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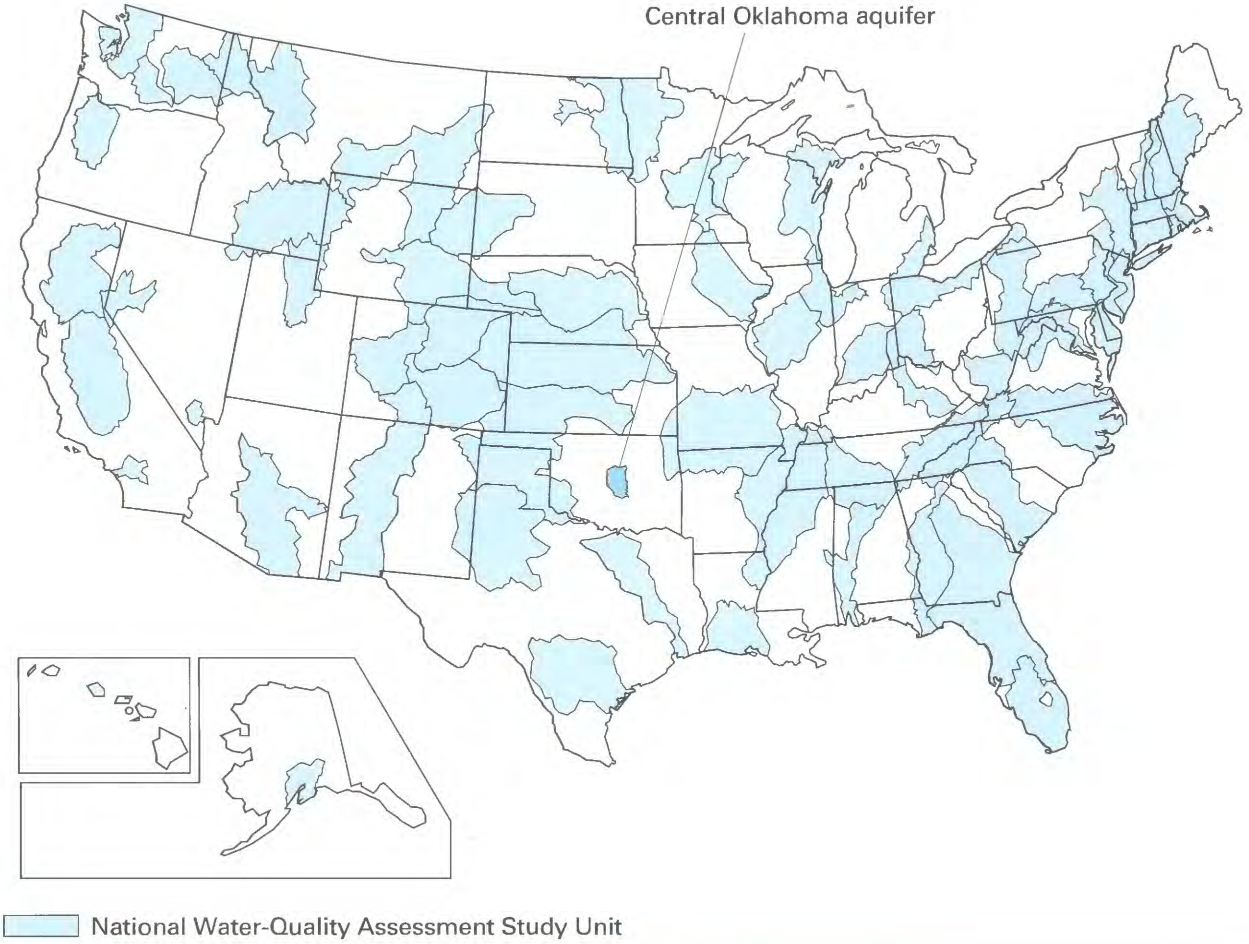
NATIONAL WATER-QUALITY ASSESSMENT—CENTRAL OKLAHOMA AQUIFER

Chapter A

Ground-Water-Quality Assessment of the Central Oklahoma Aquifer, Oklahoma: Results of Investigations

Water-Supply Paper 2357-A



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NATIONAL WATER-QUALITY ASSESSMENT—CENTRAL OKLAHOMA AQUIFER

Chapter A

Ground-Water-Quality Assessment of the Central Oklahoma Aquifer, Oklahoma: Results of Investigations

Edited by SCOTT CHRISTENSON and JOHN S. HAVENS

Water-Supply Paper 2357–A

Oklahoma City, Oklahoma
1998

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
inch (in.)	2.54	meter
foot (ft)	0.3048	meter
foot per mile (ft/mi)	0.1894	meter per kilometer
kilometer (km)	0.6214	mile
liter (L)	0.2642	gallon
liter per second (L/s)	15.85	gallon per minute
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
meter per kilometer (m/km)	5.27983	foot per mile
meter squared per day (m^2/d)	10.76	foot squared per day
mile (mi)	1.609	kilometer
millimeter (mm)	0.03937	inch
millimeter per year (mm/yr)	0.03937	inch per year
square kilometer (km^2)	0.3861	square mile
square mile (mi^2)	2.590	square kilometer

Temperature in degree Fahrenheit (°F) can be converted to degree Celsius (°C) as follows:

$$°C = (°F - 32)/1.8.$$

Temperature in degree Celsius (°C) can be converted to degree Fahrenheit (°F) as follows:

$$°F = 1.8\ °C + 32.$$

The following water-quality units and abbreviations are also used in this report:

microgram per gram (µg/g)
microgram per liter (µg/L)
micrometer (µm)
micromole per liter (µmol/L)
milliequivalent (meq)
milliequivalent per liter (meq/L)
milliequivalent per 100 grams (meq/100 g)
milligram per day (mg/d)
milligram per liter (mg/L)
milliliter per liter (mL/L)
millimole per liter (mmol/L)
mole (mol)
part per million (ppm)
percent modern carbon (pmc)
picocuries per liter (pCi/L)

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Ground-Water-Quality Assessment of the Central Oklahoma Aquifer: Summary of Investigations

By Scott Christenson

Abstract

A study of the ground-water quality of the Central Oklahoma aquifer was conducted as part of the National Water-Quality Assessment Program. The objectives of the study were to: (1) describe regional ground-water quality throughout the aquifer, (2) describe the major geochemical and geohydrologic processes operating in the aquifer, (3) identify the major factors affecting the ground-water quality, and (4) describe the location, nature, and causes of selected water-quality problems within the study unit, which were identified as naturally occurring trace substances and degradation of ground-water quality caused by urbanization.

Geochemical investigations showed that calcium, magnesium, and bicarbonate are the dominant ions in ground water from the unconfined parts of the Garber Sandstone and Wellington Formation. This water chemistry is the result of uptake of carbon dioxide from the unsaturated zone; dissolution of dolomite and, to lesser extents, the dissolution of biotite, chlorite, plagioclase, and potassium feldspar; and precipitation of kaolinite. Sodium and bicarbonate are the dominant ions in the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and Admire Groups. The sodium bicarbonate water is derived from the calcium, magnesium, and bicarbonate water by cation exchange of calcium and magnesium with sodium in clay minerals.

The overall quality of water in the aquifer is quite good, based on the small number of sampled wells that exceeded existing water-quality standards. Maximum Contaminant Levels, which are related to public health, were commonly (more than 10 percent of wells) exceeded only for nitrate in wells shallower than 30 meters completed in Permian geologic units and for selenium in wells deeper than 30 meters completed in Permian geologic units.

Although the overall quality of water in the Central Oklahoma aquifer is good, water-quality problems occur in parts of the aquifer. Many public supply wells in central Oklahoma yield water with elevated concentrations of arsenic, chromium, selenium, and uranium. These elements are widely dispersed on solid-phase materials throughout the aquifer and are mobilized under certain geochemical conditions. The quality of ground water under the urban area was found to be significantly different from that of water outside the urban area. Pesticides and volatile organic compounds were much more common in water samples from wells in the urban area than from wells outside the urban area. The types of pesticides and volatile organic compounds found in water samples were consistent with the organic compounds known to be used in the urban area.

INTRODUCTION

The Central Oklahoma aquifer underlies about 8,000 km^2 of central Oklahoma (fig. 1), where the aquifer is used extensively for municipal, industrial, commercial, and domestic water supplies. All the municipalities in central Oklahoma rely on the aquifer for all or part of their water supply. Thus, the Central

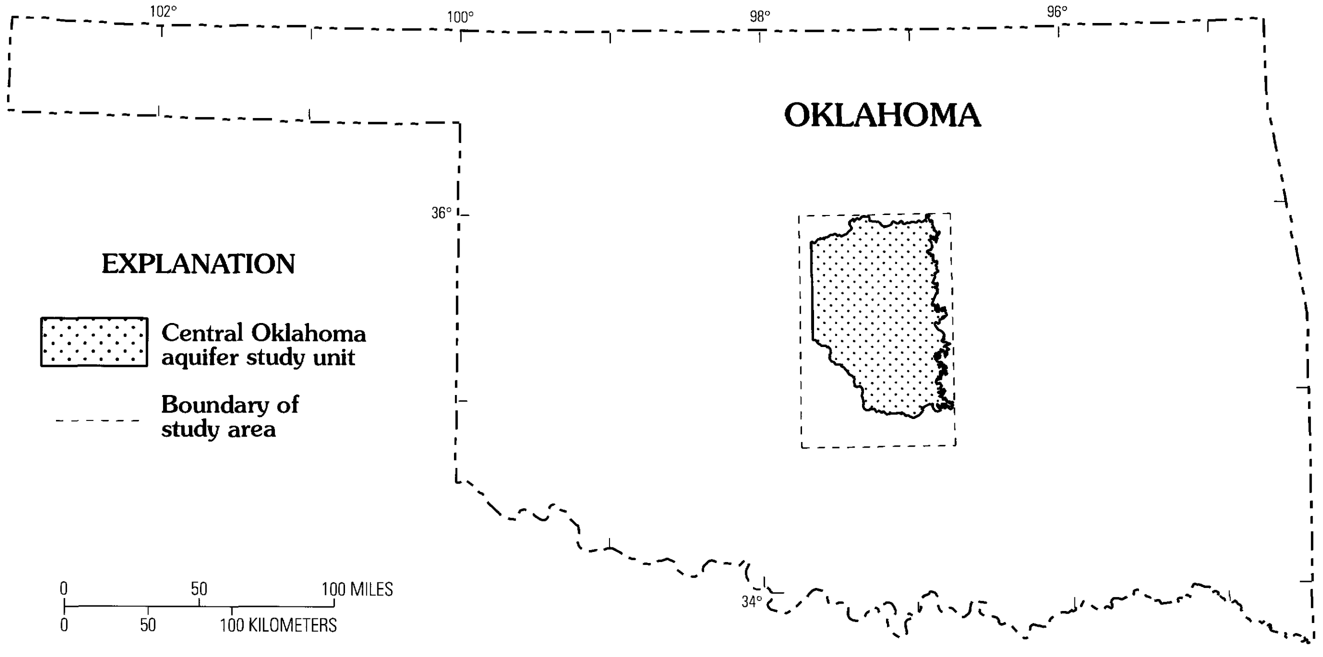


Figure 1. Location of the Central Oklahoma aquifer study unit.

Oklahoma aquifer is vitally important to the economy of central Oklahoma.

Because of its importance, the Central Oklahoma aquifer was selected as a pilot study of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The primary purpose of the NAWQA Program is to assess water quality for a large part of the Nation's water resources. The long-term goals of the NAWQA Program are to:

1. Provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources,
2. Define long-term trends (or lack of trends) in water quality, and
3. Identify, describe, and explain, as possible, the major factors that affect the observed water-quality conditions and trends.

This information, which will be obtained on a continuing basis, is available to water managers, policymakers, and the public to provide an improved scientific basis for evaluating the effectiveness of water-quality management programs and for predicting the likely effects of contemplated changes in land- and water-management practices (Hirsch, Alley, and Wilber, 1988).

The objectives of the Central Oklahoma aquifer NAWQA project, as posed by Christenson and Parkhurst (1987), were to: (1) investigate regional ground-water quality throughout the aquifer in a manner consistent with the other pilot NAWQA ground-water projects, emphasizing the occurrence and distribution of potentially toxic substances in ground water, including trace elements, organic compounds, and radioactive constituents; (2) describe the relation of ground-water quality to land use, hydrogeology, and other pertinent factors; (3) provide a general description of the location, nature, and causes of selected water-quality problems within the study unit; and (4) describe potential for water-quality degradation of ground-water zones within the study unit.

The objectives of the project were revised slightly during the life of the project as knowledge of the aquifer increased and were further revised on the basis of input from the project's liaison committee, a group of representatives from 13 Federal, State, and local governmental agencies. The liaison committee was established to ensure that the scientific information produced by the Oklahoma NAWQA project was relevant to local and regional interests. The revised objectives were to: (1) describe regional ground-water quality throughout the aquifer, (2) describe the major geochemical and geohydrologic processes operating in the aquifer, (3) identify the major factors affecting the ground-water quality, and (4) describe the location, nature, and causes of selected water-quality problems within the study unit, which were identified as naturally occurring trace substances and degradation of ground-water quality caused by urbanization.

Purpose and Scope

This collection of five papers is intended to summarize the results of the Central Oklahoma aquifer investigations and present the results of some of the investigations that are not presented in separate papers. The papers included in this collection, and a brief statement of their purposes, are as follows:

1. **Summary of Investigations:** This paper provides: (1) a basic description of the Central Oklahoma aquifer, to avoid needless duplication of common background information in the other papers in this collection, and (2) a brief overall summary of the many different investigations that were undertaken as part of the Oklahoma NAWQA project.
2. **The Diagenetic History of Permian Rocks in the Central Oklahoma Aquifer:** This paper describes the history of diagenesis of rocks of Permian age in the Central Oklahoma aquifer as inferred from a detailed mineralogic and petrographic study. This paper presents new information not discussed in other papers written as part of the NAWQA project.
3. **Geochemical Characterization of Solid-Phase Materials in the Central Oklahoma Aquifer:** This paper summarizes the extensive laboratory measurements conducted on solid-phase materials (that is, soil, outcrop, and core samples) that were essential in understanding the geochemistry of the water within the Central Oklahoma aquifer. These experiments included whole-rock digestions and sequential extractions.
4. **Summary of Geochemical and Geohydrologic Investigations of the Central Oklahoma Aquifer:** This paper summarizes investigations of the geochemistry and geohydrology of the Central Oklahoma aquifer that were done to provide the basic knowledge required to conduct a water-quality assessment of the aquifer.
5. **Arsenic, Chromium, Selenium, and Uranium in the Central Oklahoma Aquifer:** This paper summarizes investigations on naturally occurring trace substances that contaminate many wells completed in the Central Oklahoma aquifer. Although other papers written as part of the Oklahoma NAWQA project describe aspects of these investigations, this paper presents new information not discussed in other papers.

Acknowledgments

The author is indebted to many people for their cooperation and assistance in obtaining information concerning wells, ground-water withdrawals, use of water, and other pertinent data. Personnel from municipal water departments and well owners provided information and allowed personnel from the U.S. Geological Survey to measure water levels and collect water samples from their wells.

Representatives from 13 Federal, State, and local governmental agencies met on a regular basis to ensure that the scientific information produced by the Central Oklahoma NAWQA project was relevant to local and regional interests. This group formed a committee known as the Central Oklahoma aquifer NAWQA Liaison Committee. The Liaison Committee included the Association of Central Oklahoma Governments, the Bureau of Reclamation, Directorate of Environmental Management from Tinker Air Force Base, the Environmental and Ground Water Institute at the University of Oklahoma, Oklahoma Corporation Commission, Oklahoma Department of Agriculture, Oklahoma Department of Pollution Control, Oklahoma Geological Survey, Oklahoma State Department of Health, Oklahoma Water Resources Board, U.S. Army Corps of Engineers, U.S. Environmental Protection Agency, and the University Center for Water Research at Oklahoma State University. The assistance and guidance of this group are gratefully acknowledged.

DESCRIPTION OF THE STUDY UNIT

A brief description of the geography, geohydrology, and geochemistry of the Central Oklahoma aquifer is provided here. A more complete description can be found in Parkhurst, Christenson, and Breit (1993).

Geography of the Central Oklahoma Aquifer

The Central Oklahoma aquifer underlies all or parts of Cleveland, Lincoln, Logan, Oklahoma, Payne, and Pottawatomie Counties (fig. 2). The topography overlying the Central Oklahoma aquifer is

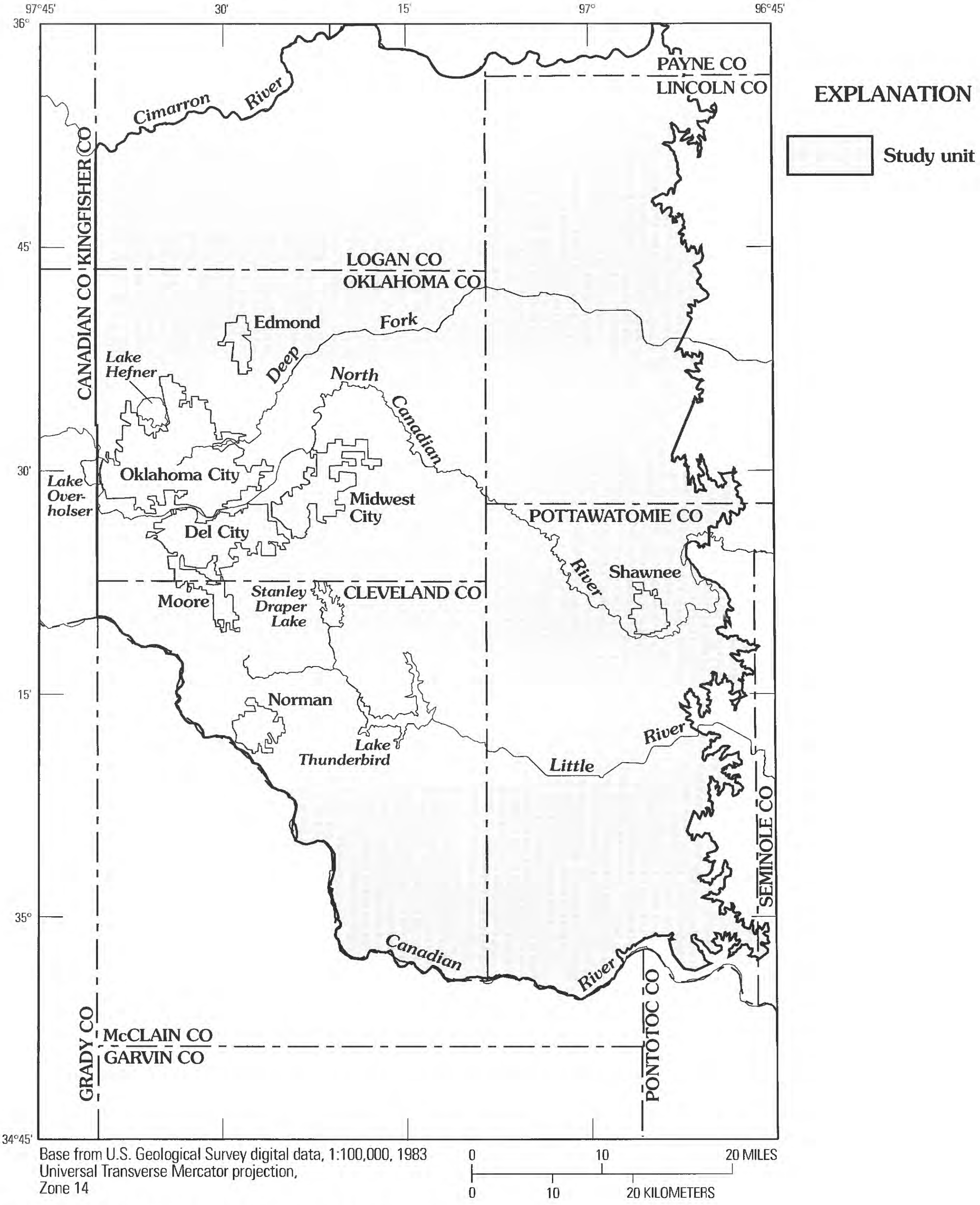


Figure 2. Major geographic features of the study unit.

characterized by low, rolling hills in the eastern two-thirds of the study unit and flat plains in the western third. The average annual temperature in the study unit is about 16 °C. The average annual precipitation is approximately 840 mm, most of which falls from April through October.

Oklahoma City, the largest city in Oklahoma, overlies the west-central part of the aquifer. Oklahoma City is the 29th largest city in the United States, based on population data from the 1990 census. Oklahoma City's population is approximately 445,000, and the city is surrounded by numerous smaller municipalities with populations as large as 80,000, as well as a large dispersed residential population outside the boundaries of the municipalities. Approximately 959,000 people live within the standard metropolitan statistical area.

Even though Oklahoma City covers a large area and is surrounded by numerous communities, the dominant land use in the study unit is agricultural. Much of the agricultural land is used for raising livestock, although grain crops (principally wheat and sorghum) are grown in the area. Land use overlying the western one-third of the aquifer is agricultural and urban, and is divided equally between agriculture and deciduous forest in the eastern two-thirds of the study unit.

All the municipalities in central Oklahoma rely on the Central Oklahoma aquifer for all or part of their water supply (although the aquifer is not used as part of Oklahoma City's public water supply, some residential areas within the Oklahoma City limits are not connected to public supplies and rely on individual domestic wells). Total ground-water withdrawals, which include municipal, industrial, and commercial use, as reported to the Oklahoma Water Resources Board, were 52,600 million liters in 1985. Domestic withdrawals are not reported but were estimated to be approximately 6,380 million liters in 1980 (Parkhurst, Christenson, and Breit, 1993).

Geohydrology and Geochemistry of the Central Oklahoma Aquifer

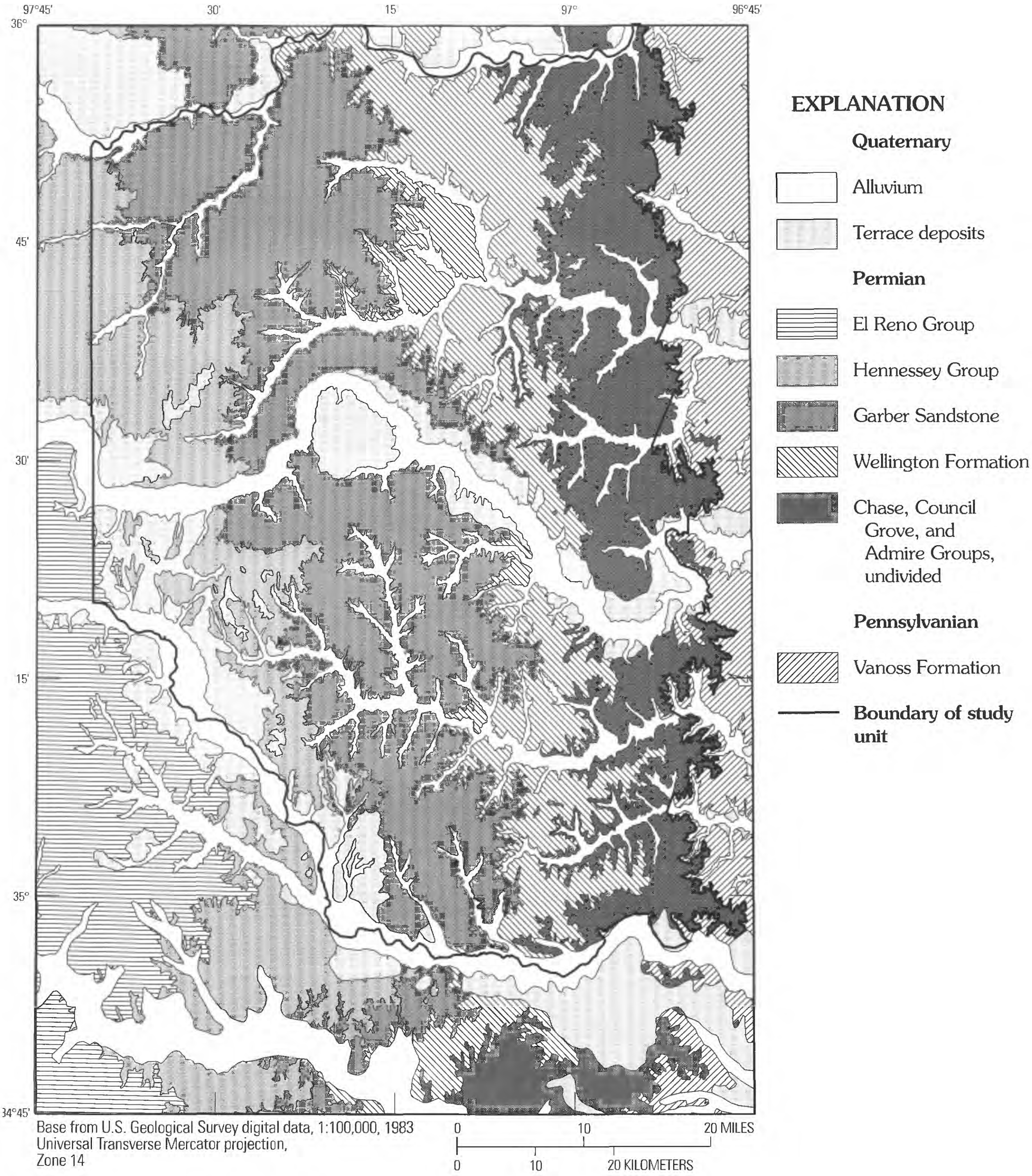
The primary purpose of the NAWQA Program is to assess the water quality for a large part of the Nation's water resources. For aquifer systems, an understanding of the major elements of the aquifer's geohydrologic and geochemical processes is necessary to conduct a water-quality assessment. Geohydrologic and geochemical investigations were performed as part of the Oklahoma NAWQA project, and the results are presented in several publications. Christenson, Morton, and Mesander (1992) present maps showing the major hydrogeologic features of the Central Oklahoma aquifer. Parkhurst, Christenson, and Breit (1993) present the results of geochemical, geohydrologic, and petrographic studies of the aquifer. The results of the geochemical and geohydrologic investigations are presented in Christenson, Parkhurst, and Breit (1995), a paper in this volume. A very brief summary of the geohydrology and geochemistry of the aquifer follows.

Geohydrology

The Central Oklahoma aquifer consists of geologic units of Permian and Quaternary ages that yield substantial volumes of water to wells from an extensive, continuous ground-water flow system in central Oklahoma (fig. 3). Most large-capacity wells completed in the Central Oklahoma aquifer are from 30 to 250 m deep and are completed in the Permian geologic units. Domestic wells typically are from 10 to 50 m deep and are completed in either the bedrock or the alluvium and terrace deposits. Ground water in this flow system originates as recharge from precipitation at a rate of about 40 mm/yr and discharges to streams and wells. The depth to water generally is less than 10 m; a map of the water table is shown in figure 4. The freshwater zone in the aquifer is as much as 275 m thick and is underlain by brine. The base of fresh ground water is shown in figure 5.

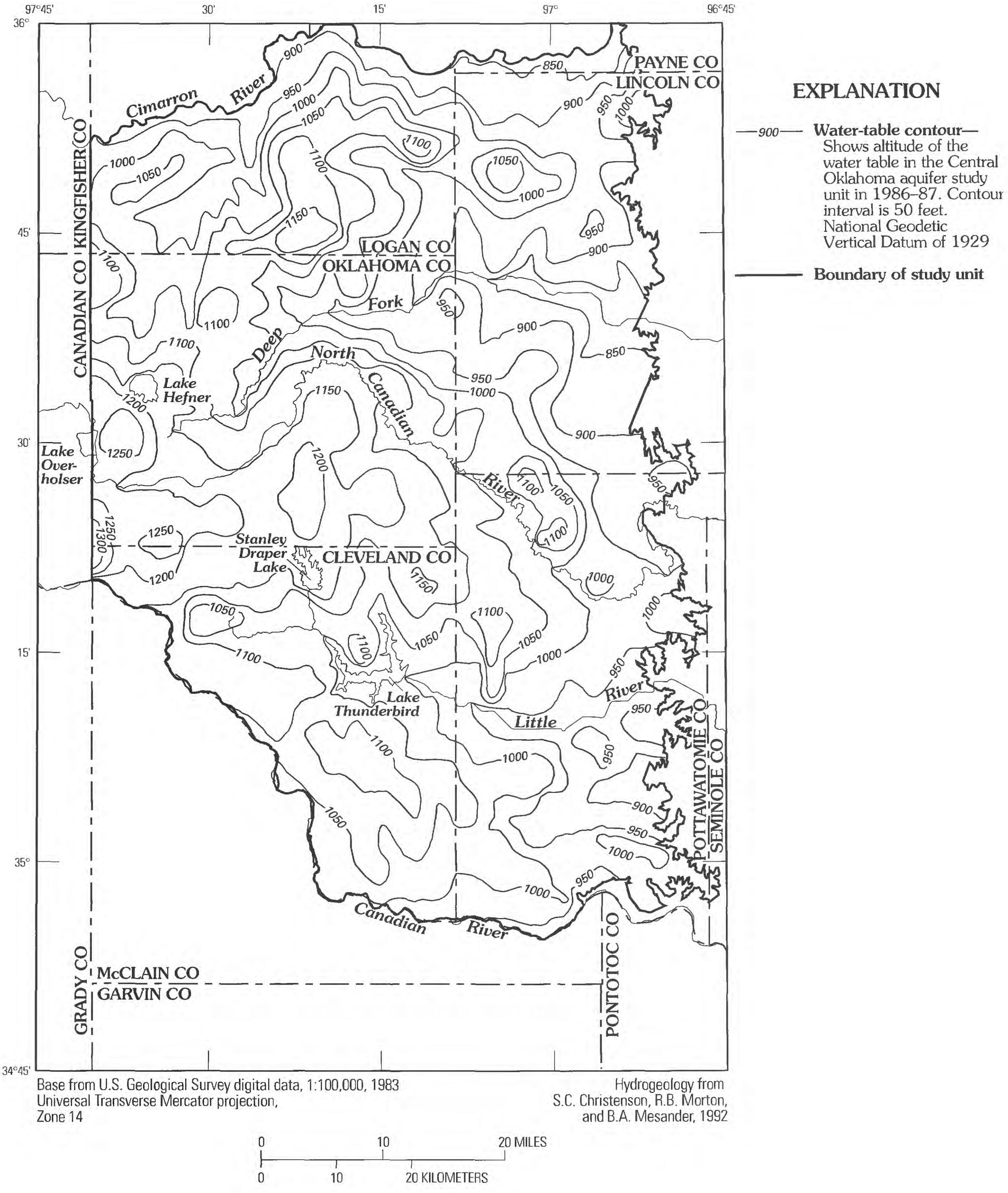
The Permian geologic units consist of lenticular beds of fine-grained, cross-bedded sandstone interbedded with siltstone and mudstone. These units were deposited in a fluvial-deltaic sedimentary environment, and the lithology is extremely variable, even over short distances. Most of the usable ground water is in the Garber Sandstone and the Wellington Formation. Where a full section of the Garber Sandstone and Wellington Formation is present in wells examined for this study, their combined thickness ranges from 355 to 490 m, and has a median thickness of 460 m (Christenson, Morton, and Mesander, 1992). A few wells completed in the Garber Sandstone and Wellington Formation yield as much as 40 L/s, but because the sandstone is fine grained, yields generally range from 10 to 25 L/s in wells designed for maximum yield. A map of the base of the Wellington Formation is shown in figure 6.

Substantial quantities of usable ground water also are in the Permian Chase, Council Grove, and Admire Groups (undivided in this report), which underlie the



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 3. Geologic map of central Oklahoma.



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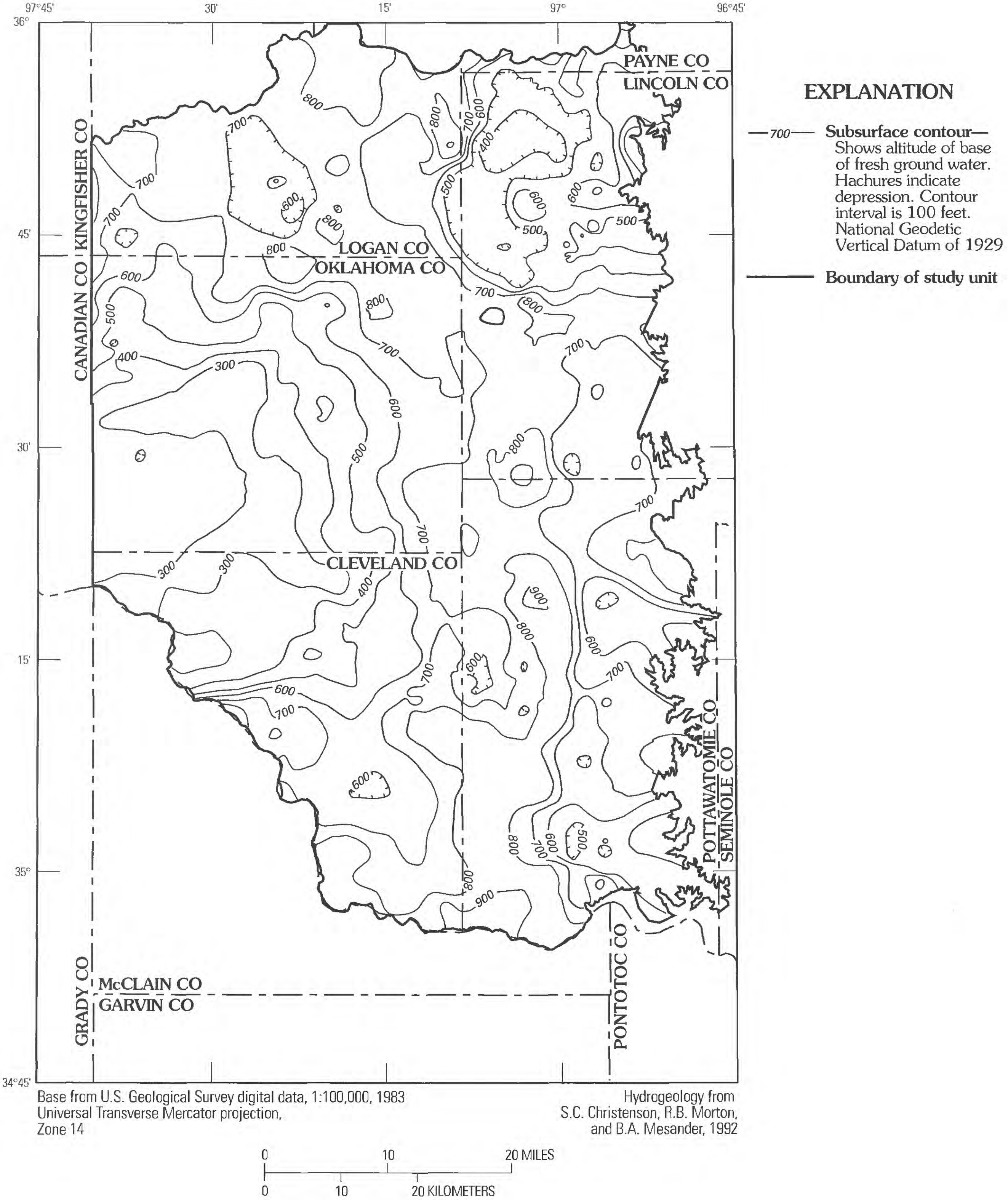
Universal Transverse Mercator projection,
Zone 14

Hydrogeology from
S.C. Christenson, R.B. Morton,
and B.A. Mesander, 1992

Figure 4. Altitude of water table in the Central Oklahoma aquifer study unit, 1986–87 (1 foot = 0.3048 meter).



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Universal Transverse Mercator projection,
Zone 14

Hydrogeology from
S.C. Christenson, R.B. Morton,
and B.A. Mesander, 1992

Figure 5. Altitude of the base of fresh ground water (1 foot = 0.3048 meter).

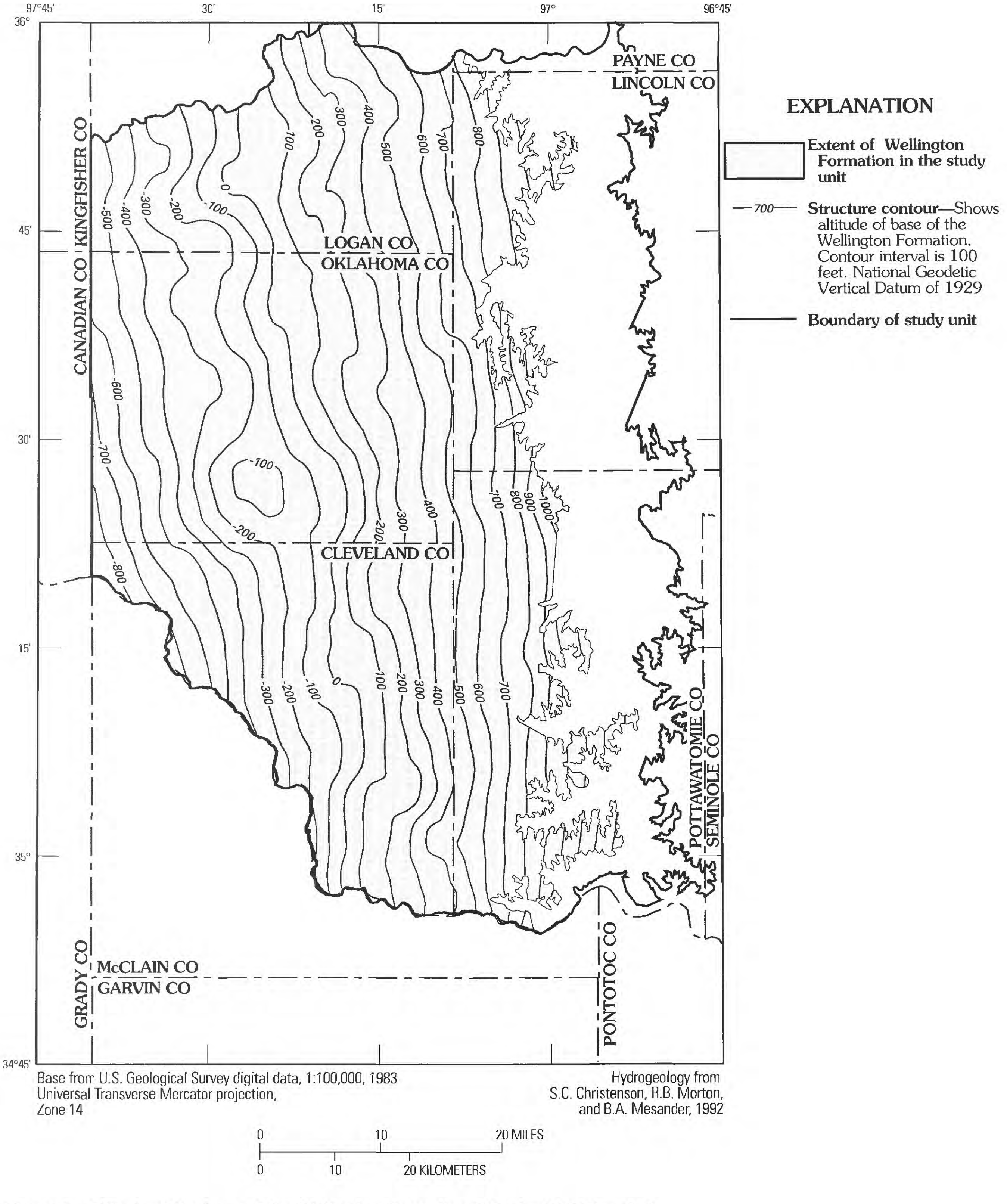


Figure 6. Altitude of the base of the Wellington Formation (1 foot = 0.3048 meter).

Garber Sandstone and Wellington Formation. Where complete sections are present in wells examined for this study, the combined thickness of these groups ranges from 170 to 290 m, with a median thickness of 230 m (Christenson, Morton, and Mesander, 1992). In surface exposures in the eastern part of the study unit, these groups have similar lithologies, consisting of beds of fine-grained, cross-bedded sandstone, shale, and thin limestone. Wells that are completed in the Chase, Council Grove, and Admire Groups generally yield 0.63 to 6.3 L/s; a few wells yield as much as 7.6 L/s. A map of the base of these groups is shown in figure 7.

Water in the western part of the aquifer is confined by the Hennessey Group, which is present in the western one-third of the study unit but has been removed by erosion in the eastern two-thirds. The Hennessey Group consists of reddish-brown shale and mudstone, with a few thin beds of very fine-grained sandstone. Because the Hennessey Group is comprised mainly of shale and mudstone, transmissivity is low, and thus, the Hennessey is a confining unit. The Hennessey Group is not considered to be part of the Central Oklahoma aquifer but is discussed in this report because it confines the aquifer. A map of the altitude of the base of the Hennessey Group is shown in figure 8.

The Permian geologic units dip to the west at approximately 10 m/km. No major faults or geologic structures are mapped in the Permian geologic units in the study unit. The simple structural geology can be seen in the geohydrologic section shown in figure 9.

Substantial quantities of usable ground water also are in the Quaternary alluvium and terrace deposits. These deposits are along streams and consist of lenticular beds of unconsolidated clay, silt, sand, and gravel. The thickness of the alluvium and terrace deposits ranges from 0 to about 30 m. Where the alluvium and terrace deposits are thickest and contain beds of gravel, wells yield as much as 40 L/s (Bingham and Moore, 1975).

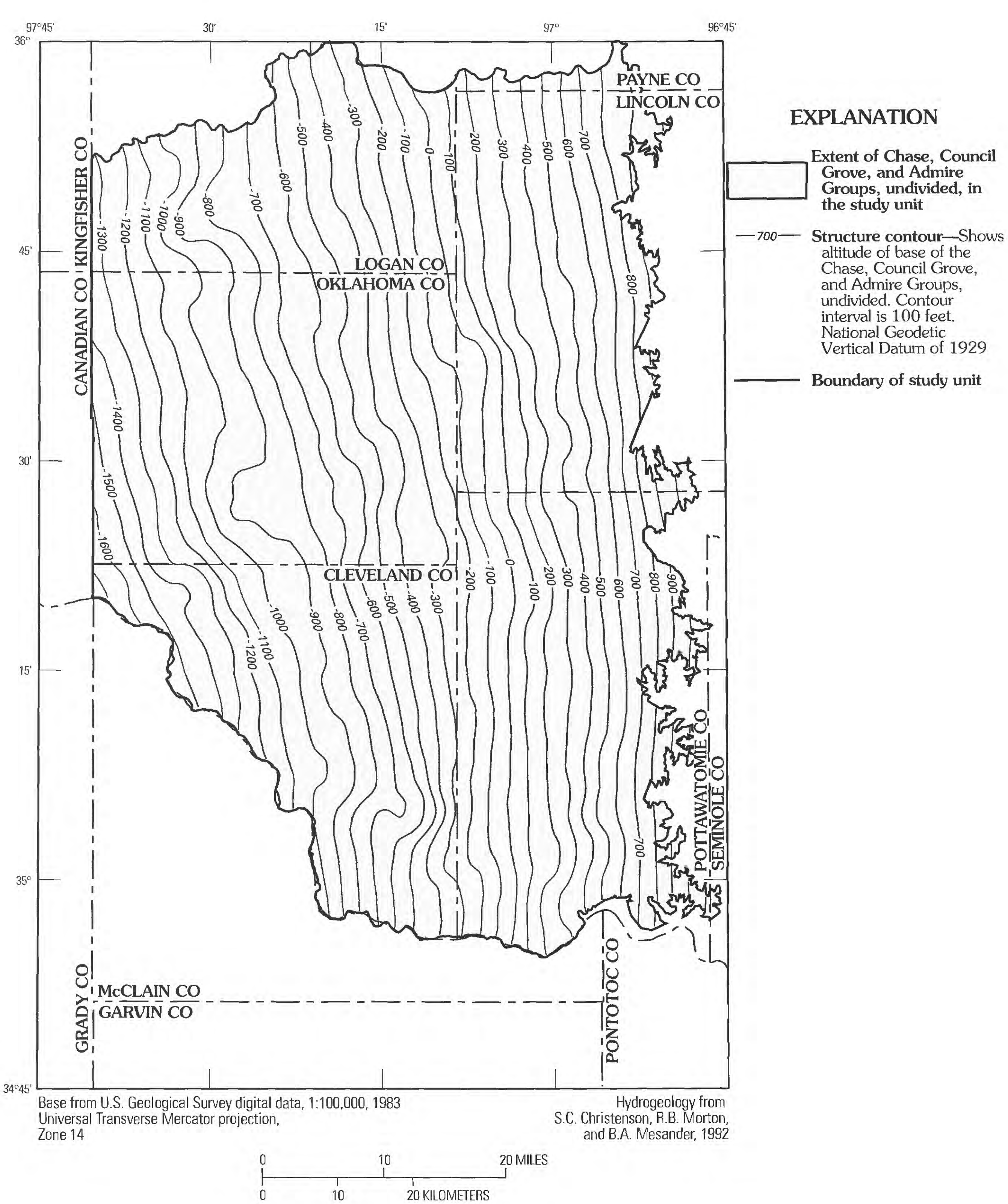
Median values for aquifer properties of Permian geologic units were estimated for the Central Oklahoma aquifer as part of the geohydrologic investigations for the NAWQA study: transmissivity of the Garber Sandstone and Wellington Formation, 24 to 42 m^2/d; horizontal hydraulic conductivity of sandstone in the study unit, 1.4 m/d; porosity of sandstone, 0.22; storage coefficient, 0.0002; recharge rate, 40 mm/yr.

A finite-difference, ground-water flow model was used in conjunction with a particle-tracking model to simulate the ground-water flow system in the Central Oklahoma aquifer. The ground-water flow and particle-tracking models, in conjunction with the results of the geochemical investigation, show that flow in the Central Oklahoma aquifer has three major components: (1) A shallow, local flow system in the unconfined part of the aquifer with transit times generally less than hundreds of years, (2) a deep, regional flow system in the unconfined part of the aquifer with transit times as much as 5,000 years or greater, and (3) a deep, regional flow system in the confined part of the aquifer with transit times ranging from thousands to tens of thousands of years.

Geochemistry

A geochemical network was designed to investigate the aqueous geochemistry of the Central Oklahoma aquifer. Wells located along suspected flowpaths were selected for inclusion in the geochemical network to measure the changes in water chemistry as ground water moves through the Central Oklahoma aquifer. Most wells in the geochemical network were water-supply wells, but a few monitoring wells also were sampled. A total of 37 wells were included in the geochemical network (fig. 10).

Petrographic evidence and mass-balance geochemical modeling were used to determine the predominant geochemical reactions in the Central Oklahoma aquifer. Calcium, magnesium, and bicarbonate are the dominant ions in ground water from the unconfined parts of the Garber Sandstone and Wellington Formation. This water chemistry is the result of uptake of carbon dioxide from the unsaturated zone (about 2.0 to 4.0 mmol/L); dissolution of dolomite (about 0.3 to 1.0 mmol/L) and, to lesser extents, the dissolution of biotite, chlorite, plagioclase, and potassium feldspar; and precipitation of kaolinite. Sodium and bicarbonate are the dominant ions in the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and Admire Groups. The sodium bicarbonate water is derived from the calcium, magnesium, and bicarbonate water by cation exchange of calcium and magnesium with sodium in clay minerals (approximately 2.0 mmol/L or more). Carbon–14 dated ages of ground water in the unconfined part of the aquifer generally are less than 10,000 years. Carbon–14 dated ages of ground water in the confined part of the aquifer range from about



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Hydrogeology from
S.C. Christenson, R.B. Morton,
and B.A. Mesander, 1992

Figure 7. Altitude of the base of the Chase, Council Grove, and Admire Groups, undivided (1 foot = 0.3048 meter).

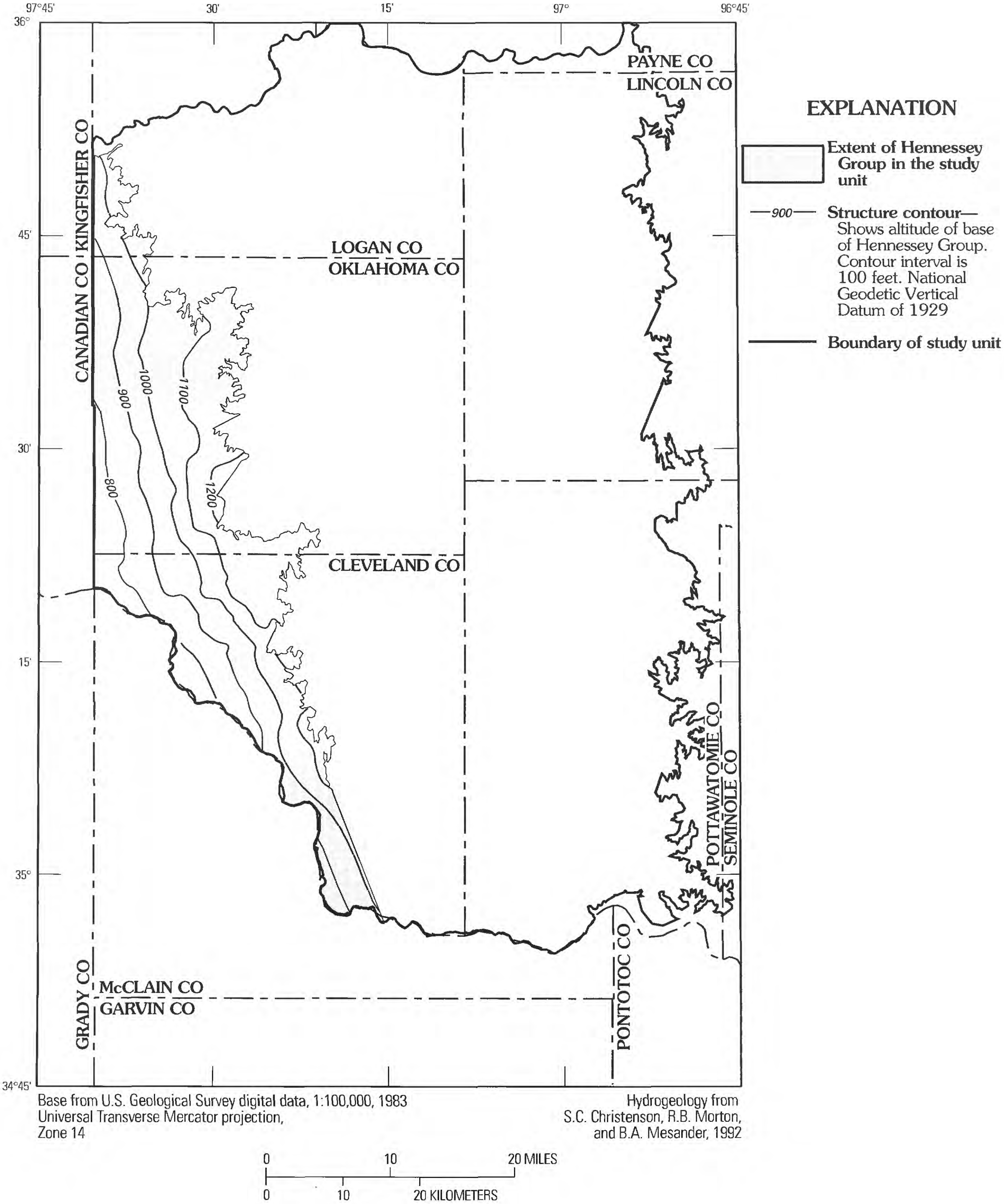


Figure 8. Altitude of the base of the Hennessey Group (1 foot = 0.3048 meter).

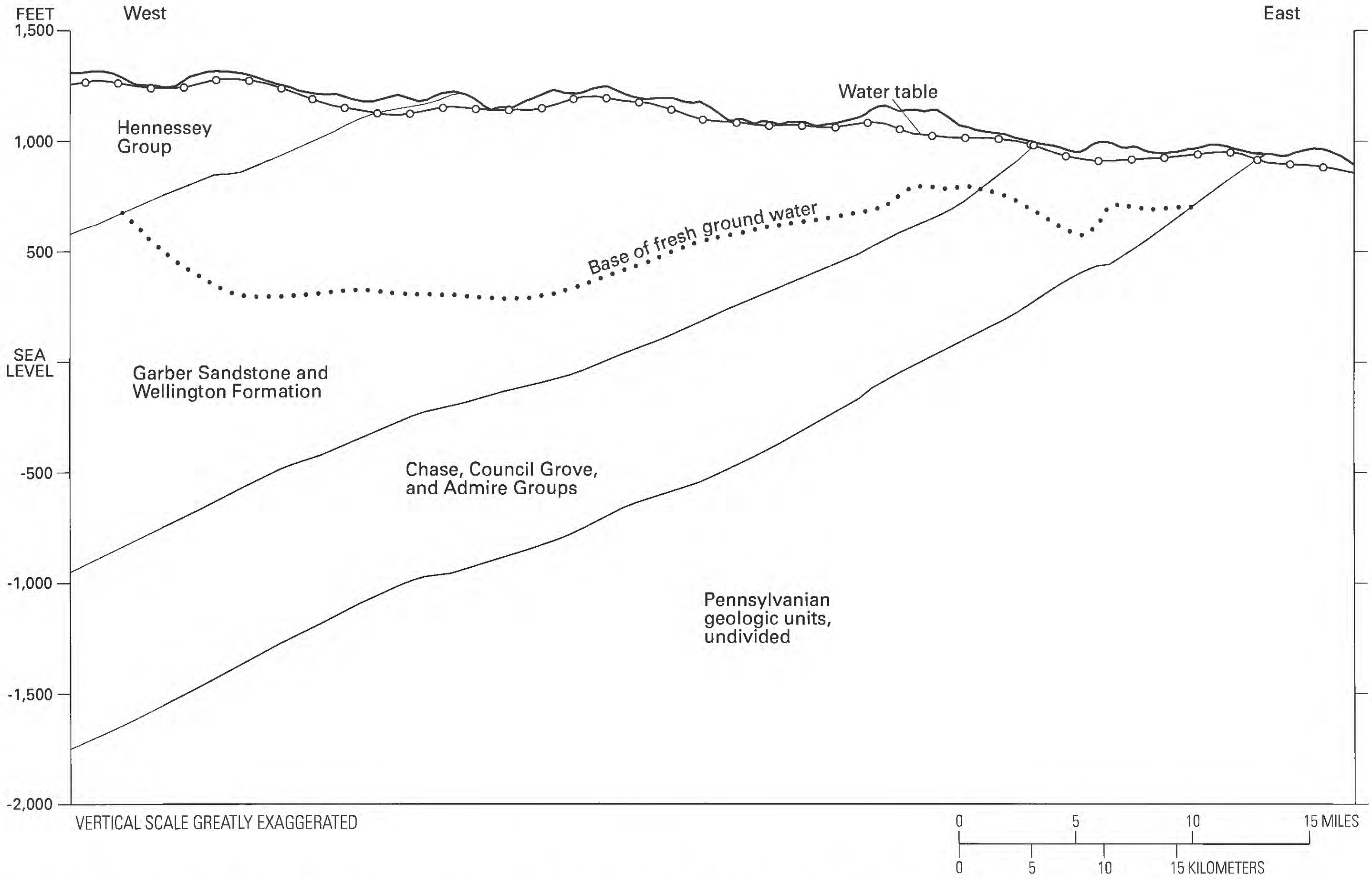
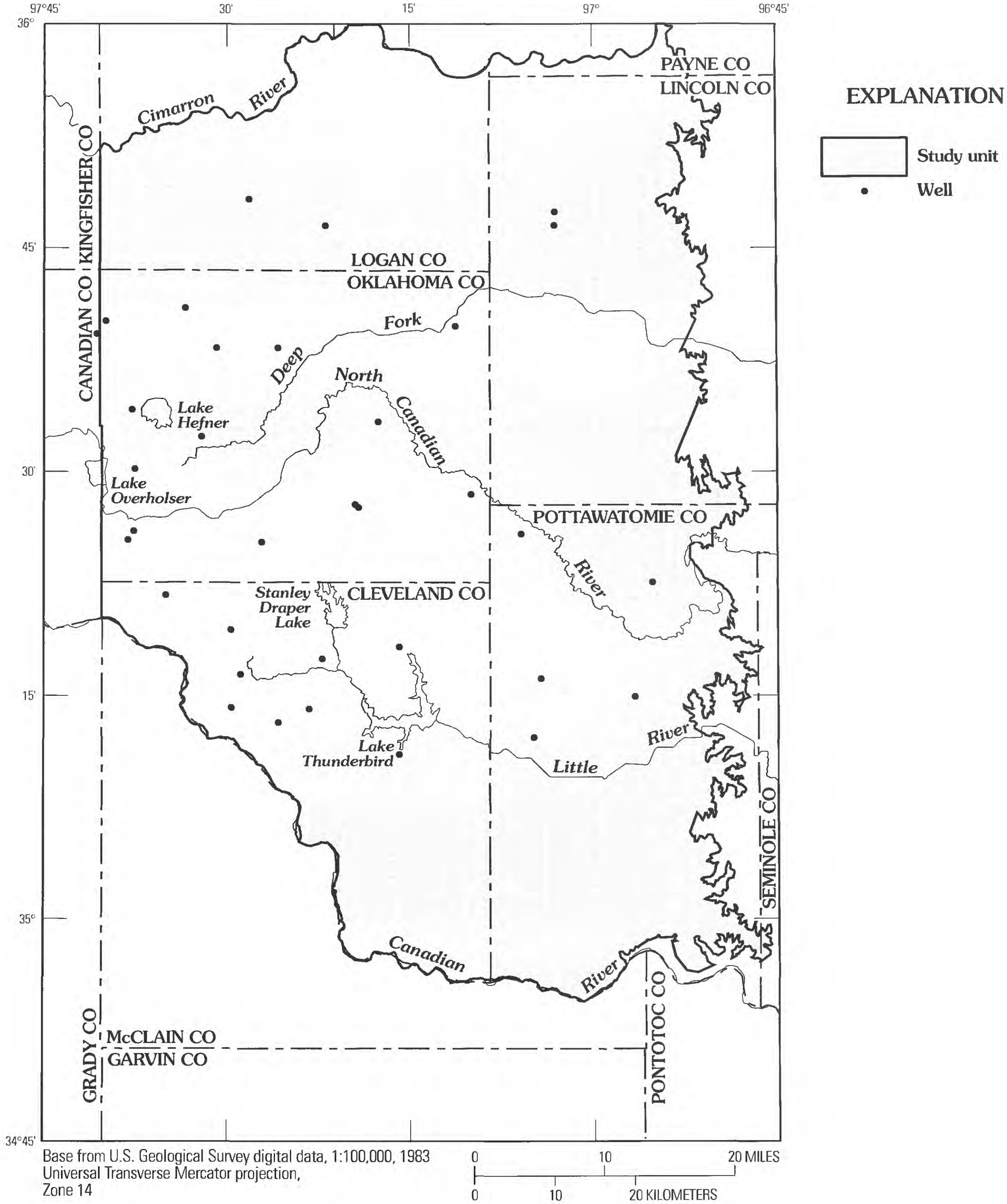


Figure 9. Geohydrologic section through central Oklahoma along latitude 35°30' (1 foot = 0.3048 meter).



