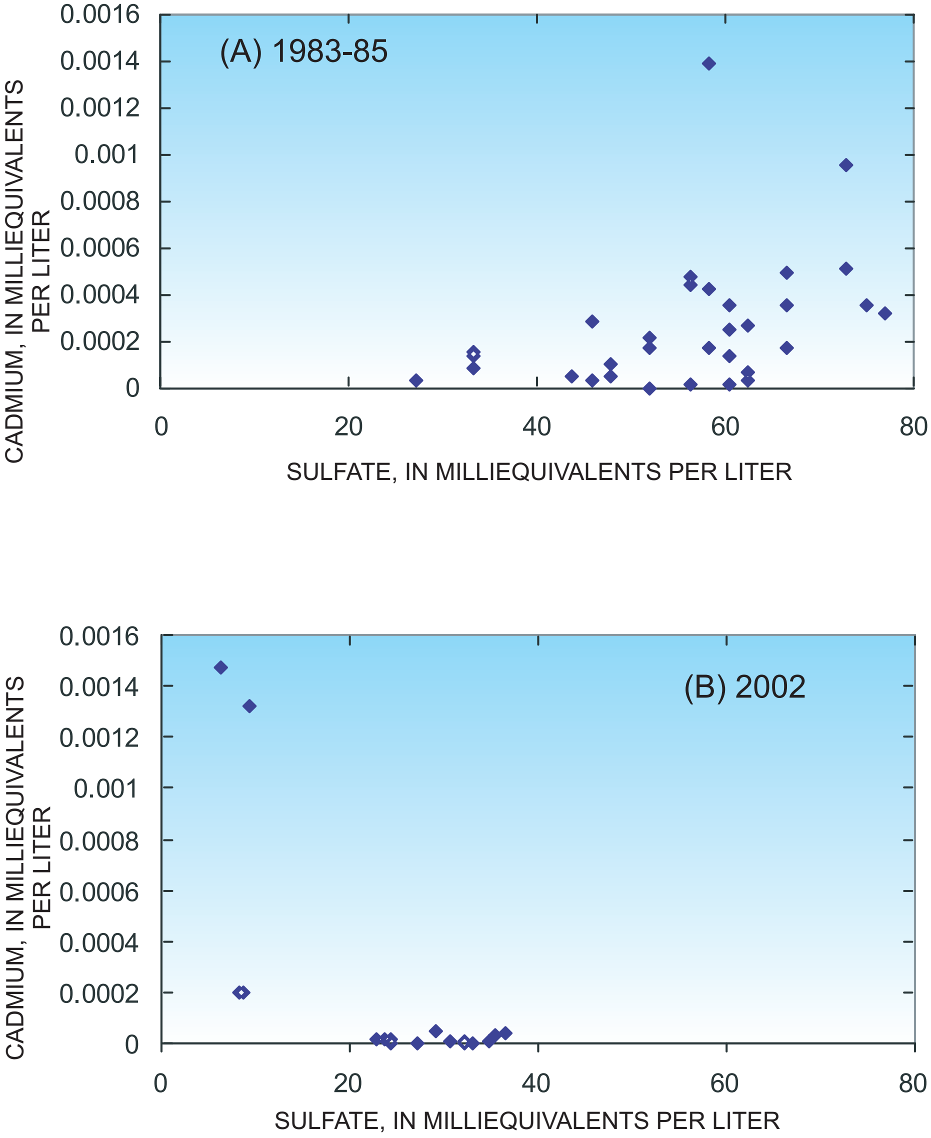


Figure 23. Relation between dissolved cadmium and dissolved sulfate concentrations in ground-water samples collected within the Picher mining district, Oklahoma, (A) 1983–85 and (B) 2002.

concentrations were greater in the 2002 water samples that had measurable concentrations of dissolved oxygen. The potential concern is these waters would typically be considered less contaminated because sulfate and iron concentrations are less and contain cadmium concentrations up to 82.6 µg/L. Geochemical processes explaining cadmium solubility in 2002 samples is poorly understood, and requires further investigation. Samples from four wells in the 2002 data set had cadmium concentrations exceeding the USEPA drinking water standards of 5 µg/L (Appendix 4).

Concentrations of lead also decreased from 1983-85 to 2002. The median value of lead in the 1983-85 data set was 11 µg/L and in the 2002 data set the median value was 0.54 µg/L (fig. 22).

Mineral Saturation in Ground Water in the Mining District

The aqueous speciation model PHREEQC (Parkhurst and Appelo, 1999) was used to calculate saturation indices of common minerals in ground-water samples collected in the mining district in 2002-03. A saturation index is the $\log_{10}$ of the ion-activity product of components of a mineral divided by the equilibrium constant for a mineral. Saturation indices greater than zero indicate that a mineral may precipitate from water (oversaturated), whereas, indices less than zero indicate that a mineral may be dissolved by water (undersaturated). If minerals readily formed and precipitated from aqueous solutions upon reaching ionic saturation, minerals would not become oversaturated. Some minerals, such as feldspars found in igneous rocks, would precipitate very slowly at low temperatures, whereas others, such as calcite and pyrite, are likely to precipitate at greater rates at temperatures typical for ground water. Another factor that may lead to substantial oversaturation of aqueous solutions with respect to some minerals is the presence of colloids. Colloids are small mineral or polymeric particles that can pass through the 0.45-micron effective pore size of the filter used in processing the water-quality samples. Rather than being true dissolved ions, colloids are microscopic mineral particles. Substantial concentrations of colloids may lead to over-estimation of what is truly dissolved in a water sample, leading to overestimation of saturation indices for minerals in water.

The carbonate minerals such as calcite ($CaCO_3$) and dolomite [$(Ca(Mg, Fe)(CO_3)_2$] are some of the most common minerals in the Boone Formation (McKnight and Fischer, 1970, p. 116-117), but were generally undersaturated (fig. 24). Carbonate minerals of cadmium (otavite), iron (siderite), lead (cerrusite), and zinc (smithsonite) were undersaturated in all samples, indicating the possible dissolution of those minerals and the release of associated metals into local ground water.

The sulfate minerals of lead (anglesite), barium (barite), cadmium, zinc (goslarite), calcium (gypsum), and iron (melanterite) were generally undersaturated in the ground-water samples (fig. 24), indicating likelihood for dissolution of those minerals and potential for associated metals to be released into ground water. The clay mineral kaolinite, which is known to form as a hydrolysis product of feldspars at low temperatures, was oversaturated in most of the samples (fig. 24), indicating that it may precipitate from local ground waters. McKnight and Fischer (1970) noted the presence of localized deposits of kaolinite in the mine workings.

Lack of eh (redox) data makes it difficult to interpret the saturation state of the ferric oxyhydroxide minerals. It is likely that the ferric oxyhydroxide minerals could be dissolving, but precipitation is unlikely due to the lack of dissolved oxygen in the mine workings.

Summary

The Picher mining district of northeastern Ottawa County, Oklahoma was the site of mining for lead and zinc ores from about 1900 until the mid-1970s. The primary source of lead and zinc were sulfide minerals disseminated in the cherty limestones and dolomites of the Keokuk and Reeds Spring Formations, otherwise known as the Boone Formation of Mississippian age, which composes the Boone aquifer. Sulfide minerals mined from the Boone Formation included: sphalerite, galena, and the accessory minerals chalcopyrite, enargite, luzonite, marcasite, and pyrite. Exposure of these minerals to oxygenated water can create acidic solutions resulting in elevated concentrations of sulfate and trace elements in the ground water, surface water, and streambed sediments.

The Boone Formation is an important aquifer in areas surrounding the Picher mining district and is the source of base-flow to streams in the Picher mining district. Water-level measurements at 20 ground-water and 9 surface-water sites within the mining district indicated that the water table is a relatively flat at approximately 800 feet above NAVD 88 in the mining district. Water levels in streams upstream from the confluence of Tar and Lytle Creeks were several feet higher than those of the surrounding ground-water altitudes, perhaps due to low-permeability streambed sediments, indicating the streams may be losing water to the mine workings in this area. Near the confluence of Tar and Lytle Creeks, the elevations of water in the stream were lower than the ground-water altitudes, and the mine water is discharging to the streams in that area.