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
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Figure 10. Location of wells sampled in the geochemical network.

10,000 to 30,000 years or older. Both confined and unconfined parts of the Central Oklahoma aquifer have an oxic or post-oxic oxidation-reduction environment as indicated by the large dissolved concentrations of oxygen, nitrate, arsenic (V), chromium (VI), selenium (VI), vanadium, and uranium.

Hydrogeochemical processes have occurred to different extents within the three flow components of the aquifer. In the shallow, local flow system, the rapid flux of water has been sufficient to remove most of the dolomite, calcite, and exchangeable sodium. In the deep, regional flow system of the unconfined part of the Garber Sandstone and Wellington Formation, the flux of water has been sufficient to remove most of the exchangeable sodium, but sufficient carbonate minerals remain to maintain dolomite and calcite equilibrium. In the confined part of the Garber Sandstone and Wellington Formation and in the less transmissive parts of the unconfined aquifer, including the Chase, Council Grove, and Admire Groups, ground-water flow is slowest, and the flux of water and extent of reactions have been insufficient to remove either the carbonate minerals or the exchangeable sodium on clay.

GROUND-WATER QUALITY

One of the primary objectives of the Oklahoma NAWQA project was to describe the quality of water in the Central Oklahoma aquifer on a regional scale. The term "regional scale" in this paper is intended to mean an area of tens to tens of thousands of square kilometers. Studies of regional water quality examine processes that affect large parts of aquifers. Regional water quality contrasts with site-specific water quality; that is, the water quality of a small area, generally hundreds of square meters to several square kilometers in area. An example of site-specific water quality might be at a contamination site where anthropogenic organic compounds, such as gasoline or trichloroethylene, leaked into the ground water from storage tanks or spills. The quality of the ground water at the contamination site would not be indicative of the water quality of the entire aquifer.

The discussion of regional ground-water quality is divided into two sections. The first section describes the sources of water-quality data used for assessment. Understanding the sources of data is important because not all water-quality data are suitable for describing regional ground-water quality. The second section provides a basic description of the regional ground-water quality of the Central Oklahoma aquifer.

Sources of Data

Two sources of water-quality data were utilized to investigate the regional ground-water quality of the Central Oklahoma aquifer: (1) data available at the beginning of the study and (2) data collected as part of the Oklahoma NAWQA project. At the beginning of the study, all readily available water-quality data for wells completed in the Central Oklahoma aquifer were compiled and placed in the U.S. Geological Survey's National Water Information System data base. The available water-quality data had some utility in assessing regional ground-water quality but were insufficient for many aspects of the assessment. For example, the only data regarding organic compounds in ground water were from the vicinity of Tinker Air Force Base near Oklahoma City, a known contamination site. No data regarding background concentrations of organic compounds in the Central Oklahoma aquifer were found. To complete the regional assessment, the Oklahoma NAWQA project established networks of wells and collected water samples; this effort was termed "survey sampling."

Available Water-Quality Data

The water-quality data available at the start of the Oklahoma NAWQA project (in late 1986 and early 1987) consisted of chemical analyses of water samples from wells completed in the Central Oklahoma aquifer, plus ancillary information such as the location of the well and its depth. The majority of the available data was obtained from six Federal, State, and local agencies: the Association of Central Oklahoma Governments, the Oklahoma State Department of Health, the Oklahoma Water Resources Board, the U.S. Department of Defense, the U.S. Department of Energy, and the U.S. Geological Survey. Some additional chemical analyses were obtained from municipalities and consulting firms. The data consist of 4,439 chemical analyses from 1,604 wells and 409 distribution systems.

The chemical analyses that were collected by the different agencies were collected for many different purposes. The suite of constituents varied greatly, some analyses having a large number of constituents and some consisting of only a single constituent. A detailed discussion of the analysis of available water-quality data can be found in Parkhurst, Christenson, and Schlottmann (1989).

Survey Sampling

The purpose of the survey sampling was to acquire data (beyond what was available at the beginning of the Oklahoma NAWQA project) needed to describe the regional ground-water quality of the Central Oklahoma aquifer. A discussion of the design of the survey sampling networks of wells is presented in Ferree and others (1992) and is summarized briefly here.

The importance of the design of sampling networks to water-quality investigations can not be over-emphasized. The target population in a regional ground-water-quality investigation is the water quality of the entire volume of water within the aquifer. Obviously, the target population cannot be known completely, so a representative sample must be obtained. Networks of wells are established to sample an aquifer, either using monitoring wells built specifically for determining regional water quality or wells already in place, such as water-supply wells.

No single network can address all water-quality issues. A network designed to address a particular water-quality issue may be totally inappropriate for investigating a different issue. For example, if the issue is the evolution of water quality along flowpaths in an aquifer, flowpaths must be identified, and wells established along the flowpaths. This flowpath network would be inappropriate to investigate the effect of urban areas on ground-water quality. For a comprehensive discussion of the design of water-quality sampling networks, see Alley (1993).

Two sampling networks were designed to study the regional ground-water quality of the Central Oklahoma aquifer—a network of wells completed in the Quaternary alluvium and terrace deposits and a network of wells completed in the Permian geologic units. To obtain water samples distributed vertically as well as areally, the Permian geologic units network was divided into three categories on the basis of well depth: (1) Shallow wells, less than 30 m in depth, (2) intermediate-depth wells, 30 m to 91 m in depth, and (3) deep wells, greater than 91 m in depth. These networks were stratified on geology and depth because the analysis of available water-quality data showed that geology and depth are related to the inorganic water quality of the aquifer (Parkhurst, Christenson, and Schlottmann, 1989). Random-selection techniques (Scott, 1990c) were used to select wells to be included in these survey sampling networks. These random-selection techniques were used to obtain water samples that were distributed throughout the study unit so that a representative sample of the water resource could be collected.

All wells sampled in the two survey-sampling networks were existing water-supply wells equipped with operational pumps. Most wells less than 91 m deep were generally but not exclusively domestic wells; most wells deeper than 91 m were generally but not exclusively public-supply wells. A total of 42 wells completed in the alluvium and terrace deposits (fig. 11) and 87 wells completed in Permian geologic units (fig. 12) were sampled.

In addition to the networks of wells established for the survey sampling, three other networks were established. Networks of wells were established as part of the geochemical, urban, and naturally occurring trace substances investigations. These networks are discussed elsewhere in this paper. In all, five networks were designed and established for the Central Oklahoma aquifer NAWQA project.

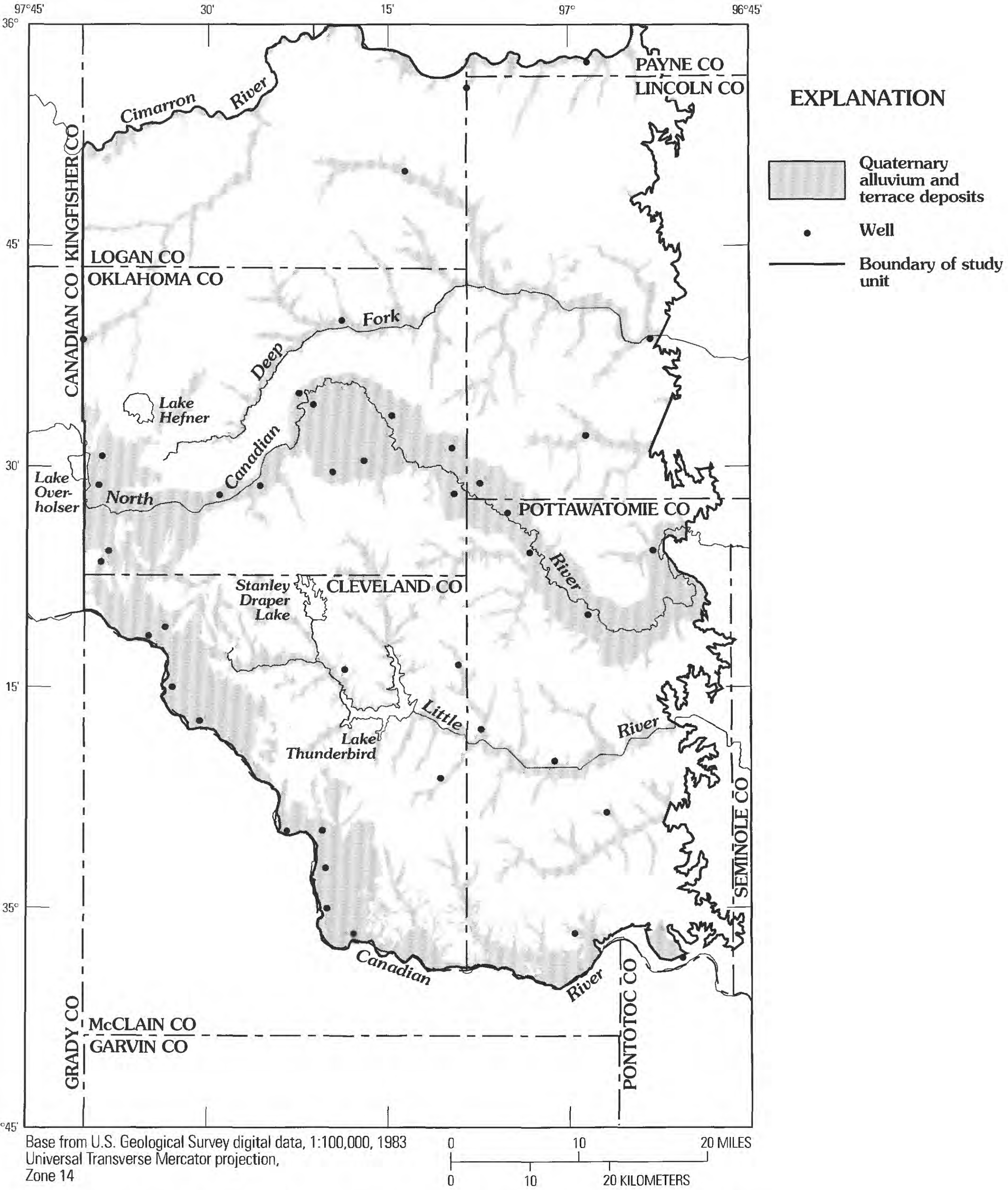
All wells were sampled between July 27, 1987, and February 5, 1990, using sampling methods described in Hardy, Leahy, and Alley (1989). The results of all chemical analyses from all networks except the naturally occurring trace-substance network can be found in Ferree and others (1992); the results of the naturally occurring trace-substance network can be found in Schlottmann and Funkhouser (1991).

Descriptive Water Quality

As previously stated, one goal of the NAWQA Program is to provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources. For this paper, the description consists of discussions of the: (1) concentrations of inorganic constituents, (2) major-ion chemistry, (3) organic compounds detected, and (4) relation of select inorganic constituent concentrations to water-quality standards.

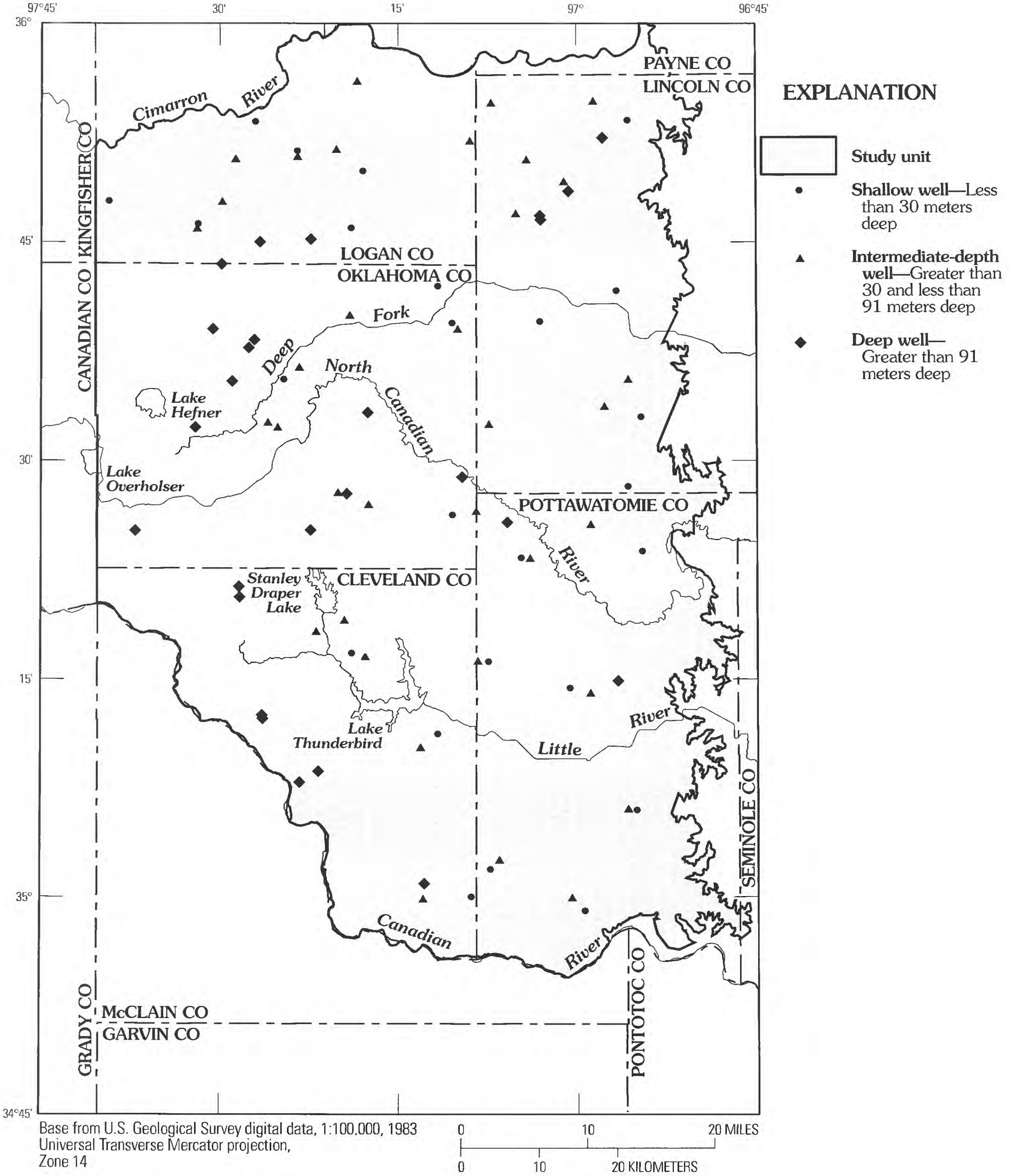
Concentrations of Inorganic Constituents

In this section, summary statistics are presented for the survey-sampling water-quality data. On the basis of the design of the survey-sampling networks, these summary statistics are considered to be representative



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 11. Location of wells sampled in the Quaternary alluvium and terrace deposits network.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
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Figure 12. Location of wells sampled in the Permian geologic units network.

of the regional water quality of the Central Oklahoma aquifer. Minimum values, selected percentiles, and maximum values were calculated for inorganic constituents for each network. Summary statistics are shown in table 1 for wells completed in alluvium and terrace deposits, in table 2 for shallow wells completed in Permian geologic units, in table 3 for intermediate-depth wells completed in Permian geologic units, and in table 4 for deep wells completed in Permian geologic units (tables 1–4 are at the end of this paper).

The chemical data for many constituents include concentrations that are reported as less than a specified minimum reporting level; these data are called censored data. If no censored data were present for a constituent, percentiles were calculated by standard methods. Percentiles below the largest minimum reporting level can not be calculated using standard methods. A procedure developed by Helsel and Cohn (1988) for calculating percentiles in data with one or more minimum reporting levels was used to calculate percentiles for any constituent with censored data. The procedure used a statistical model to calculate percentiles that were less than the largest minimum reporting level. No percentiles were calculated if more than 80 percent of the data for a constituent were censored. Tables 1–4 also list the number of analyses, the largest minimum reporting level, and the method used to calculate the percentiles for each constituent.

Major-Ion Chemistry

The major-ion chemistry of ground water in the Central Oklahoma aquifer varies over a wide range of compositions. However, there are distinct spatial patterns in water compositions that are related to geologic units. Maps were constructed to show the general areal distribution of the major-ion composition of ground water. The major ions included on the maps are sodium, calcium plus magnesium, bicarbonate, sulfate, and chloride.

Major-ion chemistry was mapped in two zones of the study unit. A shallow zone (fig. 13) was defined to include all wells in the alluvium and terrace deposits; the Hennessey Group; and the Chase, Council Grove, and Admire Groups. There are very few deep wells completed in these geologic units. The shallow zone also included wells less than 30 m in depth in the Garber Sandstone and Wellington Formation. Most deep wells in the study unit are completed in the Garber Sandstone and Wellington Formation. A deep zone (fig. 14) was defined to include only wells greater than 91 m that were completed in the Garber Sandstone and Wellington Formation.

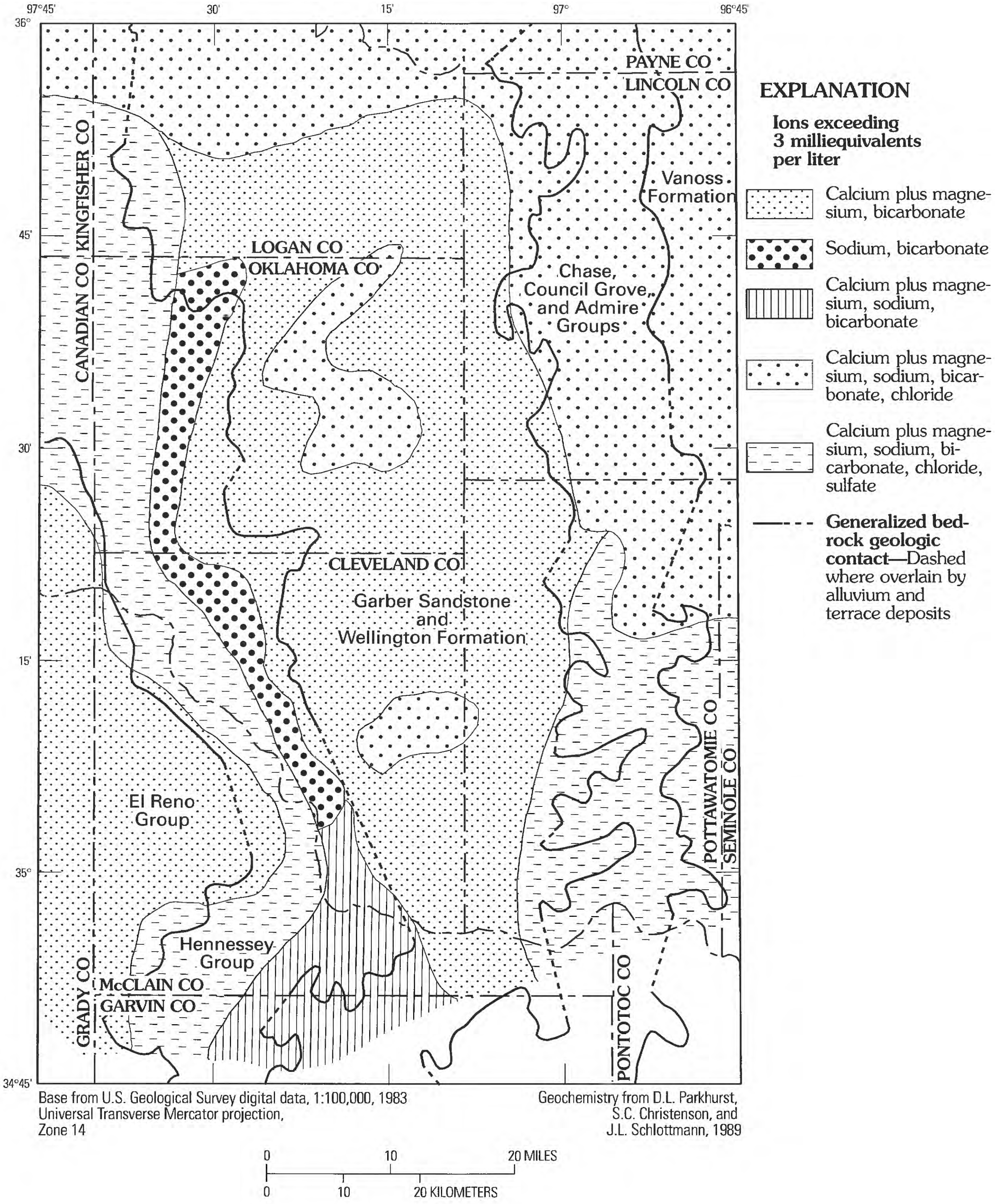
Water-quality diagrams were generated by combining the data collected in the survey sampling with the data available at the beginning of the study (fig. 15) in order to distinguish variations in water composition that are apparent in figures 13 and 14. These diagrams were made by using samples from wells completed in seven distinct parts of the study unit: (1) The alluvium and terrace deposits; (2) the Hennessey Group; (3) the shallow (depths less than or equal to 91 m; note that this definition of shallow differs from the definition in fig. 13), unconfined, (4) the deep (depths greater than 91 m), unconfined, (5) the shallow, confined, (6) the deep, confined parts of the Garber Sandstone and Wellington Formation; and (7) the Chase, Council Grove, and Admire Groups (undivided).

The water-quality diagrams show the median concentration in milliequivalents per liter of each major ion. Also shown are the 25th and 75th percentiles of each ion; 25 percent of the data are less than the 25th percentile, and 75 percent of the data are less than the 75th percentile. The percentiles are one measure of the range in concentrations that have been observed for each part of the study unit.

The following generalizations can be made from the maps of major ions and the water-quality diagrams. Calcium, magnesium, and bicarbonate are the dominant cations in the unconfined part of the Garber Sandstone and Wellington Formation. Sodium and bicarbonate are the dominant ions in the rest of the Permian geologic units; that is, the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and Admire Groups. All parts of the study unit have similar concentrations of bicarbonate. Concentrations of sulfate and chloride are relatively small in most parts of the study unit. The largest concentrations of chloride tend to occur in the shallow, confined part of the Garber Sandstone and Wellington Formation. The largest concentrations of sulfate tend to occur in the Hennessey Group and the southern part of the confined Garber Sandstone and Wellington Formation.

Organic Compounds Detected

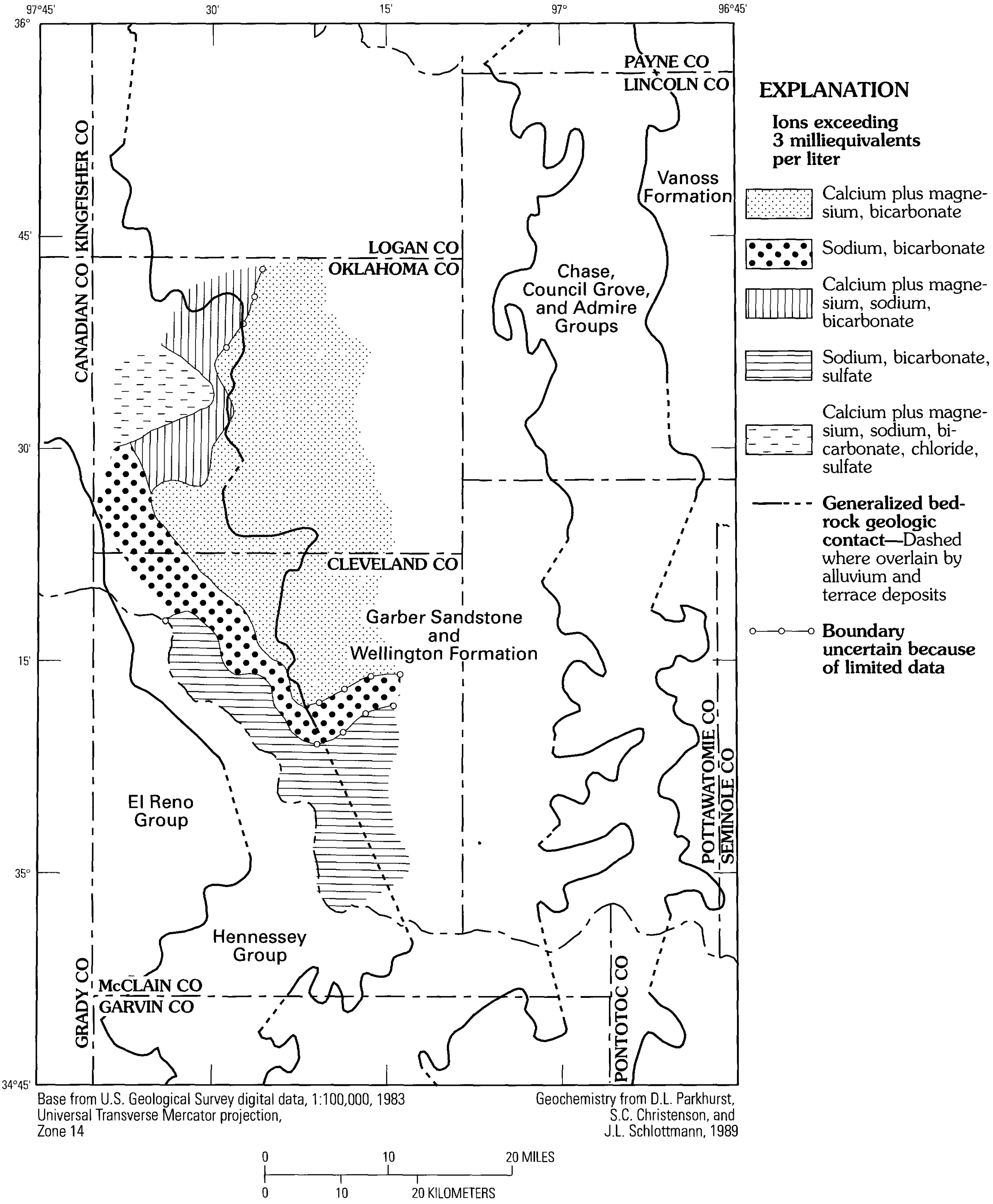
The number of wells in each network where organic compounds were reported and the maximum concentrations reported are listed in table 5. A total of 12 different pesticides (including total polychlorinated biphenyls, or PCB's, analyzed with the organochlorine



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Geochemistry from D.L. Parkhurst,
S.C. Christenson, and
J.L. Schlottmann, 1989

Figure 13. Major-ion chemistry in the shallow part (depths less than 30 meters) of the study unit.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
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Geochemistry from D.L. Parkhurst,
S.C. Christenson, and
J.L. Schlottmann, 1989

Figure 14. Major-ion chemistry in the deep part (depth greater than 91 meters) of the Garber Sandstone and Wellington Formation.

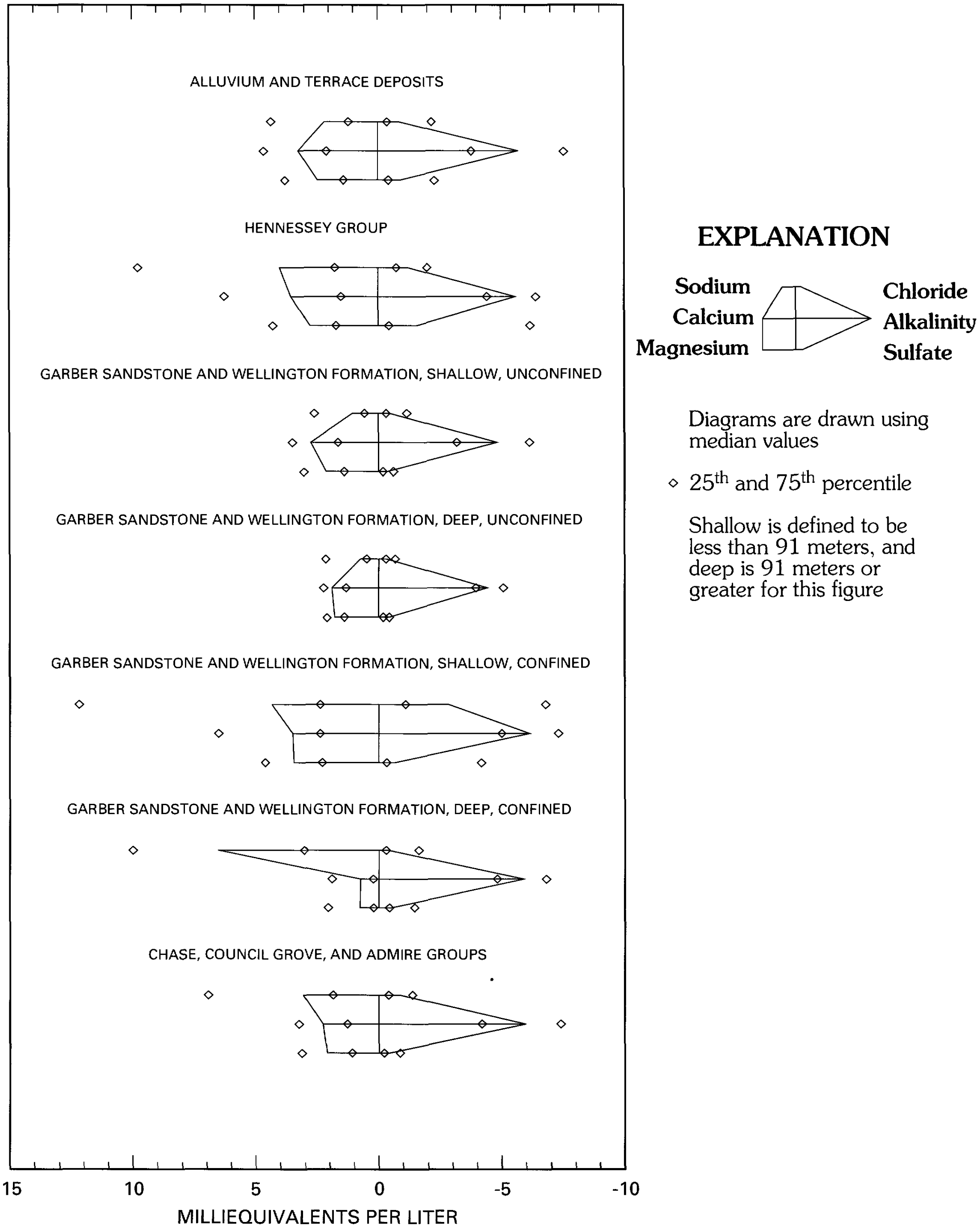

Figure 15. Median concentrations of major ions in water samples from hydrogeologic units within the Central Oklahoma aquifer.

pesticides) and 18 different volatile organic compounds (VOC's) were reported. The actual concentrations of the organic constituents were felt to be less important than their presence or absence in water samples because the presence of organic compounds in a water sample indicates that the well is vulnerable to anthropogenic contamination. Most organic compounds were reported at relatively small concentrations, with the exception of several VOC's. Large concentrations of 1,1,1-trichloroethane, trichloroethylene, and 1,1-dichloroethylene were reported from a single well, and the next-largest concentration of each of these three compounds was considerably lower than the maximum concentration

Table 5. Number of wells in Central Oklahoma aquifer survey-sampling networks in which organic compounds were reported in water samples

[µg/L, micrograms per liter]

	Sampling network					
	Quaternary alluvium and terrace deposits	Permian geologic units				
Compound		Shallow wells	Intermediate-depth wells	Deep wells	Laboratory minimum reporting level (µg/L)	Maximum concentration (µg/L)
Organochlorine compounds						
Chlordane	0	1	0	0	0.1	0.3
Dieldrin	0	1	1	0	.01	.05
DDE	0	1	0	0	.01	.01
Heptachlor epoxide	0	0	1	0	.01	.01
PCB	0	0	1	0	.1	.1
Phenoxy-acid herbicides						
2,4-D	0	2	1	0	.01	.02
2,4-DP	1	0	0	0	.01	.01
2,4,5-T	1	0	0	0	.01	.01
Picloram	1	1	0	0	.01	.02
Dicamba	1	0	1	0	.01	.01
Triazine and other nitrogen-containing herbicides						
Atrazine	2	0	1	0	.1	.3
Prometone	1	0	0	1	.1	.6
Volatile organic compounds						
Bromoform	0	0	1	2	.2	1.1
Chlorodibromomethane	0	0	1	2	.2	.7
Chloroethane	1	0	0	0	.2	.2
Chloroform	0	2	3	1	.2	6.8
Chloromethane	0	0	1	2	.2	4.4
Dichlorobromomethane	0	0	1	1	.2	.6
Dichlorodifluoromethane	1	0	0	0	.2	.2
1,1-Dichloroethane	2	0	0	0	.2	2.5
1,2-Dichloroethane	1	1	0	0	.2	.2
1,2-Dichloroethene	2	0	0	0	.2	1.0
1,1-Dichloroethylene	2	0	0	0	.2	45
Methylene chloride	2	1	0	0	.2	.6
1,1,2,2-Tetrachloroethane	0	0	1	0	.2	.3
Tetrachloroethylene	0	0	0	1	.2	.9
Toluene	0	1	0	1	.2	.2
1,1,1-Trichloroethane	1	0	0	0	.2	200
Trichloroethylene	3	0	0	2	.2	30
Trichlorofluoromethane	1	0	2	0	.2	.3
Number of wells in network	42	25	35	27		

detected. This particular well was a domestic well that apparently was contaminated by a solvent spill approximately 50 m from the well.

The presence of these organic compounds in the Central Oklahoma aquifer clearly represents anthropogenic contamination as no natural sources of these compounds exist. Organic compounds were detected most commonly in water samples from the urban sampling network. The factors that affect water quality in the Central Oklahoma aquifer are discussed in Christenson and Rea (1993).

Comparison of Selected Inorganic Constituents to Water-Quality Standards

Of considerable relevance in evaluating regional ground-water quality is a comparison of the water quality in the aquifer to water-quality standards. The water-quality standards used in this report are the Maximum Contaminant Levels (MCLs), promulgated to protect public health (U.S. Environmental Protection Agency, 1988a), and Secondary Maximum Contaminant Levels (SMCLs), promulgated for aesthetic reasons related to public acceptance of drinking water (U.S. Environmental Protection Agency, 1988b).

The number of wells in each Oklahoma NAWQA survey-sampling network that exceeded water-quality standards is shown in table 6. On the basis of the design of the Oklahoma NAWQA survey-sampling networks, the percentage of wells that exceeded the standards is considered to be representative of the overall water resource of the Central Oklahoma aquifer.

The overall quality of the water resource of the Central Oklahoma aquifer is quite good on the basis of the small percentage of wells exceeding water-quality standards. Water-quality standards were never exceeded in any survey-sampling network well for fluoride, barium, cadmium, lead, mercury, silver, 2,4-D, endrin, lindane, methoxychlor, silvex, benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, trihalomethanes, vinyl chloride, copper, and zinc. MCLs, which are related to public health, were commonly (more than 10 percent of wells) exceeded only for nitrate in the shallow Permian network and for selenium in the intermediate and deep Permian network. Nitrate concentrations exceeded the MCL of 10 mg/L for wells in the alluvium and terrace deposits and shallow and intermediate Permian geologic units networks, which is consistent with a shallow source for nitrate, probably fertilizer or septic-tank effluent. The nitrate standard of 10 mg/L is primarily a concern for infants because they are unable to metabolize nitrate. Healthy adults are less threatened by water with nitrate concentrations that exceed the MCL. The deep water resource is most likely to contain selenium in excess of the 10-µg/L standard, and unfortunately the deep resource is most likely to be used by public-supply wells. The selenium MCL of 10 µg/L was exceeded by wells in all networks, and fully one-third of the wells in the deep Permian network exceeded the standard. Deep wells are completed in the environment most likely to mobilize this element (Schlottmann, Mosier, and Breit, 1995). However, the U.S. Environmental Protection Agency has proposed raising the MCL for selenium from 10 to 50 µg/L (U.S. Environmental Protection Agency, 1989). At that concentration, no wells in the alluvium and terrace or shallow Permian network would exceed the standard, and only 2.9 percent of wells in the intermediate and 11 percent of the wells in the deep Permian networks would exceed the standard.

Arsenic and chromium exceed the MCL of 50 µg/L (for both constituents) only in wells in the deep Permian network where the geohydrologic and geochemical environment that mobilizes these elements is more likely to occur (Schlottmann, Mosier, and Breit, 1995). Residual alpha radioactivity exceeded the MCL of 15 pCi/L in a small percentage (less than 10 percent) of wells in every Permian network. The MCL for 1,1-dichloroethylene (7 µg/L) and trichloroethylene (5 µg/L) were exceeded only in a single well (the same well for both MCLs).

The Central Oklahoma aquifer is more affected by aesthetic than public health problems. The pH exceeds 8.5 in wells in all survey-sampling networks. The largest percentage (33 percent) of wells that exceeded a pH of 8.5 were wells in the deep Permian network. The pH was less than the SMCL of 6.5 in wells in the alluvium and terrace deposits and shallow and intermediate Permian networks. The largest percentage (20 percent) of wells less than the SMCL of 6.5 was in the shallow Permian network. Sulfate exceeded the SMCL of 250 mg/L in a small percentage (less than 10 percent) of wells in all networks. Chloride exceeded the SMCL of 250 mg/L in 9.5 percent of the wells in the alluvium and terrace deposits network, 12 percent of the wells in the shallow Permian network, and 2.9 percent of the wells in the intermediate Permian network. Wells in the shallower networks exceeding the standard is consistent with a shallow source of chloride, such as contamination from road salt or other surface sources, as

Table 6. Percentage of wells in Central Oklahoma aquifer survey-sampling networks that exceeded water-quality standards

		Survey-sampling network			
		Quaternary alluvium and terrace deposits	Permian geologic units		
Constituent	Type of standard[1]		Shallow (<30 meters)	Intermediate (30–91 meters)	Deep (>91 meters)
Fluoride	MCL	0	0	0	0
Nitrate	MCL	2.4	12	8.6	0
Arsenic	MCL	0	0	0	7.4
Barium	MCL	0	0	0	0
Cadmium	MCL	0	0	0	0
Chromium	MCL	0	0	0	7.4
Lead	MCL	0	0	0	0
Mercury	MCL	0	0	0	0
Selenium	MCL	4.8	4.0	11	33
Silver	MCL	0	0	0	0
Residual alpha radioactivity	MCL	0	4.0	2.9	3.7
2,4-D	MCL	0	0	0	0
Endrin	MCL	0	0	0	0
Lindane	MCL	0	0	0	0
Methoxychlor	MCL	0	0	0	0
Silvex	MCL	0	0	0	0
Benzene	MCL	0	0	0	0
Carbon tetrachloride	MCL	0	0	0	0
1,4-Dichlorobenzene	MCL	0	0	0	0
1,2-Dichloroethane	MCL	0	0	0	0
1,1-Dichloroethylene	MCL	2.4	0	0	0
1,1,1-Trichloroethane	MCL	0	0	0	0
Trichloroethylene	MCL	2.4	0	0	0
Trihalomethanes (total)	MCL	0	0	0	0
Vinyl chloride	MCL	0	0	0	0
pH > 8.5	SMCL	2.4	8.0	2.9	33
pH < 6.5	SMCL	12	20	8.6	0
Sulfate	SMCL	7.1	4.0	2.9	7.4
Chloride	SMCL	9.5	12	2.9	0
Copper	SMCL	0	0	0	0
Iron	SMCL	26	4.0	0	3.7
Manganese	SMCL	38	8.0	0	0
Zinc	SMCL	0	0	0	0
Number of wells in network		42	25	35	27

[1] MCL, Maximum Contaminant Level (U.S. Environment Protection Agency, 1988a). SMCL, Secondary Maximum Contaminant Level (U.S. Environmental Protection (1988b).

opposed to upconing of brines caused by ground-water withdrawals. Iron exceeded the SMCL of 300 µg/L in all survey networks except the intermediate Permian network, and manganese exceeded the SMCL of 50 µg/L in the alluvium and terrace and shallow Permian networks. The SMCLs for iron and manganese are very commonly exceeded (in more than 25 percent of wells) in the alluvium and terrace deposits network.

TARGETED SAMPLING

The fourth objective of the Oklahoma NAWQA project was to describe the location, nature, and causes of selected water-quality problems within the study unit, which were identified as naturally occurring trace substances and degradation of water quality due to urbanization. The investigations of these selected water-quality problems were termed "targeted sampling," as the network design, water-quality sampling, and data analyses were targeted at specific problems.

Naturally Occurring Trace Substances

The purpose of the investigation of naturally occurring trace substances was to determine the cause of elevated concentrations (in excess of MCLs) of arsenic, chromium, selenium, and gross alpha radioactivity in many wells completed in the Central Oklahoma aquifer. The results of the study of naturally occurring trace substances in the Central Oklahoma aquifer are documented in Schlottmann, Mosier, and Breit (1995) and summarized below.

The presence of elevated concentrations of these elements and gross alpha radioactivity was documented prior to the inception of the Oklahoma NAWQA project (for example, see Gates, Marsh, and Fryberger, 1983). Parkhurst, Christenson, and Schlottmann (1989) found that in the water-quality data available at the beginning of the NAWQA project, 4.3 percent of the chemical analyses exceeded the arsenic MCL, 6.8 percent exceeded the chromium MCL, 12.5 percent exceeded the selenium MCL, and 12.2 percent exceeded the gross alpha radioactivity MCL. Many of the wells affected by this problem were public-supply wells, and input from the Oklahoma NAWQA Liaison Committee indicated that the trace element/gross alpha radioactivity issue was the most serious water-quality problem in the Central Oklahoma aquifer.

An important finding of the Oklahoma NAWQA was that naturally occurring gross alpha radioactivity in water samples from the Central Oklahoma aquifer results largely from dissolved uranium (Schlottmann, Mosier, and Breit, 1995). Thus, further investigation of radioactivity in the aquifer concentrated exclusively on uranium.

Initial efforts to determine the causes of elevated concentrations of arsenic, chromium, selenium, and uranium centered on finding a simple source, such as a bed or stratum enriched in these elements. A total of 293 B-horizon soil samples and 362 outcrop rock samples were collected for chemical analysis. Eight test holes were drilled, cores were recovered, and water samples were collected from sandstone layers. The core samples were subjected to a variety of petrographic and chemical analyses, including sequential chemical extractions. As work progressed, it became clear that elevated dissolved concentrations of these trace elements could not be attributed to a simple source; rather, the elevated concentrations depended on several complex geologic and geochemical conditions, including: (1) the distribution of the elements in the solid phases, (2) the redox conditions of the water, (3) the distribution of mudstone, and (4) changes in water chemistry as water flows through the aquifer.

Average whole-rock abundances of the elements in the Central Oklahoma aquifer are similar to those of typical sedimentary rocks (Mosier and others, 1990). However, the distribution of the elements in the solid phase is not uniform, and specific rock types locally are enriched with certain elements. High concentrations of all four elements are associated with red iron-oxide grain coatings in sandstone in the aquifer. High arsenic concentrations are in yellow-brown goethite-cemented sandstone; high chromium concentrations are in mudstone and clay; and high selenium and uranium concentrations are in green-gray reduced zones in sandstone. High concentrations of any of these elements in ground water frequently are in proximity to rocks enriched in that element.

All of the elements require oxidizing redox conditions to be mobile. Most water sampled in the Permian geologic units contained greater than 1 mg/L dissolved oxygen, indicating an oxidizing condition. This condition allows the elements to be mobile in most of the aquifer.

Dissolved concentrations of the elements generally increase with pH. Arsenic, chromium, and selenium that are adsorbed onto the iron-oxide coatings of mineral grains in the aquifer tend to desorb at higher pH. Selenium desorbs at a lower pH than do arsenic and chromium. Higher pH increases carbonate-ion activity, which favors the mobilization of uranium by formation of carbonate complexes in the bicarbonate water that resides in the aquifer. High pH in the aquifer results from chemical reactions with clay and dolomite in the aquifer rock. Sodium, bound to clay, is exchanged for calcium and magnesium in water, which results in dissolved calcium and magnesium concentrations below saturation. As a result, the dolomite cement in the aquifer dissolves. Where dolomite dissolution occurs away from the atmosphere (with no carbon dioxide available), the pH increases to greater than 8.5.

High concentrations of uranium occur in some water with low pH. In this case, the exchange of sodium for calcium and magnesium occurs in the vadose zone, and the resultant dissolution of dolomite takes place in proximity to soil gas with abundant carbon dioxide. The carbon dioxide buffers the pH to near neutral, and the alkalinity increases. The increased alkalinity results in an increased carbonate-ion activity, which favors mobilization of uranium.

The distribution of mudstone is significant for three reasons: (1) mudstone frequently contains higher concentrations of chromium; (2) clay in mudstone is a site for cation exchange (where mudstone is abundant in the aquifer, the increased cation-exchange capacity results in more of the changes in ground-water chemistry that allow the elements to be mobile); and (3) the hydraulic conductivity of mudstone is lower than that of sandstone, which constitutes the producing zone in the aquifer. As a result, transmissivity is lower in parts of the aquifer with abundant mudstone, and fewer volumes of water pass through these parts of the aquifer to deplete the elements and the exchangeable sodium. Thus, more of the elements and more clay with exchangeable sodium are available in parts of the aquifer with abundant mudstone.

Concentrations of the elements generally increase with the age of ground water as it flows through the aquifer. Arsenic and chromium are found only in water that has resided in the aquifer on the order of tens of thousands of years. This relation is thought to be caused by: (1) the elements may require more time to reach elevated concentrations where the source of the elements is small concentrations disseminated throughout the aquifer, (2) the elements may require more time to oxidize, regardless of the source, or (3) water taking longer to flow through the parts of the aquifer with abundant mudstone (because the transmissivity is lower) where mudstone is the source of the elements or where mudstone is creating the geochemical environment needed to mobilize the elements. Selenium and uranium are in some young (generally less than 5,000 years) ground water because they are more available for dissolution and are mobile at low pH.

The elevated concentrations of arsenic, chromium, selenium, and uranium in the Central Oklahoma aquifer depend on several complex geologic and geochemical conditions. A detailed explanation of those conditions is presented in Schlottmann, Mosier, and Breit (1995).

Urban Ground-Water Quality

The purposes of the urban ground-water investigation were to describe the quality of ground water under the Oklahoma City urban area, to determine if the water quality under the urban area was different from the overall water quality of the Central Oklahoma aquifer, and to determine the causes of the differences, if differences existed. An urban water-quality sampling network was established in the central part of the Oklahoma City urban area. The results of the urban ground-water-quality investigation are documented in Christenson and Rea (1993) and summarized below.

An urban sampling network was designed to study water quality in the Oklahoma City urban area. The urban sampling network was established within the central part of Oklahoma City and included the downtown business district, industrial areas, and older residential areas. All wells sampled in the urban sampling network were existing water-supply wells equipped with operational pumps and were generally but not exclusively domestic wells. Forty-one randomly selected wells were sampled for the urban network (fig. 16).

Any ground-water investigation that considers land use as a factor must determine how to characterize land use at a well. Several methods were used in the urban investigation for characterizing the land use near the sampled wells. Because there was no clear best method, the results of the different methods were compared. If several of the methods indicated the same relations between urban land use and ground-water quality, then confidence in the validity of those relations was increased. Similarly, if the results of the different methods did not agree, the results could be an artifact of the methods used, rather than cause-and-

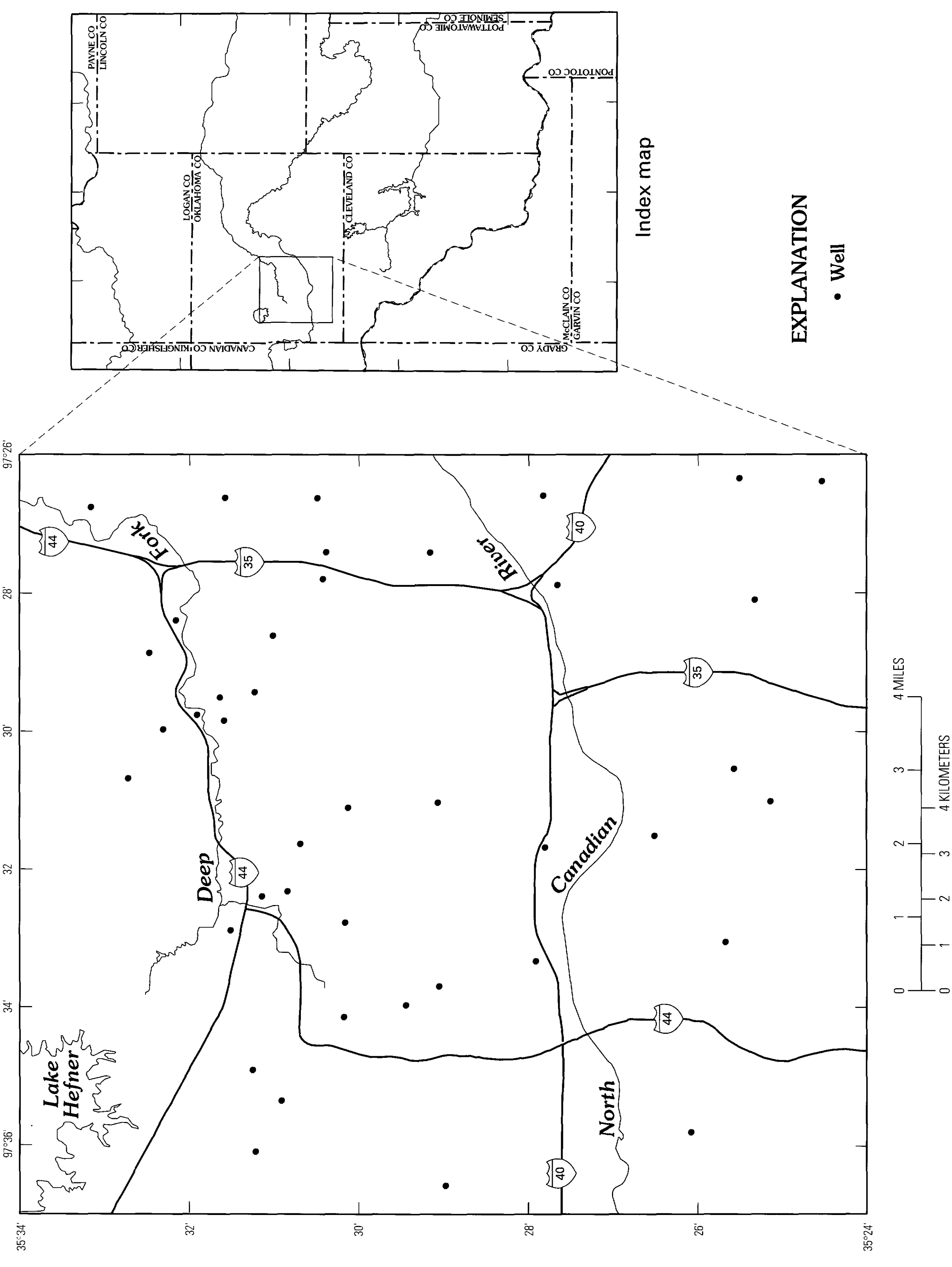

Figure 16. Location of wells sampled in the urban network.

effect relations in the hydrologic system. The methods of categorizing urban land use that were used were based on the sampling network, field sheets, point-in-polygon overlay, buffer-overlay analysis, and particle-tracking analysis. Explanation of these different methods of land-use categorization can be found in Christenson and Rea (1993).

Mann-Whitney tests were used to compare selected inorganic constituent concentrations in urban and nonurban wells. The tests indicated that there were statistically significant differences between urban and nonurban wells in the concentrations of alkalinity, calcium, magnesium, sodium, potassium, bicarbonate, chloride, iron, gross alpha radioactivity, and uranium. Median concentrations of these constituents were larger in urban than in nonurban wells. Concentrations of dissolved oxygen, carbonate, sulfate, nitrite plus nitrate, arsenic, barium, copper, lead, mercury, selenium, and silver had no significant differences in urban and nonurban wells. Whether the concentrations of pH, fluoride, cadmium, chromium, manganese, and radon were significantly different or not in urban and nonurban wells depended on the method of land-use categorization.