Mean daily streamflow in the nearby Neosho River near Commerce, Oklahoma, ranged from 20 cubic feet per second in a dry period in August 2003 to 20,000 cubic feet per second during wet periods in March, April, and May 2003. Ground-water altitudes recorded continuously for one year in two mineshafts completed in the Boone aquifer responded relatively rapidly to individual precipitation events, indicating connection between the aquifer and the land surface.

Ground-water recharge-age dates, determined by concentrations and ratios of chlorofluorocarbons and other gases dissolved in ground water, indicated that although water-level altitudes in much of the mining district were fairly flat, there tended

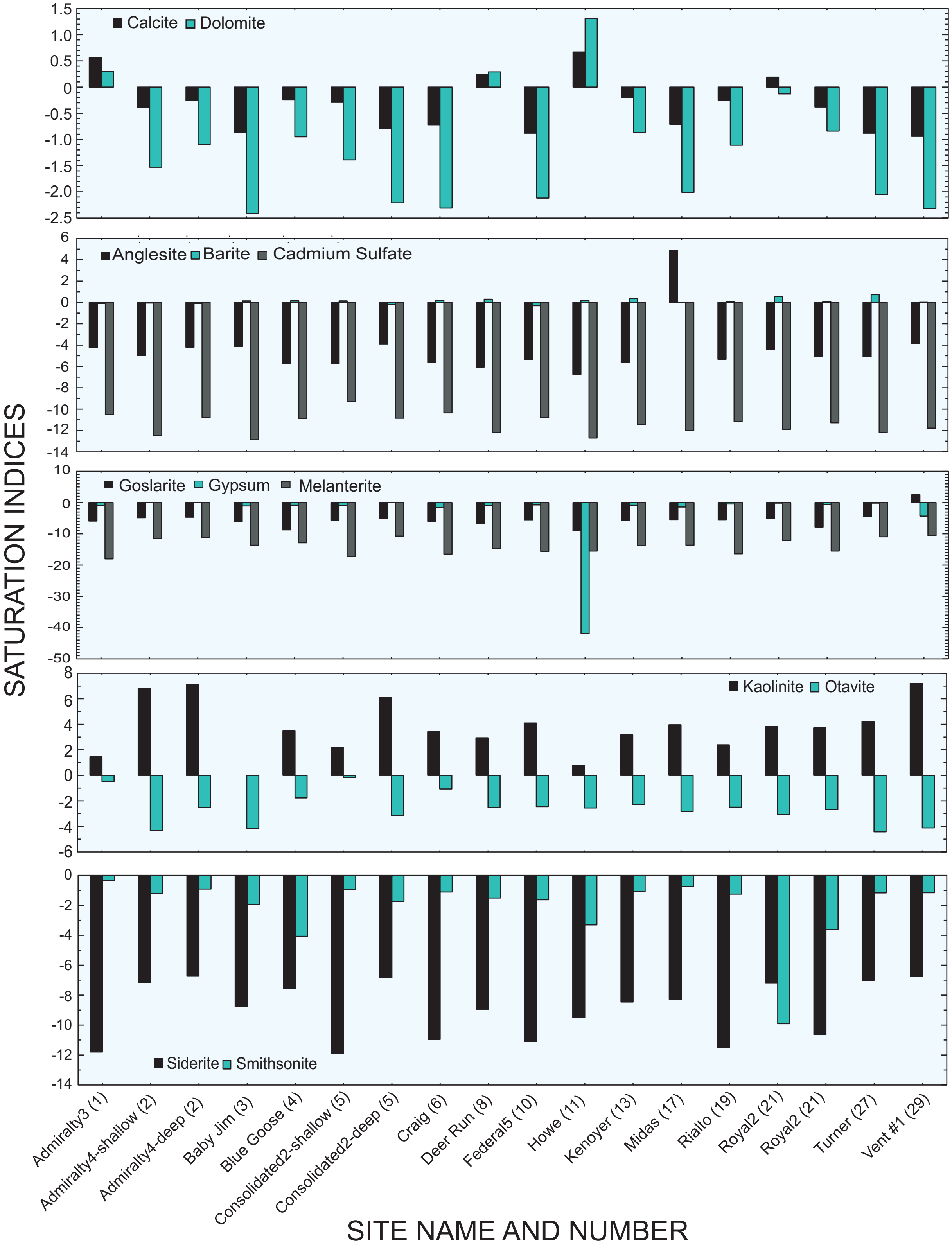


Figure 24. Saturation indices for selected minerals in ground-water samples collected within the Picher mining district, Oklahoma, 2002–03.

to be more recently-recharged ground-water in the southeastern and northeastern parts of the mining district, progressing to older ground-water in the center of the mining district on the south side of Picher and on the west side of Picher and Cardin. Variations in recharge-age dates of ground water samples may have been due to ground water flow in the aquifer or to the nature of the sites sampled. Mineshafts had larger openings than airshafts and were flush with the ground, perhaps allowing greater exchange with the atmosphere and infiltration of surface runoff than the smaller airshafts, which had casings completed above land surface.

Ground water in the mining district had large specific conductances and dissolved solids concentrations. Most of the ground-water samples, particularly those from the airshafts, had dissolved oxygen concentrations less than 1.0 milligram per liter. Small concentrations of dissolved oxygen may have been introduced during the sampling process. The low dissolved oxygen concentrations were associated with samples containing high iron concentration that indicates possible anoxic conditions in much of the aquifer.

Ground water in the mining district was dominated by calcium, magnesium, and sulfate. Sodium concentrations tended to be less than calcium and magnesium concentrations in samples. Sulfate was the dominant anion in most of the samples.

Ground-water samples from the mining district had elevated concentrations of many trace elements. Trace elements may seep with ground water to adjoining portions of the aquifer, creeks and streams in hydraulic connection with the aquifer, and to the underlying Roubidoux aquifer. Many trace elements have potential health effects, when present in sufficient quantities in drinking water. Dissolution of trace elements and sulfate in ground water within the Picher mining district in 2002-03 were primarily a function of pH and dissolved oxygen concentrations. Greater concentrations of trace elements and sulfate occurred in ground water with low pH and dissolved oxygen concentrations.

Iron was typically the metal occurring in greatest concentration in the water samples, with concentrations as much as 115,000 micrograms per liter (µg/L) being detected. About two-thirds of the samples had iron concentrations exceeding the secondary drinking-water standard of 300 µg/L. Iron concentrations had a similar distribution in the samples as sulfate, indicating possible relation to oxidation and dissolution of the iron-sulfide minerals—marcasite and pyrite. Cadmium, lead, manganese, zinc, and the other analyzed trace elements occurred in lesser concentrations than iron in water samples collected in the mining district, with most of the trace elements concentrations in the samples being less than drinking-water standards or chronic criterion concentrations designed to protect aquatic life. However, large cadmium concentrations appeared to be associated with sites that have small iron concentrations and more oxygenated waters. This is noteworthy because the small sulfate and iron concentrations in these waters could lead to conclusions that the waters are less contaminated than waters with large sulfate and iron concentrations.

Ground-water quality in the mining district was compared with subsets of samples collected in 1983-85 and in 2002 that had specific conductances greater than 2,000 µS/cm, indicating that they were from the mine workings, rather than from overlying ground water. Concentrations of most mine-water indicators such as acidity, specific conductance, magnesium, sulfate, and most trace elements concentrations decreased over that period. Calcium concentrations did not significantly change.

Mineral saturation indices indicated that the carbonate minerals calcite and dolomite, that compose much of the Boone aquifer, were likely to dissolve at most sites. The sulfate minerals of lead (anglesite), barium (barite), cadmium, zinc (goslarite), calcium (gypsum), and iron (melanterite) were generally undersaturated in the ground-water samples, indicating likelihood for dissolution of those minerals and potential for those elements to dissolve into ground water. The clay mineral kaolinite, which is known to form as a hydrolysis product of feldspars at low temperatures, was oversaturated in most of the samples, indicating that it may precipitate out of local ground waters.