A contingency-table analysis indicated that the proportion of wells with reportable pesticides or VOC's might or might not be different in urban and nonurban land uses, depending on the method used to categorize urban land use and how the VOC's were grouped. On the basis of the results of statistical tests and onsite evidence, the sources of organic contaminants commonly were near the wellhead, indicating that the shallow seals and gravel packs may provide pathways for contaminants to enter the wells.

The comparisons by sampling network (which represent the basis of the design of the urban sampling network) consistently indicated that the presence or absence of organic constituents, as well as the concentrations of many inorganic constituents, were significantly different in samples from urban and nonurban wells. Additionally, the median concentrations of all inorganic constituents that were significantly different for any method of land-use categorization, except fluoride, cadmium, and chromium, were larger in samples from urban wells than in those from nonurban wells. The proportion of wells with reportable organic compounds was higher among the urban wells than the nonurban wells, regardless of the method of land-use categorization. The possibility exists that the comparison between urban and nonurban wells contained a geologic bias for the inorganic constituents. For a more complete discussion of the effects of urbanization on the ground-water quality of the Central Oklahoma aquifer, see Christenson and Rea (1993).

SUMMARY

A study of the regional ground-water quality of the Central Oklahoma aquifer was conducted as part of the pilot National Water-Quality Assessment Program. The objectives of the study were to: (1) describe regional ground-water quality throughout the aquifer, (2) describe the major geochemical and geohydrologic processes operating in the aquifer, (3) identify the major factors affecting the ground-water quality, and (4) describe the location, nature, and causes of selected water-quality problems within the study unit, which were identified as naturally occurring trace substances and degradation of ground-water quality caused by urbanization.

The Central Oklahoma aquifer is a major source of water supply for municipalities in central Oklahoma. The aquifer consists of the Permian Garber Sandstone, Wellington Formation, and Chase, Council Grove, and Admire Groups, and Quaternary alluvium and terrace deposits. The aquifer is unconfined in the eastern two-thirds of its areal extent and confined in the western one-third by the Hennessey Group. Ground water originates as recharge from precipitation and discharges to streams and wells. Water flows rapidly through the shallow, unconfined part of the aquifer but can take tens of thousands of years to flow through the confined part of the aquifer.

The regional water quality of the aquifer was described and analyzed using data available at the start of the Oklahoma NAWQA project and networks of wells established during the project. Calcium, magnesium, and bicarbonate are the dominant ions in ground water from the unconfined parts of the Garber Sandstone and Wellington Formation. This water chemistry is the result of uptake of carbon dioxide from the unsaturated zone; dissolution of dolomite and, to lesser extents, the dissolution of biotite, chlorite, plagioclase, and potassium feldspar; and precipitation of kaolinite. Sodium and bicarbonate are the dominant ions in the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and Admire Groups. The sodium bicarbonate water is derived from the calcium, magnesium, and bicarbonate water by cation exchange of calcium and magnesium with sodium in clay minerals.

Statistically based networks of wells were established to assess the overall quality of the water resource of the Central Oklahoma aquifer. The overall quality of the resource is quite good, based on the small percentage of wells in these networks that exceeded existing water-quality standards. Maximum Contaminant Levels, which are related to public health, are commonly (more than 10 percent of wells) exceeded only for nitrate in the shallow (less than 30 m) wells completed in Permian geologic units and for selenium in wells deeper than 30 m completed in Permian geologic units. Deep (greater than 91 m) ground water is most likely to contain selenium in excess of the 10-μg/L standard, and deep ground water is most likely to be used by public-supply wells. However, the U.S. Environmental Protection Agency has proposed raising the Maximum Contaminant Level for selenium from 10 to 50 μg/L. At that concentration, only 2.9 percent of the network wells 30 to 91 m deep and 11 percent of the network wells greater than 91 m deep completed in Permian geologic units would exceed the standard. The Central Oklahoma aquifer is affected more by aesthetic than public health problems. Secondary Maximum Contaminant Levels, related to aesthetic concerns, are commonly (more than 10 percent) exceeded for pH greater than 8.5 in deep (greater than 91 m) Permian wells, pH less than 6.5 in alluvium and terrace deposits and shallow (less than 30 m) Permian wells, chloride in shallow Permian wells, and iron and manganese are very commonly (more than 25 percent) exceeded in alluvium and terrace deposits wells.

Although the overall quality of water in the Central Oklahoma aquifer is good, water-quality problems occur in parts of the aquifer. Some of these problems were investigated as part of the Oklahoma NAWQA project, including concentrations of arsenic, chromium, selenium, and uranium in excess of water-quality standards and the effect of urbanization on ground-water quality.

Many public-supply wells in central Oklahoma yield water with elevated concentrations of arsenic, chromium, selenium, and uranium. These elements are widely dispersed on solid-phase materials throughout the aquifer and are mobilized under certain geochemical conditions. Dissolved oxygen in the aquifer, which commonly exceeds 1 mg/L, oxidizes the elements to their most mobile states. The exchange of calcium and magnesium in water for sodium adsorbed on clay decreases the saturation of dolomite, which results in the dissolution of dolomite. In parts of the aquifer isolated from carbon dioxide in the atmosphere, the dissolution of dolomite increases the pH of the water. Arsenic, chromium, and selenium are desorbed from the solid aquifer matrix at elevated pH. In parts of the aquifer in contact with carbon dioxide in the atmosphere, the exchange reaction and dissolution of dolomite take place, but the reaction is buffered to neutral and the alkalinity increases. The increased alkalinity results in increased carbonate-ion activity, which favors mobilization of uranium. Because the exchange reaction requires sodium-saturated clay, the distribution of mudstone, which contains the clay, controls the location where dissolved concentrations of arsenic, chromium, selenium, and uranium are elevated.

The effect of the Oklahoma City urban area on the water quality of the Central Oklahoma aquifer was investigated. The quality of water under the urban area was found to be significantly different from that of water outside the urban area. Pesticides and VOC's were much more common in water samples from wells in the urban area than from wells outside the urban area. The types of pesticides and VOC's found in water samples were consistent with the organic compounds known to be used in the urban area. The concentrations of certain inorganic constituents were also found to be different in the urban area than in nonurban areas, but the presence of a geologic bias for inorganic constituents is possible.

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Table 1. Summary statistics of chemical constituents for water samples from wells completed in alluvium and terrace deposits of the Central Oklahoma aquifer

[Constituents and properties: mS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter, mg/L, micrograms per liter; pCi/L, picocuries per liter. Method: 1, no censored data, ordinary percentile calculation; 2, censored data present, percentiles calculated using methods of Helsel and Cohn (1988); 3, no calculation, more than 80 percent of the data were censored. Largest MRL: largest minimum reporting level (percentiles less than this value were estimated using the methods of Helsel and Cohn (1988); percentiles greater than this value are the same as ordinary percentile calculation); --, no censored data for this constituent. Percentiles: --, indicates no statistic was calculated. <, less than]

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
				Properties and major ions						
Specific conductance (μS/cm at 25°C)	1	42	--	91	109	474	668	959	2,590	6,010
pH, field (standard units)	1	42	--	5.7	5.8	6.8	7.2	7.3	8.2	8.6
Water temperature (°C)	1	42	--	15.6	16.0	16.6	17.1	17.5	18.9	19.5
Oxygen, dissolved (mg/L)	1	42	--	0	0	.1	2.4	4.7	6.9	9.0
Alkalinity, total, field (mg/L as $CaCO_3$)	1	42	--	22	27	171	276	370	529	580
Calcium, dissolved (mg/L)	1	42	--	6.4	8.9	36	55	88	180	180
Magnesium, dissolved (mg/L)	1	42	--	3.5	3.9	14	21	40	76	94
Sodium, dissolved (mg/L)	1	42	--	5.4	5.5	22	39	92	430	1,400
Potassium, dissolved (mg/L)	1	42	--	.40	.60	.80	1.3	2.2	4.9	16
Bicarbonate, field (mg/L)	1	42	--	27	32	209	337	453	646	708
Carbonate, field (mg/L)	1	42	--	0	0	0	0	0	0	14
Sulfate, dissolved (mg/L)	1	42	--	5.0	5.0	14	36	52	290	2,600
Chloride, dissolved (mg/L)	1	42	--	2.4	6.3	9.9	22	40	440	480
Fluoride, dissolved (mg/L)	1	42	--	.10	.10	.20	.30	.50	1.2	3.0
Bromide, dissolved (mg/L)	1	42	--	.030	.030	.070	.20	.20	1.3	1.5
Silica, dissolved (mg/L)	1	42	--	9.1	9.9	17	20	27	33	36
			Nutrients							
Nitrogen, nitrite, dissolved (mg/L as N)	3	42	<.010	<.010	--	--	--	--	--	.020
Nitrogen, nitrite plus nitrate, dissolved (mg/L as N)	2	42	<.100	<.100	.010	.120	1.00	3.70	8.89	34.0
Nitrogen, ammonia + organic, dissolved (mg/L as N)	2	42	<.20	<.20	.08	.20	.35	.73	2.0	2.0
Phosphorus, orthophosphate, dissolved (mg/L as P)	2	42	<.010	<.010	0	.010	.030	.060	.180	.200
			Trace elements							
Aluminum, dissolved (μg/L)	3	42	<10	<10	--	--	--	--	--	30
Antimony, dissolved (μg/L)	3	42	<1	<1	--	--	--	--	--	2
Arsenic, dissolved (μg/L)	2	42	<1	<1	.28	.52	.82	1	3	4

Table 1. Summary statistics of chemical constituents for water samples from wells completed in alluvium and terrace deposits of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Trace elements—Continued										
Barium, dissolved (µg/L)	2	42	<5	<5	37	110	220	320	590	650
Beryllium, dissolved (µg/L)	3	42	<2.5	<.5	--	--	--	--	--	<2.5
Boron, dissolved (µg/L)	1	42	--	10	20	70	140	370	3,480	9,600
Cadmium, dissolved (µg/L)	3	42	<5	<1	--	--	--	--	--	5
Chromium, dissolved (µg/L)	3	42	<25	<5	--	--	--	--	--	19
Cobalt, dissolved (µg/L)	3	42	<15	<3	--	--	--	--	--	3
Copper, dissolved (µg/L)	3	42	<50	<10	--	--	--	--	--	40
Iron, dissolved (µg/L)	2	42	<3	<3	.32	5.5	11	740	2,800	3,400
Lead, dissolved (µg/L)	3	42	<50	<10	--	--	--	--	--	20
Lithium, dissolved (µg/L)	2	42	<4	<4	6	11	16	24	69	110
Manganese, dissolved (µg/L)	2	42	<1	<1	.01	.33	6	240	1,000	1,200
Mercury, dissolved (µg/L)	3	42	<.1	<.1	--	--	--	--	--	.9
Molybdenum, dissolved (µg/L)	3	42	<50	<10	--	--	--	--	--	20
Nickel, dissolved (µg/L)	3	42	<50	<10	--	--	--	--	--	30
Selenium, dissolved (µg/L)	2	42	<1	<1	.01	.07	.25	.91	13	26
Silver, dissolved (µg/L)	2	42	<2	<1	.01	.08	.26	.89	4.8	44
Strontium, dissolved (µg/L)	1	42	--	42	49	220	340	1,100	2,500	2,800
Vanadium, dissolved (µg/L)	3	42	<30	<6	--	--	--	--	--	21
Zinc, dissolved (µg/L)	2	42	<3	<3	1.76	4	8	18	78	86
Radioactivity and radionuclides										
Gross alpha radiation, dissolved (pCi/L as Th-230)	1	42	--	.400	.510	1.78	3.34	7.77	24.8	40.4
Gross alpha, dissolved (µg/L as U-natural)	2	42	<.4	<.4	.5	1.6	3.1	7.4	24	39
Gross beta, dissolved (pCi/L as Cs-137)	2	42	<.4	<.4	1.2	3.2	7.2	15	97	200
Gross beta, dissolved (pCi/Las Sr/Y-90)	2	42	<.4	<.4	1	2.5	5.6	12	78	160
Radon-222, total (pCi/L)	2	42	<80	<80	70	160	205	460	1,385	1,400

Table 1. Summary statistics of chemical constituents for water samples from wells completed in alluvium and terrace deposits of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Radioactivity and radionuclides—Continued										
Tritium, total (pCi/L)	2	42	<0.3	<0.3	0.28	3.2	24	32	59	66
Uranium-234, dissolved (pCi/L)	2	42	<.10	<.10	.07	.20	1.2	3.7	15	19
Uranium-235, water, dissolved (pCi/L)	2	42	<.1	<.1	.02	.06	.1	.3	.6	1.3
Uranium-238, dissolved (pCi/L)	2	42	<.10	<.10	.02	.12	.45	1.6	4.1	13
Uranium, natural, dissolved (µg/L)	2	42	<.20	<.20	.09	.38	1.4	5.2	12.	40
Organic carbon										
Carbon, organic dissolved (mg/L as C)	1	40	--	.3	.3	.5	.7	1.3	5.4	9.7

Table 2. Summary statistics of chemical constituents for water samples from shallow (less than 30 meters deep) wells completed in Permian geologic units of the Central Oklahoma aquifer

[Constituents and properties: µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter, µg/L, micrograms per liter; pCi/L, picocuries per liter. Method: 1, no censored data, ordinary percentile calculation; 2, censored data present, percentiles calculated using methods of Helsel and Cohn (1988); 3, no calculation, more than 80 percent of the data were censored. Largest MRL: largest minimum reporting level (percentiles less than this value were estimated using the methods of Helsel and Cohn (1988); percentiles greater than this value are the same as ordinary percentile calculation); --, no censored data for this constituent. Percentiles: --, indicates no statistic was calculated. <, less than]

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Properties and major ions										
Specific conductance (µS/cm at 25°C)	1	25	--	144	158	318	591	896	2,200	2,210
pH, field (standard units)	1	25	--	6.1	6.1	6.5	6.9	7.3	9.0	9.1
Water temperature (°C)	1	25	--	16.5	16.5	17.0	17.0	17.5	18.5	18.5
Oxygen, dissolved (mg/L)	1	25	--	.2	.2	2.0	4.9	8.2	10.6	11.0
Alkalinity, total, field (mg/L as $CaCO_3$)	1	25	--	44	48	92	259	368	495	516
Calcium, dissolved (mg/L)	1	25	--	1.3	1.6	16	42	67	220	240
Magnesium, dissolved (mg/L)	1	25	--	.40	.67	7.9	21	42	78	82
Sodium, dissolved (mg/L)	1	25	--	4.1	4.4	12	30	98	340	390
Potassium, dissolved (mg/L)	1	25	--	.30	.33	.70	1.1	1.3	2.3	2.3
Bicarbonate, field (mg/L)	1	25	--	53	58	112	315	446	604	629
Carbonate, field (mg/L)	1	25	--	0	0	0	0	0	28	29
Sulfate, dissolved (mg/L)	1	25	--	5.8	6.0	16	18	34	280	350
Chloride, dissolved (mg/L)	1	25	--	2.8	3.6	11	19	62	320	340
Fluoride, dissolved (mg/L)	2	25	<0.10	<.10	.10	.20	.30	.40	2.2	2.9
Bromide, dissolved (mg/L)	1	25	--	.030	.030	.080	.10	.35	1.4	1.7
Silica, dissolved (mg/L)	1	25	--	8.9	9.0	14	16	20	34	36
Nutrients										
Nitrogen, nitrite, dissolved (mg/L as N)	3	25	<.050	<.010	--	--	--	--	--	<.050
Nitrogen, nitrite + nitrate, dissolved (mg/L as N)	2	25	<.100	<.100	.060	.400	.800	3.55	38.8	40
Nitrogen, ammonia + organic, dissolved (mg/L as N)	2	25	<.20	<.20	.09	.17	.20	.40	1.3	1.4
Phosphorus, orthophosphate, dissolved (mg/L as P)	2	25	<.010	<.010	0	.010	.020	.030	.160	.200

Table 2. Summary statistics of chemical constituents for water samples from shallow (less than 30 meters deep) wells completed in Permian geologic units of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	Percentiles 25	Percentiles 50	Percentiles 75	Percentiles 95	Maximum
Trace elements										
Aluminum, dissolved (µg/L)	3	25	<10	<10	--	--	--	--	--	10
Antimony, dissolved (µg/L)	3	25	<1	<1	--	--	--	--	--	3
Arsenic, dissolved (µg/L)	2	25	<1	<1	0.08	0.24	0.5	1	5	6
Barium, dissolved (µg/L)	1	25	--	30	40	97	180	380	690	700
Beryllium, dissolved (µg/L)	3	25	<.5	<.5	--	--	--	--	--	<.5
Boron, dissolved (µg/L)	1	25	--	20	20	40	80	260	5,500	7,200
Cadmium, dissolved (µg/L)	3	25	<1	<1	--	--	--	--	--	<1
Chromium, dissolved (µg/L)	3	25	<5	<5	--	--	--	--	--	<5
Cobalt, dissolved (µg/L)	3	25	<3	<3	--	--	--	--	--	<3
Copper, dissolved (µg/L)	2	25	<10	<10	5	7	8	10	20	20
Iron, dissolved (µg/L)	2	25	<3	<3	.22	1.64	5	27	1,000	1,400
Lead, dissolved (µg/L)	3	25	<10	<10	--	--	--	--	--	<10
Lithium, dissolved (µg/L)	2	25	<4	<4	4	9	13	17	35	39
Manganese, dissolved (µg/L)	2	25	<1	<1	.01	.12	.64	2	140	180
Mercury, dissolved (µg/L)	3	25	<.1	<.1	--	--	--	--	--	.2
Molybdenum, dissolved (µg/L)	3	25	<10	<10	--	--	--	--	--	30
Nickel, dissolved (µg/L)	3	25	<10	<10	--	--	--	--	--	40
Selenium, dissolved (µg/L)	2	25	<1	<1	.04	.16	.45	1	17	22
Silver, dissolved (µg/L)	3	25	<1	<1	--	--	--	--	--	2
Strontium, dissolved (µg/L)	1	25	--	17	18	89	150	370	2,200	2,600
Vanadium, dissolved (µg/L as V)	2	25	<6	<6	.03	.27	1.21	5.49	110	130
Zinc, dissolved (µg/L)	2	25	<3	<3	1.22	4	7	16	140	180
Radioactivity and radionuclides										
Gross alpha radiation, dissolved, (pCi/L as Th-230)	1	25	--	.100	.310	1.44	3.49	16.3	107	119
Gross alpha, dissolved (µg/L as U-natural)	2	25	<.4	<.4	.4	1.5	3.4	16	100	110
Gross beta, dissolved (pCi/L as Cs-137)	2	25	<.4	<.4	.4	1.8	2.5	9.8	64	73
Gross beta, dissolved (pCi/L as Sr/Y-90)	2	25	<.4	<.4	.37	1.4	1.8	7.0	43	49
Radon-222, total (pCi/L)	2	25	<80	<80	40	92	150	240	960	1,100

Table 2. Summary statistics of chemical constituents for water samples from shallow (less than 30 meters deep) wells completed in Permian geologic units of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Radioactivity and radionuclides—Continued										
Tritium, total (pCi/L)	2	25	<0.3	<0.3	0.23	2.8	27	40	80	80
Uranium-234, dissolved (pCi/L)	2	25	<.10	<.10	.01	.14	1.3	4.5	30	32
Uranium-235, water, dissolved (pCi/L)	2	25	<1	<.1	.01	.02	.06	.2	.7	.9
Uranium-238, dissolved (pCi/L)	2	25	<.10	<.10	.01	.08	.40	2.8	20	23
Uranium, natural, dissolved (µg/L)	2	25	<.20	<.20	.02	.21	1.1	8.6	60	69
Organic carbon										
Carbon, organic dissolved (mg/L as C)	1	24	--	.7	.7	.9	1.0	1.3	1.8	1.9

Table 3. Summary statistics of chemical constituents for water samples from intermediate (less than 91 meters and greater than 30 meters) depth wells completed in Permian geologic units of the Central Oklahoma aquifer

[Constituents and properties: mS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter, mg/L, micrograms per liter; pCi/L, picocuries per liter. Method: 1, no censored data, ordinary percentile calculation; 2, censored data present, percentiles calculated using methods of Helsel and Cohn (1988); 3, no calculation, more than 80 percent of the data were censored. Largest MRL: largest minimum reporting level (percentiles less than this value were estimated using the methods of Helsel and Cohn (1988); percentiles greater than this value are the same as ordinary percentile calculation); --, no censored data for this constituent. Percentiles: --, indicates no statistic was calculated. <, less than]

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Properties and major ions										
Specific conductance (µS/cm at 25°C)	1	35	--	208	243	420	666	830	2,420	2,700
pH, field (standard units)	1	35	--	6.0	6.2	7.0	7.3	7.5	8.4	9.0
Water temperature (°C)	1	35	--	15.5	16.3	17.0	17.5	17.5	19.1	19.5
Oxygen, dissolved (mg/L)	1	35	--	.2	.2	3.6	6.9	8.4	9.7	9.9
Alkalinity, total, field (mg/L as $CaCO_3$)	1	35	--	50	69	172	280	342	512	646
Calcium, dissolved (mg/L)	1	35	--	1.7	4.7	31	54	71	95	98
Magnesium, dissolved (mg/L)	1	35	--	.70	2.5	14	26	36	62	73
Sodium, dissolved (mg/L)	1	35	--	6.6	6.6	14	30	62	330	510
Potassium, dissolved (mg/L)	2	35	<0.10	<.10	.25	.70	1.0	1.6	9.7	15
Bicarbonate, field (mg/L)	1	35	--	61	84	210	342	417	578	788
Carbonate, field (mg/L)	1	35	--	0	0	0	0	0	7	36
Sulfate, dissolved (mg/L)	1	35	--	3.3	4.8	9.5	22	40	260	350
Chloride, dissolved (mg/L)	1	35	--	5.1	6.5	10	20	37	270	590
Fluoride, dissolved (mg/L)	1	35	--	.10	.10	.30	.30	.5	2.9	3.9
Bromide, dissolved (mg/L)	1	35	--	.040	.050	.10	.20	.3	.98	1.3
Silica, dissolved (mg/L)	1	35	--	9.8	10	14	16	19	23	24
Nutrients										
Nitrogen, nitrite, dissolved (mg/L as N)	3	35	<.010	<.010	--	--	--	--	--	.020
Nitrogen, nitrite + nitrate, dissolved (mg/L as N)	2	35	<.100	<.100	.040	.300	.900	3.10	44.2	85.0
Nitrogen, ammonia + organic, dissolved (mg/L as N)	2	34	<.20	<.20	.10	.19	.30	.42	.83	1.2
Phosphorus, orthophosphate, dissolved (mg/L as P)	2	35	<.010	<.010	0	.010	.010	.040	.080	.100
Trace elements										
Aluminum, dissolved (µg/L)	3	35	<10	<10	--	--	--	--	--	70
Antimony, dissolved (µg/L)	2	35	<1	<1	.06	.19	.41	.88	5	5
Arsenic, dissolved (µg/L)	2	35	<1	<1	.35	.70	1	2	5	9
Barium, dissolved (µg/L)	1	35	--	15	28	95	240	440	720	770
Beryllium, dissolved (µg/L)	3	35	<1.5	<.5	--	--	--	--	--	1.7

Table 3. Summary statistics of chemical constituents for water samples from intermediate (less than 91 meters and greater than 30 meters) depth wells completed in Permian geologic units of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Trace elements—Continued										
Boron, dissolved (µg/L)	1	35	--	20	28	50	80	370	4,080	8,000
Cadmium, dissolved (µg/L)	3	35	<3	<1	--	--	--	--	--	<3
Chromium, dissolved (µg/L)	3	35	<5	<5	--	--	--	--	--	36
Cobalt, dissolved (µg/L)	3	35	<9	<3	--	--	--	--	--	<9
Copper, dissolved (µg/L)	3	35	<30	<10	--	--	--	--	--	80
Iron, dissolved (µg/L)	2	35	<9	<3	.38	1.4	3.2	7.8	40	79
Lead, dissolved (µg/L)	3	35	<30	<10	--	--	--	--	--	10
Lithium, dissolved (µg/L)	1	35	--	5	6	11	14	19	33	34
Manganese, dissolved (µg/L)	2	35	<3	<1	.02	.11	.45	1.8	19	37
Mercury, dissolved (µg/L)	3	35	<.1	<.1	--	--	--	--	--	.9
Molybdenum, dissolved (µg/L)	3	35	<30	<10	--	--	--	--	--	20
Nickel, dissolved (µg/L)	3	35	<30	<10	--	--	--	--	--	20
Selenium, dissolved (µg/L)	2	35	<1	<1	.05	.25	.80	2	29	75
Silver, dissolved (µg/L)	3	35	<3	<1	--	--	--	--	--	1
Strontium, dissolved (µg/L)	1	35	--	48	51	110	310	590	3,100	3,800
Vanadium, dissolved (µg/L as V)	2	35	<18	<6	.55	2.37	6.54	20	120	230
Zinc, dissolved (µg/L)	2	35	<9	<3	.9	4	10	28	180	360
Radioactivity and radionuclides										
Gross alpha radiation, dissolveed (pCi/L as Th-230)	1	35	--	.800	.970	2.13	5.15	16.6	174	212
Gross alpha, dissolved (µg/L as U-natural)	1	35	--	.7	.9	2.5	5.0	16	170	210
Gross beta, dissolved (pCi/L as Cs-137)	1	35	--	.8	1.0	1.8	3.4	9.6	50	96
Gross beta, dissolved (pCi/L as Sr/Y-90)	1	35	--	.6	.8	1.2	2.4	6.6	40	67
Radon-222, total (pCi/L)	2	35	<80	<80	28	84	120	180	2,100	4,900
Tritium, total (pCi/L)	2	35	<.3		.07	.4	6.6	22	48	51
Uranium-234, dissolved (pCi/L)	2	35	<.10	<.10	.06	.40	1.2	6.0	47	65
Uranium-235 dissolved (pCi/L)	2	35	<.10	<.10	0	0	.02	.10	2.6	2.8
Uranium-238, dissolved (pCi/L)	2	35	<.10	<.10	.02	.2	.30	2.3	43	73
Uranium, natural, dissolved (pCi/L)	2	35	<.20	<.20	.05	.5	1.0	7.1	130	220
Organic carbon										
Carbon, organic dissolved mg/L as C)	1	35	--	.4	.48	.8	1	1.3	3.1	3.3

Table 4. Summary statistics of chemical constituents for water samples from deep (greater than 91 meters) wells completed in Permian geologic units of the Central Oklahoma aquifer

[Constituents and properties: mS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter, mg/L, micrograms per liter; pCi/L, picocuries per liter. Method: 1, no censored data, ordinary percentile calculation; 2, censored data present, percentiles calculated using methods of Helsel and Cohn (1988); 3, no calculation, more than 80 percent of the data were censored. Largest MRL: largest minimum reporting level (percentiles less than this value were estimated using the methods of Helsel and Cohn (1988); percentiles greater than this value are the same as ordinary percentile calculation); --, no censored data for this constituent. Percentiles: --, indicates no statistic was calculated. <, less than]

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Properties and major ions										
Specific conductance (µS/cm at 25°C)	1	27	--	381	392	484	570	678	1,420	1,470
pH, field (standard units)	1	27	--	6.9	7.1	7.5	7.8	8.8	9.2	9.2
Water temperature (°C)	1	27	--	16.5	16.7	17.0	17.5	18.5	19.8	20.0
Oxygen, dissolved (mg/L)	1	27	--	0	.1	2.0	4.0	5.9	9.4	10.0
Alkalinity, total, field (mg/L as $CaCO_3$)	1	27	--	161	165	212	262	296	394	400
Calcium, dissolved (mg/L)	1	27	--	1.0	1.0	11	33	45	120	160
Magnesium, dissolved (mg/L)	1	27	--	.30	.34	8.8	18	27	44	52
Sodium, dissolved (mg/L)	1	27	--	5.8	8.7	25	84	130	280	300
Potassium, dissolved (mg/L)	1	27	--	.40	.44	.90	1.4	2.0	3.4	3.4
Bicarbonate, field (mg/L)	1	27	--	196	202	259	311	349	415	419
Carbonate, field (mg/L)	1	27	--	0	0	0	0	12	34	34
Sulfate, dissolved (mg/L)	1	27	--	5.5	5.7	8.1	11	24	490	600
Chloride, dissolved (mg/L)	1	27	--	5.0	5.3	8.7	12	24	200	200
Fluoride, dissolved (mg/L)	1	27	--	.20	.20	.20	.30	.40	1.3	1.3
Bromide, dissolved (mg/L)	1	27	--	.020	.020	.030	.050	.090	.26	.30
Silica, dissolved (mg/L)	1	27	--	9.5	9.5	10	14	20	23	23
Nutrients										
Nitrogen, nitrite, dissolved (mg/L as N)	3	27	<.010	<.010	--	--	--	--	--	.020
Nitrogen, nitrite + nitrate, dissolved (mg/L as N)	2	27	<.100	<.050	.080	.200	.300	.400	.800	1.00
Nitrogen, ammonia + organic, dissolved (mg/L as N)	2	27	<.20	<.20	.02	.05	.10	.20	.82	.90
Phosphorus, orthophosphate, dissolved (mg/L as P)	2	27	<.010	<.010	0	0	.010	.030	.050	.060

Table 4. Summary statistics of chemical constituents for water samples from deep (greater than 91 meters) wells completed in Permian geologic units of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
			Trace elements							
Aluminum, dissolved (µg/L)	3	27	<10	<10	--	--	--	--	--	10
Antimony, dissolved (µg/L)	2	27	<1	<1	0.04	0.14	0.35	0.87	5	5
Arsenic, dissolved (µg/L)	2	27	<1	<1	.11	.71	2	14	86	110
Barium, dissolved (µg/L)	1	27	--	20	28	90	210	390	670	770
Beryllium, dissolved (µg/L)	3	27	<.5	<.5	--	--	--	--	--	2
Boron, dissolved (µg/L)	1	27	--	50	50	90	430	1,000	3,700	3,900
Cadmium, dissolved (µg/L)	3	27	<1	<1	--	--	--	--	--	<1
Chromium, dissolved (µg/L)	2	27	<5	<5	1.36	4.11	8	23	84	100
Cobalt, dissolved (µg/L)	3	27	<3	<3	--	--	--	--	--	<3
Copper, dissolved (µg/L)	3	27	<10	<10	--	--	--	--	--	<10
Iron, dissolved (µg/L)	2	27	<3	<3	.26	1.17	3	5	200	320
Lead, dissolved (µg/L)	3	27	<10	<10	--	--	--	--	--	10
Lithium, dissolved (µg/L)	2	27	<4	<4	3.84	8	10	20	39	45
Manganese, dissolved (µg/L)	2	27	<1	<1	0	.04	.18	.83	17	25
Mercury, dissolved (µg/L)	3	27	<.1	<.1	--	--	--	--	--	.4
Molybdenum, dissolved (µg/L)	3	27	<10	<10	--	--	--	--	--	40
Nickel, dissolved (µg/L)	3	27	<10	<10	--	--	--	--	--	<10
Selenium, dissolved (µg/L)	2	27	<1	<1	.12	.85	3	20	120	150
Silver, dissolved (µg/L)	3	27	<1	<1	--	--	--	--	--	<1
Strontium, dissolved (µg/L)	1	27	--	44	51	130	290	990	4,200	4,600
Vanadium, dissolved (µg/L as V)	1	27	--	6.0	6.4	11	25	120	530	560
Zinc, dissolved (µg/L)	2	27	<3	<3	.40	1.19	2.57	4	33	40

Table 4. Summary statistics of chemical constituents for water samples from deep (greater than 91 meters) wells completed in Permian geologic units of the Central Oklahoma aquifer—Continued

Physical properties and constituents	Method	Sample size	Largest MRL	Minimum	Percentiles 5	25	50	75	95	Maximum
Radioactivity and radionuclides										
Gross alpha radiation, dissolved (pCi/L as Th-230)	1	27	--	4.75	5.29	10.7	19.4	34.1	148	190
Gross alpha, dissolved (µg/L as U-natural)	1	27	--	4.5	5.0	10	19	33	150	190
Gross beta, dissolved (pCi/L as Cs-137)	1	27	--	2.8	2.8	5.1	11	17	99	110
Gross beta, dissolved (pCi/L as Sr/Y-90)	1	27	--	2.1	2.2	3.8	8.4	13	70	76
Radon-222, total (pCi/L)	2	27	<80	<80	65	110	146	188	628	820
Tritium, total (pCi/L)	2	27	<.3	<.3	0	.01	.04	.24	8.5	12
Uranium-234, dissolved (pCi/L)	1	27	--	2.4	2.4	3.5	8.6	15	51	57
Uranium-235, water, dissolved (pCi/L)	2	27	<.1	<.1	.01	.06	.1	.4	1.8	2.1
Uranium-238, dissolved (pCi/L)	1	27	--	.30	.34	.70	3.6	8.2	41	45
Uranium, natural, dissolved (µg/L)	1	27	--	1.0	1.1	2.2	11	25	120	130
Organic carbon										
Carbon, organic dissolved (mg/L as C)	1	27	--	.4	.4	.5	.6	.8	1.6	1.9

The Diagenetic History of Permian Rocks in the Central Oklahoma Aquifer

By George N. Breit

Abstract

Variations in the chemical composition of water within the Central Oklahoma aquifer are largely a result of reactions between water and solid components of the aquifer. To understand these reactions, a detailed mineralogical and petrographic study of Permian rocks in the aquifer was included as part of the Oklahoma National Water-Quality Assessment (NAWQA) project. Rock samples from eight test-hole cores were analyzed by X-ray diffraction and by optical and scanning electron microscopy.

The abundance, composition, and reactivity of solids in the aquifer reflect the sediment source unit and alteration during deposition, burial, and exposure due to erosion. During deposition of the Permian sediment, soil processes dissolved some framework silicates and precipitated iron oxides, carbonate nodules, and kaolinite. Burial and incursion of evolved seawater resulted in precipitation of dolomite, barite, quartz overgrowths, additional iron oxides, and local accumulations of selenium, uranium, and vanadium. Tertiary and Quaternary erosion exposed rocks in the aquifer to recharge by rainwater. This dilute recharge has dissolved calcite, dolomite, feldspars, and chert, and has precipitated calcite, goethite, manganese oxides, and kaolinite.

INTRODUCTION

The range of water compositions produced from Permian rocks within the Central Oklahoma aquifer (Parkhurst, Christenson, and Schlottmann, 1989) is largely a result of reactions between ground water and solid constituents of the rocks. To better understand these reactions, a detailed study of the mineralogy and petrography of these rocks was conducted as part of the National Water Quality Assessment (NAWQA) Program. This paper summarizes the petrographic and mineralogic data with particular emphasis on rock textures that record water-rock interaction. These data are to be integrated with hydrologic, aqueous geochemical, and solid-phase chemical data to understand processes that affect the quality of water in the aquifer.

Changes in the abundance and composition of solids in the aquifer that occurred from Permian to present affect modern ground-water compositions. The altered appearance of some detrital minerals and the mineralogy of solids that formed within the aquifer record these changes. The alteration of the Permian sediment began soon after deposition, continued during burial, and is continuing now because of reactions between solids and dilute recharge water. Assignment of the timing and conditions of alteration based on petrographic evidence is commonly ambiguous because many of the observed alterations can have multiple origins. Therefore, this paper presents information on the abundance and appearance of constituents of the Permian rocks and reviews the evidence for the probable timing of each type of alteration. Previous studies have described the mineralogy of Permian rocks near the study unit (Swineford, 1955; Cox, 1978; Shelton, 1979; Elrod, 1980; Lilburn and Al-Shaieb, 1983, 1984), but little is published about diagenesis within the aquifer.

Geology

The Central Oklahoma aquifer as defined by Parkhurst, Christenson, and Schlottmann (1989) includes alluvial and terrace deposits of Quaternary age and sedimentary rocks of Permian age. Major water-yielding Permian units include, from youngest to oldest, the Garber Sandstone, the Wellington Formation, and the Chase, Council Grove, and Admire Groups. The undifferentiated Chase, Council Grove, and Admire Groups of central Oklahoma have been identified in previous studies as the Pennsylvanian Oscar Group (compare Bingham and Moore, 1975), but recent stratigraphic correlations have reassigned the units (Lindberg, 1987). The Permian Hennessey Group overlies Permian rocks in the aquifer, and the Vanoss Formation of Pennsylvanian age underlies it; both units are sedimentary rocks with relatively low permeability.

The Permian units are mainly red, interbedded sandstone and mudstone, with minor amounts of conglomerate (fig. 1). The Hennessey Group consists of reddish-brown shale and mudstone with a few thin beds of very fine-grained sandstone. The Hennessey Group is underlain by Garber Sandstone, which is in turn underlain by the Wellington Formation. Because the Garber Sandstone and Wellington Formation are lithologically similar, they are described together. These units include lenticular beds of fine-grained, crossbedded sandstone that are interbedded with siltstone and mudstone. The combined thickness of a full section of the Garber Sandstone and Wellington Formation is 1,165 to 1,600 ft (Christenson, Morton, and Mesander, 1992). The amount of sandstone varies from 25 to 75 percent in this section. The Chase, Council Grove, and Admire Groups are also undifferentiated because of their lithologic similarities within the study unit. The rocks consist of mudstone; fine-grained, crossbedded sandstone; and some conglomerates. The combined thickness of these groups ranges from 570 to 940 ft (Christenson, Morton, and Mesander, 1992). The underlying Pennsylvanian Vanoss Formation consists mainly of mudstone and a few thin, fine-grained sandstone beds.

The Permian rocks were deposited in a combination of fluvial, deltaic, and marginal marine environments (Tanner, 1959). During deposition, the study unit was in a structurally stable unit on the east margin of the Anadarko Basin (fig 2; Johnson, 1989). Streams crossed the unit and transported detritus from the southeast and east toward an epeiric sea to the west and north. Most of the sediment was eroded from Paleozoic sandstone, shale, and chert in the Ouachita Uplift. Studies of Permian units outside the Central Oklahoma aquifer indicate minor contributions of sediment may have come from the Arbuckle and Ozark Uplifts (fig. 2; Self, 1966; Cox, 1978; Shelton, 1979). Fluctuations in sea level along the shallow depositional slope resulted in large changes in depositional environment. In the marine basin, rocks equivalent to those in the aquifer are finer grained and include bedded limestone and evaporite deposits.

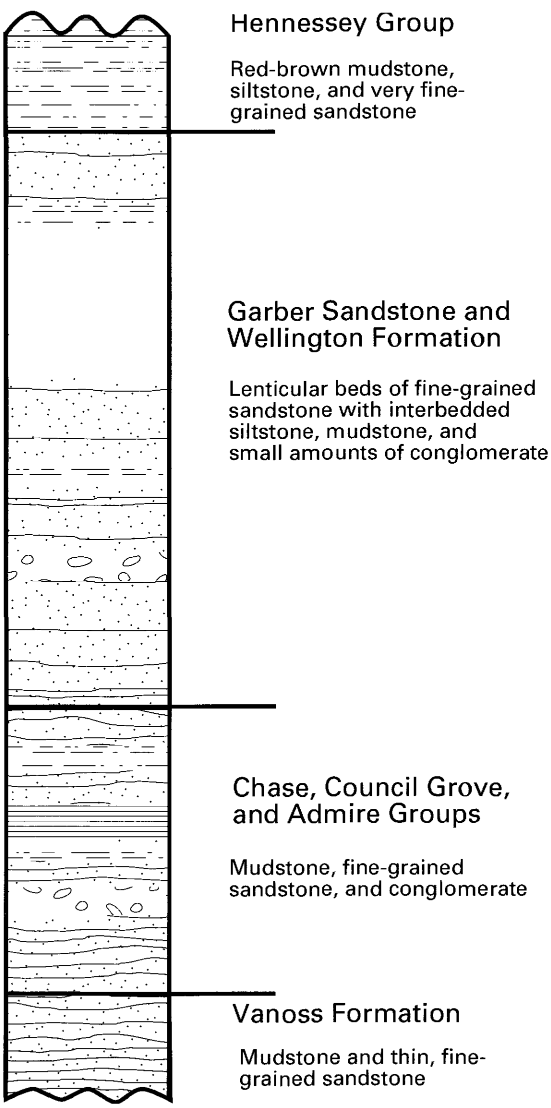


Figure 1. Generalized stratigraphic section of rock units within the Central Oklahoma aquifer.

Paleogeographic reconstructions and paleoclimatic interpretations (Ziegler, 1990) indicate that central Oklahoma was near the equator during the Permian. The unit had an alternating wet and dry climate during the Early Permian when the rocks in the aquifer were deposited. The climate shifted to consistently dry conditions during the Late Permian. Paleosols visible in core and outcrop indicate that the climate affected pedogenic processes on the Permian depositional surface (J. Schlottmann, U.S. Geological Survey, oral commun., 1989; Joeckel, 1991).

Following deposition of the Hennessey Group, a few hundred feet of Permian sediment and 1,500 to 2,000 ft of Triassic, Jurassic, and Cretaceous sediment accumulated (Johnson, 1989). Late Jurassic to Early Cretaceous and Late Cretaceous to early Tertiary were times of epeirogenic uplift during which most of the

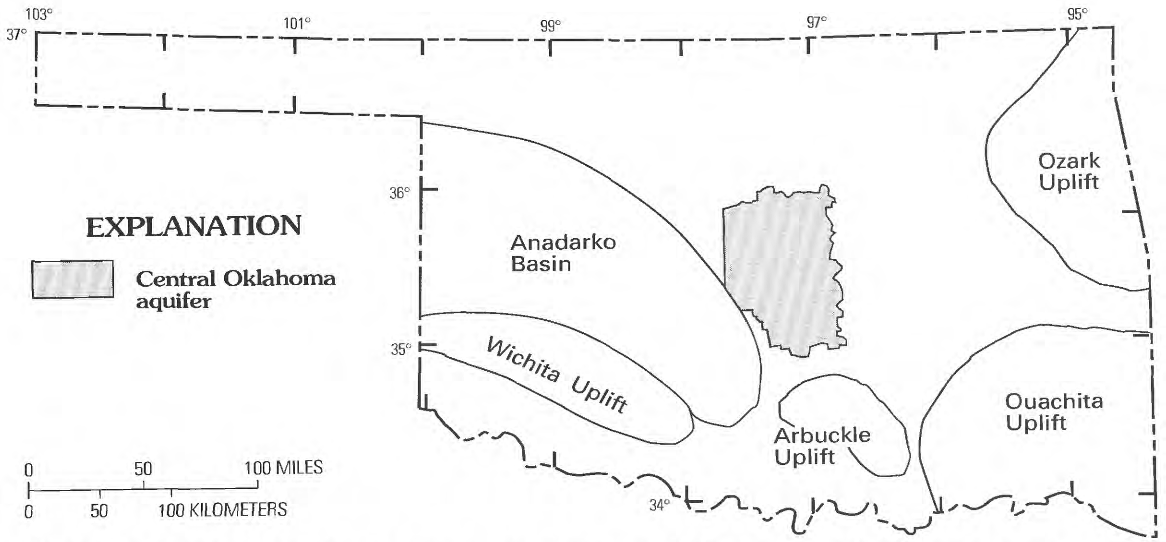


Figure 2. Approximate location of physiographic features in Oklahoma that affected deposition of Permian sedimentary rocks within the Central Oklahoma aquifer.

Mesozoic sediment was eroded (Johnson, 1989). Approximately 500 to 1,000 ft of upper Tertiary sediment were deposited and subsequently eroded. Only minor faults and folds deformed Permian rocks in the study unit.

Method of Study

Approximately 200 rock samples were collected from cores obtained from eight test holes (table 1; Schlottmann and Funkhouser, 1991) for mineralogical and petrographic study. Samples were selected to reflect lithologic, color, and diagenetic variations. Mosier (1998) summarizes the chemical composition of a larger set of core samples.

Analytical methods used to identify and describe solid constituents of Permian rocks in the aquifer and results of the analyses are presented in Breit and others (1991). Abundances of major rock-forming minerals were determined by semiquantitative X-ray diffraction (XRD) of 196 samples (Appendix 1). Estimates of mineral abundance were based on mixed standards containing varying amounts of quartz, plagioclase, illite, hematite, dolomite, calcite, and kaolinite. Samples analyzed by XRD were selected to represent the relative abundances of mudstone, sandstone, and conglomerate within each test hole. Additional compositional data were collected by point counting 160 thin sections of aquifer sandstone (Appendix 2), conglomerate, and siltstone. The thin sections were stained for ferroan carbonates (none were detected), potassium feldspar, and calcite. Optical and scanning electron microscopy (SEM) were used to determine paragenetic relations, examine mineral surfaces, and evaluate textural variations. An energy-dispersive spectrometer (EDS) attached to the SEM was used for qualitative chemical analysis of selected phases.

The clay-size (less than 2 μm) fraction was separated from 70 selected samples by centrifugation. Mineralogy of the clay fraction was determined by XRD of oriented mounts. The mounts were treated with ethylene glycol, and a few were heated to 425 °C prior to analysis. Selected subsamples were saturated with sodium, potassium, or magnesium ions prior to XRD analysis. Saturation with these ions aided in identification of mixed-layer clay minerals.

The stable isotope compositions of dolomite, calcite, and barite were determined. All isotope values are presented in del-value (δ) notation as per mil (Hoefs, 1973). Standards used in this study include Peedee belemnite for carbonate carbon and oxygen, and Cañon Diablo troilite for sulfur in barite. Samples of carbonate minerals were selected to represent textures detected during petrographic examination (table 2). The $\delta^{13}C$ and $\delta^{18}O$ of carbonate minerals were measured according to the timed phosphoric-acid-dissolution procedure of Walters, Claypool, and Chouquette (1972). Precision of the analyses is 0.1 per mil for $\delta^{13}C$ and 0.05 per mil for $\delta^{18}O$. The sulfur isotope compositions of barite were determined by standard methods after purification by the technique of Breit, Simmons, and Goldhaber (1985); results are reported in table 3. Precision of these analyses is 0.2 per mil.

Table 1. Location and description of test-hole cores used in this study

Test hole	Latitude	Longitude	Total depth (feet)	Geologic unit
1a	35°51'18"	97°25'00"	268	Garber Sandstone
2	35°44'18"	97°01'35"	277	Chase, Council Grove, and Admire Groups
3	35°40'12"	97°23'10"	195	Garber Sandstone
4	35°21'42"	97°10'35"	291	Garber Sandstone and Wellington Formation
5	35°11'42"	96°58'01"	238	Chase, Council Grove, and Admire Groups
6	35°42'08"	97°33'02"	587	Garber Sandstone
7	35°13'15"	97°25'43"	456	Hennessey Group
[1]7a	35°13'15"	97°25'42"	631	Garber Sandstone

[1] Test hole 7a was drilled next to test hole 7.

MINERALOGY

Detrital Minerals

The major detrital constituents of Permian rocks in the aquifer are quartz and illitic material (Appendix 1). Minor constituents are plagioclase, orthoclase, microcline, chlorite, and rock fragments. Rock fragments include polycrystalline quartz, schist, phyllite, chert, shale, and intraclasts of mudstone and dolostone. Trace detrital constituents include biotite, muscovite, leucoxene, ilmenite, tourmaline, monazite, chromite, and zircon. Sandstone and mudstone contain the same assemblage of minerals.

The same minerals are found in the Hennessey Group, Garber Sandstone, Wellington Formation, and Chase, Council Grove, and Admire Groups. The similar assemblage of minerals is consistent with the shared depositional environment, source unit, and burial history of the units. The relative abundance of the constituent minerals do vary among test holes (Appendices 1 and 2). This variation is accounted for largely by the varying abundance of mudstone intersected by the test holes. Cores with greater amounts of mudstone typically have more illite and less quartz. Differences that are not related to the abundance of mudstone include the relative absence of chlorite, dolomite, and plagioclase in test hole 4 and the large abundance of chlorite and plagioclase and lack of kaolinite in test hole 7 (Breit and others, 1991).

Sandstone in the aquifer (fig. 3) is classed mainly as sublitharenite with abundant clay matrix (Folk, 1980) or as lithic wackes (Dott, 1964). The sandstone is fine to very fine-grained and moderately sorted; constituent grains are mainly subangular.

Quartz is typically 50 volume percent of sandstone and 30 weight percent of mudstone. Most quartz grains have slight undulatory extinction, and approximately 30 percent are strongly undulatory. A few quartz grains have inclusions of biotite, chlorite, or tourmaline. As much as 16 volume percent of a sandstone is polycrystalline quartz that has extinction patterns suggestive of a composite metamorphic origin (Folk, 1980).

Plagioclase is the most abundant feldspar and typically is 2 volume percent of a sandstone. Orthoclase and microcline are commonly less than 0.5 percent of the rock. In thin section, two types of plagioclase were recognized—one is sericitized and albite twinned; the other has clear interiors and good cleavage. Orthoclase grains have extinction patterns that indicate they were originally part of larger, zoned crystals. Most feldspars have been at least partially dissolved (fig. 4*A*), generally leaving voids and discontinuous fragments. Feldspar grains are best preserved in samples that have an abundant clay matrix or dolomite cement.

Chert is typically present in trace amounts (less than 1 volume percent) but is as much as 30 percent of some samples from the Chase, Council Grove, and Admire Groups (Breit and others, 1991). Most chert has been partly to extensively dissolved leaving voids that are surrounded by thin rims of quartz. The dis-

Table 2. Carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope composition of carbonate minerals from the Central Oklahoma aquifer

[Data units are per mil relative to Peedee belemnite; --, not analyzed]

Test-hole number	Depth (feet)	Sample description	Calcite		Dolomite	
			$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
1a	161.5	Sparry calcite	–8.87	–4.55	--	--
	211.7	Micritic dolomite nodule	--	--	–8.22	3.00
	211.7	Sparry dolomite from nodule	--	--	–9.51	.09
	243.2	Sparry dolomite cement	--	--	–9.22	.27
2	183.5	Sparry dolomite from clast	--	--	–11.37	.92
	240.5	Micritic dolomite clast	--	--	–8.81	1.09
3	113.9	Sparry calcite	–7.84	–5.08	--	--
	123	Sparry dolomite	--	--	–8.37	1.40
	124	Sparry dolomite	--	--	–8.46	1.09
	182.7	Micritic dolomite cement	--	--	-8.60	.84
4	118	Sparry dolomite cement	--	--	–15.76	2.09
5	234.2	Micritic dolomite clasts	--	--	–9.05	.19
6	124.8	Sparry dolomite and calcite	–8.53	[1]–1.20	–9.03	9.24
	184.2	Sparry calcite cement	–8.14	–4.61	--	--
	494.8	Sparry dolomite cement	--	--	–9.12	.40
	560.6	Micritic dolomite clast	--	--	–8.67	.97
7	59	Dolomite cement	--	--	–5.18	.62
	94.5	Dolomite cement	--	--	–4.72	.45
7a	381	Sparry dolomite cement	--	--	–8.33	.84
	598	Sparry calcite cement	–8.86	–4.90	--	--

[1] Unusually large $\delta^{18}O$ value may indicate contamination from dolomite.

Table 3. Sulfur isotope ($\delta^{34}S$) composition of barite samples from the Hennessey Group and Garber Sandstone in the Central Oklahoma aquifer

[All values are reported in per mil notation relative to Cañon Diablo troilite]

Sample description		$\delta^{34}S$ (per mil)
1. Barite "veinlets" in red, silty mudstone from the lower Hennessey Group		8.0
2. Barite rose in red sandstone from the Garber Sandstone		12.8
3. Barite rose from green, argillaceous sandstone in the Garber Sandstone. Barite was visibly zoned by the abundance of hematite inclusions:		
	Core	16.9
	Middle zone	14.7
	Outer surface	14.4

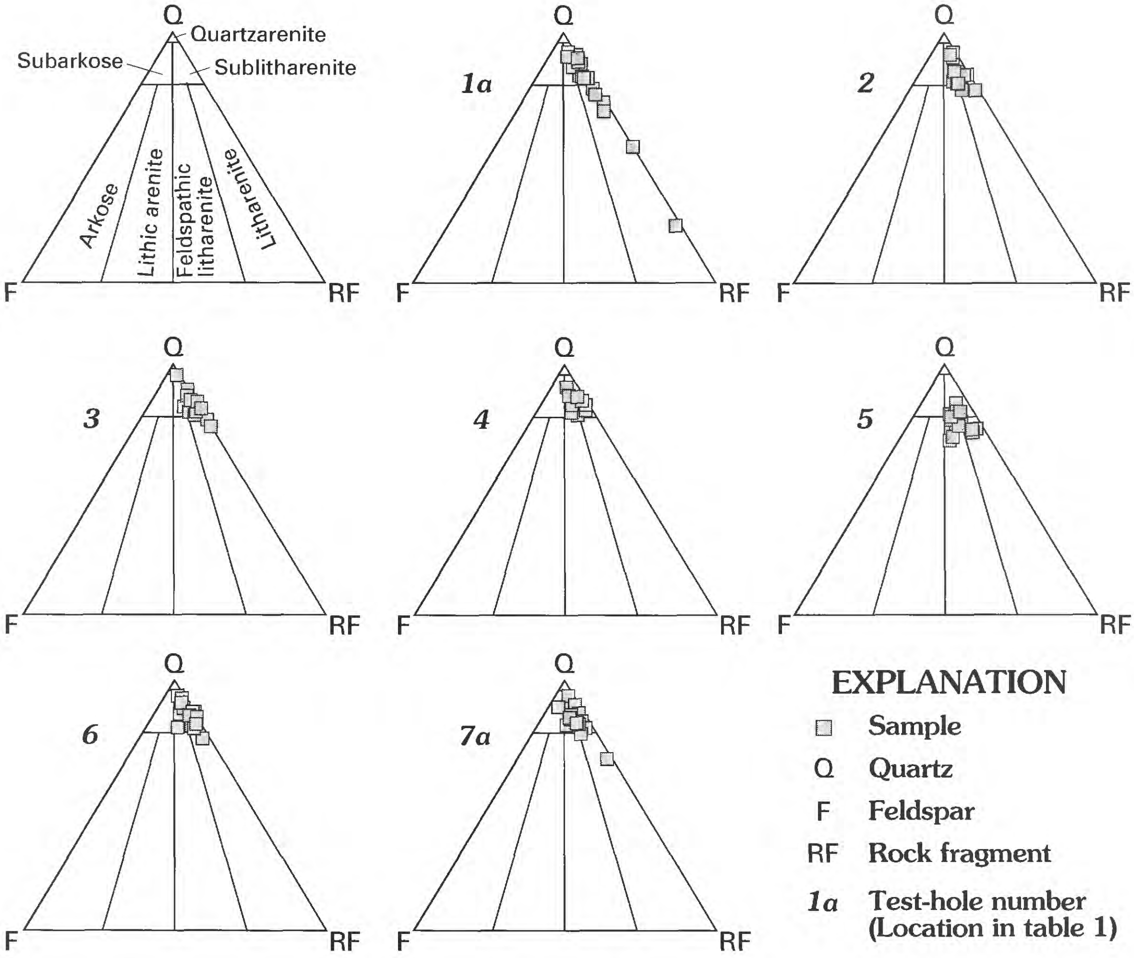


Figure 3. Composition of sandstone and conglomerate from each test hole in the Central Oklahoma aquifer. Classification scheme in upper left is modified from Folk (1980).

solved chert grains have not been compacted or replaced by authigenic minerals.

Phyllite, schist, and shale fragments total as much as 3 volume percent of the rock in a few samples. Major components of the metamorphic rock fragments are muscovite and quartz with minor amounts of biotite. In thin section, the shale fragments are green and comprised mainly of well-oriented clay and very fine quartz. The shale fragments are typically coated with thick rims of reddish-brown iron oxide in red rocks.

Intraclasts of dolostone and mudstone are the most common rock fragments in conglomerates. Micritic dolostone clasts are typically less than a few inches in diameter. Nodules similar to the clasts are common within some mudstone. The host mudstone typically contains rhizoliths and is marked by color mottling and slickensides, which are consistent with nodule formation during pedogenesis. Calcite was not detected in the nodules or clasts.

Clay minerals in mudstone and sandstone are similar and typically include kaolinite, illite, illite-smectite, and chlorite (fig. 5). Illite and chlorite lack delicate textures that are characteristic of authigenic clay, and therefore, the clay is considered detrital. This contrasts with Permian rocks elsewhere in Oklahoma reported to contain authigenic illite (Shelton, 1979; Al-Shaieb and others, 1980; Lilburn and Al-Shaieb, 1983). A few samples also contain illite-smectite, with greater than 50 percent smectite interlayers (smectite/vermiculite of Breit and others, 1991). Smectite-rich mixed-layer clay is a common component of mudstone in the Chase, Council Grove, and Admire Groups and the lower part of the Garber Sandstone. This clay was not detected in samples from the upper part of the Garber Sandstone and the Hennessey Group.

Trace amounts of detrital, sand-sized muscovite and biotite are components of all formations in the aquifer. Smaller mica fragments are common in the

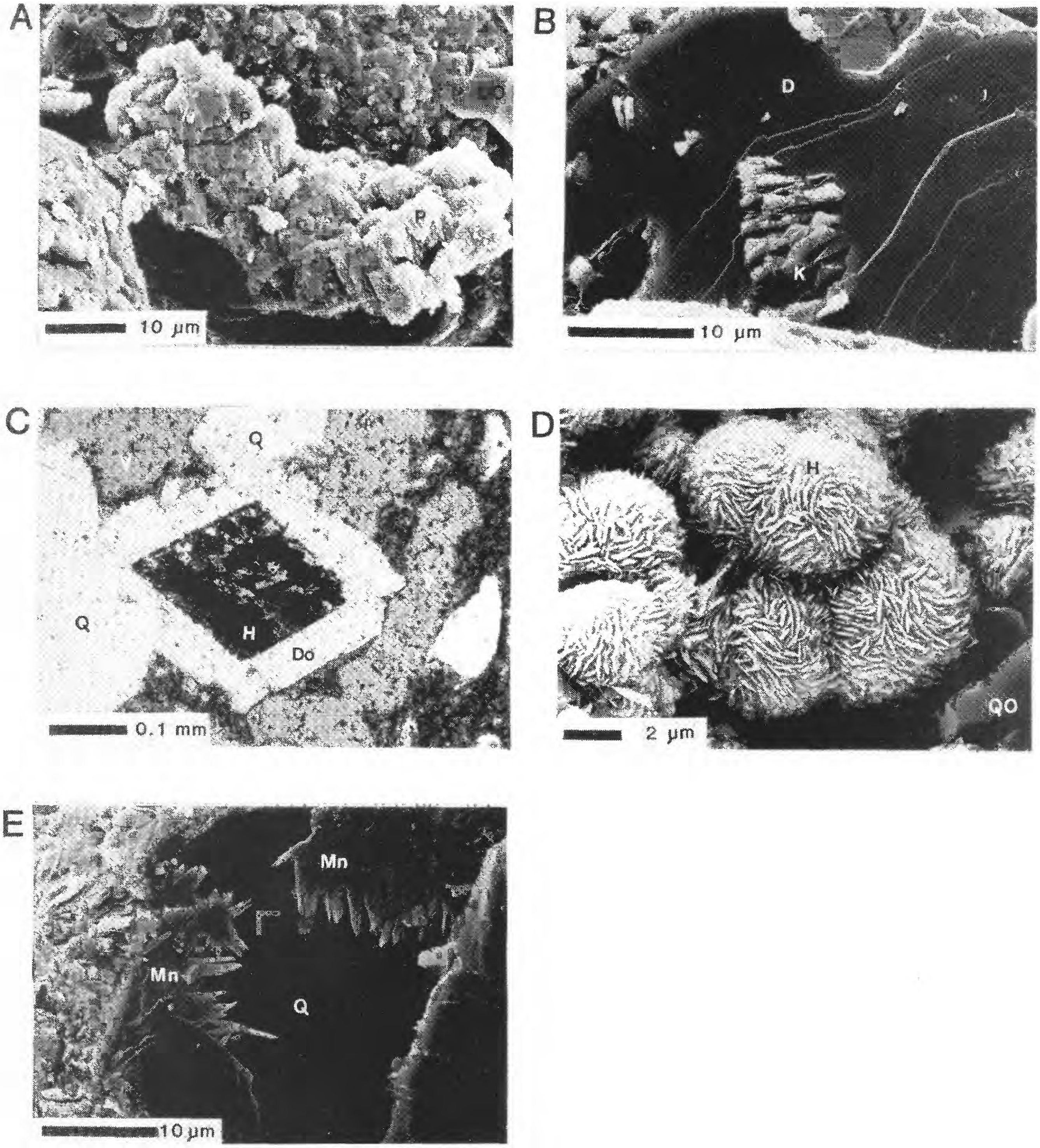
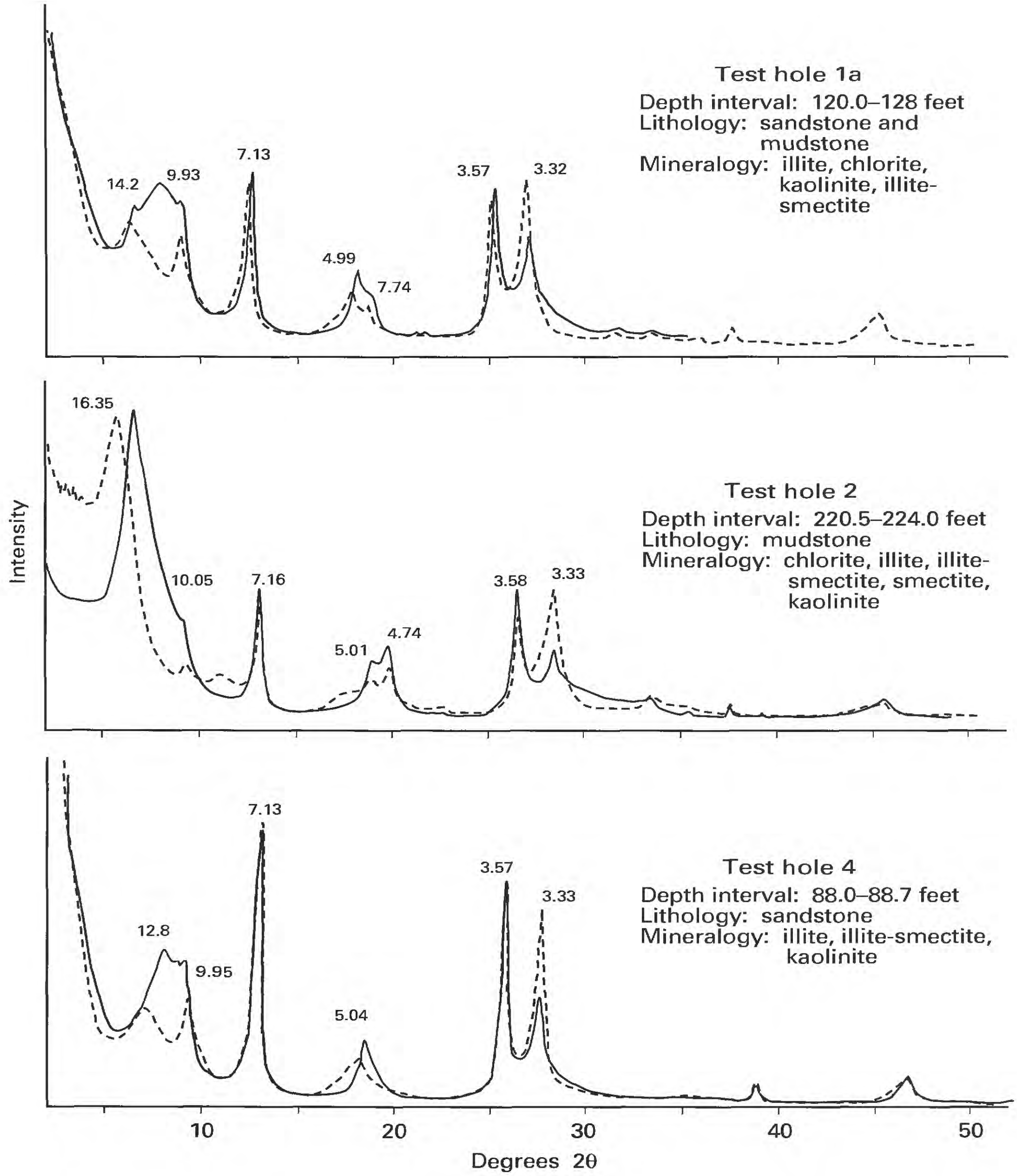


Figure 4. Examples of authigenic and altered detrital minerals detected during microscopic examination of Permian rocks from the Central Oklahoma aquifer. *A*, scanning electron micrograph of partly dissolved plagioclase (P) grain, note incipient quartz overgrowths (QO); *B*, scanning electron micrograph of kaolinite (K) within sparry dolomite (Do) cement; *C*, photomicrograph of hematite inclusions (H) within dolomite (Do), note rhombohedral outline of the inclusions (Q, quartz; V, voids); *D*, scanning electron micrograph of rosettes of hematite (H) on the surface of a quartz grain; *E*, scanning electron micrograph of manganese oxygen (Mn) that has grown within a fractured quartz grain (Q).



EXPLANATION

———— X-ray diffraction pattern after the sample was air dried

- - - - - - - X-ray diffraction pattern after the sample was treated with ethylene glycol

9.95 "d" spacing in angstroms of glycol-treated samples

Figure 5. X-ray diffraction patterns of oriented mounts of less than 2-micrometer fractions from three samples that represent the range of clay minerals detected in the Central Oklahoma aquifer. Diffractograms are plotted as degrees 2θ versus peak intensity and were obtained using CuKα radiation.

clay matrix but could not be consistently distinguished from other clay minerals. Microscopic examination revealed that the larger fragments of biotite are typically green to brown and, in red rocks, are coated with thick iron-oxide rims. Muscovite has been altered locally to kaolinite or possibly vermiculite. This alteration is most common in sandstone that lacks feldspar.

Authigenic Minerals

Dolomite, quartz overgrowths, calcite, hematite, goethite, kaolinite, manganese oxides, and barite formed within the aquifer after deposition of the host sediment. These common authigenic minerals form pore-filling cements, coatings on detrital grains, and locally replace detrital grains. Rare authigenic minerals that contain large concentrations of selenium, uranium, and vanadium are also disseminated in the aquifer within small black lenses and spherical patches.

Sparry dolomite is the most abundant authigenic mineral in the aquifer. It is present as pore-filling cement, isolated rhombs within mudstone, and replacement of micritic dolomite nodules and clasts. Manganese concentrations in sparry dolomite were determined by wet chemical analysis to be near 1 weight percent. Irregular, discontinuous patches of optically continuous pore-filling dolomite cement and etch pits on dolomite surfaces are attributed to dissolution. The age of dolomite rhombohedra in the mudstone is uncertain, but its inclusion within the boundaries of mudstone clasts suggests it formed prior to the rip-up clast. Recrystallization of micritic nodules and clasts to sparry dolomite varies from complete replacement to sparse, thin veinlets. Micritic dolomite cement is most abundant in argillaceous samples.

The spatial associations of sparry dolomite with other authigenic minerals are variable. Hematite commonly coats detrital grains cemented by dolomite. A few quartz grains have overgrowths beneath the dolomite cement. Inclusions within the dolomite include hematite, goethite, kaolinite (fig. 4*B*), and rare vanadium oxide. In several samples from the Chase, Council Grove, and Admire Groups, hematite inclusions within dolomite define a pseudorhombic outline that is interpreted to be psuedomorphic after a ferroan carbonate (fig. 4*C*).

Syntaxial quartz overgrowths are common in Central Oklahoma aquifer sandstone that lacks clay matrix. The overgrowths are responsible for the angular appearance of many quartz grains. In most samples, the overgrowths are small and can be resolved only with the SEM. Larger overgrowths are sparse and typically less than 10 µm thick. The outer surfaces of all quartz overgrowths are smooth. The larger overgrowths commonly contain inclusions of hematite and goethite. Calcite or kaolinite are common on the outer overgrowth surfaces.

Calcite is a minor to trace cement in sandstone and a trace cement in mudstone. Calcite cement in sandstone is sparry and forms optically continuous patches with circular cross section that cement as many as 50 contiguous grains. Inclusions of kaolinite and iron oxide are common within calcite. Surfaces of calcite cement are pitted and irregular in samples from shallow parts of the aquifer.

Hematite is responsible for the red color of rocks within the aquifer. Variations in rock color are attributed mainly to differences in hematite abundance, particle size, and clustering of hematite grains (Walker, Larson, and Hoblitt, 1981; Torrent and Schwertmann, 1987). Hematite in the aquifer is locally concentrated in Liesegang bands within sandstone, accumulations near burrows and root traces, and disseminated, pore-filling patches that are a few millimeters in diameter. The morphology of authigenic hematite ranges from ultrafine pigment (grains less than 0.2 µm) and microcrystalline grains to specular hematite. The red color of many rocks in the aquifer is attributed to ultrafine hematite, which could not be resolved with techniques used in this study. This pigmentary hematite is intermixed with clay minerals and is a coating on detrital grains. Microcrystalline grains typically are "buttons" up to 5 µm in diameter that have red internal reflections when illuminated by oblique light. This form of hematite is dispersed in voids, coats detrital grains (fig. 4*D*), and is included under quartz overgrowths and within dolomite. Authigenic specular hematite was identified by its silver-gray color in reflected light. It is concentrated along the rims of burrows, in rare cubic psuedomorphs of pyrite, as laterally extensive pore-filling cements, and as spheres as large as 20 µm that resemble micro-ooids. Hematite inclusions are common beneath quartz overgrowths, within barite roses or sparry dolomite cement, and around quartz grains that are cemented with calcite or dolomite.

Yellow-brown iron oxides in the aquifer include goethite and less crystalline phases. These oxides form massive coatings on detrital grains and mudstone clasts, fibrous overgrowths on hematite, and ultrafine pigment. Yellow-brown iron-oxides coat kaolinite, hematite, quartz overgrowths, and rarely dolomite. In a few samples, fibrous yellow-brown iron-oxide overgrowths on hematite were detected within sparry dolomite cement or beneath quartz overgrowths. The energy-dispersive spectrometer on the SEM detected large concentrations of arsenic in some yellow-brown iron oxides.

Kaolinite is a minor constituent that forms vermicular books as large as 60 µm and random, finer grained aggregates that fill voids. Kaolinite inclusions were seen in sparry calcite and less commonly in dolomite cement. Kaolinite is absent within partially dissolved framework grains, although grains composed entirely of kaolinite have boundaries similar to those of detrital grains. Large kaolinite books between detrital grains are deformed, apparently because of compaction. Within some siltstone laminae, interstitial kaolinite is locally abundant to the exclusion of more common interstitial clay minerals such as illite and chlorite.

Manganese oxides, mainly as dendrites, were visible in all test-hole cores. Microscopically, these oxides are massive, pore-filling cement and porous boxwork pore fillings. The massive cement penetrates quartz grains along fractures (fig. 4*E*) and replaces detrital grains. The boxwork structures have a rhombohedral habit, suggesting that it formed as dolomite dissolved. Manganese oxides coat dolomite, but no other contact relations with other authigenic minerals were seen. Romanechite ($BaMn_8O_{16}(OH)_4$) and todorokite ($(Mn,Ca,Mg)Mn_3O{\bullet}7H_2O$) were detected by XRD in an outcrop sample of a manganese-oxide-cemented siltstone.

Barite is a trace constituent of aquifer sandstone. Although barite roses locally are concentrated in layers within the aquifer (Ham and Merritt, 1944), only one rose was detected in the test-hole cores. A few samples contain small prisms of barite within interstitial pores; locally, these prisms are sufficiently large to cement a few grains. The prisms are typically embayed or segmented. Contacts of barite and other authigenic phases are sparse. Two barite roses obtained from an outcrop of the Garber Sandstone contain inclusions of hematite but lack other authigenic minerals.

Sandstone porosity within the Central Oklahoma aquifer is variable and in some samples exceeds 40 volume percent as determined by point-count analysis (Appendix 2). Many voids have rims of clay and iron oxide that resemble the outlines of detrital grains. Apparently, porosity in this sandstone is the result of primary void space and dissolution of cement and detrital grains. Samples with large amounts of porosity (greater than 16 volume percent) have consistently less clay matrix, hematite, potassium feldspar, calcite, and dolomite than those of lesser porosity.

The small (less than 1 cm in maximum dimension) black zones enriched in selenium, uranium, and vanadium are contained within green argillaceous fine-grained sandstone, mudstone, or conglomerate. Only a few percent of each core is green, and a small portion of the green rock contains the black trace-metal accumulations. The relative absence of ferric oxides and the low oxidation state of metals enriched in the black spots imply that the spots were sites of chemical reduction and, hence, are referred to as reduction zones. Similar features occur in Permian rocks elsewhere in Oklahoma (Wu, 1971; Curiale and others, 1983).

The minerals in the reduction zones in the aquifer are very fine grained and were identified by XRD on grain separates and EDS analyses on the SEM. Identified phases include clausthalite (PbSe), haggite ($V_2O_3(OH)_3$), as well as U-Ti, Cu-Se-S, and U-Si phases. Native selenium (Se), metatyuyamunite ($Ca(UO_2)_2(VO_4)_2{\cdot}H_2O$), and volborthite ($Cu_3(VO_4)_2{\cdot}3H_2O$) are found near or around the black cores of the reduction zones. The sequence of mineral precipitation is poorly defined. Clausthalite and other selenides are typically surrounded by vanadium oxides. Haggite formed after, and with quartz overgrowths, and was locally intergrown with vermicular kaolinite and dolomite. Metatyuyamunite, volborthite, and native selenium were the last-formed phases. Rare grains of pyrite that are typically less than a few micrometers wide were detected in one reduction zone and in two hematitic samples. Pyrite in the hematitic samples is pitted and rimmed by yellow-brown iron oxides.

DIAGENESIS OF PERMIAN ROCKS IN THE AQUIFER

Detrital minerals and rock fragments in Permian rocks of the Central Oklahoma aquifer are consistent with a source unit dominated by shale, sandstone, and chert. Reactions of these solids with surface and pore water altered some detrital phases and precipitated authigenic minerals. Considering the geologic history of the aquifer rocks and the petrographic data for individual minerals as summarized in table 4, the alteration reactions are divided among three sequential episodes—deposition, burial, and exposure.

Deposition

During deposition of the Permian-age sediment, surface and pore water was mainly dilute freshwater, with a component of seawater that increased westward

Table 4. Summary of evidence for mineral alteration within Permian rocks in the Central Oklahoma aquifer

Mineral	Sediment deposition	Burial	Exposure
Dolomite	**Precipitation:** micritic cement; sparry dolomite in mudstone clasts	**Precipitation:** sparry dolomite cement; $\delta^{18}O$ consistent with seawater	**Dissolution:** pitted surfaces; voids within sparry crystals
Calcite	**Precipitation(?):** probably the original mineral in pedogenic nodules	**Dolomitization:** absence of early-formed calcite	**Precipitation:** after quartz overgrowths, $\delta^{18}O$ consistent with meteoric water **Dissolution:** in shallow aquifer—voids within sparry cement, etch pits
Hematite	**Precipitation:** around burrows, oxidation of ferroan carbonates, oxidation of pyrite(?)	**Precipitation:** continued oxidation of ferroan silicates (biotite)	**Unknown**
Manganese oxides	**Unknown:** probably formed by oxidation during pedogenesis	**Dissolution(?):** high manganese content of dolomite indicates reduction of manganese in oxides	**Precipitation:** cement of quartz grains, boxwork after dolomite
Goethite	**Precipitation:** preserved in sparry dolomite cement and under quartz overgrowths, precipitated during pedogenesis?	**Recrystallization:** altered to hematite?	**Precipitation(?):** overgrowths on hematite, lining of voids that lack other cements; in outcrop, it is abundant near fractures
Kaolinite	**Precipitation:** discrete laminae in siltstone, inclusions in dolomite	**Unknown**	**Precipitation:** pore-filling clay on quartz overgrowths near dissolved feldspar
Quartz overgrowth	**Unknown**	**Precipitation:** absence of overgrowths in dolomite-cemented rocks, inclusions of iron oxide, common beneath calcite cement	**Precipitation:** likely sink of silica released from dissolved framework silicates
Chert	**Detrital phase**	**Unknown**	**Dissolution:** voids with remnant texture that are surrounded by quartz rims, not compacted or filled by other minerals
Barite	**Unknown**	**Precipitation:** replacement of gypsum; formed after hematite; $\delta^{34}S$ values are consistent with Permian seawater	**Dissolution(?):** scattered prismatic crystals in pores are irregular and embayed
Feldspar	**Dissolution:** partially dissolved grains within dolomite cement	**Unknown**	**Dissolution:** skeletal grains within voids that are not compacted, or cemented

across the study unit. Highlands to the southeast provided the dilute surface- and ground-water recharge. Reactions between the solids and freshwater dissolved framework grains formed an early generation of kaolinite and smectite-rich interlayered clay. Seawater from the epeiric sea to the west and north may have flooded parts of the depositional surface when sea level rose. Evidence of these incursions is limited to the dolomite rhombs in mudstone.

Carbonate nodules, color mottling due to iron oxides, slickensides, and destruction of depositional fabrics in fine-grained rocks are products of Permian pedogenesis. Nodules similar to those in the study unit are described in Permian mudstones elsewhere in the Midcontinent (Joeckel, 1991). Joeckel (1991) proposed that the carbonate nodules formed during slow sediment deposition and extended subaerial exposure, under the influence of a generally dry climate that included wet episodes. The dry climate is consistent with bedded Permian evaporite deposits that were deposited west of the study unit in the Anadarko Basin (Jordan and Vosburg, 1963).

The evidence of generally dry conditions is contrasted with the irregular distribution of hematite and kaolinite within the aquifer. The varying abundance of these minerals is consistent with intermittent wet conditions that enhanced chemical weathering in some intervals. Increased amounts of freshwater recharge favored release and redistribution of aluminum, silicon, and iron from framework grains (Walker, Larson, and Hoblitt, 1981; Pye, 1983). However, the variable grain size, concentration, and morphology of hematite indicate a complex history of reddening, which began during Permian soil formation but continued until deep burial limited the supply of oxidants to form ferric iron.

Kaolinite in thin layers and within some pores formed during or soon after sediment deposition. Similar early-formed kaolinite has been described in rocks west and north of the study unit (Cox, 1978; Al Shaieb and others, 1980). Kaolinite typically forms by reaction of unstable aluminosilicates with relatively dilute or low pH water (Tardy, 1982; Arditto, 1983; Kantorowicz, 1984). In the aquifer, partially dissolved feldspar grains within dolomite cement are consistent with an early dissolution of framework grains that could have been sources of aluminum and silicon. The virtual absence of kaolinite in the Hennessey Group samples indicates this unit was deposited in an environment with a greater marine influence or a drier climate.

The abundance of smectite interlayers in illite-smectite is greatest in mudstone from the oldest rocks in the aquifer. This distribution is not matched by a similar change in other detrital constituents and is, therefore, attributed to a change in weathering/alteration conditions. The smectite layers could have formed by weathering of detrital clay and mica in soil zones. A shift to drier conditions (Ziegler, 1990) during deposition of younger Permian sediment slowed this process, leaving the detrital clay assemblage less altered. The abundance of interlayer smectite in the aquifer is an important control on ion-exchange processes that affect the relative abundance of dissolved calcium, magnesium, and sodium in ground water (Parkhurst, Christenson, and Breit, 1993).

During shallow burial, local, chemically reducing pore water altered the distribution of ferric oxides. The disseminated pyrite, reduction zones, and inferred ferroan carbonates were stable under conditions where ferric iron would be reduced and dissolve. The low redox potential may have been favored by the presence of local accumulations of organic matter. Remnants of carbonaceous plant debris are rare in the aquifer, but episodes of high productivity are preserved in carbonaceous layers 25 mi north of the study unit (Tasch, 1964; Shelton, 1979). Remnants of pyrite and ferroan carbonates found in hematitic rocks imply that rocks with reducing (low Eh) pore water were more extensive than the present distribution of green rocks and reduced zones indicate. The pervasive red color of the aquifer resulted in part from periods of extended oxidation that destroyed organic matter and minerals that were stable in reducing environments.

Burial

Burial diagenesis began within a few tens of feet of the depositional surface and continued until erosion re-exposed the aquifer to meteoric water recharge. This episode was marked by precipitation of dolomite cement, quartz overgrowths, barite, and some hematite, and the accumulation of selenium, uranium, and vanadium, in the remaining zones of low Eh. Rocks in the aquifer were buried to a maximum depth of only 2,000 to 2,500 ft, so many of the diagenetic changes ascribed to deeper burial in siliclastic sequences are absent. During burial, chemically evolved seawater, which formed by evaporation, dominated pore-water compositions. Saline solutions beneath the aquifer may be remnants of this pore water (Parkhurst, Christenson, and Breit, 1993). Saline water moved into the sediment with fluctuations in sea level, or as a result of compaction of more deeply buried equivalent units in the Anadarko Basin.

Oxygen and carbon isotope data are consistent with dolomite formation through reaction of seawater with preexisting carbonates. The $\delta^{18}O$ of the water in equilibrium with dolomite was estimated using the fractionation factor of Northrop and Clayton (1966). Temperatures used in the calculation range from 15 to 40 °C; the range likely to include the temperatures from sediment deposition to maximum burial. The calculated $\delta^{18}O_{SMOW}$ of the equilibrium water ranges between 0 and +8 per mil. Values near 0 per mil are consistent with seawater; larger values suggest a water modified by evaporation. Knauth and Roberts (1991) measured a similar range of $\delta^{18}O$ values for seawater trapped within inclusions in Permian evaporite deposits of the Palo Duro Basin, Texas (O to +6 per mil).

The similar $\delta^{18}O_{SMOW}$ compositions of dolomite nodules and sparry cement (fig. 6) indicate that both formed by reaction with seawater. Coupled with the different paragenetic age relations of the two forms of dolomite, the isotopic data imply that the nodules were dolomitized after they formed in the soil zones. The distribution of dolostone nodules indicates that dolomitization of early carbonates was pervasive in the aquifer.

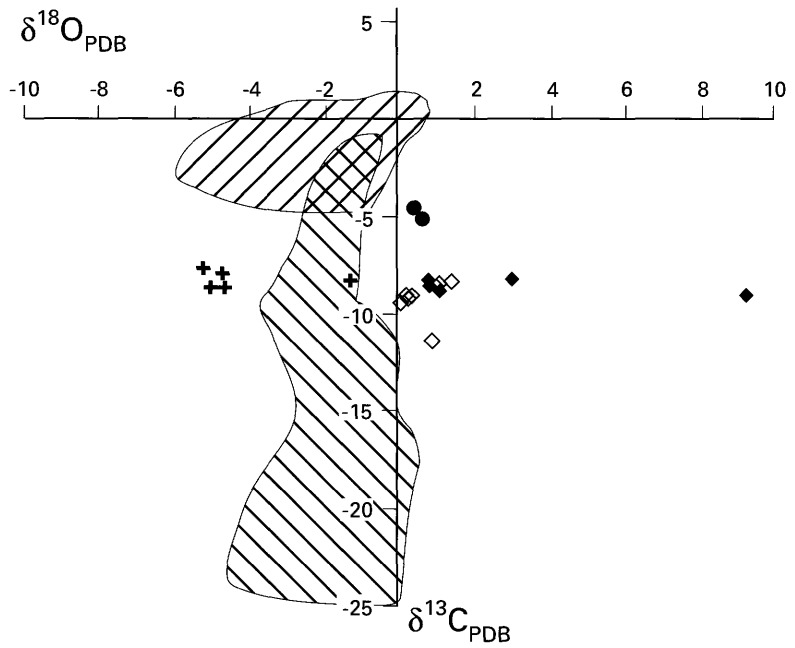
Carbon in the dolomite may have been inherited from preexisting carbonates or accumulated from carbon species dissolved in pore water. The $\delta^{13}C_{PDB}$ values (table 2; fig. 6) are distinctly more negative than the range predicted for marine inorganic carbon (-4 to +4 per mil; Hudson, 1977). The isotopically light carbon may have been inherited from preexisting pedogenic carbonates or been supplied by migrating hydrocarbons. Talma and Netterberg (1983) report $\delta^{13}C_{PDB}$ values for modern and submodern calcretes to range from +4 to -12 per mil. This range includes most of the dolomite samples from the aquifer. The $\delta^{13}C_{PDB}$ values that are less than -5 per mil are attributed to carbon that was produced by respiration of organic matter in the Permian soil zones. The mass of these early-formed carbonates in the aquifer could have dominated the carbon reservoir during dolomitization; therefore, the $\delta^{13}C_{PDB}$ value of preexisting carbonates was retained.

The effect of hydrocarbon migration on $\delta^{13}C_{PDB}$ of carbonates within Permian rocks of Oklahoma has been described by Donovan, Friedman, and Gleason (1974) and Lilburn and Al-Shaieb (1984). In contrast to results of these studies, dolomite samples in the aquifer have relatively uniform $\delta^{13}C_{PDB}$ values (-8 to -10 per mil). The narrow range of $\delta^{13}C_{PDB}$ and the small amount of iron-oxide dissolution (bleaching) detected in the test-hole cores suggest that hydrocarbon migration is not responsible for the carbon isotope composition of most dolomite in the aquifer. The less negative $\delta^{13}C_{PDB}$ of dolomite (fig. 6) in the Hennessey Group is attributed to greater inputs of dissolved carbon from seawater or increased amounts of atmospheric carbon dioxide during carbonate formation.

Quartz overgrowths formed during burial on the basis of their inclusion of iron oxides and their sparse occurrence on grains cemented with dolomite. They can be explained by redistribution of silica from altering silicate minerals, migration of warmer, silica-bearing solutions from the Anadarko Basin into the cooler aquifer, or salting out of dissolved silica as pore-water salinity increased (McBride, 1989).

Barite precipitated by reaction of seawater sulfate and barium from the Permian rocks. The origin of the sulfate is supported by the sulfur isotope data. $\delta^{34}S_{CDT}$ compositions of the two barite roses collected during this investigation range from +12.8 to +16.9 per mil. A sample of barite that is interpreted to be psuedomorphic after chicken-wire gypsum in a Hennessey Group mudstone has a $\delta^{34}S_{CDT}$ of +8.0 per mil. The range of $\delta^{34}S_{CDT}$ values spans the range of Permian seawater (+9 to +13 per mil; Claypool and others, 1980) and falls within the range measured in sulfate minerals in Permian units in southern Kansas (-3 to +16 per mil; Branam and Ripley, 1990). The large range of $\delta^{34}S_{CDT}$ values measured by Branam and Ripley (1990) is attributed to isotopic fractionation of Permian seawater sulfate during diagenesis. Similar fractionation processes probably affected dissolved sulfate within the aquifer and resulted in the heavier $\delta^{34}S_{CDT}$ than predicted for Permian seawater. Probable barium sources include feldspar and clay minerals in the Permian rocks.

During burial, selenium, uranium, and vanadium may have been transported by pore water to sites of accumulation in the reduction zones. Reduction of the dissolved forms of the metals to less-soluble oxidation states was affected by conditions that favored the formation of pyrite and ferroan carbonates elsewhere in the aquifer. Organic matter and microbial activity have been proposed to explain reduction zones in other rock units (Hofmann, 1991). Mosier and others (1991)



EXPLANATION

Samples from the Central Oklahoma aquifer (values are listed in table 2)

+	Calcite cement
◇	Sparry dolomite cement
◆	Miciritic dolomite in nodules, clasts, and cement
●	Dolomite in the Hennessey Group

Carbon and oxygen isotope values from similar rocks

▨	Pedogenic carbonates in Permian rocks in southeastern Nebraska (Joeckel, 1991)
▧	Carbonate minerals from the Wellington Formation and Garber Sandstone, near the Cement-Chickasha oil field, Caddo and Grady Counties, Oklahoma (Lilburn and Al-Shaieb, 1984)

Figure 6. Oxygen isotope composition relative to Peedee belemnite ($\delta^{18}O_{PDB}$) versus carbon isotope composition relative to Peedee belemnite ($\delta^{13}C_{PDB}$) for calcite and dolomite in the Central Oklahoma aquifer. Values for carbonate in equivalent Permian unit from elsewhere in Oklahoma and southeastern Nebraska are plotted for comparison.

determined that significant amounts of selenium, uranium, and vanadium are readily dissolved from "barren rocks" in the Central Oklahoma aquifer by treatment with weak reactants, such as solutions of 0.1-mol KH_2PO_4 or $NaHCO_3$. Changes in pore-water composition during burial may have similarly favored redistribution of selenium, uranium, and vanadium dispersed in the sediment to form the accumulations.

Exposure

During the Tertiary and Quaternary, rocks within the study unit were successively eroded, overlain by 300 to 1,000 ft of late Tertiary sediment, and subsequently re-exposed and eroded to produce the modern surface configuration. Meteoric water, supplied largely by direct precipitation, became the principal source of aquifer recharge. This freshwater dilutes and displaces saline pore water and reacts with solid phases (Parkhurst, Christenson, and Breit, 1993).

Calcite is considered a product of reaction between solids in the aquifer and meteoric recharge. The $\delta^{18}O_{SMOW}$ of water that formed most calcite is calculated to range between -5 and -1 per mil using the fractionation factor of O'Neil, Clayton, and Mayeda (1969). This range is much lower than water that formed the dolomite, 0 to +8 per mil, but is greater than present ground water, which ranges between -5 and -7 per mil (Parkhurst, Christenson, and Breit, 1993). The water that formed the calcite could have been a mixture of isotopically heavy brines with modern meteoric water, or the calcite may have formed from a meteoric water different from that currently in the aquifer. The isotopically distinct meteoric water may have been recharge that entered the aquifer during the early Tertiary when it was exposed by erosion. On the basis of their $\delta^{13}C_{PDB}$ values, both dolomite (table 2; fig. 6) and modern ground water ($\delta^{13}C_{PDB}$ = -7.7 to -20.2 per mil; Ferree and others, 1992) could be sources of the carbon in calcite.

Textural data suggest that dolomite, calcite, feldspar, chert, and possibly chlorite are dissolving by reaction with modern recharge water. Dissolution of these minerals is consistent with the chemical composition of modern ground water (Parkhurst, Christenson, and Breit, 1993). As detrital grains dissolve, aluminum and some silica recombine to form kaolinite, excess silica is precipitated as quartz overgrowths, and iron forms iron oxides. Among the test holes, the effects of dissolution are greatest in test hole 4. Although the smaller amounts of plagioclase and chlorite in test hole 4 could be attributed to provenance, no other minerals vary in abundance to support a change in the sediment source unit. Mineral dissolution may have been more intense in the unit of test hole 4 as a result of preferential flow of dilute meteoric water during the Permian. However, the absence of dolomite in this test hole favors recent dissolution because dolomite is considered a product of the pervasive incursion of seawater during burial. Hydrologic modeling of the aquifer indicates that test hole 4 is near a major recharge unit (Parkhurst, Christenson, and Breit, 1993), which is consistent with recent dissolution of the depleted minerals.

The capability of modern recharge to favor oxidation reactions is supported by the concentrations of dissolved oxygen in ground water (Parkhurst, Christenson, and Breit, 1993). Dissolved oxidants react with reduced forms of manganese, iron, and other elements to form in-place accumulations of manganese oxide, goethite, and the rare secondary selenium, uranium, and vanadium minerals. Manganese oxides are locally common and are explained most simply by the oxidation of manganese released as dolomite dissolved. Iron in goethite may have originated in nearby iron-rich silicates, such as biotite. The great abundance of goethite in yellow-brown sandstone suggests that these rocks originally contained a great abundance of ferrous iron. However, no local accumulations of ferrous iron-rich minerals have been recognized. An explanation offered to explain yellow-brown and bleached rocks elsewhere in Oklahoma is the migration of oil-field brines or petroleum (Donovan, 1974; Ferguson, 1975). These solutions could have reduced ferric oxides to form ferrous iron minerals that were subsequently re-oxidized by modern meteoric water. Alteration by hydrocarbon-bearing solutions is consistent with the abundance of yellow-brown iron oxides along small fractures that are visible in some outcrops.

SUMMARY

Changes to the solid constituents of the Central Oklahoma aquifer are the result of complex processes that began during sediment deposition and continue with the circulation of modern dilute ground water. Detrital framework grains were dissolved or altered, and authigenic minerals were precipitated and dissolved in response to changes in the composition of the pore water. These changes were products of climate and sea-level fluctuations during deposition, migration of evolved seawater during burial, and the flow of modern dilute water. Reactions between solids and dilute ground water that affect the composition of modern ground water include: dissolution of feldspar, chert, dolomite, chlorite, and calcite; ion exchange with clay minerals; oxidation of minerals with great abundances of selenium, uranium, and vanadium; and precipitation of kaolinite, quartz, goethite, and manganese oxides.

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APPENDICES

Appendix 1. Statistical summary of the mineralogical composition of the test-hole cores as determined by whole-rock X-ray diffraction

[Values were calculated for results normalized to totals of 100 percent. %, percent; <, less than the value that follows; n, number of samples; Std. Dev., standard deviation; --, data insufficient for calculation; *, abundance of kaolinite could not be determined because of interference with chlorite]

Test Hole 1a—Garber Sandstone
Location: Latitude 35°51'18"; Longitude 97°25'00"
Lithologies: Sandstone 67%, Mudstone 33%

(n= 26)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	61	21	92	56	22
Plagioclase	2	<1	8	2	2
Illite	20	2	71	29	23
Hematite	4	1	12	4	3
Dolomite	2	<.5	38	4	7
Calcite	<.5	<.5	1	--	--
Kaolinite	5	2	8	5	2

Test Hole 2—Chase, Council Grove and Admire Groups
Location: Latitude 35°44'18"; Longitude 97°01'35"
Lithologies: Sandstone 45%, Mudstone 45%, Siltstone 5%, Conglomerate 5%

(n= 21)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	39	26	83	46	20
Plagioclase	2	<1	10	2	3
Illite	41	4	61	37	21
Hematite	6	<1	9	5	3
Dolomite	1	<.5	30	3	7
Calcite	<.5	<.5	<.5	--	--
Kaolinite	6	4	10	7	2

Test Hole 3—Garber Sandstone
Location: Latitude 35°40'12"; Longitude 97°23'10"
Lithologies: Sandstone 52%; Mudstone 33%, Siltstone 10%, Conglomerate 5%

(n= 22)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	52	21	99	56	29
Plagioclase	2	<1	7	2	2
Illite	35	<1	72	32	27
Hematite	1	<1	3	1	1
Dolomite	4	<0.5	56	7	12
Calcite	<0.5	<0.5	1	--	--
Kaolinite	3	1	7	3	1

Appendix 1. Statistical summary of the mineralogical composition of the test-hole cores as determined by whole-rock X-ray diffraction—Continued

Test Hole 4—Garber Sandstone and Wellington Formation
Location: Latitude 35°21'42"; Longitude 97°10'35"
Sandstone 60%, Mudstone 36%, Siltstone 4%

(n= 25)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	68	21	99	63	26
Plagioclase	<1	<1	<1	--	--
Illite	18	<1	67	27	24
Hematite	4	<1	35	6	7
Dolomite	<.5	<.5	<.5	--	--
Calcite	<.5	<.5	.5	--	--
Kaolinite	4	1	7	4	2

Test Hole 5—Chase, Council Grove, and Admire Groups
Location: Latitude 35°11'42"; Longitude 96°58'01"
Lithologies: Sandstone 57%, Mudstone 38%, Siltstone 5%

(n= 21)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	40	18	84	47	25
Plagioclase	2	<1	11	2	3
Illite	46	<1	71	40	23
Hematite	6	<1	11	5	4
Dolomite	1	<.5	11	2	2
Calcite	<.5	<.5	<.5	--	--
Kaolinite	4	2	7	4	1

Test Hole 6—Garber Sandstone
Location: Latitude 35°42'08"; Longitude 97°33'02"
Lithologies: Sandstone 71%, Mudstone 18%, Conglomerate 8%, Siltstone 3%

(n= 36)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	78	24	99	70	23
Plagioclase	2	<1	8	2	2
Illite	12	<1	71	18	20
Hematite	2	<1	29	3	5
Dolomite	1	<.5	21	3	5
Calcite	<.5	<.5	13	--	--
Kaolinite	2	<1	6	3	2

Appendix 1. Statistical summary of the mineralogical composition of the test-hole cores as determined by whole-rock X-ray diffraction—Continued

Test Hole 7—Hennessey Group
Location: Latitude 35°13'15"; Longitude 97°25'43"
Lithologies: Sandstone 25%, Mudstone 50%, Siltstone 19%, Conglomerate 6%

(n= 16)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	40	21	64	42	14
Plagioclase	5	<1	9	5	2
Illite	42	17	73	42	17
Hematite	2	1	5	2	1
Dolomite	5	7	36	7	8
Calcite	<.5	<.5	<.5	--	--
Kaolinite*	--	--	--	--	--

Test Hole 7a—Garber Sandstone
Location: Latitude 35°13'15"; Longitude 97°25'42"
Sandstone 76%, Mudstone 14%, Siltstone 7%, Conglomerate 3%

(n= 29)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	70	28	98	67	19
Plagioclase	2	<1	8	2	2
Illite	19	<1	66	23	19
Hematite	3	<1	8	3	2
Dolomite	1	<.5	12	2	3
Calcite	<.5	<.5	4	0.3	1
Kaolinite	2	1	5	2	1

Appendix 2. Summary statistics of point-count results on sandstone collected from test-hole cores

[<, abundance is less than the value that follows; n, number of samples; --, data insufficient for calculation; Std. Dev., standard deviation; Poly-quartz, polycrystalline quartz rock fragments; Rock fragments, other than polycrystalline quartz]

Test Hole 1a—Garber Sandstone
Location: Latitude 35°51'18"; Longitude 97°25'00"

(n=17)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	35	35	56	47	7
Plagioclase	1	<.5	2	--	--
K-feldspar	<.5	<.5	1	--	--
Clay matrix	13	1	38	15	11
Poly-quartz	2	<.5	10	5	3
Rock fragments	1	<.5	4	1	1
Sparry dolomite	<.5	<.5	16	--	--
Calcite	<.5	<.5	2	--	--
Kaolinite	1	<.5	2	1	1
Hematite	5	<.5	27	7	8
Voids	20	5	35	21	9

Test Hole 2—Chase, Council Grove, and Admire Groups
Location: Latitude 35°44'18"; Longitude 97°01'35"

(n=12)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	45	29	60	44	8
Plagioclase	1	<.5	4	1	1
K-feldspar	<.5	<.5	<.5	--	--
Clay matrix	29	3	60	27	19
Poly-quartz	4	1	11	5	3
Rock fragments	1	<.5	3	1	1
Sparry dolomite	<.5	<.5	5	1	2
Calcite	0	<.5	1	--	--
Kaolinite	<.5	<.5	1	--	--
Hematite	5	<.5	17	5	5
Voids	14	<.5	33	15	12

Test Hole 3—Garber Sandstone
Location: Latitude 35°40'12"; Longitude 97°23'10"

(n=12)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	48	27	61	46	8
Plagioclase	<.5	<.5	2	1	1
K-feldspar	<	<.5	2	--	--
Clay matrix	8	.5	34	11	10
Poly-quartz	6	1	13	7	3
Rock fragments	2	<.5	14	2	3
Sparry dolomite	<.5	<.5	27	--	--
Calcite	<.5	<.5	7	--	--
Kaolinite	<.5	<.5	3	--	--
Hematite	2	<.5	45	8	13
Voids	20	2	37	20	12

Appendix 2. Summary statistics of point-count results on sandstone collected from test-hole cores—Continued

Test Hole 4—Garber Sandstone and Wellington Formation
Location: Latitude 35°21'42"; Longitude 97°10'35"

(n=22)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	52	41	59	51	5
Plagioclase	1	<.5	2	1	1
K-feldspar	1	<.5	3	1	1
Clay matrix	15	1	33	15	11
Poly-Quartz	6	<.5	16	6	3
Rock fragments	1	<.5	3	1	1
Sparry dolomite	<.5	<.5	2	--	--
Calcite	<.5	<.5	2	--	--
Kaolinite	<.5	<.5	4	--	--
Hematite	3	<.5	17	4	5
Voids	21	2	38	21	10

Test Hole 5—Chase, Council Grove and Admire Groups
Location: Latitude 35°11'42"; Longitude 96°58'01"

(n=14)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	48	38	55	47	4
Plagioclase	2	1	4	2	1
K-feldspar	1	<.5	5	2	1
Clay matrix	12	2	47	18	14
Poly-quartz	6	3	12	6	3
Rock fragments	3	1	6	3	2
Sparry dolomite	<.5	<.5	14	2	4
Calcite	<.5	<.5	<.5	--	--
Kaolinite	1	<.5	3	1	1
Hematite	1	<.5	8	2	3
Voids	11	<.5	28	18	8

Test Hole 6—Garber Sandstone
Location: Latitude 35°42'08"; Longitude. 97°33'02"

(n=31)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	48	33	66	48	7
Plagioclase	1	<.5	2	1	1
K-feldspar	<.5	<.5	2	--	--
Clay matrix	4	<.5	49	7	10
Poly-quartz	5	1	10	5	2
Rock fragments	1	<.5	3	1	1
Sparry dolomite	<.5	<.5	35	--	--
Calcite	<.5	<.5	7	--	--
Kaolinite	<.5	<.5	1	--	--
Hematite	1	<.5	10	2	3
Voids	33	4	44	29	10

Appendix 2. Summary statistics of point-count results on sandstone collected from test-hole cores—Continued

Test Hole 7a—Garber Sandstone
Location: Latitude 35°13'15"; Longitude 97°25'42"

(n=13)	Median	Minimum	Maximum	Mean	Std. Dev.
Quartz	47	38	59	48	5
Plagioclase	1	<.5	2	1	1
K-feldspar	1	<.5	2	1	1
Clay matrix	16	2	38	17	11
Poly-quartz	6	2	9	5	2
Rock fragments	2	<.5	3	2	1
Sparry dolomite	<.5	<.5	28	--	--
Calcite	<.5	<.5	3	--	--
Kaolinite	<.5	<.5	1	--	--
Hematite	1	<.5	11	2	3
Voids	22	3	41	22	12

Geochemical Characterization of Solid-Phase Materials in the Central Oklahoma Aquifer

By Elwin L. Mosier

Abstract

Surficial and subsurface solid-phase materials were collected from the area overlying the Central Oklahoma aquifer to determine the abundance and distribution of chemical constituents. These geochemical studies were conducted because, in some instances, trace elements such as arsenic, chromium, selenium, and uranium are present in the ground water at concentrations that exceed public drinking-water regulations. The surficial material sampled included B-horizon soils and outcrop rocks from the Central Oklahoma aquifer study unit. Subsurface rock samples were obtained from the cores of eight test holes drilled at selected locations in the aquifer. The solid-phase samples were analyzed by an inductively coupled plasma-atomic emission spectrometric technique for 40 elements, by hydride generation-atomic absorption spectroscopy for arsenic and selenium, and by delayed neutron activation analysis for uranium and thorium.

Analytical results show that the highest concentration of most elements are in the drill-core samples and the lowest concentrations of the elements are in the outcrop samples. Comparison of geometric means for calcium and magnesium indicate that these elements have been leached from surficial materials. Factor analysis identified element associations directly related to residence sites of the elements and variations in the composition of the solid-phase materials that relate to water quality. In drill-core samples, arsenic is strongly associated with mudstone and samples with enhanced red coloration, indicating adsorption on clay minerals and iron oxides; chromium has a strong correlation with aluminum and, therefore, is strongly associated with high clay-content mudstone and siltstone; selenium and uranium, along with vanadium, are associated with white to pale-green samples that are indicative of reduction zones; uranium also is associated with high clay-content samples.

Two partial dissolution techniques were used to study partitioning of the elements among geochemical phases likely to be affected by environmental conditions. One technique, a two-step sequential procedure, was specifically designed to mimic naturally present high pH-high bicarbonate water and to assess the importance of oxidation processes. The second procedure sequentially extracted elements into five fractions (soluble, ligand-exchangeable, acid soluble, oxidizable, and residual). Appreciable amounts of arsenic, selenium, and uranium were extracted from some samples by the soluble and ligand-exchangeable extractions, indicating that significant portions of these elements reside in phases that are readily available. The extraction results did not clearly explain the sources of readily extractable chromium or the processes involved in chromium mobilization.

The analytical results and partial dissolution studies indicate that the concentration of trace elements in ground water is affected by oxidation, adsorption-desorption, and cation-exchange reactions at mineral surfaces.

INTRODUCTION

The Central Oklahoma aquifer is of great interest to water managers and to the public because it is a major source for water supplies in central Oklahoma and because it has several known and suspected water-quality problems. The U.S. Geological Survey (USGS) has completed geochemical studies of solid-phase geologic materials collected from the Central Oklahoma aquifer study unit. These solid-phase geochemical studies were done as part of the National Water-Quality Assessment (NAWQA) Program of the

USGS. The term "solid-phase" is used to differentiate between geochemical studies of solid materials and water-chemistry studies. A description of the geographic and geologic settings of the Central Oklahoma aquifer study unit and an explanation of the long-term goals of the NAWQA Program are provided by Christenson (1998).

Solid-phase geochemical studies began in the spring of 1987 with the objective of characterizing the chemical composition of solid-phase materials in the Central Oklahoma aquifer. At many locations in the aquifer, the water contains concentrations of arsenic (As), chromium (Cr), selenium (Se), and uranium (U) that exceed the Federal drinking-water regulations of 50 µg/L As, 50 µg/L Cr, 10 µg/L Se (U.S. Environmental Protection Agency, 1986), and the proposed regulation of 20 µg/L U. The trace elements are released from solid-phase materials by ground water whose chemical composition is a product of reaction with the rock and soil gases. Although much geologic information was available concerning water quality, outcropping strata, and oil-well and well-drilling data for the study unit at the beginning of this study (Mosier and Bullock, 1988; Parkhurst, Christenson, and Schlottmann, 1989), little surface and subsurface geochemical information existed. Therefore, the chemical composition of surface and subsurface geologic materials had to be determined. Knowledge and understanding of the sites and mechanisms for the mobilization of trace elements from the geologic materials into the ground-water system were gained from the results of these analyses.

To assess areal and vertical variations in the distribution and abundance of the elements, the geologic materials studied included B-horizon soils, outcrop rocks, and drill-core samples. The B horizon in a soil profile is just below the A horizon and consists of a zone of residual accumulation of clay minerals and sesquioxides characterized by a darker, stronger, or redder coloring and a blocky or prismatic structure. B-horizon soils and outcrop samples provided information on elements that may be mobilized from the near-surface oxidizing zone. Drill-core samples were analyzed to determine whether various lithologic and geochemical environments were sources of the mobilized elements.

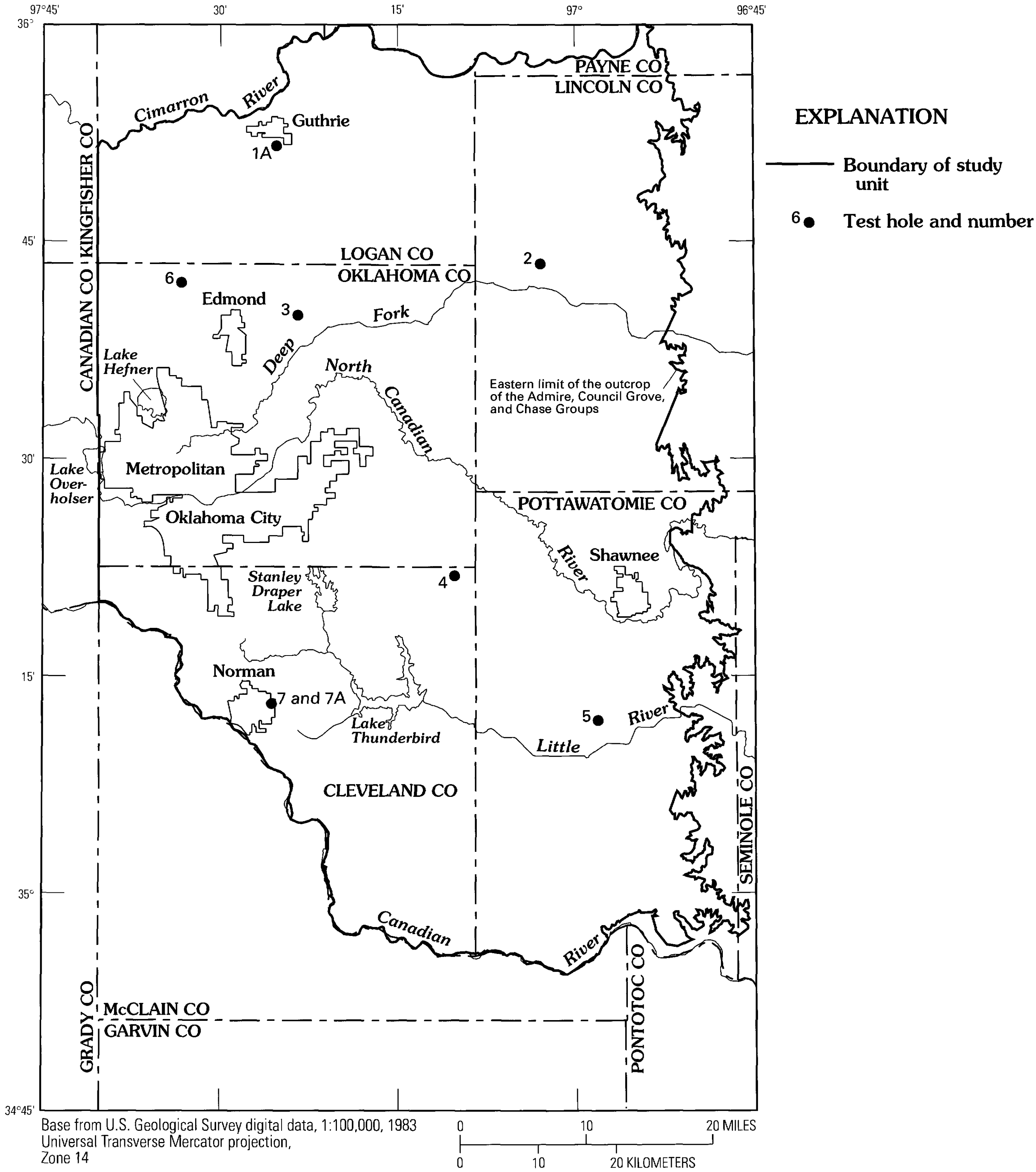
During this investigation, solid-phase geochemical data were used with data obtained from other Central Oklahoma NAWQA studies to describe the rock-water interaction and to understand the chemical composition of ground water within the aquifer (Breit and others, 1990a; Mosier and others, 1990a; Mosier and Schlottmann, 1992). This paper presents a review of the solid-phase geochemical studies.