Lack of eh (redox) data makes it difficult to try to interpret the saturation state of the ferric oxyhydroxide minerals. It is likely that the ferric oxyhydroxide minerals could be dissolving, but precipitation is unlikely due to the lack of dissolved oxygen in the mine workings.

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Appendices

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Barometric pressure (mm of Hg)	Specific conductance at 25˚C, (µS/cm)		pH (standard unit)		Temperature, water (˚C)	Oxygen, dissolved (mg/L)
							field	lab	field	lab		
Admiralty #3	1	365737094502201	10/23/2002	1320	60	766	771	744	7.8	E7.5	16.0	7.7
Admiralty #4	2	365753094504601	11/05/2002	1330	60	766	2,550	E2,360	6.5	6.3	15.6	0.3
Admiralty #4	2	365753094504601	11/05/2002	1700	200	766	2,860	2,260	6.5	5.7	15.6	0.3
Baby Jim	3	365818094505201	10/28/2002	1100	60	--	728	708	6.5	7.2	15.9	0.5
Blue Goose	4	365732094513201	11/04/2002	1245	75	766	1,580	1,550	6.8	6.9	16.1	0.3
Consolidated #2	5	365927094485901	11/18/2002	1250	80	760	695	666	7.4	7.3	17.1	8.2
Consolidated #2	5	365927094485901	11/18/2002	1540	200	760	2,540	2,580	6.0	6.1	16.2	0.7
Craig	6	365702094492901	10/22/2002	1210	60	767	463	421	6.7	E7.1	17.6	1.7
Deer Run	8	365839094492601	01/14/2003	1305	60	760	1,800	1,700	7.2	7.3	15.6	--
Federal #5	10	365803094494101	10/24/2002	1345	75	766	1,120	1,080	6.6	7.4	16.1	0.7
Howe	11	365921094505701	11/21/2002	1255	55	760	1,540	1,480	7.9	7.8	17.4	0.3
Kenoyer	13	365846094505401	10/30/2002	1138	60	760	1,230	1,230	6.8	7.3	16.1	0.8
Midas	17	365815094493601	10/29/2002	1130	75	766	553	528	6.7	6.9	16.0	0.4
Rialto	19	365807094503101	10/31/2002	1145	75	766	1,370	E1,350	7.1	7.3	17.1	3.7
Royal #2	21	365834094485302	11/19/2002	1550	80	--	2,420	2,450	6.8	6.6	16.4	0.3
Slim Jim	22	365942094504203	11/20/2002	1620	80	760	2,630	2,590	6.7	7.1	17.6	0.9
Turner	27	365855094484501	11/19/2002	1035	80	760	2,280	2,460	6.1	6.0	16.4	0.7
Vent #1	29	365844094510501	11/20/2002	1123	80	766	2,640	2,520	6.0	5.1	18.0	0.7

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Alkalinity, dissolved, field (mg/L as $CaCO_3$)	Solids, residue at 180˚C, dissolved (mg/L)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
Admiralty #3	1	365737094502201	10/23/2002	1320	60	167	564	144	13.0	3.06	0.72
Admiralty #4	2	365753094504601	11/05/2002	1330	60	180	2,480	569	60.4	28.2	2.96
Admiralty #4	2	365753094504601	11/05/2002	1700	200	259	2,870	581	91.5	43.5	4.02
Baby Jim	3	365818094505201	10/28/2002	1100	60	144	528	118	15.2	16.4	2.16
Blue Goose	4	365732094513201	11/04/2002	1245	75	268	1,080	169	33.5	125	8.98
Consolidated #2	5	365927094485901	11/18/2002	1250	80	64	529	126	11.4	4.12	0.76
Consolidated #2	5	365927094485901	11/18/2002	1540	200	225	2,690	572	80.2	36.8	4.65
Craig	6	365702094492901	10/22/2002	1210	60	150	306	79.7	6.01	4.00	2.67
Deer Run	8	365839094492601	01/14/2003	1305	60	220	1,470	245	96.1	48.7	7.36
Federal #5	10	365803094494101	10/24/2002	1345	75	100	898	161	41.4	24.9	2.13
Howe	11	365921094505701	11/21/2002	1255	55	319	1,060	90.6	49	166	14.6
Kenoyer	13	365846094505401	10/30/2002	1138	60	290	907	161	33.1	61.2	13.5
Midas	17	365815094493601	10/29/2002	1130	75	160	386	86.9	13.4	5.96	1.67
Rialto	19	365807094503101	10/31/2002	1145	75	88	1,230	273	38.6	10.2	1.22
Royal #2	21	365834094485302	11/19/2002	1550	80	362	2,380	487	90.4	52.4	5.70
Slim Jim	22	365942094504203	11/20/2002	1620	80	315	2,190	174	82.3	326	13.3
Turner	27	365855094484501	11/19/2002	1035	80	193	2,530	419	123	62.4	4.69
Vent #1	29	365844094510501	11/20/2002	1123	80	201	2,690	466	102	53.7	5.36

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Bicarbonate, dissolved, field (mg/L)	Carbonate, dissolved, field (mg/L)	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Bromide, dissolved (mg/L)
Admiralty #3	1	365737094502201	10/23/2002	1320	60	202	0	250	1.43	0.20	0.04
Admiralty #4	2	365753094504601	11/05/2002	1330	60	219	0	1,550	8.88	2.63	0.04
Admiralty #4	2	365753094504601	11/05/2002	1700	200	315	0	1,750	13.2	1.74	0.06
Baby Jim	3	365818094505201	10/28/2002	1100	60	175	0	243	2.01	0.27	0.03
Blue Goose	4	365732094513201	11/04/2002	1245	75	326	0	376	147	3.32	0.47
Consolidated #2	5	365927094485901	11/18/2002	1250	80	77	0	294	0.67	0.24	0.03
Consolidated #2	5	365927094485901	11/18/2002	1540	200	274	0	1,700	6.76	1.68	0.06
Craig	6	365702094492901	10/22/2002	1210	60	182	0	85.8	1.92	0.22	<0.02
Deer Run	8	365839094492601	01/14/2003	1305	60	268	0	794	25.0	0.38	0.13
Federal #5	10	365803094494101	10/24/2002	1345	75	121	0	517	2.54	0.21	E0.01
Howe	11	365921094505701	11/21/2002	1255	55	385	2	456	30.4	0.61	0.13
Kenoyer	13	365846094505401	10/30/2002	1138	60	353	0	370	30.4	0.73	0.11
Midas	17	365815094493601	10/29/2002	1130	75	195	0	131	1.14	0.19	E0.02
Rialto	19	365807094503101	10/31/2002	1145	75	107	0	744	1.66	0.31	0.02
Royal #2	21	365834094485302	11/19/2002	1550	80	440	0	1,300	5.94	0.40	0.06
Slim Jim	22	365942094504203	11/20/2002	1620	80	383	0	1,170	19.6	0.38	0.22
Turner	27	365855094484501	11/19/2002	1035	80	235	0	1,570	8.07	<0.17	0.10
Vent #1	29	365844094510501	11/20/2002	1123	80	244	0	1,670	14.3	2.31	0.08