GEOCHEMICAL STUDIES

Sample Media and Data Collection

During the reconnaissance geochemical sampling program for surficial materials, 293 B-horizon soil samples and 362 outcrop samples were collected in the area bounded by 34°45' and 36° north latitude, and 96°45' and 97°45' west longitude (fig. 1). The surficial sampling area extended beyond the Central Oklahoma aquifer boundaries as defined by Christenson (1998). B-horizon soil samples were collected from well-drained locations, usually at or near the crest of a hill. Most sample sites were near roads with light vehicular traffic to minimize contamination from vehicular emissions. Approximately three-fourths of the samples were collected from pasture or forested land, and the remainder were collected from cultivated land. Soil samples were air dried, disaggregated, and then sieved through a 10–mesh stainless-steel sieve. The less than 10–mesh fraction of the sample was pulverized to less than 150 mesh and analyzed.

Nearly all of the outcrop samples were collected from road cuts. Most outcrops in the study unit are small and fairly uniform in their lithologic makeup. For such outcrops, a composite sample of several rock chips was made. Where distinct lithologies were present, more than one sample was collected. Lithologies sampled include sandstone, mudstone, siltstone, and conglomerate. All geologic units exposed in the sampling area were sampled. These geologic units are, in ascending order, Upper Pennsylvanian rocks of the Vanoss Formation and Permian rocks of the Admire, Council Grove, and Chase Groups, Wellington Formation, Garber Sandstone, Hennessey Group, and the El Reno Group. The Vanoss Formation, which occupies the eastern one-eighth of the study unit, and the El Reno Group, which crops out in the western part and southwestern corner of the study unit, are not considered to be a part of the Central Oklahoma aquifer. Likewise, the shale and siltstone that make up the Hennessey Group in the western one-fourth of the study unit are not very transmissive and are not considered to be part of the aquifer. The Fairmont Shale, which is the basal formation of the Hennessey Group, is a confining



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 1. Location of test holes.

unit that overlies the aquifer. However, there is some leakage of water from the Hennessey Group into the aquifer, which affects the chemistry of the water in the aquifer (Parkhurst, Christenson, and Schlottmann, 1989). The outcrop samples were crushed in the laboratory and then pulverized to less than 150 mesh before analysis.

To characterize the chemical nature of subsurface solid-phase materials in the aquifer, 549 rock samples were obtained from the cores of test holes that were drilled specifically for the Central Oklahoma aquifer study. Eight test holes were drilled at seven locations (fig. 1). Seven of the test holes were drilled in areas where water wells were known to yield ground water with high concentrations of As, Cr, Se, and U. Test hole 4 was drilled in an area known to have ground water with low concentrations of As, Cr, Se, and U. Test holes 1A, 3, 4, and 6 intercept the undifferentiated Garber Sandstone and Wellington Formation. Test holes 1A, 3, and 4 were drilled to investigate As, Cr, Se, and U in the unconfined, shallow (less than 300 ft) part of the aquifer, and test hole 6 was drilled to study the elements in the unconfined deeper (greater than 300 ft) part of the aquifer. Test holes 2 and 5 are shallow and penetrate the undifferentiated Chase, Council Grove, and Admire Groups in the unconfined part of the aquifer. Test hole 7 was drilled to characterize the confining layer (Hennessey Group), and test hole 7A (drilled at the same location) was drilled to study As, Cr, Se, and U in that part of the aquifer confined by the Fairmont Shale.

The material collected from the cores was split and sampled on the basis of lithologic variations, for example, sandstone, mudstone, siltstone, and conglomerate, and on visible diagenetic variations such as color, reduction spots, degree of carbonate cement, or iron enrichment. Each sample is a composite of the depth interval sampled, and samples from each drill core are contiguous. The distribution of the lithologic units in linear feet and in percentage of total core is given in table 1. Sandstones constitutes nearly 62 percent of the material cored. Mudstone comprises about 24 percent of the core, and the remainder of the core is comprised of 2.9 percent conglomerate, 5.6 percent siltstone, and 5.9 percent mixed lithologies. Mixed lithologies identify locations in the core where distinct lithologies are too thinly interbedded to sample separately. Drill-core samples were crushed and then pulverized to less than 150 mesh prior to analysis.

Water samples also were collected from one to eight individual sandstone layers within each test hole. Chemical and isotopic analyses of the water samples

Table 1. Distribution by lithology of rock cored in test holes in the Central Oklahoma aquifer

[Values are in feet and parenthesized values are in percent]

Test hole (fig. 1)	Sandstone	Mudstone	Conglomerate	Siltstone	Mixed	Total
1A	174.9	47.7	11.6	1.5	15.4	251.1
	(69.7)	(19.0)	(4.6)	(0.6)	(6.1)	
2	140.9	104.8	3.8	10.0	2.5	262.0
	(53.8)	(40.0)	(1.5)	(3.8)	(1.0)	
3	95.6	79.4	1.8	2.8	0	179.0
	(53.2)	(44.2)	(1.0)	(1.6)	(0)	
4	191.8	67.6	0	1.5	8.9	269.8
	(71.1)	(24.5)	(0)	(0.5)	(3.2)	
5	106.0	98.3	13.0	4.2	1.5	223.0
	(47.5)	(44.1)	(5.8)	(1.9)	(0.7)	
6	367.2	85.6	22.0	24.5	14.8	514.1
	(71.4)	(16.7)	(4.3)	(4.8)	(2.9)	
7	11.8	25.1	1.6	52.7	63.4	154.6
	(7.6)	(16.2)	(1.0)	(34.1)	(41.0)	
7A	262.4	21.3	10.4	25.9	22.7	342.7
	(76.6)	(6.2)	(3.0)	(7.6)	(6.6)	
Total	1,350.6	529.8	64.2	123.1	129.2	2,196.9
	(61.5)	(24.1)	(2.9)	(5.6)	(5.9)	

collected from the test holes and the geophysical logs of the test holes have been reported by Schlottmann and Funkhouser (1991). The mineralogy and petrology of the rock cores are presented in Breit and others (1990b).

B-horizon soil, outcrop rock, and drill-core rock samples were analyzed by an inductively coupled plasma-atomic emission spectrometric (ICP–AES) technique for 40 elements (Lichte, Golightly, and Lamothe, 1987). Arsenic was determined by hydride generation-atomic absorption spectroscopy (HG–AAS) (Crock and Lichte, 1982). Selenium also was determined by HG–AAS (Briggs and Crock, 1986; Sanzolone and Chao, 1987). Uranium and thorium were measured using delayed neutron activation analysis (DNAA) (McKown and Millard, 1987). Geochemical results from the chemical analyses of B-horizon soil samples and outcrop samples and a summary of the results and sample location maps were reported by Mosier and others (1991a). Geochemical results from the analyses of drill-core samples were reported in and summarized by Mosier and others (1990b).

Data Presentation

Statistical summaries of the geochemical data from the analysis of B-horizon soil samples, outcrop samples, and drill-core samples are listed in table 2. Only those elements that were detected in a majority of the samples, indicated by the detection ratio, are listed. Shown in table 2 are the detection ratios, minimum and maximum values (concentration ranges), geometric means, geometric deviations, arithmetic means, and standard deviations for the elements for each of the three solid-phase sample media. If an element was not detected in all of the samples, Cohen's (1959) method was used to estimate the geometric mean and geometric deviation. The arithmetic means and standard deviations were calculated only on the noncensored data. In figure 2, the geometric means of concentrations for the elements listed in table 2 are displayed as ratios to show the relation of the geometric means among the three sample types.

A comparison of the geometric mean ratios for drill-core samples to outcrop samples and for drill-core samples to soil samples shows that the drill-core samples contain considerably higher concentrations of most elements than outcrop samples and slightly higher concentrations for most of the elements than soil samples. These ratios indicate that, on the average, the concentration levels of As, Cr, Se, and U are 2 to 2.4 times higher in drill-core samples than in outcrop samples. With the exception of Se, concentrations of these elements are slightly higher in drill-core samples than in soil samples. The geometric mean for Se is higher in soil samples than in drill-core samples and outcrop samples. Eighty percent of the soil samples had detectable (greater than or equal to 0.1 ppm) Se, whereas only 63 percent of the drill-core samples and 34 percent of the outcrop samples had detectable Se (table 2). Outcrop-to-soil geometric mean ratios indicate that soil samples contain higher concentrations of most of the elements than outcrop samples. As, Cr, Se, and U concentrations in outcrop samples are approximately one-half of soil-sample concentrations.

In the Paleozoic terrain of central Oklahoma, carbonate cements and nodules are the primary sources of calcium (Ca) and magnesium (Mg). The ratios for the geometric means for Ca and Mg indicate that they have been depleted or leached from the surficial materials, particularly from the soils.

In figure 3, the elemental distributions of the B-horizon soil, outcrop, and drill-core As, Cr, Se, and U data are shown by high-low plots. The maximum value, 95th percentile, geometric mean, and minimum value are shown for the four elements. Comparison of the maximum values and the 95th-percentile values shows that the highest concentrations of As, Cr, Se, and U are in the drill-core samples. Higher concentrations of these elements are often in discrete or isolated locations in the core that are associated with such lithologic features as yellowish-brown limonitic staining, clay enrichment, greenish-gray or white rocks, and reduction spots.The geochemical data indicate that the surface and near-surface sedimentary rocks have been altered by weathering processes and that a part of their elemental constituents have been leached. Some of these constituents may have been locally redeposited or adsorbed onto clay minerals, aluminum oxides, or iron oxides in the zone of accumulation or illuviation constituting the B horizon of the soil profile.

FACTOR ANALYSIS

R-mode factor analysis (VanTrump and Miesch, 1977) was used to aid in the interpretation of the geochemical data. R-mode factor analysis groups, within a data set, elements that are geochemically associated. This association is determined by evaluating the variance among the elements. Thus, the data set is

Table 2. Summary statistics for elements determined in B-horizon soils, outcrop rocks, and drill-core rocks from Central Oklahoma

[Detection ratio = number of reported values/number of samples in data set. All concentration values are in parts per million except for Al, Ca, Fe, K, Mg, Na, P, and Ti, which are in percent]

Element	Detection ratio	Minimum value	Maximum value	Geometric mean	Geometric deviation	Arithmetic mean	Standard deviation
			B-horizon soils (293 samples)				
Calcium (Ca)	1.0	0.01	9.4	0.23	2.63	0.45	0.91
Magnesium (Mg)	1.0	.02	5.3	.34	2.43	.48	.47
Sodium (Na)	1.0	.02	.99	.26	2.13	.33	.22
Potassium (K)	1.0	.10	2.4	.88	1.78	1.0	.48
Phosphorus (P)	.99	<.005	.06	.016	1.64	.018	.0087
Aluminum (Al)	1.0	.38	8.9	3.9	1.79	4.4	1.9
Arsenic (As)	1.0	.6	21	4.8	1.77	5.6	3.0
Barium (Ba)	1.0	47	6,400	300	1.88	400	590
Beryllium (Be)	.69	<1.0	3.0	1.2	1.58	1.5	.57
Cerium (Ce)	1.0	14	110	51	1.47	54	18
Chromium (Cr)	1.0	5.0	110	41	1.81	48	23
Cobalt (Co)	1.0	<1.0	27	7.8	1.79	9.0	4.7
Copper (Cu)	1.0	<2.0	59	10	1.84	12	7.7
Gallium (Ga)	.89	<4.0	23	9.2	1.67	11	4.0
Iron (Fe)	1.0	.18	5.8	1.8	1.86	2.1	1.0
Lanthanum (La)	1.0	7.0	51	26	1.47	28	9.0
Lead (Pb)	.97	<4.0	30	12	1.55	13	4.7
Lithium (Li)	1.0	5.0	100	26	1.76	30	16
Manganese (Mn)	1.0	24	3,400	260	2.25	350	310
Neodymium (Nd)	1.0	6.0	47	23	1.49	25	8.3
Nickel (Ni)	1.0	<2.0	61	17	1.95	21	11
Scandium (Sc)	.91	<2.0	15	5.7	1.80	7.1	3.0
Selenium (Se)	.81	< .1	1.2	.26	2.47	.43	.21
Strontium (Sr)	1.0	13	300	63	1.60	70	35
Thorium (Th)	.99	<1.6	17.3	7.88	1.58	8.66	2.93

Table 2. Summary statistics for elements determined in B-horizon soils, outcrop rocks, and drill-core rocks from Central Oklahoma—Continued

Element	Detection ratio	Minimum value	Maximum value	Geometric mean	Geometric deviation	Arithmetic mean	Standard deviation
			B-horizon soils (293 samples)—Continued				
Titanium (Ti)	1.0	0.04	0.42	0.19	1.53	0.20	0.071
Uranium (U)	1.0	.65	6.40	2.33	1.39	2.44	.72
Vanadium (V)	1.0	5.0	220	48	1.84	56	27
Ytterbium (Yb)	.88	<1.0	4.0	1.6	1.53	1.9	.60
Yttrium (Y)	1.0	3.0	43	13	1.57	14	5.4
Zinc (Zn)	1.0	3.0	79	27	1.86	31	16
			Outcrop rocks (362 samples)				
Calcium (Ca)	1.0	.008	17	.32	9.37	2.1	3.5
Manganese (Mg)	1.0	.03	9.4	.33	4.89	1.1	1.7
Sodium (Na)	1.0	.01	2.1	.16	3.92	.34	.42
Potassium (K)	1.0	.06	2.8	.41	2.27	.58	.52
Phosphorus (P)	.85	< .005	.14	.010	2.36	.017	.017
Aluminum (Al)	1.0	.43	11	2.0	1.88	2.4	1.7
Arsenic (As)	1.0	.2	28	2.4	2.27	3.3	3.1
Barium (Ba)	1.0	34	6,800	160	2.64	320	690
Beryllium (Be)	.23	<1.0	4.0	.58	2.02	1.6	.69
Cerium (Ce)	1.0	12	170	35	1.60	39	20
Chromium (Cr)	.99	<1.0	150	19	2.30	26	20
Cobalt (Co)	1.0	<1.0	38	5.8	1.90	7.2	4.9
Copper (Cu)	.93	<1.0	2,100	7.1	3.05	19	120
Gallium (Ga)	.56	<4.0	26	4.5	1.98	8.0	3.9
Iron (Fe)	1.0	.09	8.9	.92	2.18	1.2	1.1
Lanthanum (La)	1.0	6.0	86	17	1.67	20	11
Lead (Pb)	.78	<4.0	620	6.9	2.46	15	40
Lithium (Li)	1.0	4.0	76	15	1.70	18	12
Manganese (Mn)	1.0	15	13,000	260	4.50	760	1,400
Neodymium (Nd)	.99	<4.0	83	16	1.73	19	11

Table 2. Summary statistics for elements determined in B-horizon soils, outcrop rocks, and drill-core rocks from Central Oklahoma—Continued

Element	Detection ratio	Minimum value	Maximum value	Geometric mean	Geometric deviation	Arithmetic mean	Standard deviation
Outcrop rocks (362 samples)—Continued							
Nickel (Ni)	0.99	<2.0	74	9.9	1.87	12	9.0
Scandium (Sc)	.73	<2.0	18	3.1	2.05	4.9	2.8
Selenium (Se)	.34	< .1	1.1	.07	1.94	.16	.16
Strontium (Sr)	1.0	10	1,700	54	1.92	70	97
Thorium (Th)	.97	<1.4	21.6	4.62	1.70	5.32	2.94
Titanium (Ti)	1.0	.02	.55	.12	1.70	.14	.081
Uranium (U)	1.0	.34	13.2	1.26	1.73	1.47	1.02
Vanadium (V)	1.0	5.0	170	28	1.95	35	25
Ytterbium (Yb)	.57	<1.0	4.0	1.1	1.87	1.9	.74
Yttrium (Y)	1.0	2.0	73	10	1.93	13	9.3
Zinc (Zn)	.98	<2.0	290	12	2.30	19	26
Drill-core rocks (549 samples)							
Calcium (Ca)	1.0	.01	15.5	.75	4.19	1.9	2.6
Manganese (Mg)	1.0	.03	9.6	.86	3.05	1.5	1.5
Sodium (Na)	1.0	.009	1.1	.26	2.56	.36	.23
Potassium (K)	1.0	.07	2.6	.73	2.18	.94	.55
Phosphorus (P)	.95	<.005	.34	.020	2.11	.026	.022
Aluminum (Al)	1.0	.28	10.0	3.7	2.12	4.6	2.6
Arsenic (As)	1.0	.4	62	5.5	2.20	7.3	5.9
Barium (Ba)	1.0	44	5,000	240	2.22	360	510
Beryllium (Be)	.66	<1.0	4.0	1.3	1.87	2.0	.76
Cerium (Ce)	1.0	13	180	57	1.58	62	24
Chromium (Cr)	1.0	4.0	170	46	2.01	56	30
Cobalt (Co)	1.0	2.0	70	13	1.67	15	7.2
Copper (Cu)	1.0	1.0	190	11	2.16	15	15
Gallium (Ga)	.86	<4.0	28	9.8	1.98	13	6.0
Iron (Fe)	1.0	.11	14.0	2.0	2.36	2.6	1.8

Table 2. Summary statistics for elements determined in B-horizon soils, outcrop rocks, and drill-core rocks from Central Oklahoma—Continued

Element	Detection ratio	Minimum value	Maximum value	Geometric mean	Geometric deviation	Arithmetic mean	Standard deviation
			Outcrop rocks (362 samples)—Continued				
Lanthanum (La)	1.0	7.0	83	30	1.59	32	12
Lead (Pb)	.87	<4.0	160	9.7	2.14	15	15
Lithium (Li)	1.0	4.0	130	33	2.06	41	25
Manganese (Mn)	1.0	18	7,700	380	3.26	750	1,000
Neodymium (Nd)	1.0	5.0	97	28	1.61	31	12
Nickel (Ni)	.99	<2.0	71	21	2.18	27	15
Scandium (Sc)	.91	<2.0	20	6.7	2.06	9.0	4.4
Selenium (Se)	.63	<.1	110	.13	4.50	1.4	8.0
Strontium (Sr)	1.0	18	470	110	1.79	130	65
Thorium (Th)	.97	<1.30	25.0	7.77	1.75	8.96	3.94
Titanium (Ti)	1.0	.04	.47	.20	1.81	.24	.11
Uranium (U)	1.0	.345	123	2.47	1.98	3.64	8.42
Vanadium (V)	1.0	5.0	5,200	61	2.33	100	270
Ytterbium (Yb)	.86	<1.0	6.0	1.9	1.67	2.3	.78
Yttrium (Y)	1.0	3.0	78	16	1.71	18	8.9
Zinc (Zn)	.99	<2.0	550	29	2.21	38	32

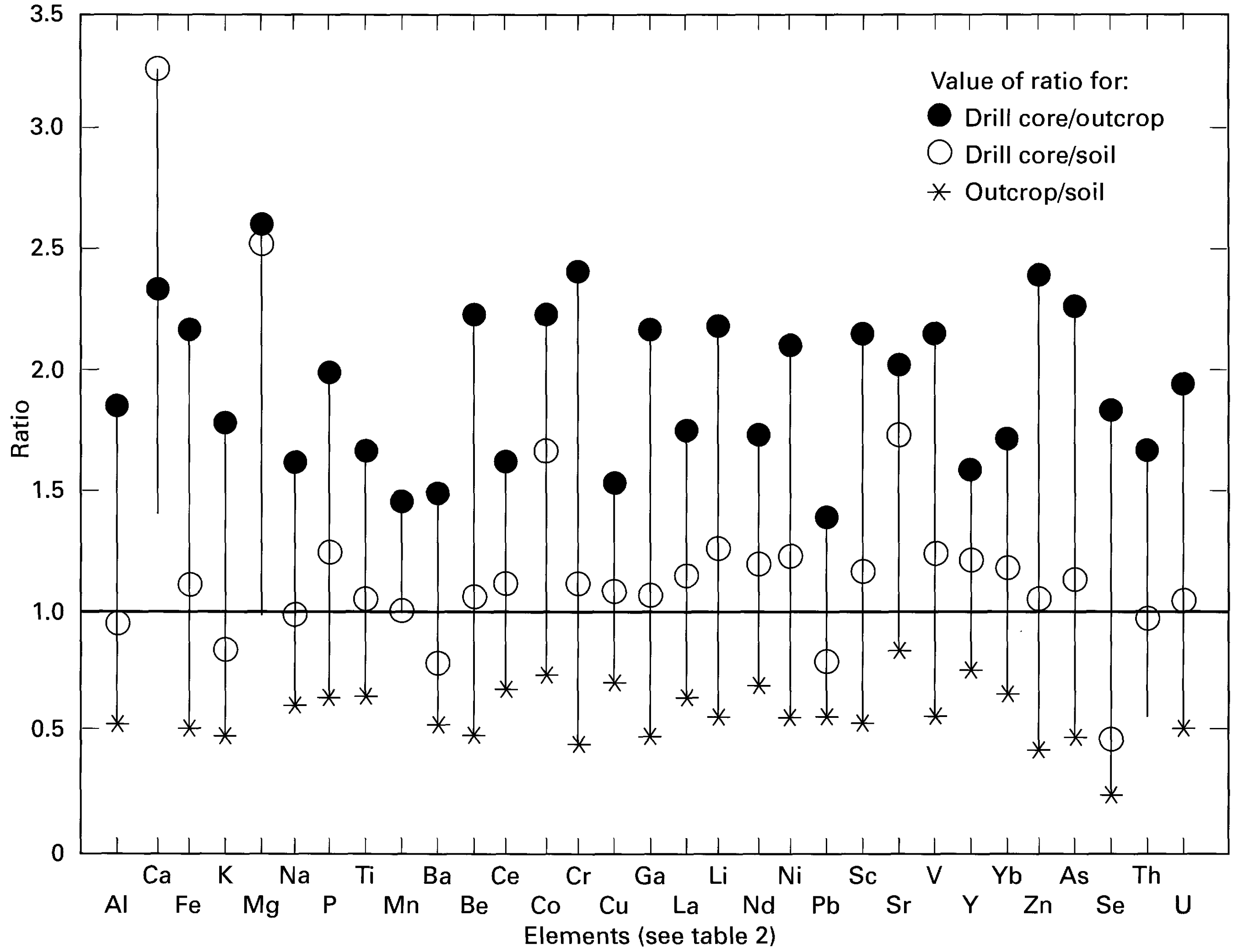


Figure 2. Relation of geometric means of chemical elements for drill-core, outcrop, and B-horizon soil samples, presented as ratios.

reduced to a smaller number of more easily presented factors. The contribution of each variable (concentration of each element) onto each factor in factor analysis is referred to as that element's factor loading. Because an element may be associated with more than one group of elements, any given element may have a high factor loading on more than one factor. The effect an individual sample has on a particular factor is represented by a factor sample-score loading. A sample with a high factor sample score indicates that the element association represented by that factor is strong. Any given sample may have a high sample score for more than one factor. The reader is referred to Davis (1986, p. 546–562) for further discussion of the factor analysis method. For the three data sets, B-horizon soil, outcrop rock, and drill-core rock, a varimax solution was used to calculate the factor scores from the log-transformed data. Only data with detection ratios (table 2) greater than 0.70 were used. In addition, beryllium (Be) (detection ratio of 0.69) was included in the B-horizon soil data set, and Se (detection ratio of 0.63) was included in the drill-core data set. Locations within the sampling area with enrichments of the elements are indicated by clusters of samples with high factor sample-score loadings from each of the three data sets. In the following sections, the geochemical and factor analysis data from B-horizon soil samples and outcrop samples are presented to evaluate the areal distribution of the geochemical factors. Data from drill-core samples are presented to evaluate vertical distribution. The major elements and As, Cr, Se, and U had high factor loadings in the first three

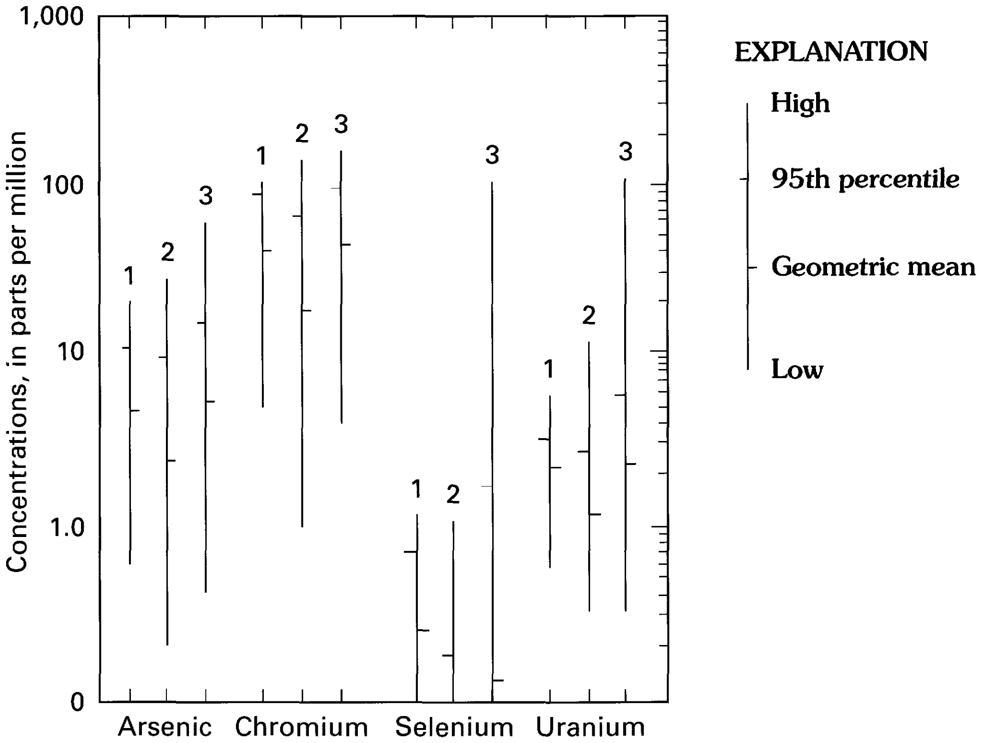


Figure 3. Concentration range, 95th percentile, and geometric mean of concentrations of arsenic, chromium, selenium, and uranium in (1) B-horizon soil samples, (2) outcrop-rock samples, and (3) drill-core rock samples.

factors of the B-horizon soil solution and in the first four factors of the outcrop and drill-core solutions. Therefore, only these factors are presented in the following discussion. The factor loadings of each factor for B-horizon soil (SF–1—SF–3), outcrop (RF–1—RF–4), and drill-core (DF–1—DF–4) data are presented in tables 3, 4, and 5, respectively.

B-Horizon Soils

The three-factor model used to examine the B-horizon soil data accounts for 83 percent of the total variance in the data set (table 3). A majority of the elements, including As, Cr, Se, and U, have high or moderate factor loadings on the first factor (SF–1). Factor SF–1 represents 72 percent of the total variance and is interpreted to be a lithologic factor that is mainly associated with aluminum- (Al) and iron- (Fe) enriched argillic B-horizon soils. Samples with high SF–1 scores have a dark-red argillic B horizon, and samples with very low SF–1 scores typically have a sandy to very sandy, cambic B horizon. Areas associated with samples that have high SF–1 sample-score loadings have soil profiles with easily distinguishable A and B horizons. Figure 4 shows the areal distribution of the B-horizon soil samples with SF–1 scores greater than or equal to 1.0. The majority of these samples were collected from the northeast quadrant of the study unit. Samples with high SF–1 scores have higher concentrations of Al and Fe indicating that these soils have a higher content of Al oxides and Fe oxides in the B-horizon zone of illuviation and that many of the trace elements with high factor loadings on the SF–1 factor may be associated with the oxides. The clay-rich B-horizon soils that developed over the Hennessey Group, in the western part of the study unit, generally have moderate to low SF–1 sample scores. These B-horizon soils exhibit a dark-brown or brownish-red color and have the pronounced blocky, columnar structure typical of a natric B horizon (Soil Survey Staff, 1975). A natric B horizon is a special kind of argillic horizon that is alkali enriched. The two types of clay-rich B-horizon soils have discrete geochemical characteristics (table 6). Soil samples developed over the Hennessey Group have markedly higher average concentrations of Ca, Mg, potassium (K), and sodium (Na) than the clay-enriched soil samples with high SF–1 scores. Therefore, because of the higher alkali content, the Hennessey Group soils should have a

Table 3. Factor loadings for the first three factors after varimax rotation of the log-transformed B-horizon soil data

[The three factors (SF–1, SF–2, and SF–3) explain 83 percent of the total variance in the data set. --, factor loadings less than 0.40, unless the value was quite close, in which case it is enclosed in parentheses (). *, element concentrations determined by hydride generation-atomic absorption; #, element concentration determined by delayed neutron activation analysis; all other element concentrations determined by inductively coupled plasma-atomic emission spectrometry]

Element	SF–1	SF–2	SF–3	Detection ratio
Calcium (Ca)	0.44	0.68	--	1.0
Magnesium (Mg)	.74	.50	--	1.0
Sodium (Na)	--	.63	0.70	1.0
Potassium (K)	--	.62	.55	1.0
Phosphorus (P)	.47	.50	.43	.99
Aluminum (Al)	.79	--	.43	1.0
Arsenic* (As)	.83	--	--	1.0
Barium (Ba)	--	.82	--	1.0
Beryllium (Be)	.76	--	--	.69
Cerium (Ce)	.68	--	.60	1.0
Chromium (Cr)	.90	--	--	1.0
Cobalt (Co)	.82	--	--	1.0
Copper (Cu)	.72	--	--	1.0
Gallium (Ga)	.86	--	--	.89
Iron (Fe)	.90	--	--	1.0
Lanthanum (La)	.68	--	.58	1.0
Lead (Pb)	.52	.40	.45	.97
Lithium (Li)	.91	--	--	1.0
Manganese (Mn)	--	.58	.42	1.0
Neodymium (Nd)	.67	--	.58	1.0
Nickel (Ni)	.91	--	--	1.0
Scandium (Sc)	.88	--	--	.91
Selenium* (Se)	.58	--	--	.81
Strontium (Sr)	.49	.72	--	1.0
Thorium# (Th)	.66	--	.61	.99
Titanium (Ti)	.69	--	.59	1.0
Uranium# (U)	.44	--	.77	1.0
Vanadium (V)	.88	--	--	1.0
Ytterbium (Yb)	.64	--	.51	.88
Yttrium (Y)	.68	--	.57	1.0
Zinc (Zn)	.76	(.38)	(.38)	1.0
Percent variance	72	7	4	

Table 4. Factor loadings for the first four factors after varimax rotation of the log-transformed outcrop-rock data

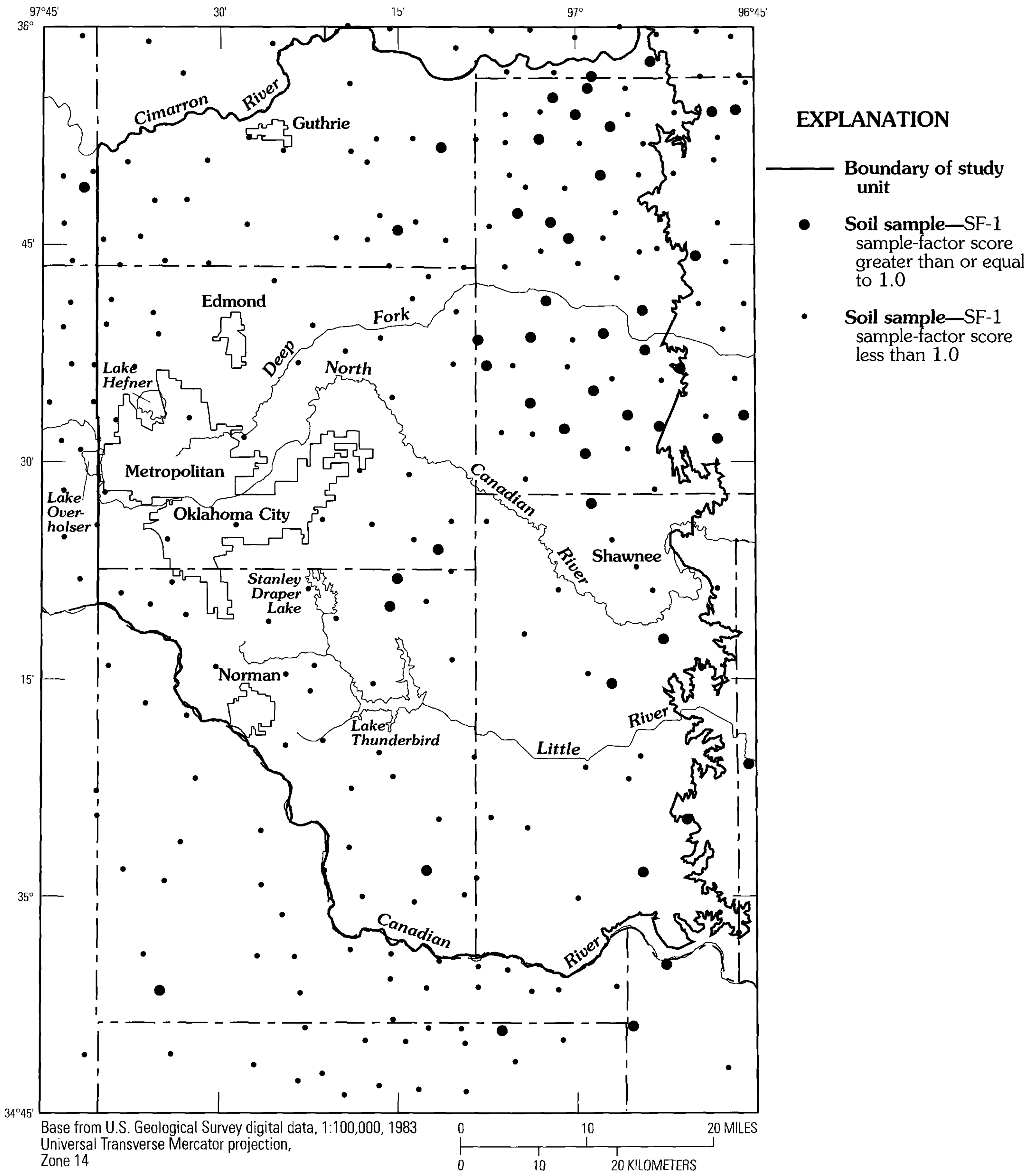
[The four factors (RF–1, RF–2, RF–3, and RF–4) explain 79 percent of the total variance in the data set. --, factor loadings less than 0.40, unless the value was quite close, in which case it is enclosed in parentheses (); *, element concentrations determined by hydride generation-atomic absorption; #, element concentration determined by delayed neutron activation analysis; all other element concentrations determined by inductively coupled plasma-atomic emission spectrometry]

Element	RF–1	RF–2	RF–3	RF–4	Detection ratio
Calcium (Ca)	--	0.93	--	--	1.0
Manganese (Mg)	--	.84	--	--	1.0
Sodium (Na)	--	.67	--	0.51	1.0
Potassium (K)	0.50	.45	--	.62	1.0
Phosphorus (P)	.42	.54	--	.42	.85
Aluminum (Al)	.63	--	--	.61	1.0
Arsenic* (As)	--	--	0.71	--	1.0
Barium (Ba)	--	.52	--	--	1.0
Cerium (Ce)	.82	--	--	--	1.0
Chromium (Cr)	.69	--	.47	--	.99
Cobalt (Co)	.42	.42	.61	--	1.0
Copper (Cu)	--	--	--	.55	.93
Iron (Fe)	.42	--	.75	--	1.0
Lanthanum (La)	.77	.50	--	--	1.0
Lead (Pb)	--	--	.59	.58	.78
Lithium (Li)	.75	--	--	.48	1.0
Manganese (Mn)	--	.77	.47	--	1.0
Neodymium (Nd)	.78	.45	--	--	.99
Nickel (Ni)	.70	--	.41	.40	.99
Scandium (Sc)	.68	.44	--	--	.73
Strontium (Sr)	.40	.65	--	--	1.0
Thorium# (Th)	.81	--	--	--	.97
Titanium (Ti)	.83	--	--	.43	1.0
Uranium# (U)	.63	--	--	--	1.0
Vanadium (V)	.46	--	.58	.41	1.0
Yttrium (Y)	.58	.68	--	--	1.0
Zinc (Zn)	--	--	--	.78	.98
Percent variance	59	9	5	6	

Table 5. Factor loadings for the first four factors after varimax rotation of the log-transformed drill-core rock data

[The four factors (DF–1, DF–2, DF–3, and DF–4) explain 83 percent of the total variance in the data set. --, factor loadings less than 0.40, unless the value was quite close, in which case it is enclosed in parentheses (); *, element concentrations determined by hydride generation-atomic absorption; #, element concentrations determined by delayed neutron activation analysis; all other element concentrations determined by inductively coupled plasma-atomic emission spectrometry]

Element	DF–1	DF–2	DF–3	DF–4	Detection ratio
Calcium (Ca)	--	0.94	--	--	1.0
Manganese (Mg)	--	.88	--	--	1.0
Sodium (Na)	0.57	(.39)	--	--	1.0
Potassium (K)	.94	--	--	--	1.0
Phosphorus (P)	.69	--	--	--	.95
Aluminum (Al)	.96	--	--	--	1.0
Arsenic* (As)	.44	--	--	0.71	1.0
Barium (Ba)	.44	--	--	--	1.0
Cerium (Ce)	.88	--	--	--	1.0
Chromium (Cr)	.92	--	--	--	1.0
Cobalt (Co)	.48	--	--	.60	1.0
Copper (Cu)	.66	--	--	.41	1.0
Gallium (Ga)	.90	--	--	--	.86
Iron (Fe)	.67	--	--	.62	1.0
Lanthanum (La)	.86	--	--	--	1.0
Lead (Pb)	--	--	--	.72	.87
Lithium (Li)	.95	--	--	--	1.0
Manganese (Mn)	--	.91	--	--	1.0
Neodymium (Nd)	.76	--	--	--	1.0
Nickel (Ni)	.94	--	--	--	.99
Scandium (Sc)	.89	--	--	--	.91
Selenium* (Se)	--	--	0.86	--	.63
Strontium (Sr)	.79	--	--	--	1.0
Thorium# (Th)	.91	--	--	--	.97
Titanium (Ti)	.95	--	--	--	1.0
Uranium# (U)	.54	--	.74	--	1.0
Vanadium (V)	.59	--	.64	--	1.0
Ytterbium (Yb)	.77	--	--	--	.86
Yttrium (Y)	.61	.58	--	--	1.0
Zinc (Zn)	.86	--	--	--	.99
Percent variance	63	10	5	5	



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 4. Distribution of B-horizon soil SF-1 sample-factor scores in the Central Oklahoma aquifer.

Table 6. Average values for soil samples with sample-factor scores greater than or equal to 1.0 for factors SF–1, SF–2, and SF–3 of a three-factor varimax factor-analysis model and for soils developed over rocks of the Hennessey Group

Element	SF–1	SF–2	SF–3	Hennessey Group
	(Concentration values are in weight percent)			
Calcium (Ca)	0.47	1.5	0.29	0.93
Manganese (Mg)	.73	1.0	.39	.90
Sodium (Na)	.22	.53	.57	.65
Potassium (K)	1.0	1.5	1.3	1.6
Phosphorus (P)	.022	.026	.021	.029
Aluminum (Al)	6.8	5.3	4.6	5.8
Iron (Fe)	3.7	2.5	1.9	2.7
Titanium (Ti)	.27	.23	.25	.26
	(Concentration values are in parts per million)			
Arsenic (As)	8.9	6.7	4.6	7.1
Barium (Ba)	370	840	400	590
Beryllium (Be)	2.0	1.5	1.0	1.6
Cerium (Ce)	69	59	66	67
Chromium (Cr)	81	55	45	61
Cobalt (Co)	15	11	8.3	11
Copper (Cu)	18	15	13	18
Gallium (Ga)	16	12	10	14
Lanthanum (La)	35	31	34	35
Lead (Pb)	15	15	14	17
Lithium (Li)	53	37	27	39
Manganese (Mn)	310	530	390	500
Neodymium (Nd)	31	28	30	31
Nickel (Ni)	38	25	17	26
Scandium (Sc)	11	8.0	6.3	8.9
Selenium (Se)	.59	.25	.31	.33
Strontium (Sr)	92	115	74	99
Thorium (Th)	10.7	8.88	10.9	10.7
Uranium (U)	2.58	2.33	3.40	2.83
Vanadium (V)	91	61	54	68
Ytterbium (Yb)	2.3	1.9	2.1	2.2
Yttrium (Y)	18	17	17	18
Zinc (Zn)	45	40	32	49

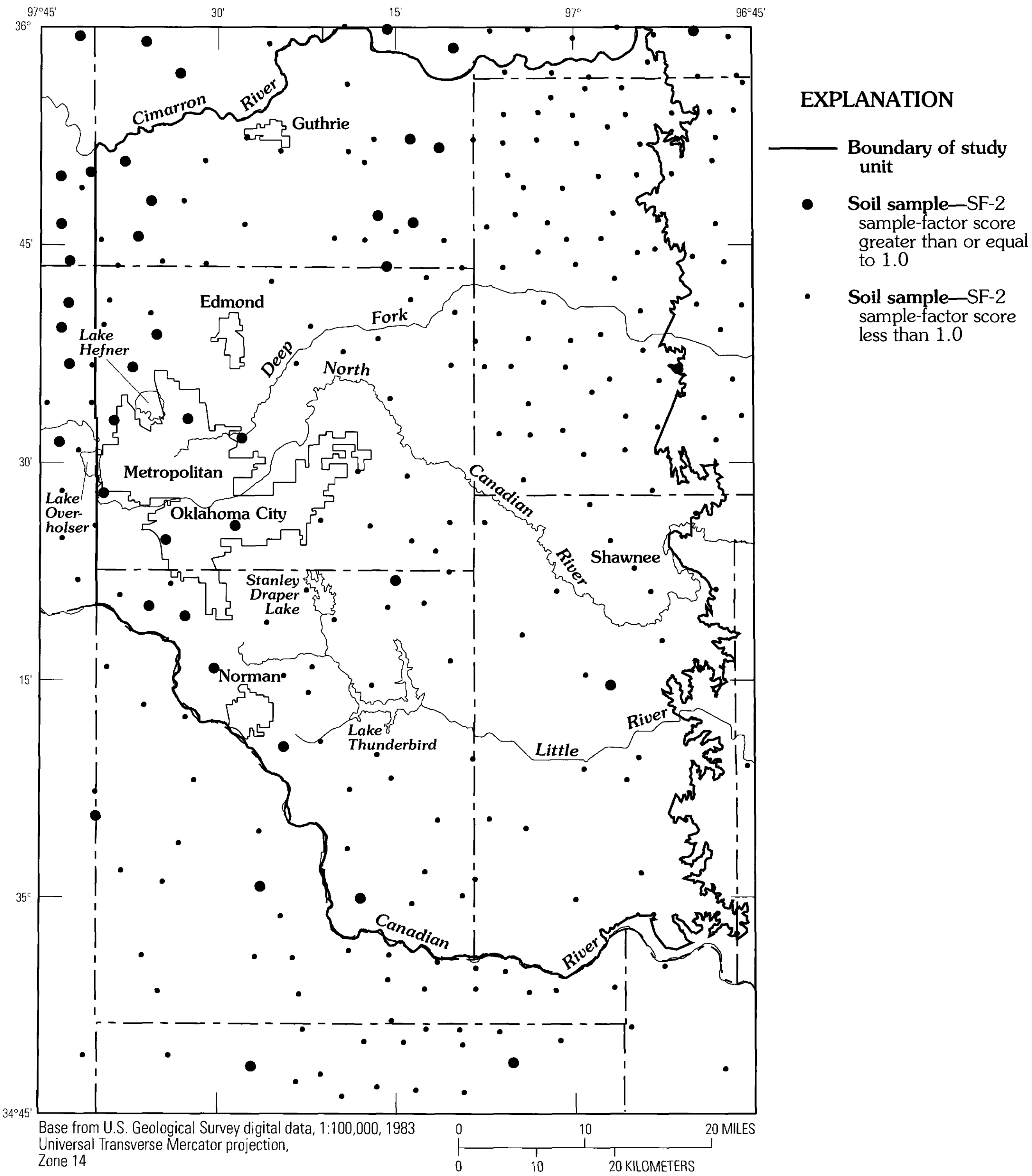
greater cation-exchange capacity than the soils with SF–1 scores greater than or equal to 1.0. These soils also contain higher concentrations of manganese (Mn) and barium (Ba) and slightly higher concentrations of strontium (Sr) and U than the soils with SF–1 scores greater than or equal to 1.0.

As a group, the geochemistry of the Hennessey Group soils best fits factor SF–2 (table 3). Factor SF–2 is a lithologic factor that has moderate to high factor loadings for Ca, K, Mg, Na, phosphorous (P), Mn, Ba, and Sr and accounts for 7 percent of the total variance. None of the four trace elements (As, Cr, Se, and U) had high factor loadings on the SF–2 factor. The areal distribution of samples with SF–2 scores greater than or equal to 1.0, shown in figure 5, indicates that many of the Hennessey Group soils, particularly those farther north, are strongly associated with the SF–2 factor. On the other hand, most of the samples collected from southern Hennessey Group soils have a SF–2 score of less than 1.0, possibly because the Hennessey Group becomes more sandy to the south, and therefore, the soils have a higher sand content. Not all samples with SF–2 scores greater than or equal to 1.0 were collected from an area where the soil had a natric B horizon. Some samples, such as those collected north of the Cimarron River, were quite sandy and contained very little illuvial clay. Samples lacking illuvial clay that have strong SF–2 factor loadings have a high Ba content. Ba has a high loading on the SF–2 factor (0.82) and is not always associated with the suite of alkali metals. The large Ba contents may be a result of disseminated barite mineralization known to be present throughout the study unit.

Factor SF–3 (table 3) is also a lithologic factor with a fairly high Na loading (0.70) and moderate Al, K, P, titanium (Ti), and Mn loadings. The rare-earth elements also have moderate loadings on the SF–3 factor, and U has a strong association with this factor. Only 4 percent of the total variance is explained by the SF–3 factor. The areal distribution of samples with SF–3 scores greater than or equal to 1.0 shows a clustering of samples south of the Canadian River in the south-central part of the study unit (fig. 6). The few samples from the Central Oklahoma aquifer part of the study unit with high SF–3 scores (greater than or equal to 1.0) are limited to the peripheral area of the aquifer. B-horizon soil samples with SF–3 scores greater than or equal to 1.0 have a brown to dark-brown or dark reddish-brown coloration, have a high to very high clay content, and often have a blocky texture. The geochemical signature for soil samples with SF–3 scores greater than or equal to 1.0 is shown in table 6. Compared to the whole B-horizon soil-sample data set (table 2), the SF–3 samples have above-average Na and K concentrations, near-average Al and Fe concentrations, and below-average Ca and Mg concentrations.

Summarizing the B-horizon soil geochemistry, three clay-enriched soil types having distinct geochemical properties are identified, and these may have a causal relation to the distribution of trace elements. All three soil types have enhanced chroma and vary slightly in their texture. The first soil type, referred to as the SF–1 soils, is enriched in Al and Fe oxides and has a below-average Na concentration. The SF–1 soils have average Ca and K concentrations but an above-average Mg concentration. Many of the trace elements, including As, Cr, and Se, are more abundant in the SF–1 soils. U, however, is only slightly enriched in the SF–1 soils. Soil type SF–2, referred to as the Hennessey Group soils, are enriched in the alkali metals (Ca, Mg, Na, and K). Although the Hennessey Group soils have above-average Al and Fe concentrations, they are not as enriched in these elements as the SF–1 soils. Of the trace elements, only Mn, Ba, and Sr have a strong association with the Hennessey Group soils. Compared to the whole B-horizon soil-sample data set (table 2), the Hennessey Group soils are slightly enriched in As and Cr, although these elements did not have strong loadings on factor SF–2. The third soil type, referred to as the SF–3 soils, differs from the other two in that they have above-average Na and K concentrations but low Ca and Mg concentrations. These soils have average Al and Fe concentrations. U is above average in these soils, whereas As, Cr, and Se approximate average concentrations obtained for these elements in the whole soil-sample data set.

The geochemistry of the soils in central Oklahoma is undoubtedly much more complicated than is presented here. A more comprehensive understanding of the physical and chemical processes in the soils of central Oklahoma would require studies beyond the scope of this investigation. Nevertheless, the current investigation shows that small amounts of major and trace elements leach from clay-enriched soils, particularly SF–1 and SF–3 soils, and contribute to the chemistry of the underlying ground-water system.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
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Figure 5. Distribution of B-horizon soil SF–2 sample-factor scores in the Central Oklahoma aquifer.

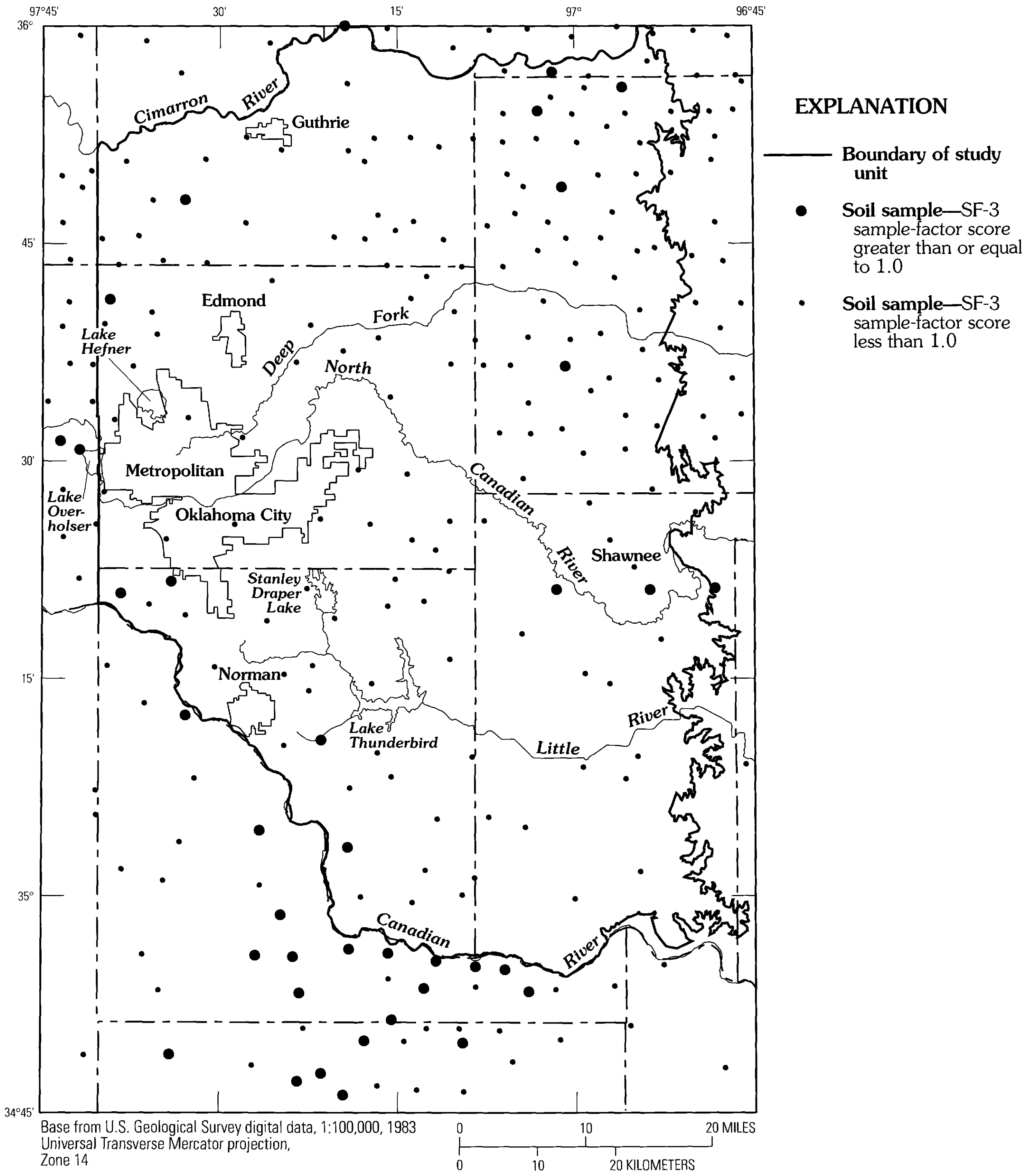

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Figure 6. Distribution of B-horizon soil SF–3 sample-factor scores in the Central Oklahoma aquifer.

Outcrop Rocks

The four-factor model used to examine the outcrop-rock data accounts for 79 percent of the total variance of the data (table 4). The average concentration for the 27 elements used in the outcrop factor-analysis model for samples with sample-factor scores greater than or equal to 1.0 in each of the four factors (RF–1 to RF–4) is given in table 7. The areal distribution of outcrop samples with scores greater than or equal to 1.0 for each of the four factors are shown in figures 7, 8, 9, and 10. Outcrop samples with high scores are more randomly distributed than were observed for the soil samples with high scores.

Eighteen of the 27 elements used in this model have moderate to high loadings on the RF–1 factor and account for 59 percent of the total data variance. Cr and U have factor loadings on the RF–1 factor of 0.69 and 0.63, respectively (table 4). Samples with RF–1 scores greater than or equal to 1.0 have average concentrations of 51 ppm Cr and 2.24 ppm U (table 7), which are greater than the total data set (table 2). High scores for factor RF–1 are in high-clay-content samples associated with mudstone rocks of the Hennessey Group in the area northwest of Oklahoma City and at scattered localities in the central and east-central regions (fig. 7). The scattered samples from the latter region generally were collected because of an unusual lithologic or diagenetic attribute, such as a clay, mudstone, or siltstone layer within a more typical friable red sandstone outcrop or a distinct color variation within a more typical red sandstone. Other than the Hennessey Group samples from the northwest region, there appears to be no correlation between samples with high scores for the RF–1 factor and geologic formation. Factor RF–2, which accounts for 9 percent of the total variance, has high loadings for Ca, Mg, Mn, Na, yttrium (Y), and Sr and moderate loadings for K, P, Ba, cobalt (Co), lanthanum (La), neodymium (Nd), and scandium (Sc). Samples with high RF–2 scores have high concentrations for elements associated with carbonates and average Al and Fe concentrations (table 7). None of the four trace elements (As, Cr, Se, and U) have high factor loadings on the RF–2 factor. The average concentrations of 4.0 ppm As, 24 ppm Cr, and 1.66 ppm U in samples with RF–2 scores greater than or equal to 1.0 (table 7) approximate average values of 3.3 ppm As, 26 ppm Cr, and 1.47 ppm U reported for the total sample set (table 2). Only 34 percent of the outcrop samples have detectable Se (0.1 to 1.1 ppm). Therefore, near-surface rocks probably are not contributing to high ground-water Se concentrations. The areal distribution of samples with RF–2 scores greater than or equal to 1.0 (fig. 8) shows that these samples generally are associated with outcrops peripheral to the study unit.

Factor RF–3 (table 4) is interpreted to reflect Fe oxides and accounts for 5 percent of the total data variance. In addition to Fe, the RF–3 factor has strong loadings for As and Co and moderate loadings for Mn, Cr, nickel (Ni), lead (Pb), and vanadium (V) (table 4). Average concentrations of the elements associated with the RF–3 factor for outcrop samples with sample scores greater than or equal to 1.0 (table 7) are approximately twice as high as average concentrations for the total outcrop-sample set (table 2). Figure 9 shows the areal distribution of the outcrop samples with RF–3 scores greater than or equal to 1.0. The majority of the samples (35 out of 48) with high RF–3 scores are scattered throughout the central part of the study unit within the Garber Sandstone and Wellington Formation. Many of these samples were collected from a smaller layer within a typical porous, friable, red, sandstone outcrop. This layer was selected because its color indicated Fe enrichment.