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Silica, dissolved (mg/L)	Aluminum, dissolved (μg/L)	Antimony, dissolved (μg/L)	Arsenic, dissolved (μg/L)	Barium, dissolved (μg/L)	Beryllium, dissolved (μg/L)
Admiralty #3	1	365737094502201	10/23/2002	1320	60	9.50	<2	0.34	<2	14	<0.06
Admiralty #4	2	365753094504601	11/05/2002	1330	60	12.3	81	<0.30	9	8	0.14
Admiralty #4	2	365753094504601	11/05/2002	1700	200	13.1	112	<0.60	27	7	0.23
Baby Jim	3	365818094505201	10/28/2002	1100	60	13.2	M	<0.30	<2	24	<0.06
Blue Goose	4	365732094513201	11/04/2002	1245	75	6.72	4	<0.30	<2	23	E0.04
Consolidated #2	5	365927094485901	11/18/2002	1250	80	10.8	<2	E0.19	<2	22	<0.06
Consolidated #2	5	365927094485901	11/18/2002	1540	200	12.5	126	<0.60	27	6	0.24
Craig	6	365702094492901	10/22/2002	1210	60	12.4	<2	E0.18	<2	58	<0.06
Deer Run	8	365839094492601	01/14/2003	1305	60	13.4	<2	<0.30	<2	47	<0.06
Federal #5	10	365803094494101	10/24/2002	1345	75	21.8	<2	<0.30	<2	6	<0.06
Howe	11	365921094505701	11/21/2002	1255	55	6.81	<2	<0.30	<2	23	<0.06
Kenoyer	13	365846094505401	10/30/2002	1138	60	9.08	<2	<0.30	<10	38	<0.06
Midas	17	365815094493601	10/29/2002	1130	75	19.1	<2	<0.30	<2	23	<0.06
Rialto	19	365807094503101	10/31/2002	1145	75	7.21	<2	<0.30	<2	15	<0.06
Royal #2	21	365834094485302	11/19/2002	1550	80	21.2	<2	<0.30	6	38	<0.06
Slim Jim	22	365942094504203	11/20/2002	1620	80	12.7	<3	<0.60	<2	13	<0.12
Turner	27	365855094484501	11/19/2002	1035	80	8.00	15	<0.30	51	50	0.24
Vent #1	29	365844094510501	11/20/2002	1123	80	21.3	267	<0.60	41	10	0.3

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Cadmium dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobalt, dissolved (µg/L)	Copper, dissolved (µg/L)	Iron, dissolved (µg/L)	Lead, dissolved (µg/L)	Manganese, dissolved (µg/L)
Admiralty #3	1	365737094502201	10/23/2002	1320	60	9.34	<0.8	0.33	2.4	<10	16.9	0.6
Admiralty #4	2	365753094504601	11/05/2002	1330	60	0.05	<0.8	37.1	6.8	45,400	<0.08	1,870
Admiralty #4	2	365753094504601	11/05/2002	1700	200	2.44	<0.8	38.8	8.4	92,100	0.56	1,370
Baby Jim	3	365818094505201	10/28/2002	1100	60	<0.04	<0.8	3.07	1.4	1,220	1.58	694
Blue Goose	4	365732094513201	11/04/2002	1245	75	<0.04	<0.8	0.40	2.3	12,200	<0.08	209
Consolidated #2	5	365927094485901	11/18/2002	1250	80	113	<0.8	0.33	1.2	<10	<0.08	17.6
Consolidated #2	5	365927094485901	11/18/2002	1540	200	1.97	<0.8	26.8	3.8	76,900	0.77	1,630
Craig	6	365702094492901	10/22/2002	1210	60	24.1	<0.8	0.21	2.7	<10	0.19	2.8
Deer Run	8	365839094492601	01/14/2003	1305	60	E0.03	<0.8	6.15	2.3	3,100	0.11	4,680
Federal #5	10	365803094494101	10/24/2002	1345	75	3.00	<0.8	0.73	2.4	<10	E0.05	59.0
Howe	11	365921094505701	11/21/2002	1255	55	<0.04	<0.8	0.24	0.9	1,370	<0.08	214
Kenoyer	13	365846094505401	10/30/2002	1138	60	0.93	<0.8	1.68	2.2	5,160	0.11	904
Midas	17	365815094493601	10/29/2002	1130	75	0.43	<0.8	5.72	1.3	3,600	0.68	551
Rialto	19	365807094503101	10/31/2002	1145	75	1.11	<0.8	1.64	3.9	10	<0.08	178
Royal #2	21	365834094485302	11/19/2002	1550	80	E0.02	<0.8	39.9	3.0	23,500	0.94	2,840
Slim Jim	22	365942094504203	11/20/2002	1620	80	<0.07	<0.8	1.90	2.1	<10	<0.16	321
Turner	27	365855094484501	11/19/2002	1035	80	0.09	<0.8	34.0	3.6	60,600	E0.05	711
Vent #1	29	365844094510501	11/20/2002	1123	80	0.24	<0.8	74.2	4.2	115,000	0.81	2,340

Appendix 1. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Molybdenum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Selenium dissolved (µg/L)	Silver, dissolved (µg/L)	Zinc, dissolved (µg/L)	Uranium, dissolved (µg/L)
Admiralty #3	1	365737094502201	10/23/2002	1320	60	E0.3	13.1	<3	<0.2	2,230	0.87
Admiralty #4	2	365753094504601	11/05/2002	1330	60	3.0	283	<3	<0.2	6,340	2.37
Admiralty #4	2	365753094504601	11/05/2002	1700	200	3.3	319	<3	<0.4	9,550	9.00
Baby Jim	3	365818094505201	10/28/2002	1100	60	0.5	16.0	<3	<0.2	724	0.13
Blue Goose	4	365732094513201	11/04/2002	1245	75	E0.3	6.15	<3	<0.2	2	0.25
Consolidated #2	5	365927094485901	11/18/2002	1250	80	E0.3	11.1	<3	<0.2	1,930	0.14
Consolidated #2	5	365927094485901	11/18/2002	1540	200	2.2	199	E2	<0.4	4,560	8.39
Craig	6	365702094492901	10/22/2002	1210	60	0.8	7.95	<3	<0.2	2,340	0.66
Deer Run	8	365839094492601	01/14/2003	1305	60	<0.7	40.5	<3	<0.2	373	0.13
Federal #5	10	365803094494101	10/24/2002	1345	75	E0.2	26.4	<3	<0.2	1,900	0.21
Howe	11	365921094505701	11/21/2002	1255	55	0.5	3.55	<3	<0.2	2	0.16
Kenoyer	13	365846094505401	10/30/2002	1138	60	0.3	22.4	<13	<0.2	1,740	1.49
Midas	17	365815094493601	10/29/2002	1130	75	0.5	10.6	<3	<0.2	5,790	0.24
Rialto	19	365807094503101	10/31/2002	1145	75	0.4	22.4	E1	<0.2	1,830	0.31
Royal #2	21	365834094485302	11/19/2002	1550	80	1.4	56.2	E2	<0.2	4,320	10.3
Slim Jim	22	365942094504203	11/20/2002	1620	80	<0.7	14.3	E2	<0.4	8	0.51
Turner	27	365855094484501	11/19/2002	1035	80	2.9	207	E2	<0.2	14,800	0.36
Vent #1	29	365844094510501	11/20/2002	1123	80	3.7	633	E1	<0.4	20,100	0.52

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Sampling depth (feet)	Barometric pressure (mm of Hg)	Specific conductance at 25˚C, (µS/cm)		pH (standard unit)		Temperature, water (˚C)
								field	lab	field	lab	
Federal #5	10	365803094494101	10/24/2002	1345	E	75	766	1,120	1,080	6.6	7.4	16.1
Federal #5	10	365803094494101	10/24/2002	1346	R	75	766	1,120	1,090	6.6	7.4	16.1
		RPD						0.0	0.9	0.0	0.0	0.0
Kenoyer	13	365846094505401	10/30/2002	1138	E	60	760	1,230	1,230	6.8	7.3	16.1
Kenoyer	13	365846094505401	10/30/2002	1139	R	60	760	1,230	1,230	6.8	6.9	16.1
		RPD						0.0	0.0	0.0	5.6	0.0
Turner	27	365855094484501	11/19/2002	1035	E	80	760	2,280	2,460	6.1	6.0	16.4
Turner	27	365855094484501	11/19/2002	1036	R	80	760	2,280	2,430	6.1	6.3	16.4
		RPD						0.0	1.2	0.0	4.9	0.0
Baby Jim	3	365818094505201	12/17/2003	1240	B	--	--	--	E4	--	6.4	--