Eleven elements have factor loadings greater than 0.4 on factor RF–4. However, As, Cr, Se, and U do not have high factor loadings on RF–4 (table 4). Some elements (Al, K, P, Ti, lithium (Li), Ni, and V) that have moderate to high loadings on factor RF–1 also have moderate to high loadings on factor RF–4. Factor RF–4 differs from factor RF–1 in that factor RF–4 has higher Na and K loadings than factor RF–1. Factor RF–4 also has moderate loadings for copper (Cu), Pb, and zinc (Zn), which are three of the few elements that have low loadings on factor RF–1. Samples with RF–4 scores greater than or equal to 1.0 are clustered in the area where the Hennessey Group crops out northwest of Oklahoma City and in the vicinity of the southeast corner of the sampling area (fig. 10). Samples from these two general areas have different lithologic characteristics. The Hennessey Group samples are platy or blocky red mudstones that are fairly uniform in their geochemical composition and, because of their generally higher clay content, have higher concentrations of many of the trace elements. However, samples from the southeast corner of the sampling area are light-tan to pale-green sandstone, some containing carbonate cement and, although not noticeably clay rich, containing elevated Na and K concentrations. Many of the samples from the southeast corner have anomalous

Table 7. Average values for outcrop-rock samples with sample-factor scores greater than or equal to 1.0 for a four-factor varimax factor-analysis model

Element	RF–1	RF–2	RF–3	RF–4
	(Concentration values are in weight percent)			
Calcium (Ca)	2.0	7.8	3.2	2.9
Manganese (Mg)	1.4	3.5	1.8	1.6
Sodium (Na)	.48	.58	.18	1.0
Potassium (K)	1.0	.76	.55	1.4
Phosphorus (P)	.025	.023	.023	.032
Aluminum (Al)	4.5	2.7	2.6	5.0
Iron (Fe)	2.1	1.2	2.6	2.0
Titanium (Ti)	.26	.13	.15	.23
	(Concentration values are in parts per million)			
Arsenic (As)	4.4	4.0	7.4	5.0
Barium (Ba)	250	520	430	400
Cerium (Ce)	65	47	46	48
Chromium (Cr)	51	24	36	43
Cobalt (Co)	11	9.0	13	11
Copper (Cu)	16	13	19	67
Lanthanum (La)	32	28	22	26
Lead (Pb)	12	12	33	39
Lithium (Li)	34	17	19	34
Manganese (Mn)	490	2,220	1,920	690
Neodymium (Nd)	30	28	23	23
Nickel (Ni)	24	11	16	23
Scandium (Sc)	7.6	4.8	4.9	7.0
Strontium (Sr)	91	130	71	130
Thorium (Th)	9.38	5.74	5.18	7.52
Uranium (U)	2.24	1.66	1.63	2.19
Vanadium (V)	56	38	64	56
Yttrium (Y)	18	24	17	15
Zinc (Zn)	31	16	32	56

concentrations of Cu, Pb, or Zn that may reflect mineralization.

Drill-Core Rocks

A four-factor model accounting for 83 percent of the total variance in the data set was used to interpret the drill-core rock data. The factor loadings (DF–1 to DF–4) are given in table 5. Element associations are much more clearly defined by factor analysis of the drill-core rock data than was observed for the soil and outcrop-rock data. The average values for the 30 elements used in the drill-core factor analysis model for samples with scores greater than or equal to 1.0 in each of the four factors are given in table 8.

Sixty-three percent of the total variance is contained in the first factor (DF–1 in table 5). Twenty-five elements have factor loadings greater than 0.4 in factor DF–1. Only Ca, Mg, Mn, Pb, and Se have loadings less than 0.4. Of the 79 samples with DF–1 scores greater than or equal to 1.0, 69 were mudstone; the rest were either siltstone or clay-enriched sandstone. Approximately 24 percent of the rocks cored for this study were mudstone. Although some white or pale-green

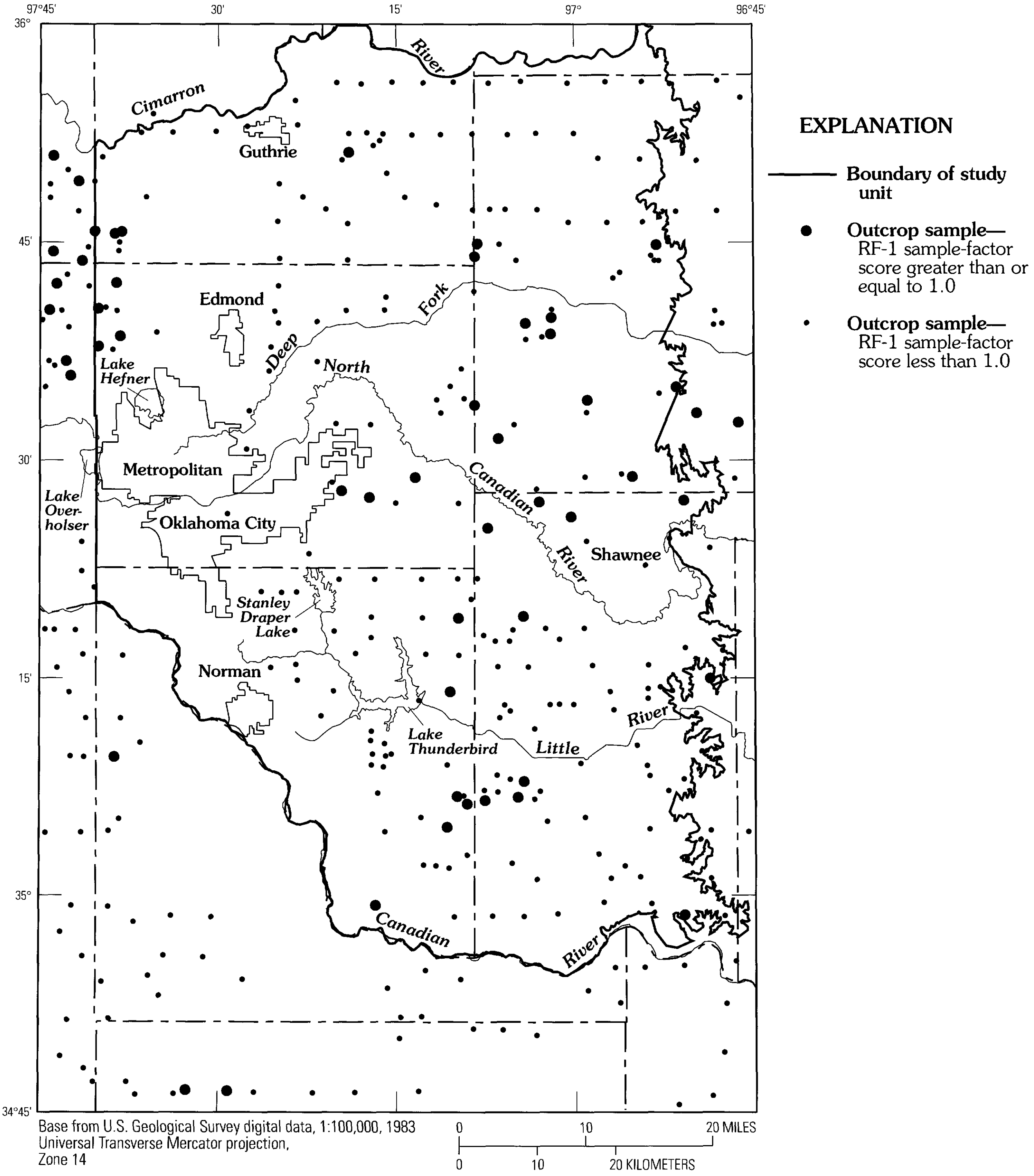

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Figure 7. Distribution of outcrop RF–1 sample-factor scores in the Central Oklahoma aquifer study unit.

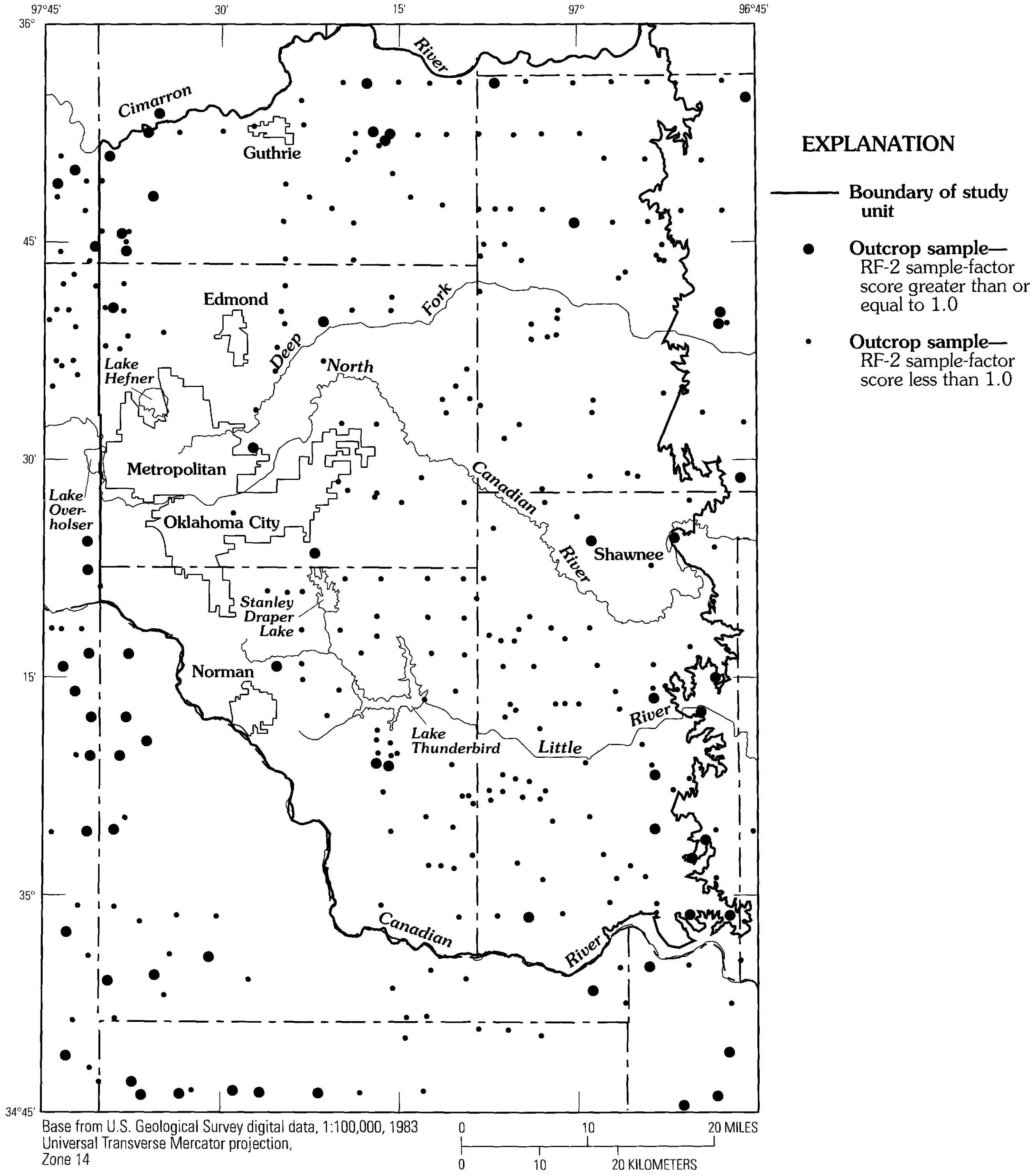

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Figure 8. Distribution of outcrop RF–2 sample-factor scores in the Central Oklahoma aquifer study unit.

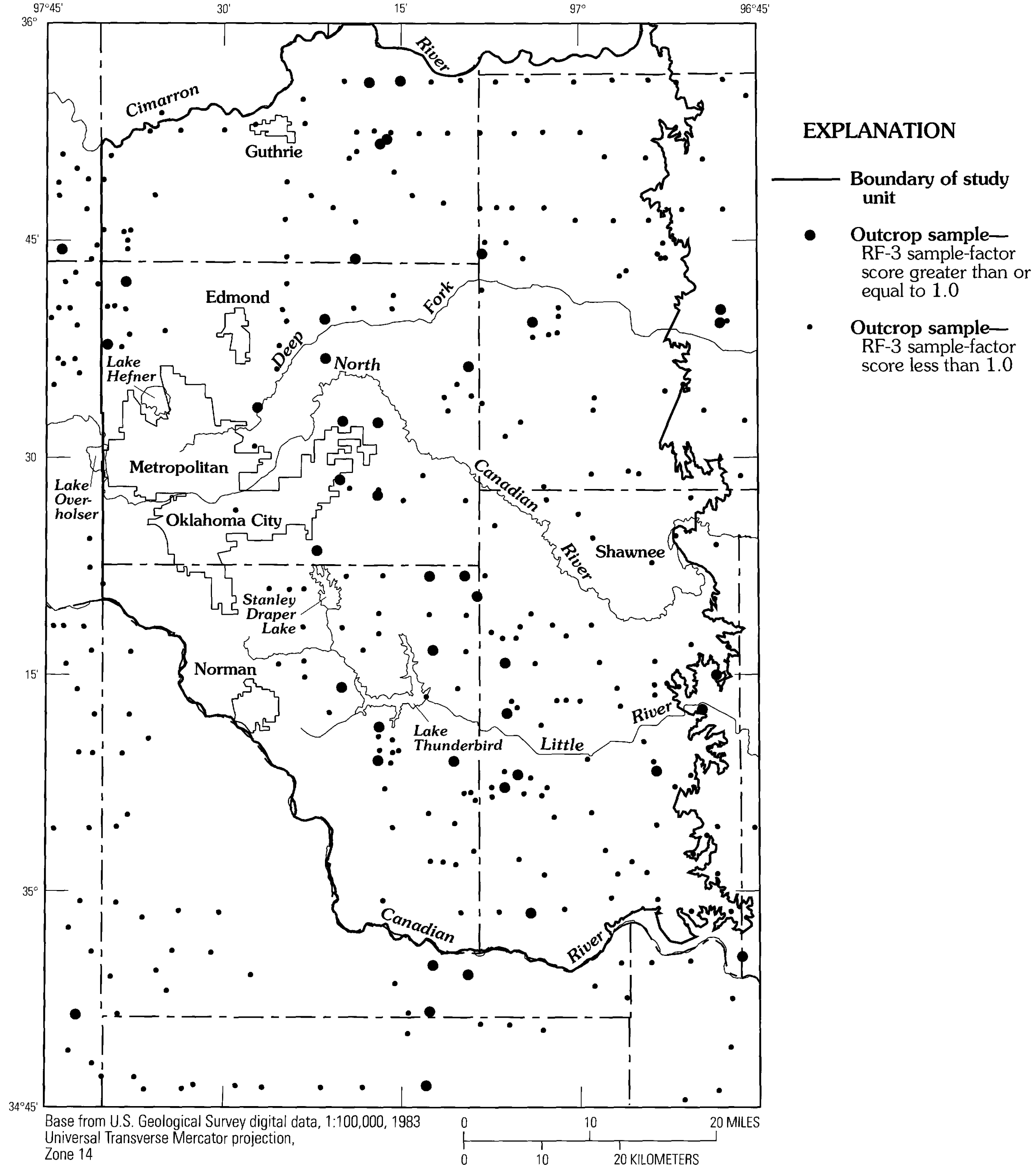

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Figure 9. Distribution of outcrop RF–3 sample-factor scores in the Central Oklahoma aquifer study unit.

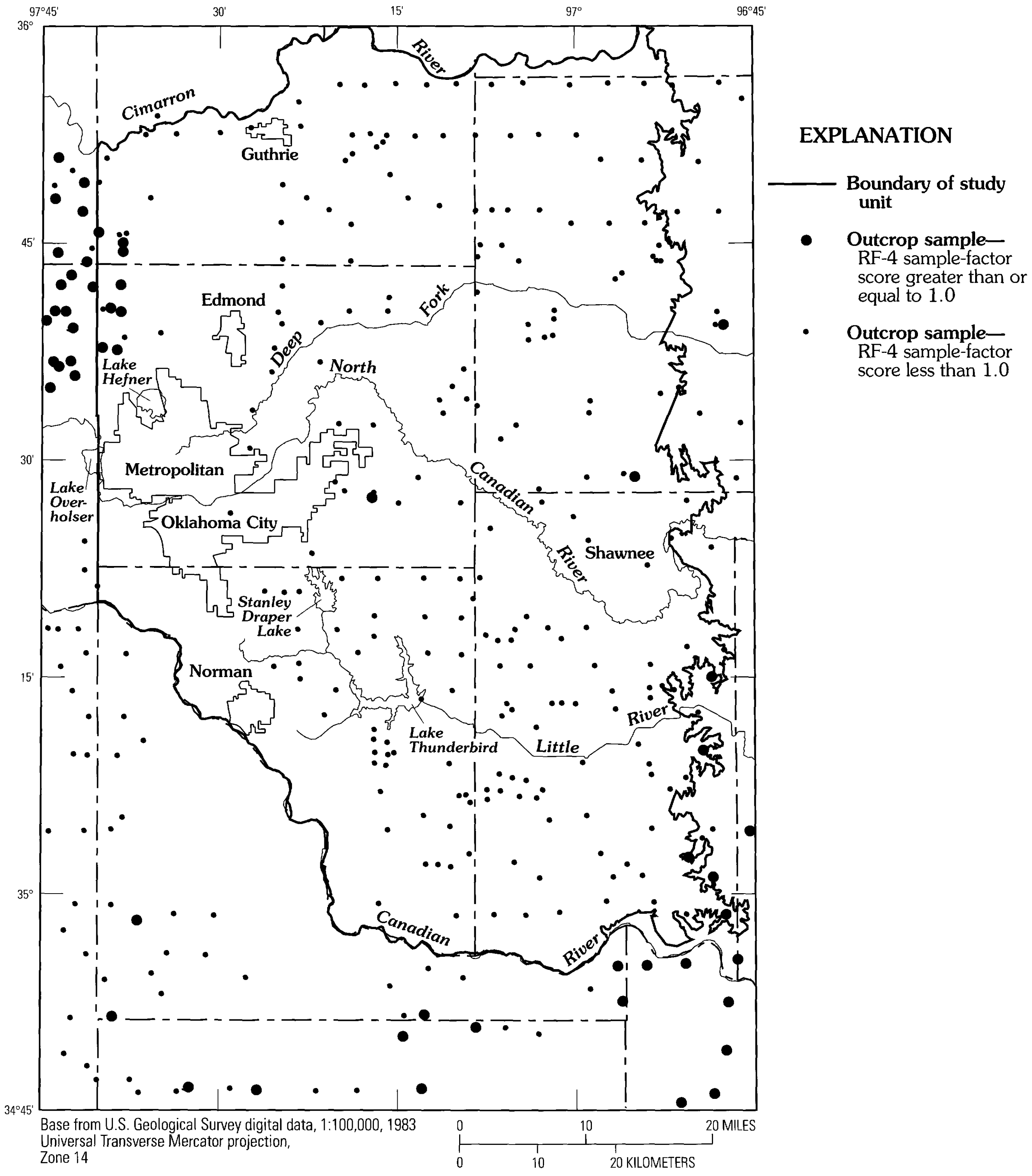

Figure 10. Distribution of outcrop RF–4 sample-factor scores in the Central Oklahoma aquifer study unit.

Table 8. Average values for drill-core rock samples with sample-factor scores greater than or equal to 1.0 for a four-factor varimax factor-analysis model

Element	DF–1	DF–2	DF–3	DF–4
	(Concentration values are in weight percent)			
Calcium (Ca)	0.84	6.6	2.3	2.9
Manganese (Mg)	1.5	4.0	1.7	1.9
Sodium (Na)	.49	.38	.44	.21
Potassium (K)	1.6	.79	.87	.77
Phosphorus (P)	.040	.026	.032	.029
Aluminum (Al)	8.5	3.6	4.3	3.8
Iron (Fe)	4.5	2.5	2.8	4.4
Titanium (Ti)	.38	.17	.22	.20
	(Concentration values are in parts per million)			
Arsenic (As)	9.7	7.3	8.0	15
Barium (Ba)	340	590	490	290
Cerium (Ce)	85	57	66	63
Chromium (Cr)	95	43	54	50
Cobalt (Co)	21	14	16	22
Copper (Cu)	25	14	15	15
Gallium (Ga)	22	11	11	11
Lanthanum (La)	45	33	35	34
Lead (Pb)	11	17	25	32
Lithium (Li)	79	32	39	36
Manganese (Mn)	410	2,500	1,000	1,400
Neodymium (Nd)	40	36	34	35
Nickel (Ni)	50	19	24	25
Scandium (Sc)	15	7.4	8.1	8.0
Selenium (Se)	.17	.76	5.8	.7
Strontium (Sr)	190	140	140	120
Thorium (Th)	13.8	7.05	8.79	7.44
Uranium (U)	4.07	2.75	12.1	2.78
Vanadium (V)	120	69	340	100
Ytterbium (Yb)	2.9	2.5	2.3	2.2
Yttrium (Y)	22	27	21	22
Zinc (Zn)	71	27	40	38

mudstone layers were intercepted, the majority of the mudstones are reddish brown because of hematite and goethite. Sample scores greater than or equal to 1.0 for factor DF–1 are almost exclusively in these Fe-rich mudstone samples. When compared to average concentrations for the total drill-core sample set (table 2), samples with DF–1 scores greater than or equal to 1.0 have elevated average concentrations for all the elements that are associated with factor DF–1 (table 8). It is assumed that the trace elements with strong loadings on factor DF–1 (mudstone) are adsorbed either on clay particles or on Fe oxides, such as goethite, that are associated with the mudstone. Of the four trace elements (As, Cr, Se, and U), only Se is not associated with the factor DF–1 suite of elements. Selenium has an average concentration of 0.17 ppm for the samples with DF–1 scores greater than or equal to 1.0 compared to an average concentration of 0.90 ppm in the total drill-core sample set. Samples with DF–1 scores greater than or equal to 1.0 have average concentrations of 9.7 ppm As, 95 ppm Cr, and 4.07 ppm U (table 8) compared to average concentrations of 7.3 ppm As, 56 ppm Cr, and 3.64 ppm U in the total drill-core sample set (table 2).

The distribution of rock cored in each of the eight test holes with sample-factor scores greater than or equal to 1.0 for each of the four drill-core factors is shown in table 9. Mudstone comprises 24 percent of the total core from the eight test holes (table 1), and samples with DF–1 scores greater than or equal to 1.0 comprise 17 percent of the cores (table 9). Drill cores from test holes 2, 3, and 5 have the most mudstone. Drill cores from test holes 1A and 4 have intermediate mudstone contents of 19 percent and 24.5 percent, respectively, and samples with DF–1 scores greater than or equal to 1.0 comprise 16 percent of the core from test hole 1A and 12 percent of the core from test hole 4.

Factor DF–2, which accounts for 10 percent of the total variance in the drill-core data, has strong factor loadings for Ca (0.94), Mg (0.88), and Mn (0.91) (table 5) and is considered a carbonate factor. Yttrium, the only other element with a strong factor loading on factor DF–2, has a factor loading of 0.58. Carbonate is present as cement in the rocks or as concretions and is most prevalent in conglomerates and in the siltstone and sandstone of the Hennessey Group. Test hole 7 was drilled in the Hennessey Group, and test hole 7 core samples with DF–2 scores greater than or equal to 1.0 make up 36.4 percent of the core (table 9). Of the 41 conglomerate samples collected from the eight cores, 29 had DF–2 sample scores greater than or equal to 1.0. The 89 samples with DF–2 scores greater than or equal to 1.0 comprise 10.8 percent of the total core. It is interesting to note that the core from test hole 4, from the area of good ground water, contained no samples with high DF–2 scores (table 9) and that carbonate-pebble conglomerates were not present in the test hole 4 core (table 1).

Table 9. Distribution of rock cored in the eight test holes with sample-factor scores greater than or equal to 1.0

[Values are in feet, and values in parentheses () are in percent]

Test hole (fig. 1)	DF–1	DF–2	DF–3	DF–4
1A	40.8	16.7	23.0	21.2
	(16.2)	(6.6)	(9.2)	(8.4)
2	119.8	10.7	23.3	0
	(45.7)	(4.1)	(8.9)	(0)
3	41.7	22.1	1.5	0.8
	(23.3)	(12.3)	(0.8)	(0.4)
4	31.4	0	0	70.1
	(11.6)	(0)	(0)	(26.0)
5	68.4	20.5	7.7	4.4
	(30.7)	(9.2)	(3.5)	(2.0)
6	29.8	84.8	69.3	87.5
	(5.8)	(16.5)	(13.5)	(17.0)
7	13.1	56.2	18.9	0
	(8.5)	(36.4)	(12.2)	(0)
7A	35.4	26.0	15.7	10.5
	(10.3)	(7.6)	(4.6)	(3.1)
Total	380.4	237.0	159.4	194.5
	(17.3)	(10.8)	(7.3)	(8.9)

Only Se (0.86), U (0.74), and V (0.64) have strong loadings on factor DF–3 (table 5). Factor DF–3 is related to mineral suites (for example, clausthalite [PbSe], native Se, tyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$], häggite [$V_2O_2(OH)_3$]; Breit and others, 1990b) and accounts for 5 percent of the total variance in the data. The 67 samples with DF–3 scores greater than or equal to 1.0 have average concentrations of 5.8 ppm Se and 12.1 ppm U (table 8) compared to 0.90 ppm Se and 3.64 ppm U in the total drill-core sample set (table 2). Most often, high scores for factor DF–3 are in samples that have reduction spots, in samples that have visible green mineralization, or in samples that are white to pale green. Of the 67 samples with DF–3 scores greater than or equal to 1.0, 42 are associated with the above diagenetic attributes. Many of the samples with DF–3 scores greater than or equal to 1.0 were collected subjectively because of their distinct color or because of visible green mineralization and represent only 0.1 to 1 ft of core. Samples with DF–3 scores greater than or equal to 1.0 comprise 7.3 percent of the total rock cored. With the exception of the core from test hole 4, all the cores contained samples with DF–3 scores greater than or equal to 1.0 (table 9). All lithologic classifications, but mostly sandstone, contain samples with DF–3 scores greater than or equal to 1.0. The core from test hole 6 contains 69.3 linear ft of rock with DF–3 scores greater than or equal to 1.0 (table 9). Although green rocks were encountered and green mineralization was observed, the samples from the core of test hole 6 with DF–3 scores greater than or equal to 1.0 were mostly red sandstones and conglomerates.

Factor DF–4, which accounts for 5.0 percent of the total variance in the drill-core data, has strong loadings for Fe, Co, Cu, Pb, and As (table 5) and is interpreted to reflect Fe oxides and adsorbed elements. Of particular interest to this study is the relationship between Fe and As. The 64 samples with DF–4 scores greater than or equal to 1.0 have average concentrations of 4.4 percent Fe and 15 ppm As (table 8) compared to 2.6 percent Fe and 7.3 ppm As in the total drill-core sample set (table 2). Factor DF–1 also has a high loading for Fe and a moderate loading for As, yet only 5 of the 549 samples had sample-factor scores greater than or equal to 1.0 for both DF–1 and DF–4 factors (4 mudstone samples from the core of test hole 4 and a mudstone sample from the core of test hole 5). High loadings for factor DF–4 are often in samples with distinct deep-red, purplish-red, dark-purple, or yellow-brown color due to abundant Fe oxides. Samples with DF–4 scores greater than or equal to 1.0 represent 8.9 percent of the total core. Drill cores from test holes 2 and 7 do not contain samples with DF–4 scores greater than or equal to 1.0, the core from test hole 3 contained only one sample, and the core from test hole 5 contained just two samples with DF–4 scores greater than or equal to 1.0. Most of the samples with DF–4 scores greater than or equal to 1.0 were obtained from the cores of test holes 1A, 4, 6, and 7A, (table 9). The samples from the cores of test holes 1A, 6, and 7A with high DF–4 scores are primarily sandstones and conglomerates, whereas the samples from the core of test hole 4 with high DF–4 scores are mostly mudstones or claystones. Independent of lithology, the core from test hole 4 differs from the rest of the cores in that the core from test hole 4 contains far less Ca, Mg, and Na. Samples from the core of test hole 4 contain average concentrations of 0.22 percent Ca, 0.40 percent Mg, and 0.04 percent Na (Mosier and others, 1990b) compared to 1.9 percent Ca, 1.5 percent Mg, and 0.36 percent Na in the total drill-core sample set (table 2). In general, the samples with DF–4 scores greater than or equal to 1.0 are sandstones and conglomerates that are enriched with Fe oxides, and the samples with DF–1 scores greater than or equal to 1.0 are mudstone similarly enriched in Fe oxides. In both groups of samples the association between Fe and As is probably due to As adsorption onto Fe oxides, such as goethite.

In summary, the subsurface distribution of the As, Cr, Se, and U is associated with lithologic and diagenetic attributes that are independent of the geologic formation. Arsenic is primarily associated with two types of subsurface rocks. In general, the highest concentrations of As are in Fe-enriched sandstones and conglomerates. Such rocks are most prevalent in the part of the aquifer consisting of the unconfined Garber Sandstone. Although mudstone has a lower average As content than sandstone, a larger volume of subsurface rocks with an As association are Fe-enriched mudstones. These mudstones most commonly are in the undifferentiated Chase, Council Grove, and Admire Groups but are found in all the geologic formations. Samples with high Cr content are also high in Al. Mudstones have the highest Cr and Al content, and sandstones have the lowest, indicating that clay is the main residence of Cr. The highest concentrations of Se and U are found in green rocks that often are present in isolated or localized sites within a larger volume of rock. However, there appears to be no direct relation between the two elements. High Se and U concentrations are found in all lithologies and geologic formations but comprise a very small percentage of the rock mass. However, the core from test hole 4, from the area of good water quality, did not contain this type of Se or U occurrence. Se was not detected in amounts greater than 0.1 ppm in the core from test hole 4. U also has a weak association with high clay-content mudstone, claystone, and siltstone, and higher concentration of Se often are found in red sandstone and conglomerates.

PARTIAL DISSOLUTION STUDIES

The above discussion concerning the abundance and distribution of As, Cr, Se, and U deals with total element concentration. Use of total concentration to assess the potential for these elements to contaminate the ground-water system indicates that all forms of a given element have an equal effect on the environment, which is not the case. The mobility and transport of elements is dependent on factors such as mode of occurrence, changes in the pH and Eh (redox potential), formation of organic or inorganic complexes, biological interactions, and the presence of highly sorptive materials such as organic matter, Fe oxides, Mn oxides, and clay minerals. Two partial dissolution techniques were used to study partitioning of the trace elements among discrete geochemical phases likely to be affected by environmental conditions. One technique, a two-step sequential procedure, was designed to mimic naturally present high pH-high bicarbonate water and the high oxidizing potential of some water in the Central Oklahoma aquifer (Mosier and others, 1991b). In step 1, the samples were extracted at room temperature for 30 minutes with a bicarbonate solution (0.3 mol of sodium carbonate, Na_2CO_3, and 0.7 mol of sodium bicarbonate, $NaHCO_3$, per liter of water, pH=9). In step 2, the washed residues from step 1 were extracted for 1 hour in a boiling water bath with a sodium hypochlorite/bicarbonate solution (0.3 mol of Na_2CO_3 and 0.7 mol of $NaHCO_3$ per liter of 0.7*M* sodium hypochlorite, NaOCl, pH=9).

The second procedure, developed by Chao and Sanzolone (1989), sequentially extracts elements into five fractions:

Step 1. Soluble. The sediment was extracted at room temperature by continuous agitation for 30 minutes with 0.25*M* potassium chloride solution. Potassium chloride (0.25*M* KCl) will dissolve water-soluble elements. Nonspecifically adsorbed anions are replaced by the chloride ion through anion exchange, and cations are exchanged for the potassium ion.

Step 2. Ligand Exchangeable. Residues from step 1 were extracted at room temperature for 30 minutes by continuous agitation with 0.1*M* potassium dihydrogen phosphate solution. Potassium dihydrogen phosphate (0.1*M* KH_2PO_4) is effective in exchanging anions specifically adsorbed on clay minerals and hydrated oxides of iron and manganese through ligand-exchange reaction and anion competition.

Step 3. Acid Extractable. Residues from step 2 were extracted for 45 minutes with hot 4*M* hydrochloric acid. Hydrochloric acid (4*M* HCl) will dissolve to varying degrees a variety of rock constituents including Fe, Mn, and Al oxides, amorphous materials, carbonates, and mono sulfides.

Step 4. Oxidative Acid Decomposable. Residues from step 3 were extracted at room temperature for 45 minutes with potassium chlorate and concentrated hydrochloric acid. A combination of potassium chlorate ($KClO_3$) and concentrated hydrochloric acid (HCl) makes a strong oxidizing reagent capable of dissolving sulfide minerals and oxidizing and dissolving reduced elemental and residual organic material.

Step 5. Mixed-Acid Digestible. Residues from step 4 were digested with a hot mixed-acid solution until near dryness. A mixed-acid solution of hydrofluoric acid (HF), nitric acid (HNO_3), and perchloric acid ($HClO_4$) is the strongest liquid chemical reagent used in the sequential procedure. It is capable of destroying the silicate lattice and solubilizing elements imbedded within the silicate structure. These matrix-bonded elements are considered to be highly resistant to changes in environmental conditions.

The KCl, KH_2PO_4, and $NaHCO_3$ treatments are mild chemical action procedures. Elements that are dissolved from the samples by KCL, KH_2PO_4, and $NaHCO_3$ treatments are considered to be readily extractable. These elements are held in relatively labile forms associated with various reaction sites. These labile-reaction sites are loci of chemical or physicochemical reaction where elements released during weathering are held in place through mechanisms such as adsorption, precipitation, surface complex formation, and ion exchange (Chao, 1984). Readily soluble elements will be mobilized without significant changes in geochemical conditions within the aquifer.

The HCl, HCl+$KClO_3$, and $NaHCO_3$ + NaOCl treatments dissolve elements that are conditionally soluble. Conditionally soluble elements are bound in minerals and require a more drastic chemical action dissolution. Sites that contain conditionally soluble elements include structural sites or inclusions within iron oxides, carbonate minerals, weakly soluble clay minerals, and minerals that require oxidation prior to or simultaneous with dissolution. The host or armoring mineral must dissolve or be oxidized before the conditionally soluble element can be released.

Residual nonextractable elements generally reside in the mineral lattice. A severe chemical action such as the $HF+HNO_3+HClO_4$ treatment that breaks down a silicate lattice is required to release residual elements.

Eighty-six drill-core samples, representing typical and enriched concentrations of As, Cr, Se, and U in various lithologic categories, were selected for the partial dissolution studies (Mosier and others, 1991b). The samples were collected from the drill cores of test holes 1A, 2, 5, 6, 7, and 7A. Table 10 summarizes the extraction data for As, Cr, Se, and U and provides comparisons among the subsets of data representing the individual drill cores. Shown in table 10 are the mean concentrations in parts per million for the 549 sample set and the mean concentrations and extraction results (as percentage extracted) for the 86 samples in the extraction set and for the subsets of data from the individual drill cores. Extraction results for Se are limited to those samples that contained greater than or equal to 0.2 ppm Se. The $NaHCO_3/NaOCl$ extraction was not executed on cores from test holes 7 and 7A. The following text summarizes the extraction results.

Arsenic

The 86 samples used for the extraction studies have a mean concentration of 11.6 ppm As (total) compared to 7.3 ppm As (total) in the complete drill-core sample set. The majority of the As was either conditionally extracted by the HCl treatment (41 percent) or was in the residual phase (47 percent). Substantial amounts of As were mobilized from the rocks by ligand exchange and possibly by increased pH. This mobile As is most likely adsorbed on Fe oxides, and its mobility is probably limited by accessibility of circulating ground water to mineral surfaces. Under oxidizing conditions and over a wide pH range, As in the +5 oxidation state can exist in ground water as monovalent and divalent anionic species, $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Cherry, Gillham, and Barber, 1984). On the average, approximately 7 percent of the As was readily extractable by the KCl and KH_2PO_4 extractions. Treatment with KH_2PO_4 extracted a greater percentage of As than treatment with $NaHCO_3$, 5.1 percent compared to 3.4 percent, indicating that phosphate ligand exchange is more important than increase in pH and carbonate ligand exchange for release of As from Fe oxides. Tests comparing readily extractable As with lithologies indicated that readily extractable As was similarly extracted from sandstones (7.2 percent), mudstones (7.2 percent), and siltstones (6.9 percent), whereas conglomerates (4.9 percent) contain the least readily extractable As. The association of Fe and As, evident by whole-rock concentrations and factor analysis, is probably a result of As contained within the structure of authigenic Fe oxides. This As is largely immobile and is extracted by the HCl extraction step. However, the association between the amount of extracted As and the relative amount of Fe released during the various extraction steps generally were not well defined. Regression analysis showing the relation between HCl extractable As and HCl extractable Fe produced a r^2 value of only 0.2 (a value of 1 is optimal). Also, the amount of As extracted was not predictable by rock color or lithologic attributes.

Chromium

Significant amounts of Cr were dissolved from the samples by the HCl (33 percent), but the majority of the Cr (64 percent) was dissolved from the residual phase. The analytical procedure used for determining Cr concentrations had a relatively high detection limit (6 ppm for the five-step sequential procedure and 3 ppm for the bicarbonate procedure). As a result, none of the samples had detectable Cr extracted by the KCl or KH_2PO_4 treatments, and only a few of the samples had detectable Cr extracted by the bicarbonate treatments.

Cr content closely parallels Al content. Regression analysis of total extractable Cr against total extractable Al has a $r^2 = 0.8$, indicating a strong correlation. Mudstone and siltstone have higher concentrations of Cr and Al than sandstone and conglomerates, indicating that clay minerals are the main residence of Cr. However, this does not preclude the adsorption of small concentrations of Cr onto Fe-oxide surfaces that may be released under favorable geochemical conditions. Under oxidizing conditions, Cr in the +6 oxidation state is present as monovalent ($HCrO_4^-$) and divalent (CrO_4^{2-}) anionic species that are relatively soluble and

Table 10. Summary of sequential extraction results for 86 selected drill-core samples from the Central Oklahoma aquifer

[Mean concentrations for sample set are in parts per million (ppm), and extraction results are in percentage extracted. Blanks indicate that the result was less than the analytical detection level, and dashes (--) indicate that the analytical procedure was not performed. Number in parentheses () indicates number of samples in sample set]

Sample set	Mean (ppm)	Percentage of element extracted							
		KCl	KH_2PO_4	Readily extracted	HCl	HCl + $KClO_3$	Mixed Acid	$NaHCO_3$	$NaHCO_3$ + NaOCl
					Arsenic				
Total sample set (549)	7.3								
Sequential extraction sample set (86)	11.6	1.7	5.1	6.8	41	5.7	47	3.4	5.4
Test hole 1A (12)	16.9	.5	3.0	3.5	38	10.9	48	1.4	4.2
2 (11)	8.7	4.4	5.5	9.9	40	6.6	44	2.4	4.9
5 (3)	1.7	7.2		7.2	16		77	2.5	5.0
6 less than 300 feet (2)	15.5	1.8	3.6	5.4	53	5.7	36	1.9	7.8
6 greater than 300 feet (26)	12.6	1.3	3.1	4.4	45	6.4	45	2.1	6.0
7 (11)	6.8	1.9	7.8	9.7	24	2.0	64	5.6	--
7A (21)	12.6	.4	8.2	8.6	50	4.3	37	5.6	--
					Chromium				
Total sample set (549)	56								
Sequential extraction sample set (86)	61				33	2.9	64		
Test hole 1A (12)	53				41		59		
2 (11)	69				29	4.6	67		
5 (1)	27				26		74		
6 less than 300 feet (1)	49				37		63		
6 greater than 300 feet (25)	43				30	3.0	67		
7 (11)	78				30	4.5	66		--
7A (21)	78				39	3.0	58		--
					Selenium				
Total sample set (549)[1]	0.90								
Sequential extraction sample set (64)	6.3	4.6	2.1	6.7	8.5	52	33	6.8	5.9
Test hole 1A (12)	1.3	1.4	1.1	2.5	14	33	50	5.1	7.0
2 (8)	14.7	10.8	6.7	17.5	4.3	58	20	12.4	10.2
5 (3)	2.6	1.3		1.3	5.8	90	2.9		11.1
6 less than 300 feet (2)	1.2				42	22	36	3.2	1.8
6 greater than 300 feet (25)	8.8	.7	.5	1.2	7.6	58	34	4.9	4.2
7 (6)	1.2	12.0	5.8	17.8	3.3	42	37	10.2	--
7A (8)	2.8	13.6	2.4	16.0	2.5	58	23	9.5	--
					Uranium				
Total sample set (549)	3.64								
Sequential extraction sample set (86)	9.2	.2	4.7	4.9	47	3.3	45	11.3	8.5
Test hole 1A (12)	3.8		7.4	7.4	44	4.9	44	6.1	6.5
2 (11)	9.4		3.9	3.9	53	4.6	40	11.4	11.3
5 (3)	6.0		5.9	5.9	66	4.2	24	14.2	20.6
6 less than 300 ft. (2)	2.5	5.9		5.9	27		67	2.3	
6 greater than 300 ft. (26)	10.7		8.5	8.5	47	2.6	42	11.4	8.2
7 (11)	25.1		1.7	1.7	52	5.1	41	19.0	--
7A (21)	2.9		.8	.8	42	1.8	55	10.3	--

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[1] Of the 549 samples, 346 samples had detectable selenium greater than or equal to 0.1 ppm. The mean for the 346 values was 1.4 ppm (Mosier and others, 1990b).

undergo little retardation by adsorption (Cherry, Gillham, and Barber, 1984).

Selenium

Se was detected at concentrations greater than or equal to 0.1 ppm in 346 of the drill-core samples. The mean concentration for the 346 samples with detectable Se was 1.4 ppm (total) (Mosier and others, 1990b) compared to a mean concentration of 6.3 ppm (total) (table 10) for the 64 samples used in the partial dissolution study that contained greater than or equal to 0.2 ppm Se. A large portion of the Se (52 percent) in all analyzed rocks was solubilized during oxidative dissolution (HCl + $KClO_3$). This conditionally extractable Se is present in red as well as green rocks and may be native Se and clausthalite (PbSe), which were detected in the aquifer (Breit and others 1990b). Reduction spots and small localized lenses of green rocks have the highest concentrations of Se. Approximately 90 percent of Se in these rocks was solubilized by the oxidative dissolution step, indicating that the Se was primarily in a reduced form. However, a large amount of Se that was extracted by the oxidative dissolution step is contained in volumetrically much larger bodies of rock and is not lithologically or color dependent.

Samples containing readily extractable Se were irregularly distributed. Of the 28 samples that contained Se extractable by the KCl or the KH_2PO_4 treatments, 19 were comprised of green or white rock or were a mixture of green and red or white and red rock. No other common parameter was characteristic of the rocks with mobile Se. The percentage of readily extractable values (KCl + KH_2PO_4) and the percentage extraction value for $NaHCO_3$ were compared and were not consistent; however, the average amount of Se released by both groups are similar, 6.7 versus 6.8 percent. An oxidizing treatment ($NaHCO_3$/NaOCl) released additional Se subsequent to the $NaHCO_3$ extraction but perhaps not to the extent expected, considering the amount mobilized by the HCl/$KClO_3$ treatment. The adsorption edge for Se (VI) onto Fe oxyhydroxide is near pH 7 (Balistrieri and Chao, 1990), which is lower than most of the ground water in the aquifer. Therefore, adsorption on Fe oxides is not a factor for Se mobility, and in fact, goethitic rocks (those that are yellow-brown or reddish brown) typically have low Se content. Factor analysis studies indicate an association between Se and U (table 5). However, empirical tests using scatter diagrams and regression analysis suggest that Se and U behave independently. Regression analysis showing the relationship between total extractable Se and total extractable U using the 64 sample Se greater than or equal to 0.2 ppm data set has a r^2 of 0.11.

Uranium

The 86 extraction sample set has a mean concentration of 9.2 ppm U (total), and the total drill-core sample set has a mean concentration of 3.64 ppm U (total). Approximately equal proportions of U were solubilized by the HCl extraction step (47 percent) and the residual dissolution step (45 percent). For most samples, the KCl treatment was ineffective at leaching U. The $NaHCO_3$ extraction was far more effective at mobilizing U than the KH_2PO_4 extraction, 11.3 percent compared to 4.7 percent of contained U. At typical ligand concentrations in ground water, the most important uranyl complexes are formed with fluoride, phosphate, and carbonate under acid, near-neutral, and alkaline conditions, respectively (Langmuir, 1978). In the presence of phosphates and carbonates and at neutral to alkaline pH's and intermediate Eh's, oxidation and leaching of uraninites, UO_2 to U_3O_8, and coffinite, $USiO_4$, are greatly enhanced to form uranyl complexes (Langmuir, 1978). Lithology was not a major control on uranium content. All lithologic classifications had at least a few samples with enriched U, although conglomerates tend to have the least enrichment. The highest concentrations of U are in green rocks or in rocks with visible green mineralization. Higher U concentrations tend to increase the amount of HCl extractable and readily extractable U, particularly $NaHCO_3$ extractable. Uranyl carbonate complexes greatly increase the mobility of U. Water samples collected from the test holes had pH values ranging from 7.3 to 9.6 and bicarbonate concentrations ranging from 242 to 566 ppm (Schlottmann and Funkhouser, 1991). Where oxidized ground water with high pHs and high bicarbonate concentrations is present in the Central Oklahoma aquifer, uranyl di- and tri-carbonate complexes probably dominate.

TRACE-ELEMENT MOBILIZATION

The solid phases involved in soil-rock/water interactions in a natural system consist of heterogenic mixtures of various minerals and organic debris with a wide range of inherent chemical properties. Weathering processes, primarily chemical and biological, in the surficial environment of central Oklahoma together with the mechanical processes by which the products of weathering are eroded, transported, and redeposited elsewhere are controlling factors in ground-water chemistry. Perhaps the most important processes in rock/water interactions are adsorption-desorption and cation-exchange reactions at mineral surfaces. The concentrations of many trace elements are believed to be controlled by adsorption-desorption reactions at mineral surfaces, with the equilibrium strongly affected by pH.

In the temperate climate of central Oklahoma, plant respiration and decay cause increases in the partial pressure of carbon dioxide in the soil gas (Parkhurst, Christenson, and Breit, 1993). This gas combines with moisture in the surficial environment to form carbonic acid, which contributes to chemical weathering of surficial materials. The geometric means for many elemental constituents in outcrop and soil samples, particularly Ca and Mg, are considerably lower than the geometric means in subsurface rock samples, indicating chemical weathering of the surficial materials. Some of these constituents are entering the ground-water system during recharge of the aquifer causing changes in the ground-water chemistry. The depletion of Ca and Mg in surficial material probably is due to dissolution of dolomite by carbonic acid, which results in the near-neutral Ca plus Mg bicarbonate water that is predominant in the shallow zone of the Garber Sandstone and Wellington Formation part of the aquifer (Parkhurst, Christenson, and Schlottmann, 1989). In the clay-rich confined and unconfined parts of the aquifer, the sediment contains high concentrations of Na. At these locations, Ca and Mg exchange for Na on the clay minerals, resulting in the development of a Na-bicarbonate water that is undersaturated with respect to dolomite causing additional dolomite dissolution. The dissolution of dolomite in the absence of carbon dioxide gas causes a rise in pH from near neutral to the 8.5 to 9.1 range.

Oxygen is not entirely depleted from recharge water by the poorly saturated soils that overly the aquifer, so that much of the water in the aquifer contains measurable oxygen (Parkhurst, Christenson, and Breit, 1993). Because of the oxic environment of the aquifer, it is assumed that the labile species of As, Cr, Se, and U are in their highest oxidation states (Schlottmann and Funkhouser, 1991; Parkhurst, Christenson, and Breit, 1993). Cherry, Gillham, and Barber (1984) show that under oxidizing conditions and normal pH conditions, As and Cr exist as monovalent and divalent anionic species ($H_2AsO_4^-$ at pH 3 to 7; $HAsO_4^{2-}$ at pH 7 to 12; $HCrO_4^-$ at pH 1 to 6; CrO_4^{2-} at pH 6 to 12). Se also exists as monovalent and divalent anionic species but has no solubility constraints under oxidizing conditions. In ground water that has an oxidizing redox condition and has appreciable carbonate alkalinity, U in the +6 oxidation state is present predominantly as anionic complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Langmuir, 1978; Cherry, Gillham, and Barber, 1984).

SUMMARY

Geochemical investigations were conducted in the area of the Central Oklahoma aquifer. One of the purposes of these investigations was characterizing the solid-phase materials in the aquifer. As, Cr, Se, and U are present in water in the aquifer at concentrations that in some instances exceed public drinking-water standards. The sites and mechanisms for the mobilization of environmentally important, naturally present trace elements into the ground water are among key questions concerning the water quality of the aquifer. To address these questions, surficial and subsurface solid-phase materials were collected from the Central Oklahoma aquifer to determine the abundance and distribution of their chemical constituents. The surficial materials sampled included B-horizon soils and outcrop rocks from the Central Oklahoma aquifer study unit. Subsurface rock samples were collected from eight drill cores obtained from test holes drilled at various locations in the aquifer. Seven of the test holes were placed at locations with known water-quality problems, and one test hole was located in an area in which ground water is known to have low concentrations of As, Cr, Se, and U. The solid-phase samples were analyzed for their chemical constituents by an inductively coupled plasma-atomic emission spectrometric technique for 40 elements, by hydride generation-atomic absorption spectroscopy for As and Se, and by delayed neutron activation analysis for U and Th.

The surficial materials from the area of the Central Oklahoma aquifer show typical abundances for both major and trace elements. R-mode factor analysis was used to identify geochemical associations in the surficial-sample data sets. Although neither major nor trace elements were abnormally enriched in the surficial materials from the Central Oklahoma aquifer, areal distribution plots of samples with high factor-analysis sample scores show clustering of samples that have similar chemical characteristics and identify areas of local enrichment of the environmentally important elements.

R-mode factor analysis applied to the drill-core data set identified element associations directly related to residence sites of the environmentally important elements and variations in the composition of the rocks that relate to water-quality problems. The subsurface rocks have median concentrations of 6.2 ppm As, 55 ppm Cr, 0.1 ppm Se, and 2.59 ppm U. Abundances as great as 62 ppm As, 170 ppm Cr, 110 ppm Se, and 123 ppm U were detected; however, all elements are not necessarily enriched in any one sample. The enriched samples were mostly isolated limonitic sandstone lenses and small grayish-green reduction spots.

The mobility of the elements in both typical and enriched subsurface rocks was assessed using a $NaHCO_3$ partial extraction technique and a five-step sequential extraction procedure. The $NaHCO_3$ extraction technique was used to mimic water in the aquifer and was effective in extracting small amounts of As, Se, and U. Sequential extractions provide information about the mode of occurrence, availability, mobilization, and transport of trace elements. The sequential extraction procedure includes steps for dissolving elements contained in soluble (KCl), ligand-exchangeable (KH_2PO_4), acid-soluble (HCl), oxidizable ($HCl–KClO_3$), and residual ($HF–HNO_3–HClO_4$) phases on or in solid materials. Appreciable amounts of As, Se, and U were extracted from some samples by the soluble and ligand-exchangeable extractions, indicating that significant quantities of these elements reside in phases that are readily available. Cr was not detected in the soluble or ligand-exchangeable extraction steps, possibly because of a higher analytical detection level for Cr than for the other elements.

As water moves through the aquifer, its chemical composition changes, mainly owing to dissolution of carbonate cements and to ion exchange with clay minerals. These changes and the presence of dissolved oxygen cause As, Cr, Se, and U to be oxidized to more soluble forms. The high pH of some aquifer water (pH greater than or equal to 8.5) augment desorption of the elements; thus, this process facilitates mobilization of the elements in the ground water.

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Summary of Geochemical and Geohydrologic Investigations of the Central Oklahoma Aquifer

By Scott Christenson, David L. Parkhurst, *and* George N. Breit

Abstract

Petrographic evidence and mass-balance geochemical modeling were used to determine the predominant geochemical reactions in the Central Oklahoma aquifer, and flow modeling, in combination with tritium and carbon-14 dating of water, was used to determine the rates and directions of ground-water flow. Calcium, magnesium, and bicarbonate are the dominant ions in water from the unconfined parts of the Garber Sandstone and Wellington Formation. This water chemistry is the result of uptake of carbon dioxide from the unsaturated zone (about 2.0 to 4.0 millimoles per liter; dissolution of dolomite (about 0.3 to 1.0 millimoles per liter) and, to lesser extents, dissolution of biotite, chlorite, plagioclase, and potassium feldspar, and precipitation of kaolinite. Sodium and bicarbonate are the dominant ions in water in the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and in the Chase, Council Grove, and Admire Groups. The sodium bicarbonate water is derived from the calcium, magnesium, and bicarbonate water by cation exchange of calcium and magnesium with sodium in clay minerals (approximately 2.0 millimoles per liter or more). Carbon-14-determined ages of water in the unconfined part of the aquifer generally are less than 10,000 years. Carbon-14 ages of water in the confined part of the aquifer range from about 10,000 to 30,000 years or older. Both confined and unconfined parts of the Central Oklahoma aquifer have an oxic or post-oxic oxidation-reduction environment as indicated by the large dissolved concentrations of oxygen, nitrate, arsenic (V), chromium (VI), selenium (VI), vanadium, and uranium.

Median values were estimated for the following aquifer properties: transmissivity of the Garber Sandstone and Wellington Formation, 24 to 42 meters squared per day; horizontal hydraulic conductivity of sandstone in the study unit, 1.4 meters per day; ratio of horizontal to vertical hydraulic conductivity, 10,000; porosity of sandstone, 0.22; storage coefficient, 0.0002; recharge rate, 41 millimeters per year.

A finite-difference ground-water flow model was used in conjunction with a particle-tracking model to simulate flow of ground water in the Central Oklahoma aquifer. Results of these models combined with the results of the geochemical investigation show that flow in the Central Oklahoma aquifer has three major components: (1) a shallow, local flow system in the unconfined part of the aquifer with transit times of tens to hundreds of years, (2) a deep, regional flow system in the unconfined part of the aquifer with transit times as much as 5,000 years or greater, and (3) a deep, regional flow system in the confined part of the aquifer, with transit times ranging from thousands to tens of thousands of years. Hydrogeochemical processes have occurred to different extents within these three flow systems in the aquifer. In the shallow, local flow system, the rapid flux of water has been sufficient to remove most of the dolomite, calcite, and exchangeable sodium. In the deep, regional flow system of the unconfined part of the Garber Sandstone and Wellington Formation, the flux of water has been sufficient to remove most of the exchangeable sodium, but sufficient carbonate minerals remain to maintain dolomite and calcite equilibrium. In the confined part of the Garber Sandstone and Wellington Formation and in the less transmissive parts of the unconfined aquifer, including the Chase, Council Grove, and Admire Groups, ground-water flow is slowest, and the flux of water and extent of reactions have been insufficient to remove either the carbonate minerals or the exchangeable sodium on clay minerals.

INTRODUCTION

One of the stated goals of the National Water-Quality Assessment (NAWQA) Program is to "identify, describe, and explain, as possible, the major factors that affect the observed water-quality conditions and trends" in the NAWQA study units (Hirsch, Alley, and Wilber, 1988). The existing state of knowledge concerning the geochemistry and geohydrology of the Central Oklahoma aquifer was recognized early in the planning phase of the study to be insufficient to meet this goal of the NAWQA Program (Christenson and Parkhurst, 1987, p. 19–20). To provide this basic knowledge, geochemical and geohydrologic investigations of the Central Oklahoma aquifer were initiated.