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Oxygen, dissolved (mg/L)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
Federal #5	10	365803094494101	10/24/2002	1345	E	0.7	161	41.4	24.9	2.13
Federal #5	10	365803094494101	10/24/2002	1346	R	0.7	161	41.5	24.9	2.11
		RPD				0.0	0.0	0.2	0.0	0.9
Kenoyer	13	365846094505401	10/30/2002	1138	E	0.8	161	33.1	61.2	13.5
Kenoyer	13	365846094505401	10/30/2002	1139	R	0.8	161	33.3	61.2	13.5
		RPD				0.0	0.0	0.6	0.0	0.0
Turner	27	365855094484501	11/19/2002	1035	E	0.7	419	123	62.4	4.69
Turner	27	365855094484501	11/19/2002	1036	R	0.7	425	125	63.1	4.94
		RPD				0.0	1.4	1.6	1.1	5.2
Baby Jim	3	365818094505201	12/17/2003	1240	B	--	0.02	0.01	E0.05	<0.16

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Bromide, dissolved (mg/L)	Silica, dissolved (mg/L)
Federal #5	10	365803094494101	10/24/2002	1345	E	517	2.54	0.21	E0.01	21.8
Federal #5	10	365803094494101	10/24/2002	1346	R	515	2.63	0.21	E0.01	21.8
		RPD				0.4	3.5	0.0	0.0	0.0
Kenoyer	13	365846094505401	10/30/2002	1138	E	370	30.4	0.73	0.11	9.08
Kenoyer	13	365846094505401	10/30/2002	1139	R	372	30.7	0.80	0.14	9.09
		RPD				0.5	1.0	9.2	24.0	0.1
Turner	27	365855094484501	11/19/2002	1035	E	1,570	8.07	<0.17	0.10	8.00
Turner	27	365855094484501	11/19/2002	1036	R	1,570	7.99	<0.20	0.10	8.13
		RPD				0.0	1.0	--	0.0	1.6
Baby Jim	3	365818094505201	12/17/2003	1240	B	<0.2	<0.20	<0.17	<0.16	E0.03

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Aluminum, dissolved (µg/L)	Antimony, dissolved (µg/L)	Arsenic, dissolved (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium dissolved (µg/L)
Federal #5	10	365803094494101	10/24/2002	1345	E	<2	<0.30	<2	6.0	<0.06	3.00
Federal #5	10	365803094494101	10/24/2002	1346	R	<2	<0.30	<2	6.0	<0.06	2.97
		RPD				--	--	--	0.0	--	1.0
Kenoyer	13	365846094505401	10/30/2002	1138	E	<2	<0.30	<10	38	<0.06	0.93
Kenoyer	13	365846094505401	10/30/2002	1139	R	<2	<0.30	E1	37	<0.06	0.94
		RPD				--	--	--	2.7	--	1.1
Turner	27	365855094484501	11/19/2002	1035	E	15	<0.30	51	50	0.24	0.09
Turner	27	365855094484501	11/19/2002	1036	R	14	<0.30	50	47	0.25	0.09
		RPD				6.9	--	2.0	6.2	4.1	0.0
Baby Jim	3	365818094505201	12/17/2003	1240	B	E1.4	<0.20	<2	<0.2	<0.06	<0.04

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Chromium, dissolved (µg/L)	Cobalt, dissolved (µg/L)	Copper, dissolved (µg/L)	Iron, dissolved (µg/L)	Lead, dissolved (µg/L)	Manganese, dissolved (µg/L)
Federal #5	10	365803094494101	10/24/2002	1345	E	<0.8	0.73	2.4	<10	E0.05	59.0
Federal #5	10	365803094494101	10/24/2002	1346	R	<0.8	0.73	2.4	<10	<0.08	59.1
		RPD				--	0.0	0.0	--	--	0.2
Kenoyer	13	365846094505401	10/30/2002	1138	E	<0.8	1.68	2.2	5,160	0.11	904
Kenoyer	13	365846094505401	10/30/2002	1139	R	<0.8	1.65	2.0	5,190	0.11	894
		RPD				--	1.8	9.5	0.6	0.0	1.1
Turner	27	365855094484501	11/19/2002	1035	E	<0.8	34.0	3.6	60,600	E0.05	711
Turner	27	365855094484501	11/19/2002	1036	R	<0.8	33.8	3.4	61,400	E0.07	694
		RPD				--	0.6	5.7	1.3	33.3	2.4
Baby Jim	3	365818094505201	12/17/2003	1240	B	<0.8	0.04	E0.3	<10	0.11	1.1

Appendix 2. Water-quality constituent concentrations from quality-assurance ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data; RPD, relative percent difference; E, environmental; R, replicate, B, equipment blank]

Station name	Site number (as in figure 1)	Station number	Date	Time	Type of sample	Molybdenum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Selenium dissolved (µg/L)	Silver, dissolved (µg/L)	Zinc, dissolved (µg/L)	Uranium, dissolved (µg/L)
Federal #5	10	365803094494101	10/24/2002	1345	E	E0.2	26.4	<3	<0.2	1,900	0.21
Federal #5	10	365803094494101	10/24/2002	1346	R	E0.2	26.8	<3	<0.2	1,870	0.21
		RPD				0.0	1.5	--	--	1.6	0.0
Kenoyer	13	365846094505401	10/30/2002	1138	E	0.3	22.4	<13	<0.2	1,740	1.49
Kenoyer	13	365846094505401	10/30/2002	1139	R	E0.3	22.4	<3	<0.2	1,720	1.47
		RPD				0.0	0.0	--	--	1.2	1.4
Turner	27	365855094484501	11/19/2002	1035	E	2.9	207	E2	<0.2	14,800	0.36
Turner	27	365855094484501	11/19/2002	1036	R	2.9	202	E2	<0.2	13,400	0.36
		RPD				0.0	2.4	0.0	--	9.9	0.0
Baby Jim	3	365818094505201	12/17/2003	1240	B	E0.4	0.72	<3	<0.2	0.7	<0.04

Appendix 3. Chlorofluorocarbon (CFC) concentrations and calculated age dates from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03

[pg/kg, picograms per kilogram; NP, not possible; Contam, contaminated, greater than 2001 air; Modern, possible range of modern air; --, no data, A, sample from shallow part of aquifer; B, sample from deep part of aquifer]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Concentration in Solution (pg/kg)			Model piston-flow dates (excess air corrected) Dual dates are possible for CFC-11, CFC-113				
						CFC-11	CFC-12	CFC-113	CFC-11		CFC-12	CFC-113	
Admiralty #3	1	365737094502201	10/23/2002	1600	60	469.2	279.5	155.2	1985.5	NP	Modern	Contam	Contam
Admiralty #3	1	365737094502201	10/23/2002	1600	60	825.0	291.5	903.0	Contam	Contam	Contam	Contam	Contam
Admiralty #3	1	365737094502201	10/23/2002	1600	60	855.4	331.4	138.1	Contam	Contam	Contam	Contam	Contam
Admiralty #4A	2	365753094504601	11/05/2002	1300	60	30.9	4,706.2	101.1	1961.5	NP	Contam	Contam	Contam
Admiralty #4A	2	365753094504601	11/05/2002	1300	60	29.8	4,643.3	72.0	1961.5	NP	Contam	1991.5	2001
Admiralty #4B	2	365753094504601	11/06/2002	1300	200	104.2	2,804.2	69.0	1968.5	NP	Contam	1990.5	NP
Baby Jim	3	365818094505201	10/28/2002	1331	60	--	659.1	357.8	NP	NP	Contam	Contam	Contam
Blue Goose	4	365732094513201	11/04/2002	1245	75	6.5	50.1	1,066.1	1954	NP	1968	Contam	Contam
Consolidated #2A	5	365927094485901	11/18/2002	1400	80	609.2	252.3	72.4	Modern	Modern	1991.5	1991.5	2000
Consolidated #2A	5	365927094485901	11/18/2002	1400	80	596.2	253.0	70.1	1993	1993	1991.5	1990.5	NP
Consolidated #2B	5	365927094485901	11/18/2002	1645	200	561.6	242.4	49.5	1989	2002	1989.5	1987	NP
Consolidated #2B	5	365927094485901	11/18/2002	1645	200	576.4	261.2	52.2	1990.5	1997.5	1993.5	1987.5	NP
Deer Run	8	365839094492601	01/14/2003	1350	60	23.4	52.6	10.2	1960	NP	1968	1974.5	NP
Deer Run	8	365839094492601	01/14/2003	1350	60	4.3	54.9	7.7	1953	NP	1968.5	1972.5	NP
Deer Run	8	365839094492601	01/14/2003	1350	60	24.8	42.6	7.5	1960.5	NP	1966.5	1972.5	NP
Howe	11	365921094505701	11/21/2002	1400	55	14.6	29.9	12.9	1957	NP	1964	1976.5	NP
Midas	17	365815094493601	10/29/2002	1300	75	1,268.8	416.8	134.2	Contam	Contam	Contam	Contam	Contam
Rialto	19	365807094503101	10/31/2002	1230	75	61.3	159.8	90.5	1965	NP	1981	Contam	Contam
Royal #2	21	365834094485302	11/19/2002	1650	80	4.1	356.6	4.3	1953	NP	Contam	1968.5	NP
Royal #2	21	365834094485302	11/19/2002	1650	80	2.1	367.8	7.4	1951	NP	Contam	1972.5	NP
Royal #2	21	365834094485302	11/19/2002	1650	80	6.6	354.5	5.2	1954.5	NP	Contam	1970	NP
Slim Jim	22	365942094504203	11/20/2002	1630	80	196.3	216.4	36.2	1973	NP	1987	1984.5	NP
Slim Jim	22	365942094504203	11/20/2002	1630	80	117.8	161.5	22.3	1969.5	NP	1981	1980.5	NP
Slim Jim	22	365942094504203	11/20/2002	1630	80	405.6	154.1	24.1	1982.5	NP	1980	1981	NP
Turner	27	365855094484501	11/19/2002	1200	80	19.8	--	9.8	1959	NP	Contam	1974.5	NP
Turner	27	365855094484501	11/19/2002	1200	80	30.1	--	39.6	1961.5	NP	Contam	1985	NP
Turner	27	365855094484501	11/19/2002	1200	80	20.8	--	12.5	1959.5	NP	Contam	1976.5	NP
Turner	27	365855094484501	11/19/2002	1200	80	46.6	--	75.8	1963.5	NP	Contam	1995	1995

Appendix 3. Chlorofluorocarbon (CFC) concentrations and calculated age dates from ground-water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[pg/kg, picograms per kilogram; NP, not possible; Contam, contaminated, greater than 2001 air; Modern, possible range of modern air; --, no data, A, sample from shallow part of aquifer; B, sample from deep

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Concentration in Solution (pg/kg)			Model piston-flow dates (excess air corrected) Dual dates are possible for CFC-11, CFC-113				
						CFC-11	CFC-12	CFC-113	CFC-11		CFC-12	CFC-113	
Vent #1	29	365844094510501	11/20/2002	1225	80	22.7	3,152.0	8.8	1960	NP	Contam	1973.5	NP
Vent #1	29	365844094510501	11/20/2002	1225	80	24.8	3,237.9	8.2	1960.5	NP	Contam	1973.5	NP
Vent #1	29	365844094510501	11/20/2002	1225	80	79.8	3,202.1	12.1	1967	NP	Contam	1976	NP

Appendix 3. Chluorofluorocarbon (CFC) concentrations and calculated age dates from water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[pg/kg, picograms per kilogram; NP, not possible; Contam, greater than 2001 air; Modern, possible range of modern air; ***, no data]

Station name	Station number	Date	Time	Sampling depth (feet)	Probable Age based on CFC 11, 12, or 113	Comments	Assigned Age
Admiralty #3	365737094502201	10/23/2002	1600	60	CFC-12, 113	Modern	2001
Admiralty #3	365737094502201	10/23/2002	1600	60			
Admiralty #3	365737094502201	10/23/2002	1600	60			
Admiralty #4A	365753094504601	11/05/2002	1300	60	CFC-113	Early 1990s	1992
Admiralty #4A	365753094504601	11/05/2002	1300	60			
Admiralty #4B	365753094504601	11/05/2002	1300	200	CFC-113	Early 1990s	1991
Baby Jim	365818094505201	10/28/2002	1331	60	CFC-113	Modern	2001
Blue Goose	365732094513201	11/04/2002	1245	75	CFC-12	Mid-early to mid-1960s	1968
Consolidated #2A	365927094485901	11/18/2002	1400	80	All	Early 1990s	1992
Consolidated #2A	365927094485901	11/18/2002	1400	80			
Consolidated #2B	365927094485901	11/18/2002	1645	200	CFC-113	Early 1990s	1987
Consolidated #2B	365927094485901	11/18/2002	1645	200			
Deer Run	365839094492601	01/14/2003	1350	60	CFC-12, 113	Mid to late 1960s	1968
Deer Run	365839094492601	01/14/2003	1350	60			
Deer Run	365839094492601	01/14/2003	1350	60			
Howe	365921094505701	11/21/2002	1400	55	CFC-12	Early to mid-1960s	1964
Midas	365815094493601	10/29/2002	1300	75	CFC-113	Modern	2001
Rialto	365807094503101	10/31/2002	1230	75	CFC-12	Early 1980s	1981
Royal #2	365834094485302	11/19/2002	1650	80	CFC-113	Late 1960s to early 1970s	1970
Royal #2	365834094485302	11/19/2002	1650	80			
Royal #2	365834094485302	11/19/2002	1650	80			
Slim Jim	365942094504203	11/20/2002	1630	80	CFC-12, 113	Early 1980s	1980
Slim Jim	365942094504203	11/20/2002	1630	80			
Slim Jim	365942094504203	11/20/2002	1630	80			
Turner	365855094484501	11/19/2002	1200	80	CFC-113	Mid-1970s or younger	1975
Turner	365855094484501	11/19/2002	1200	80			
Turner	365855094484501	11/19/2002	1200	80			
Turner	365855094484501	11/19/2002	1200	80			

Appendix 3. Chluorofluorocarbon (CFC) concentrations and calculated age dates from water samples collected in the Picher mining district, Oklahoma, 2002–03—Continued

[pg/kg, picograms per kilogram; NP, not possible; Contam, greater than 2001 air; Modern, possible range of modern air; ***, no data]

Station name	Station number	Date	Time	Sampling depth (feet)	Probable Age based on CFC 11, 12, or 113	Comments	Assigned Age
Vent #1	365844094510501	11/20/2002	1225	80	CFC-113	Early to mid-1970s or younger	1974
Vent #1	365844094510501	11/20/2002	1225	80			
Vent #1	365844094510501	11/20/2002	1225	80			