Purpose and Scope

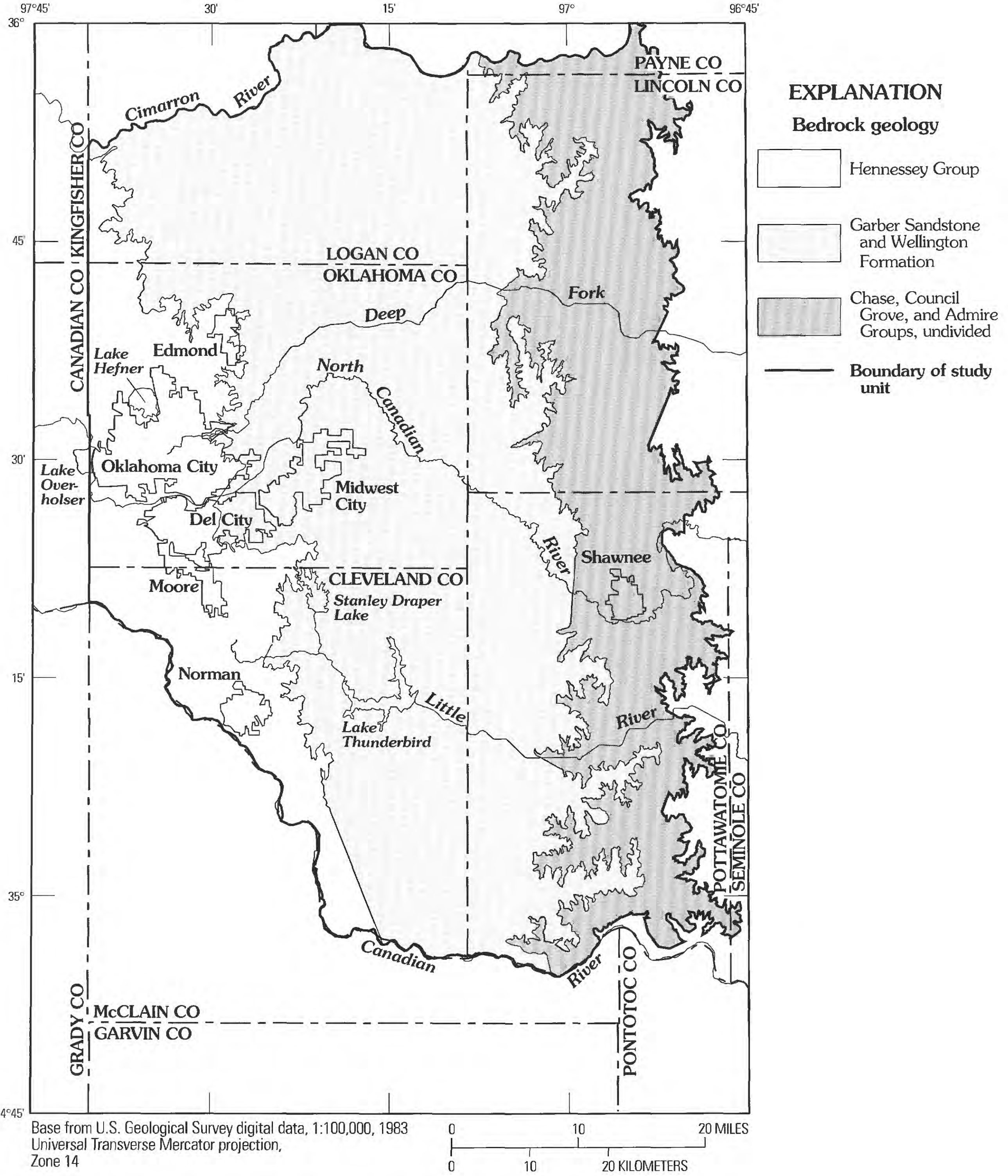
This report summarizes results of the geochemical and geohydrologic investigations of Permian geologic units of the Central Oklahoma aquifer that were described in detail in Parkhurst, Christenson, and Breit (1993). In the geochemical investigation, core material was examined and chemical and isotopic analyses of ground water were made to identify the major geochemical reactions in the aquifer and to develop mass-balance models that quantify the extent to which these reactions occur. In addition, the mass-balance models were used with measurements of tritium and carbon-14 to estimate ground-water ages. In the geohydrologic investigation, geologic and hydrologic data were examined to define the geometry, stratigraphy, lithology, and hydraulic properties of the aquifer, the distribution of hydraulic head, and the rates of recharge and discharge. These aquifer properties were used to develop a conceptual model, which was the basis of numerical flow and particle-tracking models; these models then were used to quantify the rates and directions of ground-water flow. The results of the two investigations were combined to provide a consistent explanation of the long-term hydrogeochemical processes that are occurring in the aquifer.

Definition and Extent of the Central Oklahoma Aquifer

A comprehensive description of the Central Oklahoma aquifer and the area studied by the Central Oklahoma NAWQA are provided in this volume by Christenson (1997). Brief definitions of the aquifer, the "study area," and the "study unit" are provided here.

The Central Oklahoma aquifer is defined by the limits of freshwater flow in the geologic units of central Oklahoma (fig. 1). Most of the freshwater within the aquifer is in the Permian Garber Sandstone and the Wellington Formation. Substantial quantities of freshwater also are present in the Permian Chase, Council Grove, and Admire Groups, which are stratigraphically below the Garber Sandstone and Wellington Formation, and in Quaternary alluvium and terrace deposits, which are associated with the major streams in the study area. To the north and south of the study unit, the transmissivities of the Garber Sandstone, Wellington Formation, and Chase, Council Grove, and Admire Groups decrease to the extent that these geologic units no longer yield large quantities of water to wells. The Cimarron and Canadian Rivers define the northern and southern extent of the aquifer because transmissivity decreases at the approximate location of these rivers and because available data indicate no ground-water underflow beneath these rivers. The eastern boundary of the aquifer is the eastern edge of the outcrop of the Chase, Council Grove, and Admire Groups. The presence of brine in the western part of the study unit and below the aquifer indicates the extent of the freshwater flow system in these directions. The aquifer is unconfined in the eastern two-thirds of its areal extent and confined in the western one-third by the Hennessey Group.

Two terms are used in this report to describe the limit of the study in relation to the Central Oklahoma aquifer—"study area" and "study unit." The term "study area" is used to describe the area bounded by 34°45′ and 36°00′ north latitude, and 96°45′ and 97°45′ west longitude. The term "study unit" is used to define the volume of earth between land surface and the base of fresh ground water, bounded by the extent of the Central Oklahoma aquifer. Data were collected beyond the boundaries of the Central Oklahoma aquifer to determine the effects of adjacent geologic units on the geochemistry and geohydrology of the aquifer. Thus, the study area is larger than the area overlying the study unit. The study unit contains a large volume of the Hennessey Group, which is not part of the Central Oklahoma aquifer. However, water in the Hennessey Group affects water quality in parts of the Central Oklahoma aquifer.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 1. Bedrock geology and major features of the Central Oklahoma aquifer study unit.

GEOCHEMISTRY

The Central Oklahoma aquifer is unconfined in the eastern two-thirds of its areal extent and confined in the western one-third by the Hennessey Group. Calcium, magnesium, and bicarbonate are the dominant ions in water in the unconfined parts of the Garber Sandstone and Wellington Formation and the alluvium and terrace deposits (fig. 2). Sodium and bicarbonate are the dominant ions in water in the other Permian geologic units that overlie or are part of the Central Oklahoma aquifer; that is, in the Hennessey Group, the confined part of the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and Admire Groups (fig. 2).

The predominant source of recharge to the aquifer is rainfall. A comparison of the concentrations of major elements in rainwater to those in shallow ground water indicates that rainwater cannot be an important source of chemical constituents unless evapotranspiration concentrates the constituents. Most of the rainfall that enters the unsaturated zone of the study unit is returned to the atmosphere through evapotranspiration. If evapotranspiration concentrates the chemical constituents of rainwater tenfold or more, rainwater can account for most of the potassium, sulfate, phosphate, and nitrogen species in ground water. Rainwater is not a major source of calcium, magnesium, sodium, alkalinity, or chloride in ground water.

The bromide-to-chloride ratios in water from the Central Oklahoma aquifer are consistent with a brine source for dissolved bromide and chloride in ground water. Brine underlies the Central Oklahoma aquifer and is present in fluid inclusions or dead-end pores within the aquifer. The brine most likely is derived from seawater by evaporation and other diagenetic processes. The bromide-to-chloride ratios of the brine indicate that evaporation of seawater proceeded to the point of halite precipitation (Carpenter, 1978).

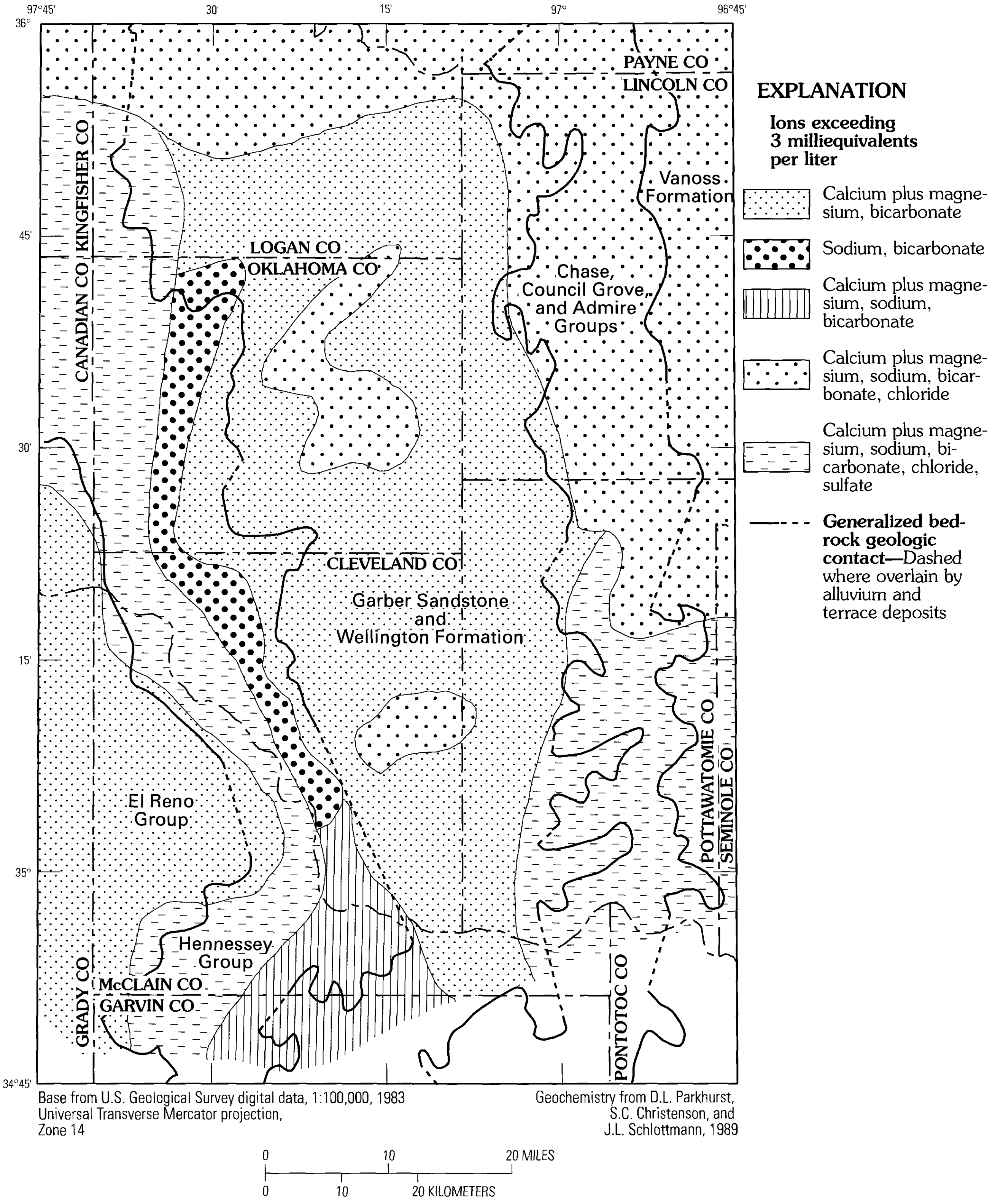
Nearly all of the Central Oklahoma aquifer has an oxic or post-oxic oxidation-reduction environment as indicated by the large dissolved concentrations of oxygen, nitrate, arsenic (V), chromium (VI), selenium (VI), vanadium, and uranium. Post-oxic environments, in which the ground water lacks measurable dissolved oxygen, were most common in the alluvium and terrace deposits, the Chase, Council Grove, and Admire Groups, and in the confined and deep, unconfined parts of the Garber Sandstone and Wellington Formation. Sulfidic and methanic environments are virtually absent, and minerals with elements in reduced oxidation states are restricted to very small, rare reduced zones (less than 1 cm in diameter).

Saturation indices and petrographic observations indicate that several minerals may be reacting throughout most of the aquifer. Etch pits, dissolution voids, and variations in mineral abundances indicate that dolomite, calcite, sodic plagioclase, potassium feldspars, chlorite, rock fragments, and micas are dissolving. In contrast, euhedral, smooth-faced kaolinite and quartz overgrowths are due to precipitation of these minerals as a result of dissolution of aluminosilicate minerals.

Clay minerals constitute as much as 30 percent of the aquifer material; the largest percentages of these minerals are in mudstone. The dominant exchangeable cations in most clay samples are calcium and magnesium. Sodium can account for as much as 50 percent of the exchangeable cations in some mudstone samples. Exchangeable sodium tends to be greater in clay minerals within sandstone from the deep part of the aquifer than in clay minerals within sandstone from the shallow part of the aquifer. Variations in the quantity of exchangeable sodium in clay minerals indicate that cation exchange is occurring within the aquifer.

Gypsum may be present locally within the aquifer, as indicated by water that contains large concentrations of sulfate. Gypsum was not found in core samples collected for this study but has been identified within the Hennessey Group. Saturation indices indicate gypsum should dissolve, if present. Although most water samples are saturated with barite, relatively little barite was found in core samples. Iron and manganese oxides are present as alteration products derived from unstable silicate and carbonate minerals.

Mass-balance models were derived for two sets of ground-water samples: (1) recharge samples, as determined by young tritium or carbon-14 ages (0 to 3,000 years), and (2) carbonate-saturated samples, which were older and included all other samples. Mass-balance models quantitatively account for the geochemical evolution of recharge water by uptake of carbon dioxide from the unsaturated zone (about 2.0 to 4.0 mmol/L); dissolution of dolomite (about 0.3 to 1.0 mmol/L), and to lesser extents, dissolution of biotite, chlorite, plagioclase, and potassium feldspar; and precipitation of kaolinite and, perhaps, a pure silica phase. Cation exchange of calcium and magnesium for sodium occurs to a limited extent locally (usually less than 1.0 mmol/L). Small quantities of sulfate are derived from rainwater or dissolution of gypsum.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Geochemistry from D.L. Parkhurst,
S.C. Christenson, and
J.L. Schlottmann, 1989

Figure 2. Major-element chemistry in the shallow part (depths less than 30 meters) of the study area.

Large concentrations of nitrate and chloride in some recharge samples indicate recent contamination.

The reactants and products in the mass-balance models for the recharge samples are consistent with the results of petrographic studies of aquifer material and saturation indices. The mass-balance models also are consistent with the carbon-isotope data. The models imply reasonable isotopic compositions for carbon dioxide gas in the unsaturated zone (–16.0 to –25.0 per mil, $\delta^{13}C$ [carbon-13] relative to the Peedee belemnite standard). The assumption of equilibrium isotopic fractionation between the aqueous phase and unsaturated-zone carbon dioxide gas fits the data better than the assumption of no isotopic fractionation.

The uptake of carbon dioxide and dissolution of dolomite results in recharge water in which bicarbonate is the dominant anion and equimolar calcium and magnesium are the dominant cations. About half of the recharge water is undersaturated with dolomite and calcite. Recharge water that is undersaturated with carbonate minerals has pH values that range from 6.0 to 7.3, and, in the absence of cation exchange, recharge water that is in equilibrium with carbonate minerals has pH values that are about 7.5. By the time recharge water enters the deeper parts of the flow system, it is saturated or supersaturated with dolomite and calcite.

Mass-balance modeling of carbonate-saturated samples, which include all of the samples from wells more than 91 m deep, indicates that, following carbonate-mineral equilibration, cation exchange of calcium and magnesium for sodium is the dominant geochemical reaction. However, cation exchange occurs to a substantial extent only in parts of the aquifer. Mass transfers by cation exchange tend to be less than 2.0 mmol/L in the unconfined part of the Garber Sandstone and Wellington Formation; mass transfers of more than 2.0 mmol/L cation exchange occur in the confined part of the Garber Sandstone and Wellington Formation and in less transmissive parts of the aquifer, including the Chase, Council Grove, and Admire Groups. Other reactions derived from mass-balance modeling of the carbonate-saturated samples include dissolution of small quantities of dolomite, calcite, biotite, chlorite, plagioclase, and potassium feldspar and precipitation of kaolinite and a silica phase. Gypsum dissolution or leakage of sulfate-rich water from the Hennessey Group can account for sulfate concentrations, and sodium chloride brine can account for chloride concentrations. The mass-balance models for the carbonate-saturated samples are consistent with the petrographic data and, except for some models for one sample, all of the models are consistent with the available $\delta^{13}C$ data.

The cation-exchange reaction accounts for the transition from calcium magnesium bicarbonate to sodium bicarbonate water compositions. The decrease in calcium and magnesium concentrations leads to the dissolution of carbonate minerals, which, in combination with dissolution of aluminosilicate minerals, tends to increase the pH of ground water. Ground water in the confined Garber Sandstone and Wellington Formation and parts of the Chase, Council Grove, and Admire Groups commonly has pH values that range from 8.6 to 9.1.

Carbon-14 ages of water in the unconfined part of the Central Oklahoma aquifer generally are less than 10,000 years. Carbon-14 ages of water in the confined part of the aquifer range from about 10,000 to 30,000 years or older. These ages produce a time trend in δD (deuterium) values that is qualitatively consistent with the timing of the transition from the last glacial maximum to the present interglacial period.

GEOHYDROLOGY

A conceptual model of the flow system in the Central Oklahoma aquifer was developed from information about the lithology and geometry of the geohydrologic units, the water table, the hydraulic properties of the aquifer, and recharge and discharge; a summary of this information is presented in this volume by Christenson (1998). The conceptual model is based on the hydraulic properties, primarily transmissivities, of the geologic units. The most transmissive units are the Permian Garber Sandstone and Wellington Formation, and Quaternary alluvium and terrace deposits; the Permian Chase, Council Grove, and Admire Groups are less transmissive on the basis of the available specific-capacity data. The transmissivities of the Permian geologic units depend largely on the percentage of sandstone in the units. The percentage of sandstone is greatest in the central part of the aquifer and decreases outward in all directions. Because of large mudstone and siltstone contents, the Permian Hennessey Group and the Pennsylvanian Vanoss Formation are assumed to be confining units above and below the aquifer.

Aquifer properties were evaluated using data collected as part of this study and data from other sources including Wood and Burton (1968), Gates, Marsh, and Fryberger (1983), and drillers' logs. Estimates of transmissivity for the Garber Sandstone and Wellington Formation ranged from 2.0 to 330 m^2/d, and median values (depending on the source of data) ranged from 24 to 42 m^2/d. Estimates of the horizontal hydraulic conductivity of sandstone in the study unit ranged from 0.049 to 37 m/d, and had a median of 1.4 m/d. The median porosity of sandstone in the Permian geologic units was determined from point counts of thin sections to be 0.22. The median storage coefficient calculated from data from six aquifer tests in the Garber Sandstone and Wellington Formation was 0.0002 (Gates, Marsh, and Fryberger, 1983). The median recharge rate estimated from measurements of base flow to streams was 41 mm/yr.

A digital ground-water flow model was used to simulate the Central Oklahoma aquifer flow system. The model simulates flow in three dimensions and uses a block-centered, finite-difference approach. The Central Oklahoma aquifer flow model contains 40 columns, 60 rows (fig. 3), and, because vertical flow is significant, 12 layers. In the x- and y-dimensions, cells are 2,000 m on a side, and cell spacing is constant throughout the modeled area. The model layers do not correspond to individual, dipping geologic units, as in many flow models. Instead, the layers are horizontal, and each cell is assigned to represent the geologic unit that is the thickest in that cell. Every layer is 30 m thick.

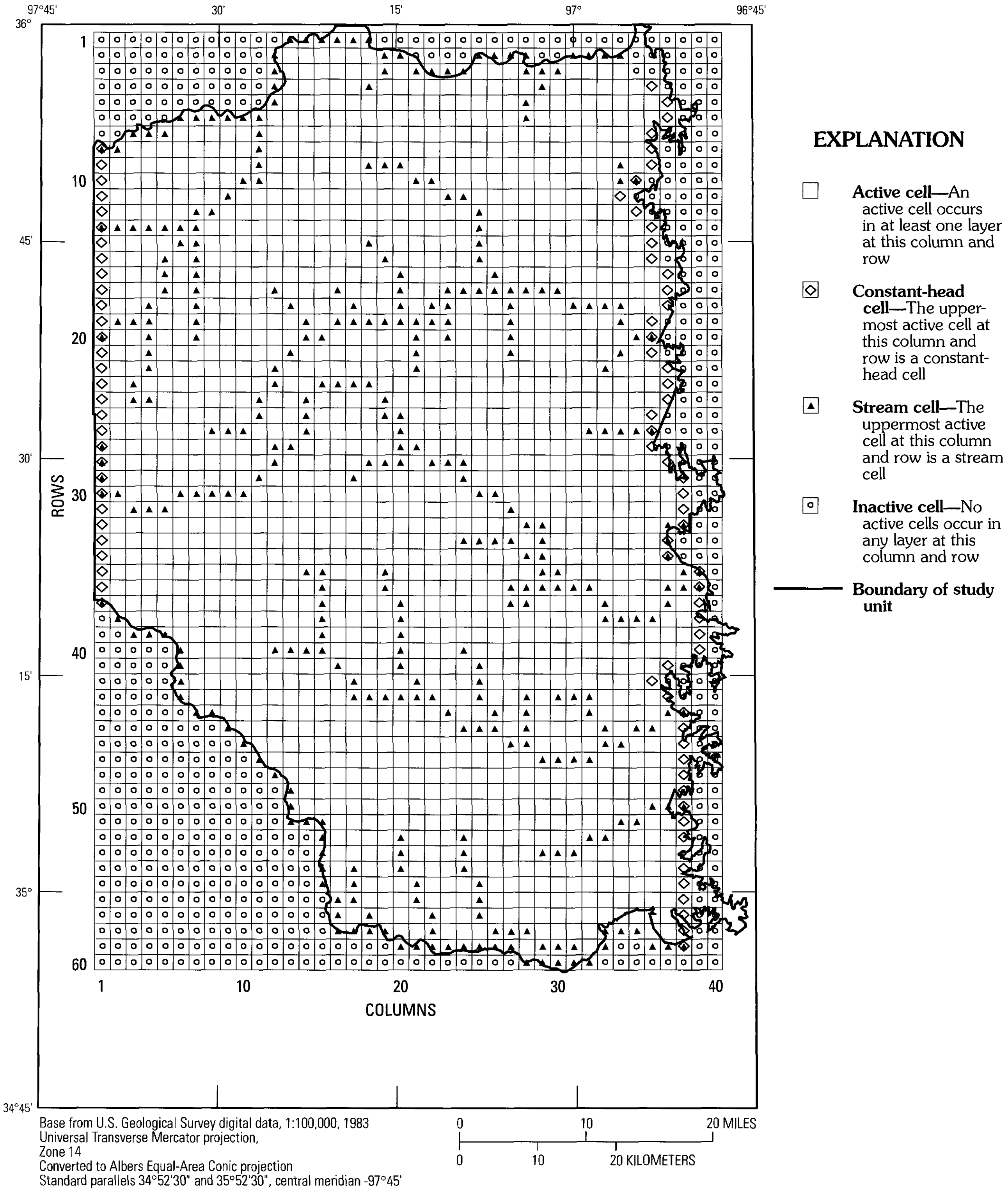
In conjunction with the digital ground-water flow model, a particle-tracking model was used to calibrate the flow model, assist in visualizing flowlines in the ground-water flow system, and integrate the results of the flow model with the analysis of the geochemistry of the Central Oklahoma aquifer. The particle-tracking model generates pathlines, which are the routes of hypothetical "particles" of water moving through the flow system simulated by the flow model. In addition to calculating the position of pathlines, the particle-tracking model was used to compute the time of travel of water along flowlines.

The ground-water flow and particle-tracking models were calibrated to match observed hydraulic heads (water levels), sulfate concentrations, and ages of ground water (based on carbon-14 and tritium concentrations). The model calibration proved to be particularly sensitive to the ratio of horizontal to vertical hydraulic conductivity. The ratio that resulted in the best calibration was 10,000.

The calibrated models were used to visualize flowlines in the Central Oklahoma aquifer. Pathlines were generated by placing particles at selected locations in the recharge area, which is the unconfined, eastern two-thirds of the aquifer (fig. 4).

The ground-water flow and particle-tracking models, in conjunction with the results of the geochemical investigation, show that flow in the Central Oklahoma aquifer has three major components:

1. *A shallow, local flow system in the unconfined part of the aquifer*—In this flow system, ground water is recharged by infiltration from precipitation and moves relatively quickly along short flowlines from the point of recharge to the point of discharge at the nearest stream. Transit times are tens to hundreds of years. Many water samples from shallow wells contain large concentrations of tritium, which indicate ground-water ages of less than 40 years.
2. *A deep, regional flow system in the unconfined part of the aquifer*—In this flow system, water takes more time to move along longer flowlines than in the shallow, local flow system. Most of the water in this flow system is recharged along ridges that correspond to ground-water divides between drainage basins. Transit times for water recharging the aquifer along some ridges is greater than 5,000 years. The model simulations also indicate water in the deep, regional flow system in the unconfined part of the aquifer flows under some streams (such as from south to north under the North Canadian River) to discharge at other streams at lower elevations.
3. *A deep, regional flow system in the confined part of the aquifer*—This flow system in the confined part of the Garber Sandstone and Wellington Formation is recharged from a small part of the outcrop area of the Garber Sandstone (located at about 35°23′ north latitude, 97°23′ west longitude). From the recharge area, water flows west under the confining unit to discharge to streams as far away as the Cimarron River. Flowpaths are relatively long, as long as 80 km. The transit times in this flow system range from thousands to tens of thousands of years. The modeled pathlines for water reaching some wells in the confined part of the aquifer indicate some flow through the Hennessey Group. Large sulfate concentrations in water samples from these wells are consistent



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14
Converted to Albers Equal-Area Conic projection
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Figure 3. Finite-difference grid used to simulate the Central Oklahoma aquifer ground-water flow system.

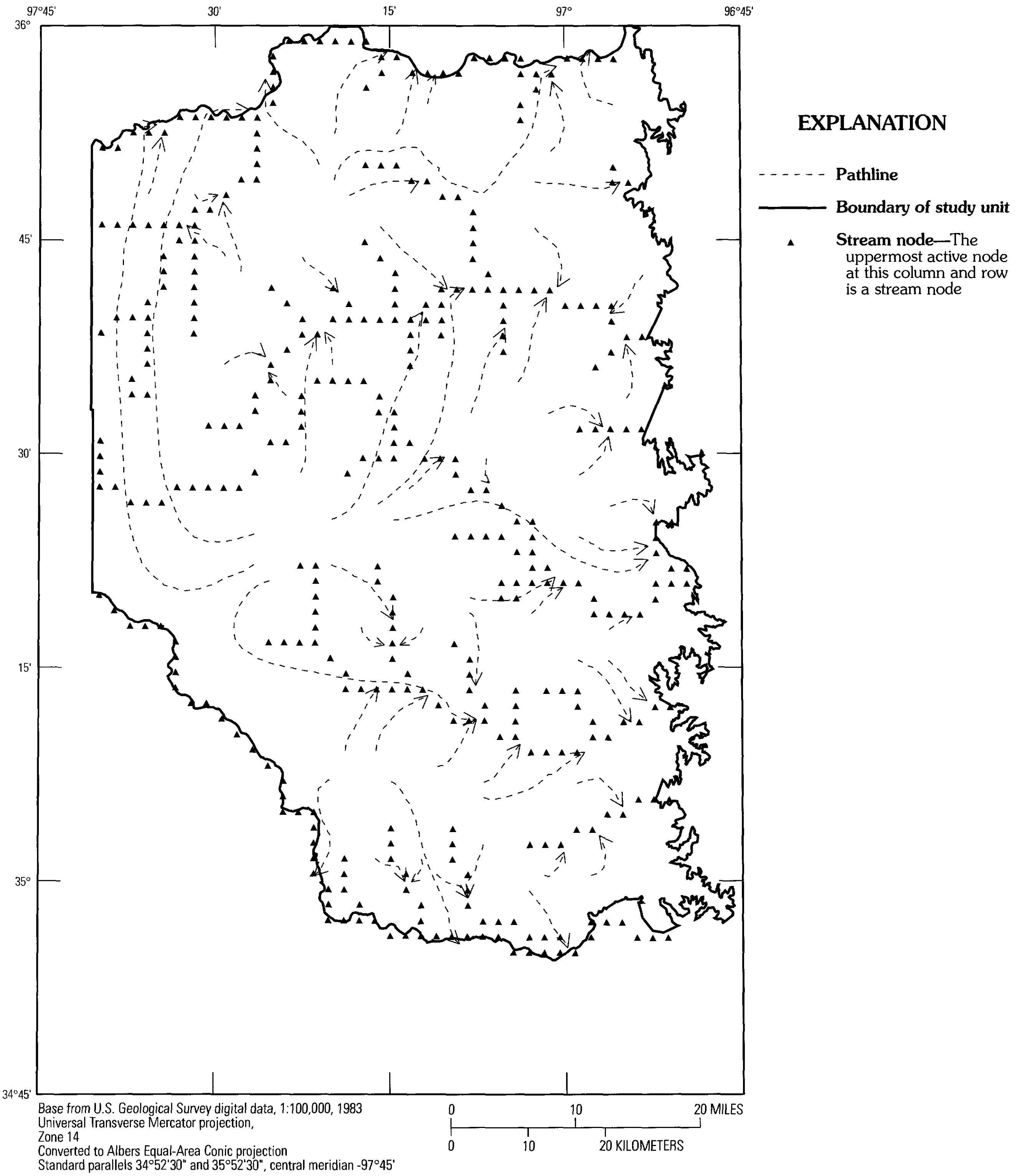

Figure 4. Selected pathlines generated by the particle-tracking model by placing a particle in selected cells that correspond to the unconfined part of the Central Oklahoma aquifer.

with a small flux of sulfate-rich water from the Hennessey Group.

CONCLUSIONS

Geochemical and petrographic data, combined with the results of a numerical flow model, provide a consistent description of the hydrogeochemical processes active in the Central Oklahoma aquifer. In the shallow, local flow system, ground water recharges the aquifer and discharges to nearby streams. Flow model and tritium ages indicate that the rate of flow and the flux of water are greatest in the local flow system. Continuous geochemical reactions associated with the large ground-water flux have been sufficient to deplete dolomite, calcite, unstable aluminosilicate minerals, and exchangeable sodium in many parts of the local flow system. The depletion of the carbonate minerals is demonstrated by large numbers of samples from shallow wells that are undersaturated with dolomite and calcite and by extensive dissolution textures visible in these minerals in core material. Petrographic examination determined that, in addition to carbonate minerals, chlorite and feldspars have been depleted in parts of the aquifer that have rapid, local flow systems. The small mass transfers of cation exchange in mass-balance models for recharge samples indicate that exchangeable sodium largely has been removed by exchange of calcium and magnesium (derived from dissolution of carbonates) for sodium. Concentrations of exchangeable sodium in clay minerals tend to be smallest in the shallow parts of the aquifer, which indicates that exchangeable sodium has been removed.

Carbon-14 and tritium ages of ground-water samples and flow-model results indicate that flow is slower and flowlines are longer in the deep, regional flow system of the unconfined Garber Sandstone and Wellington Formation than in the shallow, local flow system. In this regional flow system, ground water flows under nearby streams to discharge to streams at lower elevations. The flux of ground water through this regional flow system has not been sufficient to remove carbonate minerals. All ground-water samples from the deeper parts of the unconfined Garber Sandstone and Wellington Formation are saturated with dolomite, which indicates that this mineral is present and reactive. However, small mass transfers of cation exchange in the mass-balance models for samples from the deeper parts of the unconfined Garber Sandstone and Wellington Formation indicate exchangeable sodium largely has been removed.

Carbon-14 ages and flow-model results indicate that flow is slowest in the confined part of the Garber Sandstone and Wellington Formation and in the less transmissive parts of the unconfined flow system, including parts of the Chase, Council Grove, and Admire Groups. In the confined part of the aquifer, ground water recharges from a small area of the unconfined part of the aquifer, transits long flowlines, and discharges to streams at great distances from the recharge location. The flux of ground water through the confined part of the aquifer has not been sufficient to completely remove carbonate minerals (although petrographic data indicate carbonate minerals are dissolving) or exchangeable sodium. Mass-balance models for samples from these parts of the aquifer have large mass transfers of cation exchange, and the composition of the ground water generally has sodium as the dominant cation. Cation-exchange data indicate that exchangeable sodium is most abundant in mudstone; the large quantities of cation exchange that occur in the confined part of the aquifer and the large ratios of horizontal to vertical conductivity needed to model ground-water flow in the confined part of the aquifer are consistent with a substantial amount of flow through mudstone in the confined part of the aquifer.

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Arsenic, Chromium, Selenium, and Uranium in the Central Oklahoma Aquifer

By Jamie L. Schlottmann, Elwin L. Mosier, *and* George N. Breit

Abstract

The Central Oklahoma aquifer is a major source of drinking water for central Oklahoma. Concentrations of dissolved arsenic, chromium, selenium, and uranium in regions of the aquifer commonly exceed the 1986 Federal drinking-water standards for arsenic, chromium, and selenium and the 1991 proposed standard for uranium. Historical water analyses and analyses for water samples collected from 141 wells and from several depth intervals in 8 test holes were used to investigate the distribution and cause of the high concentrations of these elements. Rock core from the test holes was examined to determine sources of the elements in water and to define processes that transferred the elements from the rock to the water. The high concentrations of dissolved arsenic, chromium, selenium, and uranium were found to be a result of natural processes that are affected by: (1) the distribution of the elements in the solid phases, (2) the redox conditions, (3) the distribution of mudstone, and (4) changes in water chemistry as the water flows through the aquifer.

The Central Oklahoma aquifer is dominantly interbedded red-bed sandstone and mudstone of Permian age that gently dip west. Major and minor minerals in these rocks that affect water chemistry include mixed-layer illite-smectite, hematite, goethite, gypsum, and dolomite. Low-permeability rocks of the Hennessey Group confine the western third of the aquifer and overlie the sandstone-rich Garber Sandstone and Wellington Formation. Mudstone-rich rocks of the Chase, Council Grove, and Admire Groups underlie the Wellington Formation. Recharge to the aquifer is from precipitation, most of which enters the unconfined part of the aquifer and is discharged into nearby streams; a small part of the recharge enters near the aquifer center and flows along long regional flowpaths through the confined part of the aquifer to discharge into streams after thousands of years.

The base of the aquifer is the contact between fresh ground water and underlying sodium chloride brine that once filled the aquifer. Residual chloride from the brine and sulfate from dissolution of gypsum remain in mudstone-rich, poorly flushed regions of the aquifer. On the basis of spatial variations of water chemistry with depth, geologic unit, and confined or unconfined conditions, the aquifer is divided into six geohydrologic zones including: (1) shallow (less than 300 ft deep) unconfined Garber-Wellington, (2) deep (greater than or equal to 300 ft deep) unconfined Garber-Wellington, (3) shallow confined Garber-Wellington, (4) deep confined Garber-Wellington, (5) shallow Chase-Admire, and (6) deep Chase-Admire.

Concentrations of arsenic, chromium, selenium, and uranium in the ground water generally increase with depth in the unconfined zones of the aquifer and are highest in samples collected from near the base of freshwater. Higher concentrations are near the aquifer top in confined zones of the aquifer. Water in the shallow zones of the aquifer typically has only low arsenic and chromium concentrations. Water from all three shallow geohydrologic zones contains high selenium and uranium concentrations. Shallow wells with water that exceeds the drinking-water standards for arsenic, chromium, or selenium in unconfined zones of the aquifer are near major streams where old ground water that has traveled along long regional flowpaths discharges, which indicates that such high concentrations develop along long

flowpaths. Some shallow wells in unconfined zones of the aquifer with water that exceeds the proposed uranium standard are not near regional discharging streams, which indicates that high uranium concentrations can develop along short, local flowpaths. High concentrations of all four elements are common in the deep confined Garber-Wellington zone with the highest concentrations in the far western part of the ground-water flow system, in distal parts of regional flowpaths, and near the base of the confining layer.

High concentrations of solid-phase arsenic, chromium, selenium, and uranium were found in specific rock types. High arsenic concentrations are in yellow-brown goethite-cemented sandstones, high chromium concentrations are in mudstones and chromium-rich clays, and high selenium and uranium concentrations are in pale greenish-grey vanadium-rich reduced zones. High concentrations of all four elements also were associated with some red iron-oxide grain coatings in sandstone. Sequential extraction results indicated the elements are mobile in oxidizing, high-pH, bicarbonate type water.

Oxidizing conditions, which are indicated by concentrations of dissolved oxygen greater than 1 milligram per liter in most aquifer water, cause arsenic, chromium, selenium, and uranium to be in their relatively soluble, highest oxidation states. Spatial variations in redox conditions are related to mudstone distribution. Recharge through poorly drained clay-rich soils derived from the outcrop of the Chase, Council Grove, and Admire Groups and parts of the confining Hennessey Group is depleted of dissolved oxygen, which locally limits the mobility of chromium and selenium.

Distribution of mudstone in the aquifer also affects the major-element water chemistry as well as the abundance of dissolved arsenic, chromium, selenium, and uranium through decreases in permeability and increases in cation-exchange capacity. Low hydraulic conductivity in mudstones results in less flushing and higher residual concentrations of soluble arsenic, chromium, selenium, and uranium in solid phases and ground water than in sandstones.

As water flows into and through the Central Oklahoma aquifer, dolomite and carbon dioxide gas dissolve, and sodium bound to mixed-layer clays is exchanged for dissolved calcium and magnesium from dolomite. This results in water types ranging from calcium magnesium bicarbonate to sodium bicarbonate. Where the water is isolated from soil carbon dioxide in the deep and confined zones of the aquifer, these reactions result in pH values greater than 8.5 that favor desorption of oxidized arsenic, chromium, and selenium from iron oxides. Increased carbonate-ion activity at high pH favors the mobilization of uranium by carbonate complexation. High concentrations of selenium and uranium also are found in water with pH less than 8.0 in shallow unconfined zones of the aquifer where abundant mudstone interbeds create a clay-rich vadose zone. In this clay-rich vadose zone, cation exchange and dolomite dissolution occur in the presence of carbon dioxide, resulting in water with a near-neutral pH, but with a high alkalinity. The high alkalinity results in relatively high carbonate-ion activities that favor uranium mobilization. Oxidized selenium desorbs from iron-oxide surfaces at near-neutral pH.

High concentrations of arsenic, chromium, selenium, and uranium are common in specific regions of the aquifer. Individual sandstone layers yield water that exceeds the drinking-water standards for one or more of the elements, whereas vertically adjacent layers yield water of acceptable quality. Analysis of water samples collected from discrete sandstone layers through test wells before installation of public-supply wells could identify sandstone layers with high concentrations of the elements so that these layers can be isolated. Observation of test-hole drill cuttings and onsite measurement of sodium concentration, pH, and alkalinity may indicate which sand layers are likely to yield water that exceeds a drinking-water standard.

INTRODUCTION

The Central Oklahoma aquifer is a major source of drinking water. The aquifer is composed of clastic sedimentary rocks and underlies about 3,000 mi^2 in central

Oklahoma. Concentrations of dissolved arsenic, chromium, selenium, and uranium in the confined and deep zones of the aquifer commonly exceed the 1986 Federal drinking-water standards of 50 µg/L arsenic, 50 µg/L chromium, 10 µg/L selenium, and the 1991 proposed standard of 20 µg/L uranium (U.S. Environmental Protection Agency, 1986, 1991a). Dissolved selenium and uranium concentrations commonly exceed 10 µg/L and 20 µg/L in unconfined zones of the aquifer. These natural water-quality problems were studied by the U.S. Geological Survey as part of the National Water-Quality Assessment (NAWQA) Program. The study investigated the distribution of the four elements in water and rock in the aquifer, the water and rock characteristics associated with high dissolved concentrations of the elements, and the processes that transfer the elements from the rock into the water. The goal of the study was to provide information for area water managers to use in water exploration to avoid water that exceeds existing or proposed drinking-water standards for the four elements.

Arsenic, chromium, selenium, and uranium are toxic to humans after chronic exposure to high concentrations (National Academy of Science, 1977; Gough, Shacklette, and Case, 1979; U.S. Environmental Protection Agency, 1986, 1991a, b). The U.S. Environmental Protection Agency (EPA) has included them in a list of trace elements to be regulated in drinking water (U.S. Environmental Protection Agency, 1986, 1991a, b). A drinking-water standard is the maximum allowable concentration of an element in public drinking-water supplies. The drinking-water standard is exceeded when the concentration of the element is equal to or greater than the standard (U.S. Environmental Protection Agency, 1986).

Arsenic is thought to be essential for humans, and a minimum consumption of 25 to 50 mg/d has been recommended (U.S. Environmental Protection Agency, 1986). However, arsenic is known to be toxic to humans at high concentrations [400 to 10,000 µg/L in drinking water (Gough, Shacklette, and Case, 1979)] and is carcinogenic (U.S. Environmental Protection Agency, 1985). The toxicity of inorganic arsenic depends on its oxidation state. Trivalent arsenic species [arsenic (-III) and arsenic (III)] are most toxic, pentavalent arsenic [arsenic (V)] is less toxic, and native arsenic [arsenic (0)] is least toxic. In 1986, 50-µg/L arsenic was established as the primary drinking-water standard on the basis of studies of toxicity and carcinogenicity (U.S. Environmental Protection Agency, 1986). This concentration was considered to be safe for long-term use and would still meet the proposed minimum nutritional requirement.

The physiological effect of chromium on humans depends on its oxidation state. Trivalent chromium [chromium (III)] is essential for humans for maintenance of proper blood-sugar levels. Hexavalent chromium [chromium (VI)] can be toxic to organisms (U.S. Environmental Protection Agency, 1975). In 1986, 50 µg/L was established as the primary drinking-water standard for chromium on the basis of studies of chronic toxicity and carcinogenicity of chromium (VI) (U.S. Environmental Protection Agency, 1986). However, in 1989 a new standard of 100 µg/L was proposed because of a lack of data to suggest that ingested chromium is carcinogenic (U.S. Environmental Protection Agency, 1989). In 1991 the standard was increased to 100 µg/L (U.S. Environmental Protection Agency, 1991b). Because this study was conducted before the 100-µg/L standard was adopted, the distribution of chromium will dominantly be described for concentrations exceeding the previous 1986 standard of 50 µg/L, with comments concerning the distribution of water exceeding the 1991 100-µg/L standard.

Though elemental selenium [selenium (0)] is virtually nontoxic, long-term exposure to tetravalent selenium [selenium (IV)], hexavalent selenium [selenium (VI)], or organic complexes of selenium have been shown to be toxic (National Academy of Sciences, 1977; Gough, Shacklette, and Case, 1979; Hammond, 1979). Most historical cases of selenium toxicity resulted from consuming seleniferous plants or grains (Trelease and Beath, 1949). Because of indications of toxicity at an intake of 700 to 7,000 mg/d, a drinking-water standard of 10 µg/L was set by the Safe Drinking Water Act amendments of 1986 (U.S. Environmental Protection Agency, 1986). Selenium is an essential trace element, and some studies have indicated that selenium also may help to prevent certain types of cancer. The National Academy of Science has estimated an adequate and safe level of selenium consumption in water for human adults is 50 to 200 µg/L on the basis of studies of selenium toxicity and deficiency in China (U.S. Environmental Protection Agency, 1985). The EPA in 1985 proposed increasing the drinking-water standard to 45 µg/L, in order to meet this recommended level of consumption, and in 1989 rounded the proposed value up to 50 µg/L (U.S. Environmental Protection Agency, 1989). In 1991 the standard was increased to 50 µg/L (U.S.

Environmental Protection Agency, 1991b). Because this study was conducted before the 50-µg/L standard was adopted, the distribution of selenium dominantly will be described for concentrations exceeding the 1986 standard of 10 µg/L, with brief comments describing the 1991 50-µg/L standard.

Unlike the other elements investigated, uranium has not been shown to be an essential element. Uranium, taken internally, is a kidney toxin (National Academy of Sciences, 1980; U.S. Environmental Protection Agency, 1991a). Uranium also is a radionuclide, which results in an additional risk of cancer (U.S. Environmental Protection Agency, 1991a). Although there is little direct evidence that natural environmental uranium is carcinogenic, it is known that uranium deposits in the kidneys and bone over time give off ionizing radiation in amounts that can be estimated, knowing the decay rate of uranium isotopes. This radioactivity results in a potential cancer risk at high uranium activities (greater than 160 pCi/L) (U.S. Environmental Protection Agency, 1991a). On the basis of this knowledge, the EPA has proposed a drinking-water standard of 20 µg/L or 30 pCi/L uranium (30 pCi/L is estimated to be the radioactivity resulting from 20 µg/L uranium in most water) (U.S. Environmental Protection Agency, 1991a). At this writing (June 1994), the proposed 20-µg/L standard has not been adopted.

Spatial variation in concentrations of dissolved arsenic, chromium, selenium, and uranium in the Central Oklahoma aquifer is a result of: (1) the distribution of solid phases enriched with the elements, (2) the redox conditions, (3) the distribution of mudstone, and (4) changes in water chemistry as the water flows through the aquifer, particularly increases in pH and carbonate-ion activity.

PURPOSE AND SCOPE

This report describes the distribution of arsenic, chromium, selenium, and uranium in the ground water, sources of the four elements in the rock, the effects of redox conditions in the aquifer on the elements' mobility, the relation of lithology to the elements' distribution in rock and water, geochemical processes that result in the transfer of the elements from the rock into the water, and the resulting water chemistry associated with concentrations of the elements that exceed the 1986 or proposed 1991 drinking-water standards in the Central Oklahoma aquifer. The report also describes considerations for ground-water development in the aquifer on the basis of the known distribution of dissolved arsenic, chromium, selenium, and uranium. Maps show the distribution of sandstone and mudstone in the aquifer. Maps and contingency tables illustrate the distribution of the four elements in the aquifer. Tables summarize the distribution of the four elements in the aquifer and the redox conditions in wells with water that exceeds proposed or existing drinking-water standards. Piper diagrams show the relation of high element concentrations to water type, and graphs show the relation to pH, carbonate-ion activity, water age, and vanadium and boron concentration.

HYDROGEOLOGY

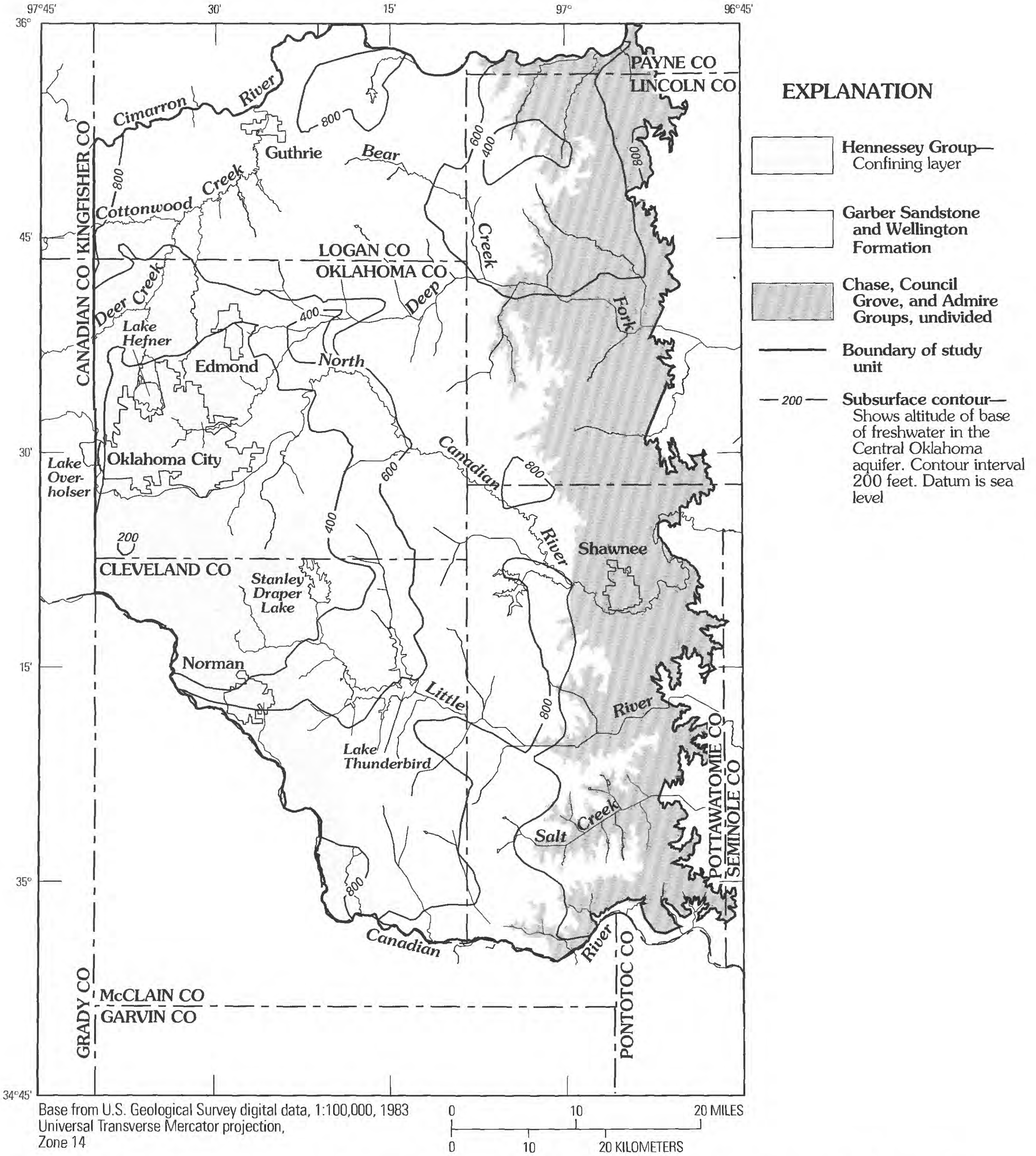
Geology

The Central Oklahoma aquifer underlies about 3,000 mi^2 in central Oklahoma. The aquifer is composed of Quaternary alluvium and terrace deposits and the underlying Permian sandstone and mudstone (see Christenson, 1998). The alluvium and terrace deposits were not included in this study because they typically do not contain water with high concentrations of arsenic, chromium, selenium, or uranium. Geologic units of Permian age include the Garber Sandstone, the Wellington Formation, and undivided rocks of the Chase, Council Grove, and Admire Groups. These dominantly red Permian units dip to the west at approximately 50 ft/mi. The western one-third of the aquifer is confined by the Permian Hennessey Group (fig. 1).

Petrography and Mineralogy

The aquifer is composed primarily of fine- and very fine-grained quartz-litharenite sandstone, lenticularly interbedded with mudstone. The mudstone is composed dominantly of mixed-layer illite-smectite.

Authigenic minerals that significantly affect water chemistry are hematite, goethite, gypsum, and dolomite (Breit, 1998). The most notable diagenetic feature of the aquifer is the pervasive red color that is caused by abundant grain-coating ferric oxides [dominantly hematite (Fe_2O_3)] and indicates the generally oxidized nature of the rocks. Locally, yellow-brown goethite [FeO(OH)] grain coatings color thick sequences of sandstone. Notable also are reduced zones and spots that represent local nonoxidized conditions in the rock. The reduced zones and spots are white or pale greenish



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 1. Major geographic and geologic features of the study unit and altitude of base of freshwater in the Central Oklahoma aquifer (modified from Christenson, Morton, and Mesander, 1992).

gray because of a lack of ferric oxides. Reduced zones typically are composed of very fine-grained sandstone or conglomerate. Reduced zones are most common in paleo-root zones and channel deposits in clay-rich parts of the aquifer. Reduced spots are in mudstone, are roughly spherical, typically are 1 to 4 cm in diameter, and have a dark-green or black mineralized center. Gypsum ($CaSO_4$) is present in evaporite beds in the confining Hennessey Group. Dolomite [$CaMg(CO_3)_2$] is present as nodules and geodes in mudstones, in conglomerate clasts, and as a diagenetic cement in conglomerate and some sandstone.

Distribution of Lithologies

The distribution of sandstone and mudstone in the aquifer affects ground-water flow and water chemistry. Maps depicting the distribution of thickness and percentage of sandstone are shown in figures 2 and 3. The maps are based on natural gamma-ray logs for water wells and test holes in areas where logs were available and on drillers' lithologic logs in areas where gamma-ray logs were not available. Gamma-ray logs were used because these logs commonly are recorded for water wells in the aquifer and because they are capable of differentiating sandstone and mudstone layers. Only the deepest wells were used for making the maps.

Total sandstone and mudstone thicknesses were determined by selecting a clean-sand line and mudstone baseline on the gamma-ray logs and drawing a dividing line halfway between these delimiting lines (fig. 4). Log intervals deflecting to the left of the dividing line (indicating low gamma counts) were considered to be sandstone; intervals deflecting to the right (indicating increased gamma counts) as mudstone. This definition was based on comparison of gamma-ray logs of test holes, drilled as part of this study, to the rock core. The method slightly underestimates thickness of clayey very fine-grained sandstone because some of these sandstones have higher gamma counts than other sandstones in the aquifer but is good for differentiating fine-grained sandstone and clean, very fine-grained sandstone from mudstone. Thin beds of conglomerate are not differentiated from sandstone by the gamma-ray log and were not considered in map preparation.

Total sandstone thickness ranges from less than 50 ft in the Chase, Council Grove, and Admire Groups to more than 600 ft at one location in the Garber Sandstone (fig. 2). Individual sandstone beds in the Chase, Council Grove, and Admire Groups typically are less than 25 ft thick, although some beds are as much as 100 ft thick locally. Individual sandstone beds in the Garber Sandstone and Wellington Formation typically are 20 to 60 ft thick; some sandstone beds are as thick as 300 ft in south-central Oklahoma County. The thickest total accumulations of sandstone (greater than 550 ft) are in central and south-central Oklahoma County. These thick accumulations lie within a large region of the aquifer where total sandstone thicknesses greater than 250 ft underlie all of the western half of Oklahoma County, south-central Oklahoma County, and the northwestern third of Cleveland County. The base of the aquifer is deepest in this region.

Sandstone percentage ranges from about 16 percent in the Chase, Council Grove, and Admire Groups to nearly 88 percent in a small region underlying southwestern Oklahoma County (fig. 3). The sandstone percentage decreases generally in all directions from southwestern Oklahoma County. On the basis of this spatial distribution, the aquifer can be divided into a clay-rich part (less than 40 percent sandstone) in the east, dominantly in the Chase, Council Grove, and Admire Groups, and a sand-rich part (greater than 40 percent sandstone) in the west.