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Barometric pressure (mm of Hg)	Specific conductance at 25˚C, (µS/cm)		pH (standard unit)		Temperature, water (˚C)	Oxygen, dissolved (mg/L)
							field	lab	field	lab		
Admiralty #3	1	365737094502201	07/17/2002	1115	197	760	2,750	2,270	5.9	5.6	15.4	0.3
Admiralty #4	2	365753094504601	11/05/2002	1330	60	766	2,550	E2,360	6.5	6.3	15.6	0.3
Admiralty #4	2	365753094504601	11/05/2002	1700	200	766	2,860	2,260	6.5	5.7	15.6	0.3
Admiralty #4	2	365753094504601	07/19/2002	0920	40	760	2,630	2,400	6.1	5.9	15.3	0.9
Admiralty #4	2	365753094504601	07/19/2002	1005	100	760	2,630	2,400	6.1	5.9	15.3	0.5
Admiralty #4	2	365753094504601	07/19/2002	1030	170	760	2,640	2,410	6.1	5.8	15.3	0.3
Admiralty #4	2	365753094504601	07/19/2002	1100	190	760	2,670	2,400	6.1	5.8	15.3	0.3
Admiralty #4	2	365753094504601	07/19/2002	1135	200	760	2,690	2,440	6.1	5.8	15.3	0.3
Admiralty #4	2	365753094504601	07/19/2002	1200	205	760	2,780	2,430	6.1	5.8	15.4	0.2
Baby Jim	3	365818094505201	07/18/2002	1620	150	760	2,270	2,010	6.2	6.5	15.9	0.2
Baby Jim	3	365818094505201	07/18/2002	1650	160	760	2,330	2,080	6.2	6.2	15.9	0.2
Baby Jim	3	365818094505201	07/18/2002	1730	170	760	2,520	2,150	6.1	6.1	15.9	0.2
Consolidated #2	5	365927094485901	11/18/2002	1540	200	760	2,540	2,580	6.0	6.1	16.2	0.7
Consolidated #2	5	365927094485901	07/16/2002	1550	227	759	2,640	684	6.2	6.9	15.7	1.1
Consolidated #2	5	365927094485901	07/16/2002	1610	230	759	2,780	915	6.1	6.5	15.8	0.3
Federal #5	10	365803094494101	07/17/2002	1830	200	760	2,640	899	6.0	6.9	16.1	0.1
Federal #5	10	365803094494101	07/17/2002	1850	210	760	2,800	898	6.1	6.7	16.1	0.1
Royal #2	21	365834094485302	11/19/2002	1550	80	--	2,420	2,450	6.8	6.6	16.4	0.3
Slim Jim	22	365942094504203	11/20/2002	1620	80	760	2,630	2,590	6.7	7.1	17.6	0.9
Turner	27	365855094484501	11/19/2002	1035	80	760	2,280	2,460	6.1	6.0	16.4	0.7
Vent #1	29	365844094510501	11/20/2002	1123	80	766	2,640	2,520	6.0	5.1	18.0	0.7

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Alkalinity, dissolved, (mg/L as $CaCO_3$)	Solids, residue at 180˚C, dissolved (mg/L)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
Admiralty #3	1	365737094502201	07/17/2002	1115	197	59	2,330	479	52.2	23.9	2.54
Admiralty #4	2	365753094504601	11/05/2002	1330	60	180	2,480	569	60.4	28.2	2.96
Admiralty #4	2	365753094504601	11/05/2002	1700	200	259	2,870	581	91.5	43.5	4.02
Admiralty #4	2	365753094504601	07/19/2002	0920	40	80	2,580	563	59.7	27.7	3.28
Admiralty #4	2	365753094504601	07/19/2002	1005	100	78	2,580	569	60.2	27.9	3.39
Admiralty #4	2	365753094504601	07/19/2002	1030	170	63	2,590	551	58.0	26.6	3.38
Admiralty #4	2	365753094504601	07/19/2002	1100	190	63	2,560	556	58.9	27.1	3.37
Admiralty #4	2	365753094504601	07/19/2002	1135	200	71	2,660	556	62.1	29.2	3.31
Admiralty #4	2	365753094504601	07/19/2002	1200	205	70	2,630	557	63.6	30.2	3.22
Baby Jim	3	365818094505201	07/18/2002	1620	150	123	1,930	368	56.2	27.6	3.18
Baby Jim	3	365818094505201	07/18/2002	1650	160	133	1,960	374	56.6	27.4	3.15
Baby Jim	3	365818094505201	07/18/2002	1730	170	138	2,050	382	56.3	27.8	3.13
Consolidated #2	5	365927094485901	11/18/2002	1540	200	225	2,690	572	80.2	36.8	4.65
Consolidated #2	5	365927094485901	07/16/2002	1550	227	68	551	136	12.4	4.78	0.93
Consolidated #2	5	365927094485901	07/16/2002	1610	230	70	782	190	18.2	7.65	1.24
Federal #5	10	365803094494101	07/17/2002	1830	200	86	751	149	32.1	16.7	2.08
Federal #5	10	365803094494101	07/17/2002	1850	210	88	713	141	33.3	17.6	2.22
Royal #2	21	365834094485302	11/19/2002	1550	80	362	2,380	487	90.4	52.4	5.70
Slim Jim	22	365942094504203	11/20/2002	1620	80	315	2,190	174	82.3	326	13.3
Turner	27	365855094484501	11/19/2002	1035	80	193	2,530	419	123	62.4	4.69
Vent #1	29	365844094510501	11/20/2002	1123	80	201	2,690	466	102	53.7	5.36

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; µS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Bicarbonate, dissolved, field (mg/L)	Carbonate, dissolved, field (mg/L)	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Bromide, dissolved (mg/L)
Admiralty #3	1	365737094502201	07/17/2002	1115	197	--	--	1,400	9.88	2.24	0.06
Admiralty #4	2	365753094504601	11/05/2002	1330	60	219	0	1,550	8.88	2.63	0.04
Admiralty #4	2	365753094504601	11/05/2002	1700	200	315	0	1,750	13.2	1.74	0.06
Admiralty #4	2	365753094504601	07/19/2002	0920	40	--	--	1,550	9.72	2.59	0.06
Admiralty #4	2	365753094504601	07/19/2002	1005	100	--	--	1,550	9.97	2.67	0.06
Admiralty #4	2	365753094504601	07/19/2002	1030	170	--	--	1,550	9.54	2.67	0.05
Admiralty #4	2	365753094504601	07/19/2002	1100	190	--	--	1,470	9.52	2.84	0.06
Admiralty #4	2	365753094504601	07/19/2002	1135	200	--	--	1,590	10.2	2.73	0.08
Admiralty #4	2	365753094504601	07/19/2002	1200	205	--	--	1,590	10.7	2.53	0.06
Baby Jim	3	365818094505201	07/18/2002	1620	150	--	--	1,100	10.5	1.77	0.05
Baby Jim	3	365818094505201	07/18/2002	1650	160	--	--	1,140	11.6	1.94	0.06
Baby Jim	3	365818094505201	07/18/2002	1730	170	--	--	1,170	10.9	2.17	0.06
Consolidated #2	5	365927094485901	11/18/2002	1540	200	274	0	1,700	6.76	1.68	0.06
Consolidated #2	5	365927094485901	07/16/2002	1550	227	--	--	298	1.34	0.35	0.03
Consolidated #2	5	365927094485901	07/16/2002	1610	230	--	--	453	1.61	0.53	E.03
Federal #5	10	365803094494101	07/17/2002	1830	200	--	--	415	2.19	0.26	E.02
Federal #5	10	365803094494101	07/17/2002	1850	210	--	--	400	2.28	0.25	E.02
Royal #2	21	365834094485302	11/19/2002	1550	80	440	0	1,300	5.94	0.40	0.06
Slim Jim	22	365942094504203	11/20/2002	1620	80	383	0	1,170	19.6	0.38	0.22
Turner	27	365855094484501	11/19/2002	1035	80	235	0	1,570	8.07	<0.17	0.10
Vent #1	29	365844094510501	11/20/2002	1123	80	244	0	1,670	14.3	2.31	0.08

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Silica, dissolved (mg/L)	Aluminum, dissolved (µg/L)	Antimony, dissolved (µg/L)	Arsenic, dissolved (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)
Admiralty #3	1	365737094502201	07/17/2002	1115	197	17.6	241	0.07	26	6	0.29
Admiralty #4	2	365753094504601	11/05/2002	1330	60	12.3	81	<0.30	9	8	0.14
Admiralty #4	2	365753094504601	11/05/2002	1700	200	13.1	112	<0.60	27	7	0.23
Admiralty #4	2	365753094504601	07/19/2002	0920	40	12.1	93	<0.05	14	8	0.21
Admiralty #4	2	365753094504601	07/19/2002	1005	100	12.3	96	<0.05	14	8	0.21
Admiralty #4	2	365753094504601	07/19/2002	1030	170	11.7	136	<0.05	19	7	0.28
Admiralty #4	2	365753094504601	07/19/2002	1100	190	11.8	130	<0.05	19	7	0.24
Admiralty #4	2	365753094504601	07/19/2002	1135	200	12.3	121	<0.05	21	7	0.22
Admiralty #4	2	365753094504601	07/19/2002	1200	205	12.4	149	0.05	21	6	0.16
Baby Jim	3	365818094505201	07/18/2002	1620	150	10.3	31	0.05	14	14	0.17
Baby Jim	3	365818094505201	07/18/2002	1650	160	10.6	36	0.06	15	13	0.14
Baby Jim	3	365818094505201	07/18/2002	1730	170	10.9	33	0.09	15	13	0.14
Consolidated #2	5	365927094485901	11/18/2002	1540	200	12.5	126	<0.60	27	6	0.24
Consolidated #2	5	365927094485901	07/16/2002	1550	227	12.0	3	0.20	<2	16	<0.06
Consolidated #2	5	365927094485901	07/16/2002	1610	230	11.2	9	0.19	2	16	<0.06
Federal #5	10	365803094494101	07/17/2002	1830	200	19.1	<1	0.14	<2	8	<0.06
Federal #5	10	365803094494101	07/17/2002	1850	210	19.1	<1	0.07	<2	8	<0.06
Royal #2	21	365834094485302	11/19/2002	1550	80	21.2	<2	<0.30	6	38	<0.06
Slim Jim	22	365942094504203	11/20/2002	1620	80	12.7	<3	<0.60	<2	13	<0.12
Turner	27	365855094484501	11/19/2002	1035	80	8.0	15	<0.30	51	50	0.24
Vent #1	29	365844094510501	11/20/2002	1123	80	21.3	267	<0.60	41	10	0.3

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data]

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Cadmium dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobalt, dissolved (µg/L)	Copper, dissolved (µg/L)	Iron, dissolved (µg/L)	Lead, dissolved (µg/L)	Man-ganese, dissolved (µg/L)
Admiralty #3	1	365737094502201	07/17/2002	1115	197	2.56	<0.8	35.8	6.9	56,200	2.08	1,020
Admiralty #4	2	365753094504601	11/05/2002	1330	60	0.05	<0.8	37.1	6.8	45,400	<0.08	1,870
Admiralty #4	2	365753094504601	11/05/2002	1700	200	2.44	<0.8	38.8	8.4	92,100	0.56	1,370
Admiralty #4	2	365753094504601	07/19/2002	0920	40	0.10	1.6	35.4	32.0	49,200	<0.08	1,440
Admiralty #4	2	365753094504601	07/19/2002	1005	100	0.14	<0.8	35.6	75.7	50,000	E0.05	1,420
Admiralty #4	2	365753094504601	07/19/2002	1030	170	0.60	<0.8	38.9	52.4	49,900	0.54	1,230
Admiralty #4	2	365753094504601	07/19/2002	1100	190	0.47	<0.8	37.9	11.6	50,400	0.36	1,190
Admiralty #4	2	365753094504601	07/19/2002	1135	200	0.20	<0.8	35.6	12.1	54,800	0.96	1,130
Admiralty #4	2	365753094504601	07/19/2002	1200	205	0.22	<0.8	39.4	19.0	56,300	0.55	1,300
Baby Jim	3	365818094505201	07/18/2002	1620	150	0.78	<0.8	29.9	18.2	44,200	1.05	935
Baby Jim	3	365818094505201	07/18/2002	1650	160	0.98	<0.8	30.7	8.6	45,100	1.13	940
Baby Jim	3	365818094505201	07/18/2002	1730	170	0.98	<0.8	29.0	4.8	45,400	2.01	893
Consolidated #2	5	365927094485901	11/18/2002	1540	200	1.97	<0.8	26.8	3.8	76,900	0.77	1,630
Consolidated #2	5	365927094485901	07/16/2002	1550	227	82.6	<0.8	1.79	1.7	3,820	E0.07	105
Consolidated #2	5	365927094485901	07/16/2002	1610	230	74.5	<0.8	4.24	2.2	10,600	0.12	253
Federal #5	10	365803094494101	07/17/2002	1830	200	11.2	<0.8	0.74	21.5	22	0.13	54.1
Federal #5	10	365803094494101	07/17/2002	1850	210	11.1	1.7	0.60	6.2	<30	0.13	57.9
Royal #2	21	365834094485302	11/19/2002	1550	80	E0.02	<0.8	39.9	3.0	23,500	0.94	2,840
Slim Jim	22	365942094504203	11/20/2002	1620	80	<0.07	<0.8	1.90	2.1	<10	<0.16	321
Turner	27	365855094484501	11/19/2002	1035	80	0.09	<0.8	34.0	3.6	60,600	E0.05	711
Vent #1	29	365844094510501	11/20/2002	1123	80	0.24	<0.8	74.2	4.2	115,000	0.81	2,340

Appendix 4. Water-quality concentrations from ground-water samples collected in the Picher mining district, Oklahoma, 2002 —Continued

[mm of Hg, millimeters of mercury; ˚C, degrees Celsius; mS/cm, microSiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; E, estimated value; --, no data

Station name	Site number (as in figure 1)	Station number	Date	Time	Sampling depth (feet)	Molyb-denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Selenium dissolved (µg/L)	Silver, dissolved (µg/L)	Zinc, dissolved (µg/L)	Uranium, dissolved (µg/L)
Admiralty #3	1	365737094502201	07/17/2002	1115	197	4.4	265	4	<1	9,250	3.16
Admiralty #4	2	365753094504601	11/05/2002	1330	60	3.0	283	<3	<0.2	6,340	2.37
Admiralty #4	2	365753094504601	11/05/2002	1700	200	3.3	319	<3	<0.4	9,550	9.00
Admiralty #4	2	365753094504601	07/19/2002	0920	40	3.7	324	3	<1	9,680	2.77
Admiralty #4	2	365753094504601	07/19/2002	1005	100	3.6	324	3	<1	9,630	2.77
Admiralty #4	2	365753094504601	07/19/2002	1030	170	4.0	358	4	<1	10,300	3.07
Admiralty #4	2	365753094504601	07/19/2002	1100	190	4.0	362	4	<1	10,300	3.03
Admiralty #4	2	365753094504601	07/19/2002	1135	200	4.1	345	5	<1	9,890	3.48
Admiralty #4	2	365753094504601	07/19/2002	1200	205	4.2	344	5	<1	11,100	3.13
Baby Jim	3	365818094505201	07/18/2002	1620	150	1.2	234	3	<1	9,050	2.81
Baby Jim	3	365818094505201	07/18/2002	1650	160	1.3	240	3	<1	8,550	3.42
Baby Jim	3	365818094505201	07/18/2002	1730	170	1.4	235	3	<1	7,970	3.91
Consolidated #2	5	365927094485901	11/18/2002	1540	200	2.2	199	E2	<0.4	4,560	8.39
Consolidated #2	5	365927094485901	07/16/2002	1550	227	0.3	20.3	E1	<1	1,900	0.84
Consolidated #2	5	365927094485901	07/16/2002	1610	230	0.5	37.7	E1	<1	2,270	1.94
Federal #5	10	365803094494101	07/17/2002	1830	200	<0.2	28.0	E1	<1	2,180	0.29
Federal #5	10	365803094494101	07/17/2002	1850	210	<0.2	24.2	E1	<1	2,050	0.27
Royal #2	21	365834094485302	11/19/2002	1550	80	1.4	56.2	E2	<0.2	4,320	10.3
Slim Jim	22	365942094504203	11/20/2002	1620	80	<0.7	14.3	E2	<0.4	8	0.51
Turner	27	365855094484501	11/19/2002	1035	80	2.9	207	E2	<0.2	14,800	0.36
Vent #1	29	365844094510501	11/20/2002	1123	80	3.7	633	E1	<0.4	20,100	0.52