Observation of gamma-ray logs showed that mudstone interlayers not only increase to the east where the Chase, Council Grove, and Admire Groups crop out, but also increase at depth in the Garber Sandstone and Wellington Formation near the base of freshwater. Mudstone interlayers also increase gradationally from the Garber Sandstone into the Hennessey Group.

Hydrology

The base of the Central Oklahoma aquifer (fig. 1) is defined as the base of freshwater that is marked by the transition from the bicarbonate type water that contains less than 5,000 mg/L dissolved solids to underlying sodium chloride brine (Hart, 1966). It is assumed that the brine once filled all geologic units that make up the aquifer and that the brine was slowly flushed from the aquifer by freshwater recharge (Parkhurst, Christenson, and Breit, 1993). Depth to the base of freshwater is greatest in the west-central part of the aquifer. In this sand-rich part of the aquifer, the base of freshwater lies as much as 1,000 ft below land surface, and the percentage of sandstone is generally greater than 60 (fig. 3). Increased transmissivity in this sand-rich part of the aquifer is thought to have resulted

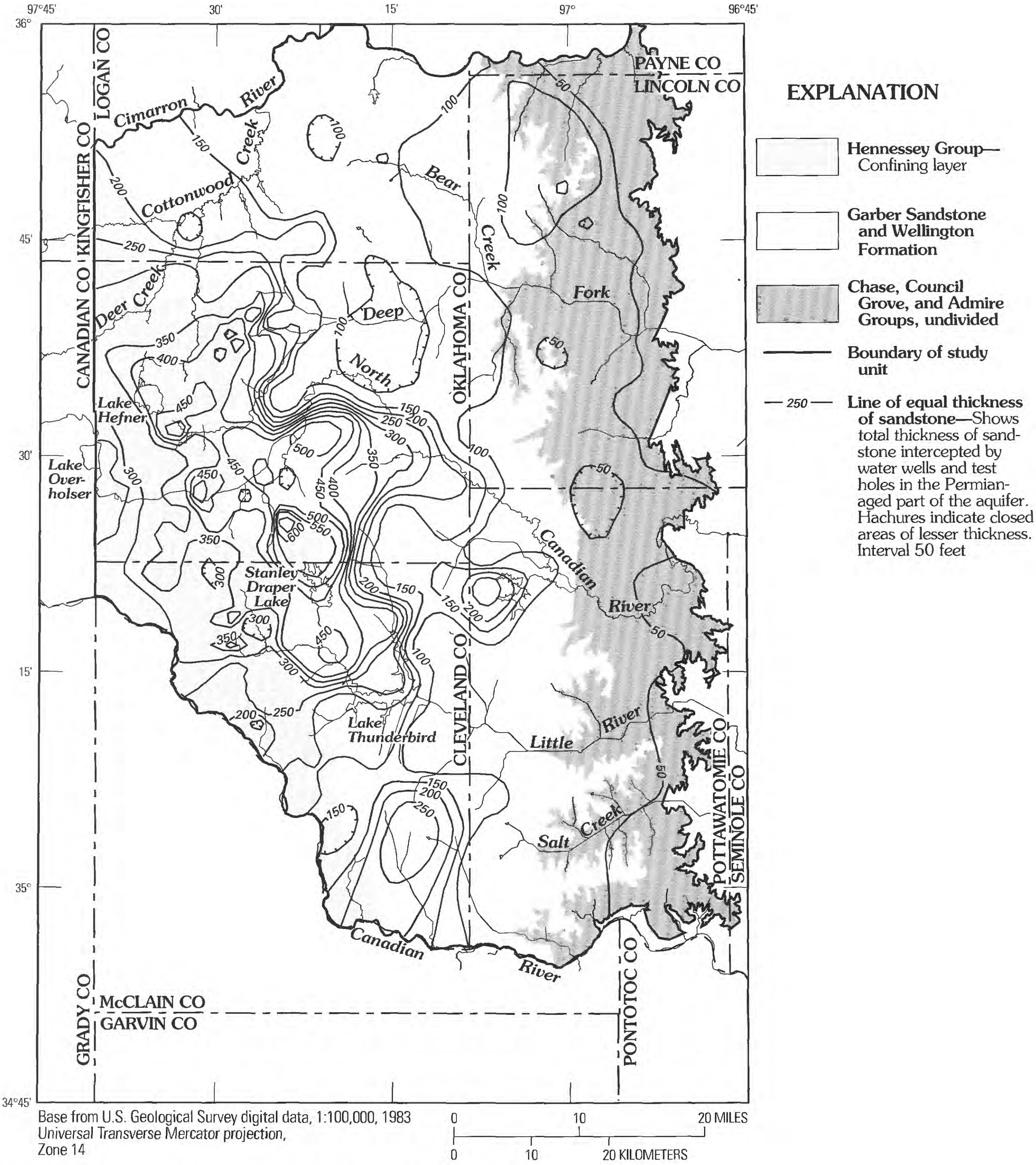


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Figure 2. Thickness of sandstone in the Central Oklahoma aquifer.

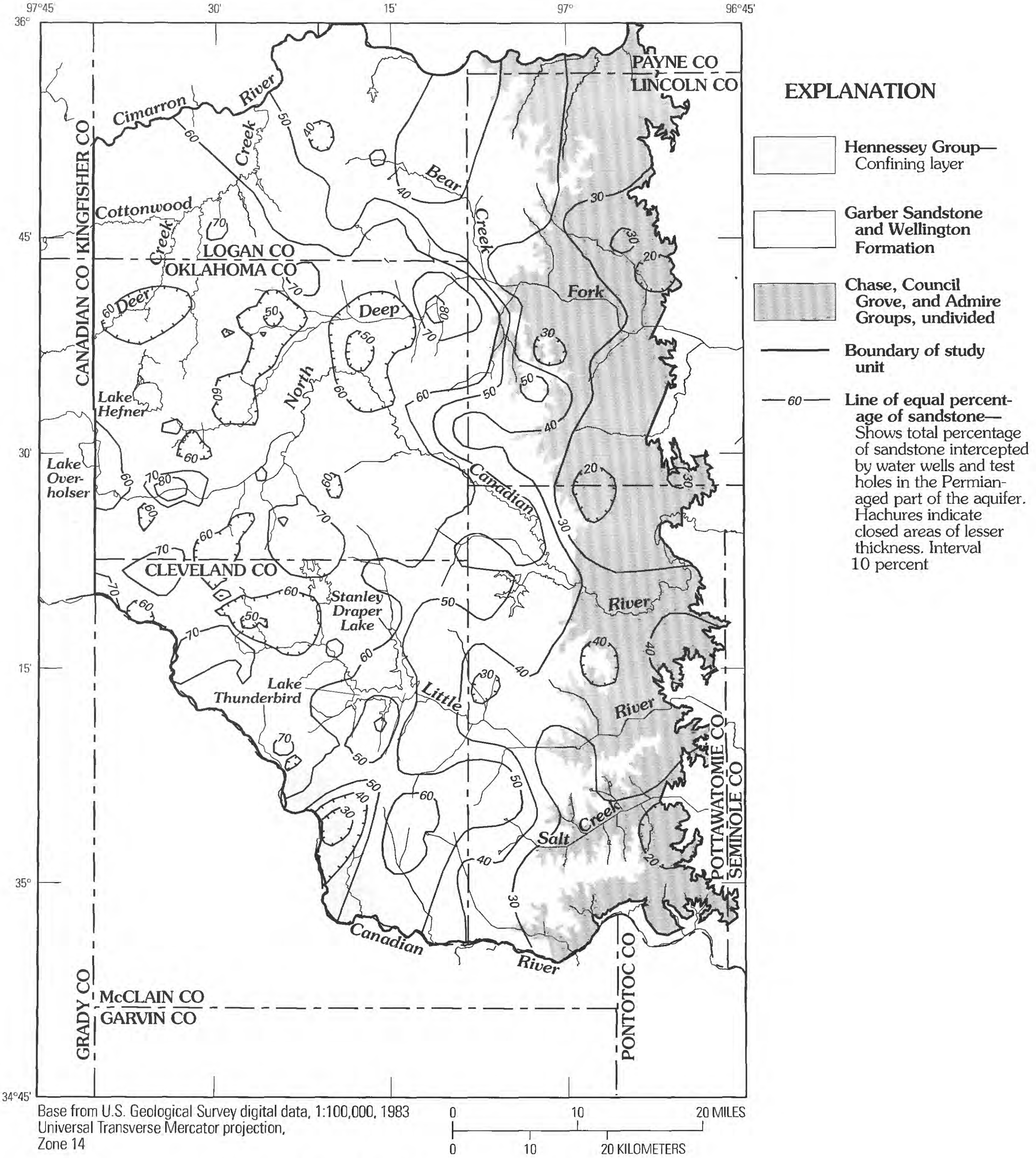

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Figure 3. Percentage of sandstone in the Central Oklahoma aquifer.

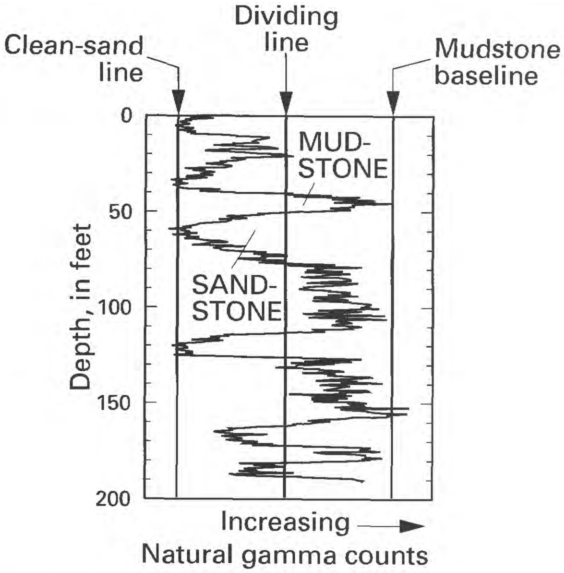

Figure 4. Lines used to differentiate sandstone and mudstone on gamma-ray logs.

in the great depth of flushing by freshwater. The base of freshwater becomes shallower to the north, south, and east where the percentage of sandstone decreases and the aquifer becomes more clay rich because of the increased percentage of mudstone interbeds. Decreased transmissivity related to increased numbers of mudstone interbeds reduces the depth of flushing by freshwater in clay-rich parts of the aquifer.

Recharge to the Central Oklahoma aquifer is dominantly from precipitation. Results of flow modeling (Parkhurst, Christenson, and Breit, 1993) indicate that most of the recharge enters the unconfined part of the aquifer and discharges into nearby streams within years to thousands of years. The Deep Fork and the Little River are major drains for the aquifer. The oldest water in the unconfined part of the aquifer is near the base of the aquifer and in the distal parts of regional flowpaths. The flow model indicates that, in the unconfined part of the aquifer, flow velocity is lowest near the base of freshwater (Scott Christenson, U.S. Geological Survey, oral commun., 1993).

A small part of the recharge flows west from the unconfined central sand-rich part of the Central Oklahoma aquifer into the confined part (fig. 5). The water flow then diverges to the north and south under the confining layer to discharge into streams. Water flowing to the north discharges into the Deep Fork, into the Cimarron River, and into Deer and Cottonwood Creeks. Water flowing to the south discharges into the Little River. Water that discharges from the confined part of the aquifer entered the aquifer as much as tens of thousands of years ago (Parkhurst, Christenson, and Breit, 1993). The flow model indicates that flow velocity and thus flow volume are lowest near the base of freshwater in the confined part of the aquifer, just below the base of the confining layer, and near the westernmost extent of flow (Scott Christenson, U.S. Geological Survey, oral commun., 1993). For a more detailed description of the hydrology of the aquifer, see Christenson, Parkhurst, and Breit (1998). Flow volume also is less in sandstone lenses that are surrounded by mudstone because the volume of flow entering the sandstone is decreased by the low permeability of the mudstone.

The Central Oklahoma aquifer can be divided into six geohydrologic zones on the basis of geohydrologic variation between confined or unconfined conditions, mudstone interbedding in geologic units, and variations in major-ion chemistry with depth described by Parkhurst, Christenson, and Schlottmann (1989) (fig. 6). For this report, confined conditions are assumed in the part of the aquifer overlain by the confining layer. The six zones include: (1) the unconfined zone of the shallow [less than or equal to 300 ft in depth (originally defined as shallow and medium depths in Parkhurst, Christenson, and Schlottmann, 1989)] Garber Sandstone and Wellington Formation (Garber-Wellington); (2) the confined zone of the shallow Garber-Wellington; (3) the unconfined zone of the deep (greater than 300 ft in depth) Garber-Wellington; (4) the confined zone of the deep Garber-Wellington; (5) the shallow (less than or equal to 300 ft in depth) Chase, Council Grove, and Admire Groups, undivided (Chase-Admire); and (6) the deep (greater than 300 ft in depth) Chase-Admire. The shallow and deep Chase-Admire are in the unconfined zone of the aquifer. Variations in water chemistry between these zones are described below. Deep geohydrologic zones are not present everywhere to the north, south, and east of the west-central part of the aquifer because the base of freshwater becomes shallower beneath those areas.

Major-Ion Geochemistry

Dominant water types in the Garber Sandstone, the Wellington Formation, and the Chase, Council Grove, and Admire Groups range from calcium magnesium bicarbonate to sodium bicarbonate. Calcium magnesium bicarbonate water types are most common in shallow (less than 300 ft) unconfined zones and sand-rich parts of the Central Oklahoma aquifer, and

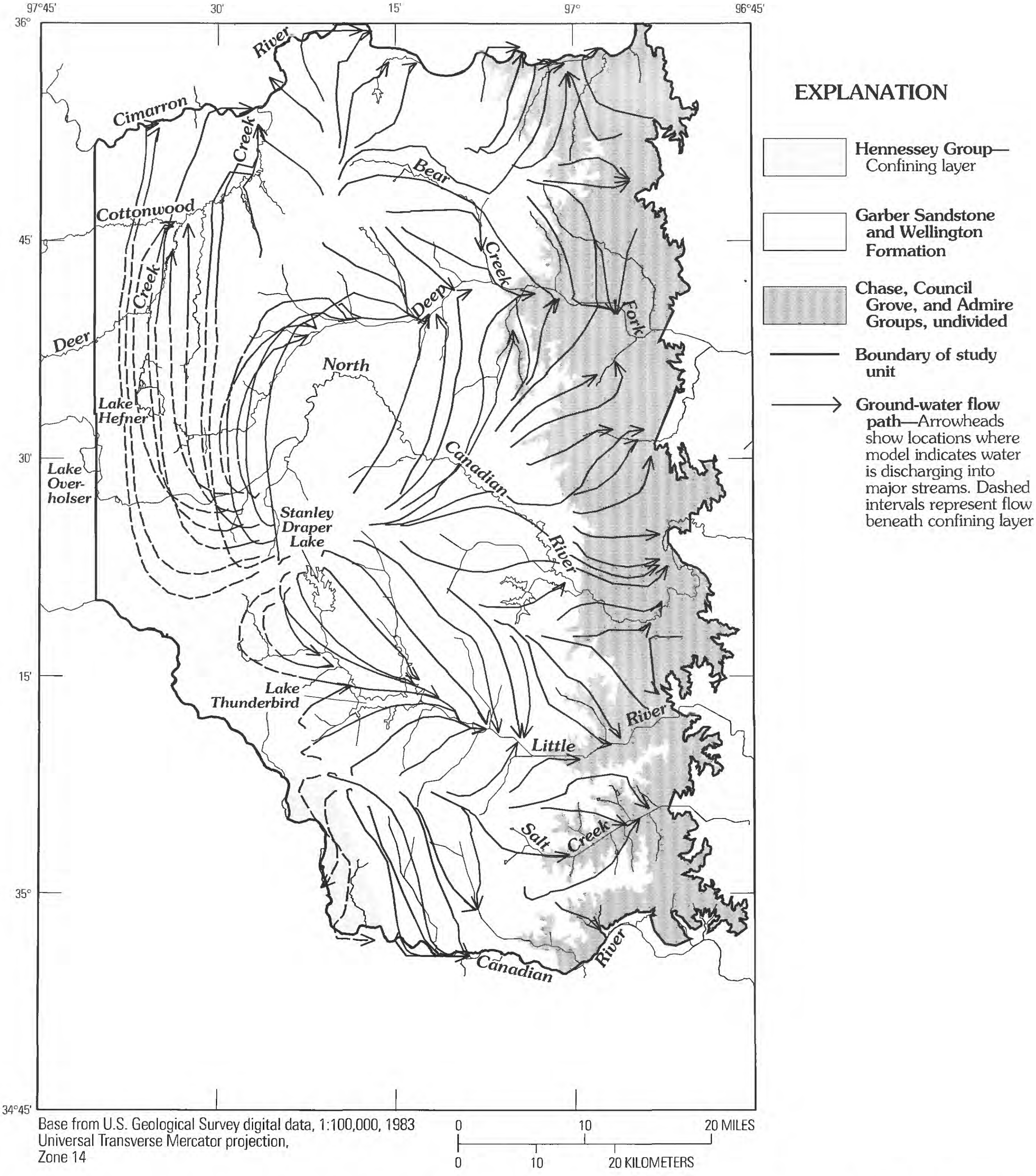

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Figure 5. Selected pathlines of flow in the Central Oklahoma aquifer generated by the particle-tracking model by placing a particle at the center of selected cells in the unconfined part of the Central Oklahoma aquifer (from Parkhurst, Christenson, and Breit, 1993).

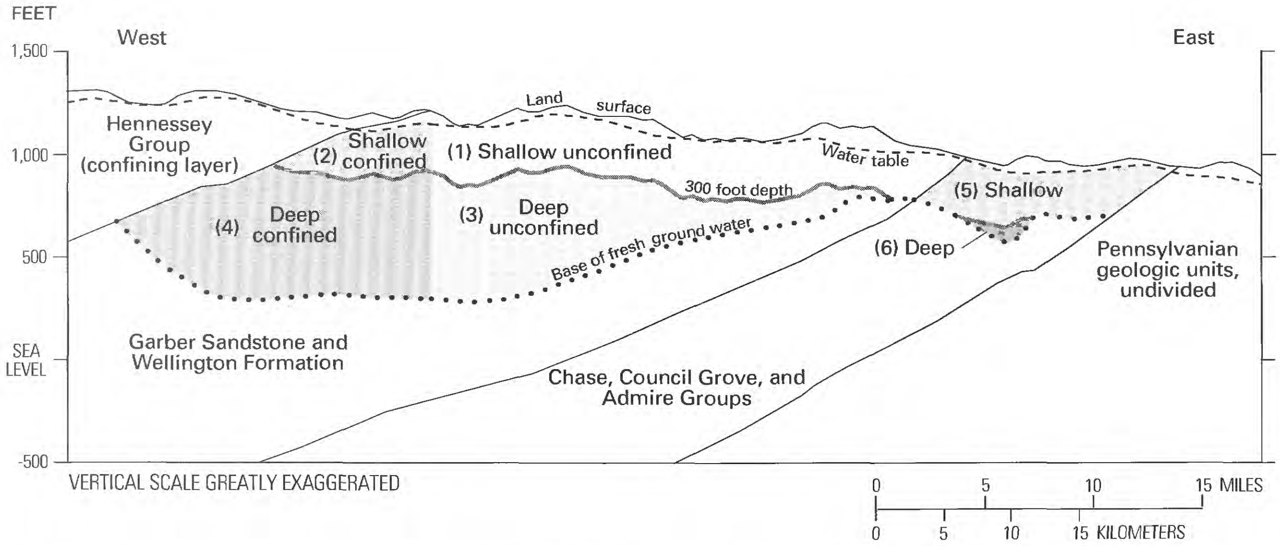


Figure 6. Geohydrologic section along latitude 35°30′ showing the six geohydrologic zones in the Central Oklahoma aquifer.

sodium bicarbonate in deep and confined zones of the aquifer (Parkhurst, Christenson, and Schlottmann, 1989). The pH of water in the aquifer ranges from 6.0 to 9.6 (Schlottmann and Breit, 1992). Summary statistics for major water constituents are shown in table 1.

High concentrations (greater than 600 mg/L) of chloride or sulfate are not common. Moderately high chloride concentrations (48 to 590 mg/L) are present near the base of freshwater, near the base of the confining layer, in the clay-rich Chase, Council Grove, and Admire Groups in the east, and in some shallow wells within 2 mi of Cottonwood Creek, the Deep Fork, or the Little River where the flow model indicates regional ground-water flow discharges (fig. 5). Sulfate (40 to 420 mg/L) is present at some locations near the base of freshwater, near the base of the confining layer, and where gypsum is dissolving in the southeast part of the study unit (Parkhurst, Christenson, and Breit, 1993). The presence of higher chloride and sulfate in these regions of the aquifer is consistent with results of the flow model that show reduced flow velocity near the base of the aquifer and the base of the confining layer where mudstone interbedding increases. Reduced velocity results in less water passing through or flushing the rock, leaving higher residual chloride and sulfate concentrations and undissolved gypsum. At some locations chloride greater than 250 mg/L near the water table results from regional ground-water discharge, a shallow base of freshwater, or anthropogenic sources. Bromide-to-chloride ratios of aquifer water are consistent with freshwater dilution of seawater-derived brine. The source of most of the aquifer chloride is assumed to be a brine that is leaching from fluid inclusions or dead-end pores (Parkhurst, Christenson, and Breit, 1993). The presence of chloride indicates brine once filled the aquifer and now remains only in less-flushed regions of the aquifer.

METHODS OF STUDY

During 1987–89, 143 wells penetrating the Permian part of the Central Oklahoma aquifer were sampled (fig. 7). Major and trace elements and selected radioisotopes were determined by the U.S. Geological Survey's National Water-Quality Laboratory. Ferree and others (1992) and Christenson (1998) list the analyses performed. Selected samples were analyzed for ^{3}H (tritium), δ^{18}O and δD [oxygen-18/16 and deuterium/hydrogen (^{2}H/^{1}H) relative to standard mean ocean water (SMOW)], or carbon-14 and carbon-13 to estimate the age of water, and for chromium (VI) to determine the oxidation state of dissolved chromium. Specific conductance, pH, alkalinity, dissolved oxygen, and temperature were determined onsite (Ferree and others, 1992). Data from two wells were not representative of the aquifer drinking-water resource because of high concentrations of chloride (greater than 1,500 mg/L) and were not used in this study.

Eight test holes were drilled in the Central Oklahoma aquifer (fig. 7) to provide additional information about arsenic, chromium, selenium, and uranium in the ground water. Seven holes were drilled near wells with high arsenic, chromium, selenium, or uranium concentrations (concentrations exceeding a 1986 drinking-

Table 1. Summary statistics for major water constituents using data from 141 wells sampled for the present study in the Central Oklahoma aquifer

[All determinations are in milligrams per liter unless otherwise noted; μS/cm, indicates microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; <, concentration is less than specified value. All samples analyzed by the National Water-Quality Laboratory of the U.S. Geological Survey unless otherwise noted]

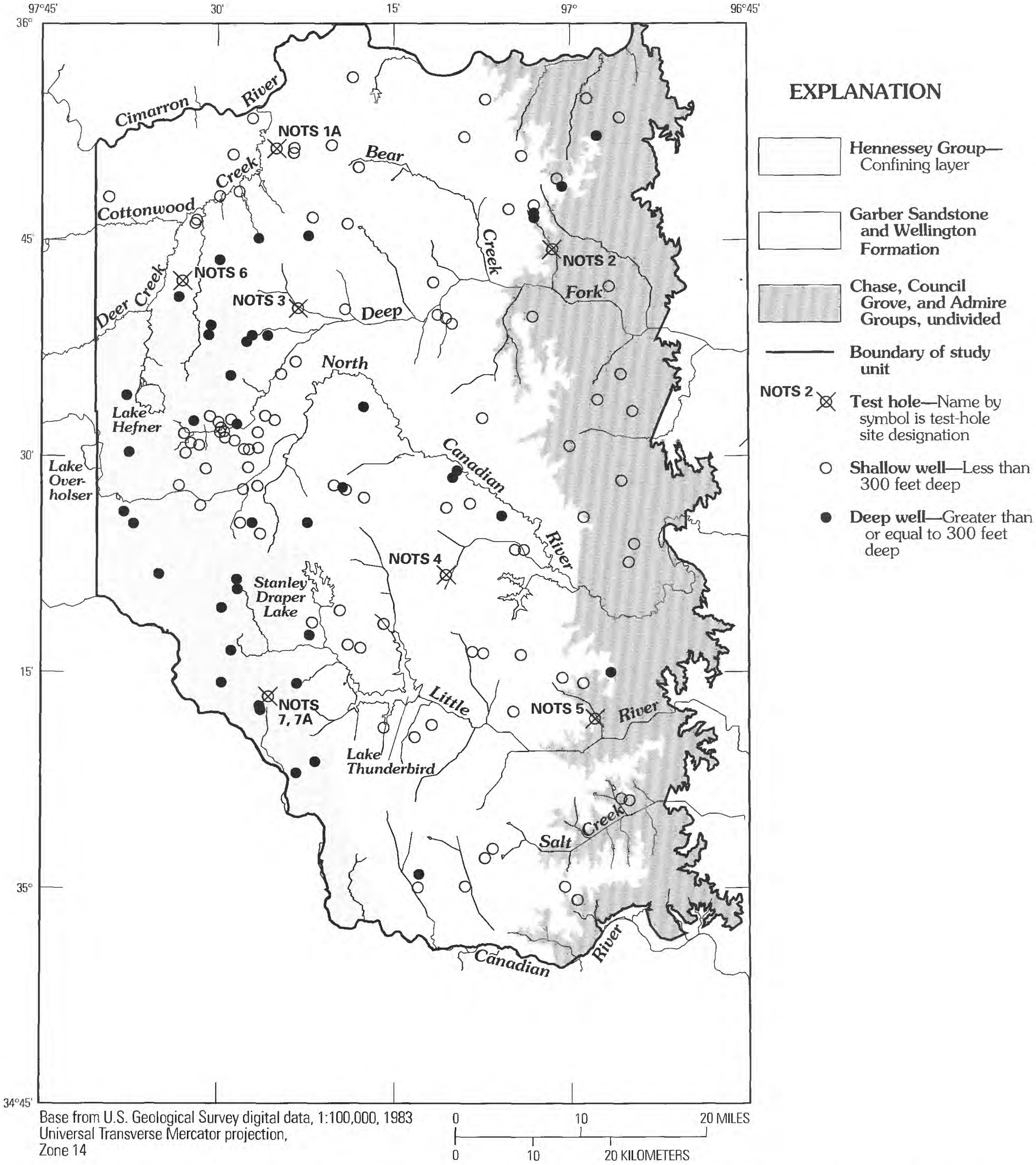
Constituents	Sample size	Minimum value	Percentiles							Maximum value
			5	10	25	50	75	90	95	
Specific conductance, μS/cm[1]	141	144	274	351	463	634	950	1,290	1,810	2,700
pH, standard units[1]	141	6.0	6.2	6.6	7.1	7.4	7.8	8.8	9.0	9.2
Dissolved oxygen[1]	140	<.1	.2	.7	2.9	5.4	8.0	8.8	9.5	13
Calcium	141	1.0	1.7	4.0	21	44	68	94	120	240
Magnesium	141	.33	.73	1.5	12	22	35	50	59	82
Sodium	141	4.1	7.4	11	17	49	130	210	270	510
Potassium	141	<.1	.4	.5	.7	1.2	2.0	3.1	3.4	15
Alkalinity, mg/L as $CaCO_3$[1]	141	44	76	106	210	276	341	399	429	646
Bicarbonate, mg/L as $CaCO_3$[1]	141	53	93	130	255	324	410	468	510	788
Carbonate, mg/L as $CaCO_3$[1]	141	<1	<1	<1	<1	<1	<1	18	31	43
Chloride	141	2.8	5.7	7.1	10	20	49	170	250	590
Sulfate	141	3.3	5.9	7.0	11	20	40	130	260	600
Fluoride	141	<.1	.1	.2	.2	.3	.4	.7	1.3	3.9

[1] Determined at sample site.

water standard or proposed standard), and one test hole was drilled as a control in a region known to have only low concentrations of the elements. The control well provides data on background lithologic, mineralogic, and geochemical characteristics of the aquifer for comparison with characteristics where arsenic, chromium, selenium, or uranium are present at high concentrations. Test-hole descriptions are listed in table 2. The test holes are named the NOTS test holes as an acronym of Naturally Occurring Trace Substances. Data for two water samples from the base of one test hole (NOTS 5) were not used in this study because the samples contained greater than 5,000 mg/L dissolved solids and were considered to be from below the base of fresh ground water.

Sandstone layers in the test holes were isolated using inflatable packers, and water samples were collected. These samples were analyzed in the same manner as samples from the 141 wells. Arsenic and selenium oxidation states were determined in selected samples (Schlottmann and Funkhouser, 1991). Results of chemical analyses for the test-hole samples were used to determine: (1) water chemistry associated with high concentrations of arsenic, chromium, selenium, and uranium; (2) how water chemistry changed with depth and between sandstone layers; and (3) the spatial relation between high concentrations of the elements in rock to high concentrations in water. Test-hole results were not included in the general descriptive statistics (table 3) because the test-hole locations were selected for their high arsenic, chromium, selenium, or uranium concentrations.

Rock core was collected for the entire depth of each test hole and described at the site. Vertically contiguous samples from the cores were analyzed to determine chemical composition and mineralogy. Cation-exchange capacity was determined on clay-sized separates from 18 selected samples. Methods used and results are summarized by Mosier and others (1990) and Breit and others (1990). Sequential chemical extractions were performed on 86 core samples to provide additional information on arsenic, chromium, selenium, and uranium residences in the aquifer rock and the processes by which the elements are mobilized or transferred from the rock into the ground water. The methods used and constituents extracted are summarized in the following paragraph. A more detailed description of the methods and an interpretation of the results are presented by Mosier (1998); extraction results are listed in Mosier and others (1991).



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
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Figure 7. Location of 141 wells and 8 test holes sampled for analysis of water quality in the Central Oklahoma aquifer, 1987–90.

Table 2. Description of test holes in the Central Oklahoma aquifer and number of geochemical samples collected from intervals in each hole

[deg, degrees; min, minutes; sec, seconds; Geologic units penetrated: Garber, Garber Sandstone; CCGA, Chase-Council Grove-Admire Groups, undivided; Wellington, Wellington Formation; Hennessey, Hennessey Group. Number of duplicate water samples collected at each test hole is shown in parentheses next to number of water samples collected]

Test-hole name (fig. 7)	Location		County	Altitude of land surface (feet above sea level)	Depth of hole (feet)	Geologic units penetrated	Depth-interval cored (feet)	Core-interval analyzed (feet)	Number of water-geochemistry samples	Number of rock-geochemistry samples
	Latitude (deg min sec)	Longitude (deg min sec)								
NOTS 1A	35 51 18	97 25 00	Logan	1,045	268	Garber	15–268	15–268	2	82
NOTS 2	35 44 18	97 01 35	Lincoln	900	277	CCGA	15–277	15–277	1	60
NOTS 3	35 40 12	97 23 10	Oklahoma	1,035	195	Garber	15–195	15–195	2(1)	53
NOTS 4	35 21 42	97 10 35	Cleveland	1,145	291	Garber	15–192	15–192	3	41
						Wellington	192–290	192–290	1	14
NOTS 5	35 11 42	96 58 01	Pottawatomie	945	238	CCGA	15–238	15–238	1(1)	57
NOTS 6	35 42 08	97 33 02	Oklahoma	1,085	587	Garber	20–587	20–587	8(1)	115
NOTS 7	35 13 15	97 25 43	Cleveland	1,172	456	Hennessey	21–185	21–185	0	35
						Garber	185–456	185–196	1	1
NOTS 7A	35 13 15	97 25 42	Cleveland	1,172	631	Hennessey	0	0	0	0
						Garber	175–631	175–631	3(1)	91

The sequential extractions included two procedures. One procedure involved five extraction steps: (1) Soluble components, including nonspecifically adsorbed anions and exchangeable cations, were extracted using room-temperature 0.25 *M* potassium chloride (KCl); (2) ligand-exchangeable components, including specifically adsorbed anions on clay minerals, hydrated iron (Fe), and manganese (Mn) oxides, were extracted using room-temperature 0.1 *M* potassium dihydrogen phosphate (KH_2PO_4); (3) acid-extractable components, including Fe, Mn, and aluminum (Al) oxides, amorphous materials, carbonates, and mono sulfides, were extracted using hot 4 *M* hydrochloric acid (HCl); (4) oxidative-acid decomposable components, including sulfide minerals and reduced elemental and residual organic material, were extracted using room-temperature potassium chlorate and concentrated HCl ($KClO_4$–HCl); and (5) mixed-acid digestible components or elements incorporated in the silicate structure were extracted using hot hydrofluoric (HF), nitric (HNO_3), and perchloric ($HClO_4$) acids. The other extraction procedure was a two-step bicarbonate extraction designed to mimic high-pH (pH 9) and high-pH oxidizing conditions in the aquifer. Samples were extracted using room-temperature 1 *M* sodium bicarbonate ($NaHCO_3$) at pH 9 to extract components that are soluble, form soluble carbonate complexes, or are specifically adsorbed. Residues from the $NaHCO_3$ extraction were washed and extracted using 0.7 *M* sodium hypochlorite (NaOCl) and 1 *M* $NaHCO_3$ to extract components that must be oxidized before they can be extracted by a high-pH bicarbonate solution.

Historical water-chemistry data for wells, test holes, and public drinking-water supply distribution systems used in this report were from the Association of Central Oklahoma Governments (ACOG), the Oklahoma State Department of Health (OSDH), the Oklahoma Water Resources Board (OWRB), the Department of Energy (DOE), and the U.S. Geological Survey. Distribution-system analyses were included only for systems that use well water. Distribution systems were allocated to geohydrologic categories on the basis of location and depth of wells used by the system. Distribution maps of high dissolved concentrations of arsenic, chromium, selenium, and uranium in the aquifer were made from these historical data as described by Parkhurst, Christenson, and Schlottmann (1989) combined with data obtained by this study. The highest measured concentration for each element was used to highlight problem regions for wells or distribution systems with multiple historical analyses. Multiple concentration ranges were mapped to provide an image of the element's concentration distribution for potential

Table 3. Summary statistics for arsenic, chromium, selenium, and uranium using data from the present study (test-hole data are not included)

[Dissolved, indicates sample was filtered; µg/L, micrograms per liter; As, arsenic; Cr, chromium; Se, selenium; U, uranium; <, indicates concentration is less than specified value; *, indicates samples exceeded proposed drinking-water standard. All samples analyzed by the National Water-Quality Laboratory of the U.S. Geological Survey]

Constituents	Sample size	Minimum value	Percentiles 5	10	25	50	75	90	95	Maximum value	Number that exceeded standard
Arsenic, dissolved (µg/L as As)	141	<1	<1	<1	<1	1	2	19	43	110	5
Chromium, dissolved (µg/L as Cr)	141	<1	<5	<5	<5	<5	7	32	46	100	7
Selenium, dissolved (µg/L as Se)	141	<1	<1	<1	<1	1	5	28	70	190	27
Uranium, dissolved (µg/L as U)	141	<.2	<.2	<.2	.9	3.8	13	56	82	220	29*

use in water exploration. Concentration ranges mapped include (1) less than one-half the 1986 arsenic, chromium and selenium or the 1991 proposed uranium drinking-water standard, (2) one-half the standard concentration to just below the standard, (3) the drinking-water standard to just below the 1991 drinking-water standard for chromium and selenium or to a much higher concentration for arsenic and uranium (to highlight regions where the greatest concentrations are present), and (4) values greater than the 1991 proposed standard or a selected higher concentration.

Contingency-table analysis with a chi-square test statistic (P–STAT, Inc., 1989) was used to examine differences in the distribution of pH and dissolved arsenic, chromium, selenium, and uranium among various geohydrologic categories. The contingency table presents a concise tabulation of available information in addition to testing a hypothesis (for a discussion of contingency tables, see Iman and Conover, 1983, p. 291–322). The null hypotheses tested were that the proportion of wells that exceeded the 1986 arsenic, chromium, or selenium drinking-water standards, the 1991 selenium or proposed uranium standards, or a pH of 8.5 were the same for each geohydrologic category. The tables are divided into cells. Each cell contains statistics for one concentration range (exceeds or does not exceed the drinking-water standard) and one geohydrologic category.

The attained significance level or "*p*-value" (less than 0.05) for the overall chi-square statistic (listed in each table footnote) is used to determine whether to accept or reject the null hypothesis. A small *p*-value (less than 0.05) suggests that the null hypothesis can be rejected. Rejections of the null hypotheses indicate that the concentrations of arsenic, chromium, selenium, and uranium were significantly different among geohydrologic categories.

In addition to the *p*-value, the contingency table presents the number of analyses in each cell, the expected number of analyses in each cell (cell expected frequency), the chi-square statistic for each cell, and the percentage of analyses that exceeded the concentration of the 1986 standard or the 1991 proposed standard for each geohydrologic category. The number of analyses in each cell is the observed number of analyses that exceeded (or did not exceed) the drinking-water standard. The expected value is the number of analyses that will exceed (or not exceed) the standard if the element concentration is distributed equally among all categories. The cell chi-square statistic increases with increased deviation of the observed value from the expected value.

For the contingency-table analysis, historical analyses from wells, test holes, and public drinking-water distribution systems were divided into two groups depending on whether or not they exceeded the 1986 drinking-water standard or the 1991 proposed standard for each element. The highest measured concentration was used for wells, test holes, or distribution systems with multiple analyses. The highest measured concentration within a depth range (less than or greater than 300 ft) was used for test holes with samples from multiple sample depths. Geohydrologic categories included wells, test-hole sample intervals, or distribution systems with wells completed in: (1) the unconfined zone of the shallow (less than or equal to 300 ft in depth) Garber-Wellington; (2) the confined zone of the shallow Garber-Wellington; (3) the unconfined zone of the deep (greater than 300 ft in depth) Garber-Wellington; (4) the confined zone of the deep Garber-Wellington; (5) the shallow (less than or equal to 300 ft in depth) Chase-Admire; and (6) the deep (greater than 300 ft in depth) Chase-Admire. Shallow and deep categories of the Chase-Admire category were combined if a cell's expected frequency for the deep category was less than one.

Contingency-table analyses for arsenic, chromium, selenium, and uranium were made only on historical data and were made in a manner consistent with methods used by Parkhurst, Christenson, and Schlottmann (1989); however, for this study, the geohydrologic categories were further divided to separate confined and unconfined zones of the Central Oklahoma aquifer, and only wells completed within the Permian part of the aquifer were included. Historical data were not combined with data obtained from wells and test holes by this study for the contingency-table analyses because the historical data were not collected by methods consistent with this study. Historical data were not used to prepare the statistical summary in table 3, to determine water characteristics associated with high concentrations of the elements, or to determine the processes mobilizing the elements because: (1) Historical data from ACOG, OSDH, OWRB, and the U.S. Geological Survey were clustered near population centers or in areas where a problem was studied, and the DOE sampled only the shallow zones of the aquifer and thus the samples are not representative of the aquifer; and (2) a consistent set of water-quality constituents, including major ions and arsenic, chromium, selenium, and uranium, was not analyzed in all historical samples, and methods used for analyses varied among agencies and samples. Well samples collected for this study were representative of the aquifer and were analyzed for a consistent set of water-quality constituents using the same analytical methods throughout the study period.

Separate contingency-table analyses were not made on data collected for this study because: (1) The tables containing only study data did not fit the requirements for a good approximation of the distribution in geohydrologic categories because there were not enough samples and thus the expected frequency for more than one cell was less than one for every element and (2) samples from the NOTS test holes were collected where arsenic, chromium, selenium, and uranium concentrations were known to be high and would bias the data. The distribution of arsenic, chromium, selenium, and uranium between geohydrologic zones indicated by this study are discussed in the text and compared with historical results shown in the contingency tables.

DISTRIBUTION OF ARSENIC, CHROMIUM, SELENIUM, AND URANIUM IN THE GROUND WATER

A statistical summary of arsenic, chromium, selenium, and uranium concentrations found in the 141 wells sampled for this study is presented in table 3. Fewer than 4 percent of the wells yielded water that exceeded the 1986 arsenic or chromium standards. The 1986 selenium standard was exceeded in 18 percent, and the 1991 proposed uranium standard was exceeded in 21 percent of the wells. When the four elements are considered, water from 36 of the wells in this study (26 percent) exceeded at least one standard or proposed standard. These 36 wells are clustered in specific regions of the aquifer.

The distributions of arsenic, chromium, selenium, and uranium concentrations in the Central Oklahoma aquifer are shown in figures 8 through 13, 15, and 16. Wells and test holes sampled for this study and wells or public drinking-water distribution systems with historical analyses were divided into two groups depending on the well depth. The first group comprises shallow wells (less than 300 ft in depth) and public drinking-water distribution systems that are supplied by water from shallow wells. This depth includes most domestic wells in the aquifer and includes both the shallow- and medium-depth wells from Parkhurst, Christenson, and Schlottmann's (1989) classification. These shallow wells may penetrate the entire thickness of the aquifer where the base of freshwater is near the land surface. The second group are deep wells (300 ft or more in depth) and public drinking-water distribution systems that are supplied by water from deep wells. Most wells greater than 300 ft deep are public-supply wells. Wells completed in the Garber-Wellington were further divided into unconfined and confined categories depending on whether they are completed in the unconfined part of the aquifer or below the confining layer.

Arsenic

Contingency-table statistics for historical arsenic data (table 4) indicate that the proportion of analyses that exceeded the 1986 50-μg/L drinking-water standard was significantly different among the geohydrologic categories (*p*-value less than 0.001, null hypothesis rejected). Overall, only 6.9 percent of 477 analyses exceeded the 1986 drinking-water standard. However, 30.2 percent of the analyses in the confined zone of the deep Garber-Wellington exceeded the standard. Few analyses exceeded the standard in other geohydrologic categories. These historical data indicate that arsenic concentrations greater than the 50-µg/L standard are common at depths greater than 300 ft in the confined part of the Garber-Wellington but are rare in the rest of the aquifer. This is consistent with well data collected for this study. All five of the arsenic determinations that exceeded the standard (table 3) were from wells in the confined zone of the deep Garber-Wellington.

The few shallow wells or test-hole intervals that yielded water that exceeded the 1986 arsenic standard were completed in the Garber Sandstone in the western part of the study unit (fig. 8). The distribution of deep wells, distribution systems, and test holes for which arsenic determinations are available is clustered along the west side of the confined part of the aquifer, in the northeast quarter of the confined part of the aquifer, north of the confined part of the aquifer, in the northeast corner of the aquifer, and near the aquifer center. Deep data are sparse in the north, east, and south because the base of the aquifer is shallower below those areas and because there is less urban development in those areas, fewer deep wells are required. Deep wells and distribution systems that produced water that exceeded the arsenic standard are located near the western boundary of the freshwater flow system, at locations where water is inferred to discharge from below the confining layer, or in the geographic area around the headwaters of the Deep Fork (figs. 5 and 9). Arsenic concentrations exceeding the standard were not found in deep wells near the aquifer center. This arsenic distribution suggests that (1) the source of arsenic is present only in the regions where high dissolved concentrations are found, (2) water chemistry in regions of the aquifer below recharge areas is not appropriate to cause the transfer of arsenic from the solid phase to the ground water, or (3) the water must travel some distance, which would require many years, and be exposed to a large volume of rock to acquire enough arsenic to exceed the 50-µg/L standard.

NOTS test-hole water samples provide additional information on the vertical distribution of arsenic (table 5) as compared to results for the 141 well samples. Arsenic concentrations are highest in the deepest samples collected from unconfined test holes NOTS 1A, 3, and 6. The deepest samples from NOTS 1A and 6 contain chloride at concentrations above the 75th percentile and sulfate concentrations above the 50th percentile (table 1) for the 141 wells sampled for this study, indicating that those samples may be from an interval near the base of freshwater or in a less-flushed area of the aquifer.

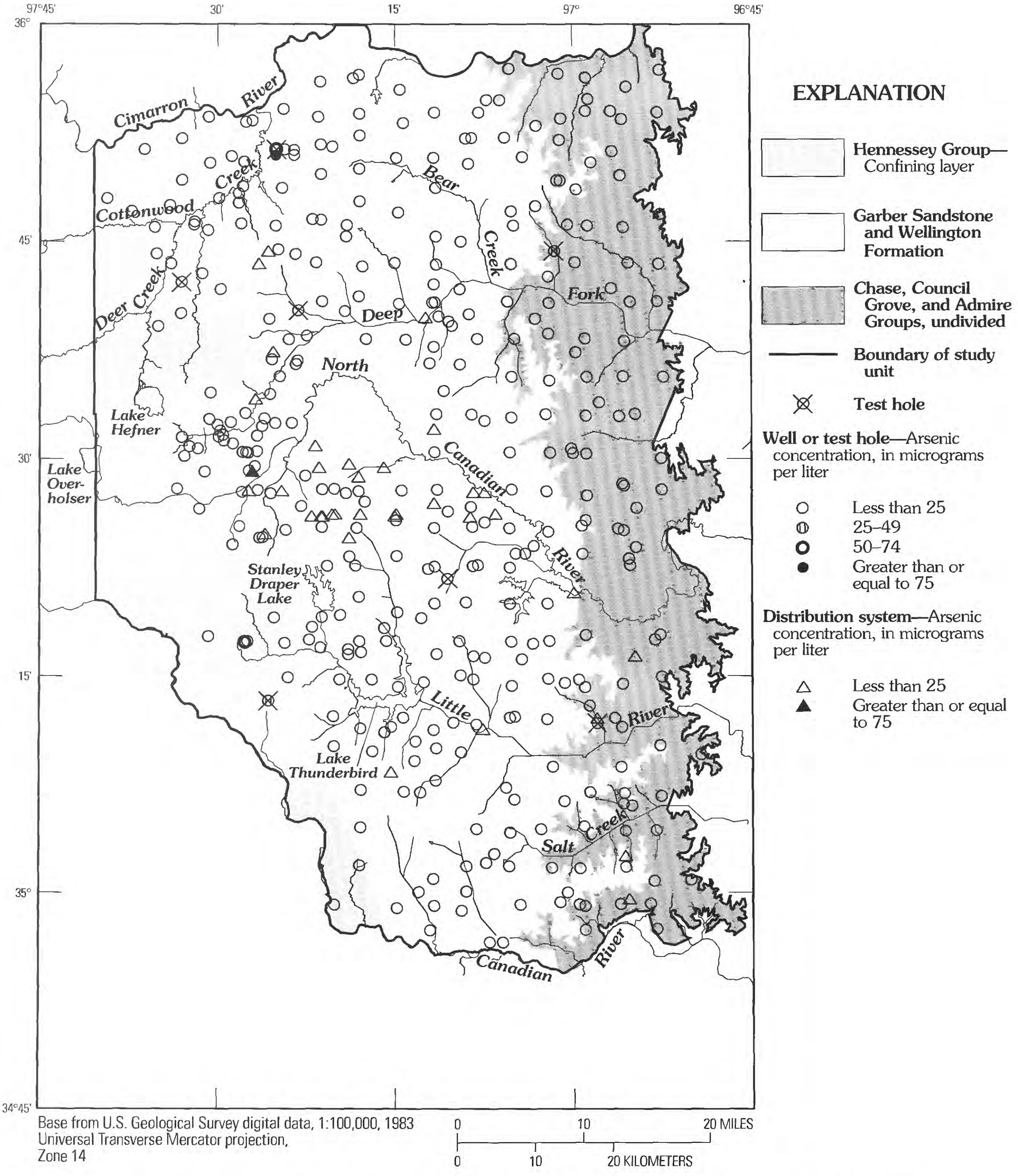
Water samples from test holes NOTS 7 and 7a, from the confined part of the Central Oklahoma aquifer, show a different distribution. Higher concentrations are near the top of the confined part of aquifer (depth to the base of the confining layer is 187 ft at this

Table 4. Contingency table of arsenic concentrations in the Central Oklahoma aquifer by geohydrologic category

[Data include historical filtered and unfiltered arsenic analyses. Each analysis represents a distribution system, a well, or a geohydrologic category within a well. The four Garber-Wellington categories were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer. Chase-Admire, Chase, Council Grove, and Admire Groups, undivided; <, less than; ≥, greater than or equal to; µg/L, micrograms per liter]

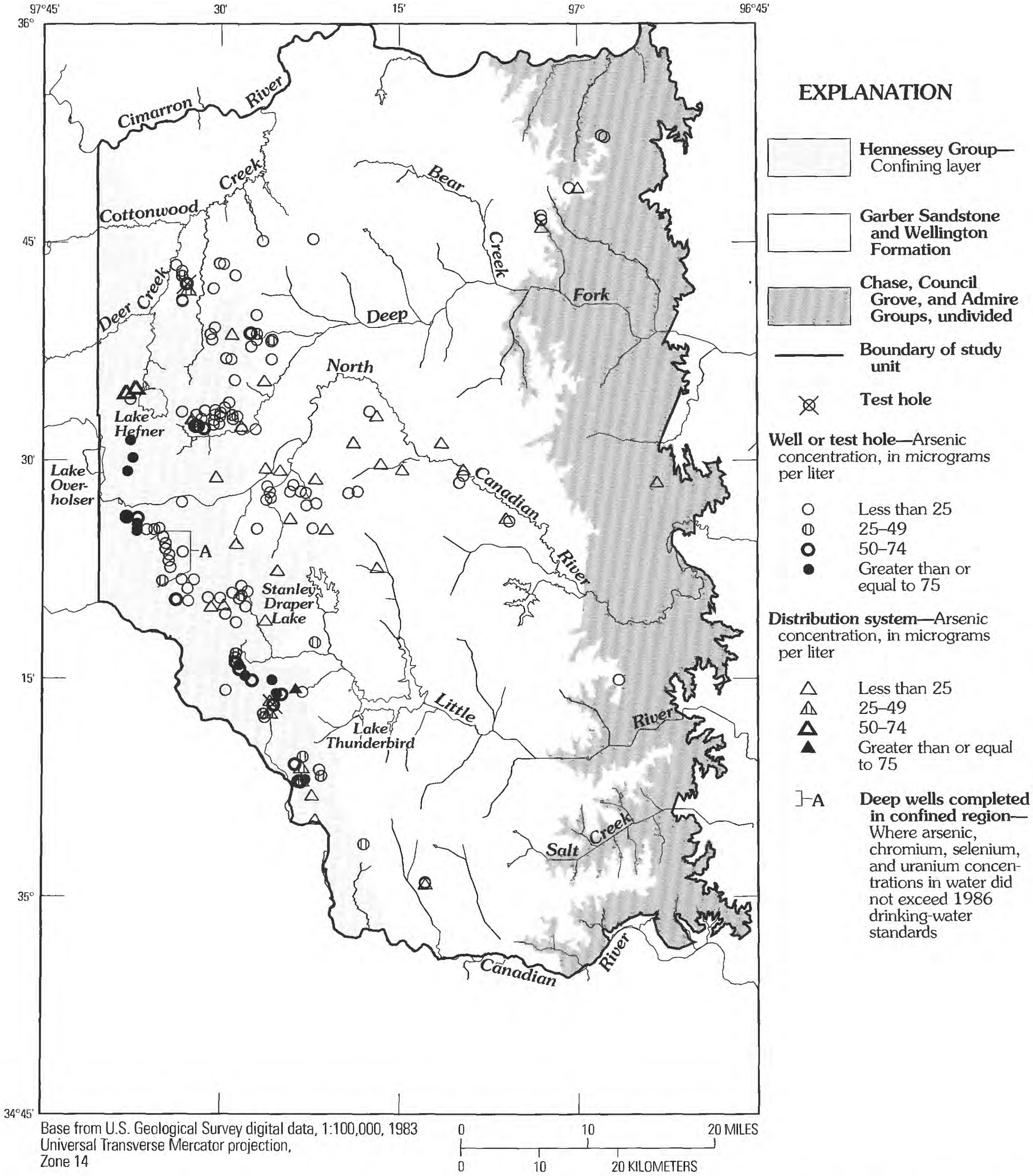
		Geohydrologic category					
		Garber-Wellington					
Arsenic concentration	Statistic	Shallow		Deep		Chase-Admire	Row totals
		Unconfined	Confined	Unconfined	Confined		
< 50 µg/L	Number of analyses	217	11	41	60	87	416
	Expected value	204.7	11.2	39.1	80.0	81.0	
	Cell chi square	.7	0	.1	5.0	.4	
≥ 50 µg/L	Number of analyses	3	1	1	26	0	31
	Expected value	15.3	.8	2.9	6.0	6.0	
	Percent ≥ 50 µg/L	1.4	8.3	2.4	30.2	0	6.9
	Cell chi square	9.8	0	1.3	67.3	6.0	
	Total number of analyses	220	12	42	86	87	447

Overall statistics: chi square 90.8; attained significance level less than 0.001; smallest expected value 0.8; degrees of freedom 4.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 8. Areal distribution of arsenic concentrations in water from shallow (less than 300 feet) wells, test holes, and distribution systems supplying water from the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 9. Areal distribution of arsenic concentrations in water from deep (greater than or equal to 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

location), and the lower concentrations are from the deeper part of the test hole. The highest arsenic concentration in test hole NOTS 7A was in the second sandstone layer below the base of the confining layer. The layer yielded water with sulfate concentration greater than the 75th percentile and chloride concentration less than the 50th percentile. All samples collected from the confined part of the aquifer for this study that exceeded the 1986 arsenic standard showed this sulfate-chloride relation. The first sandstone layer below the base of the confining layer was sampled in test hole NOTS 7. Water from that sandstone and the third sandstone below the confining layer contained 33 and 20 µg/L arsenic. This indicates that isolated lenses of water with high concentrations of arsenic are present in some individual sandstone layers between layers with lesser arsenic concentrations. The sample from test hole NOTS 2 from the shallow Chase, Council Grove, and Admire Groups contained 20 µg/L arsenic, indicating that although arsenic does not tend to exceed the standard for arsenic in water from these groups, elevated concentrations are present. Altogether, the arsenic data indicate that the arsenic standard is exceeded in the Garber Sandstone near the base of freshwater and in some sandstone layers near the base of the confining layer in the westernmost part of the flow system.

Table 5. Concentrations of arsenic, chromium, selenium, and uranium and major characteristics of water from the test holes in the Central Oklahoma aquifer

[Sampling depth interval, sampling interval below land surface; dissolved, indicates sample was filtered; µg/L, micrograms per liter; mg/L, milligrams per liter; <, indicates concentration is less than specified value; *, indicates value from unfiltered sample; --, indicates no data available; Na, sodium; Ca, calcium; Mg, magnesium; HCO_3, bicarbonate. Geohydrologic zones: SUGW, shallow (less than 300 feet) unconfined Garber-Wellington; SCA, shallow Chase-Admire; DUGW, deep (greater than 300 feet) unconfined Garber-Wellington; SCGW, shallow confined Garber-Wellington; DCGW, deep confined Garber-Wellington. All samples analyzed by the National Water-Quality Laboratory of the U.S. Geological Survey unless otherwise noted]

Test-hole name (fig. 7)	Sampling depth interval (feet)	Arsenic, dissolved (µg/L as As)	Chromium, dissolved (µg/L as Cr)	Selenium, dissolved (µg/L as Se)	Uranium, dissolved (µg/L as U)	pH[1], standard units	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Water type	Geohydrologic zone
NOTS 1A	166.0 – 186.0	53	80	75	66 ± 10	8.8	29	27	Na HCO_3	SUGW
	210.0 – 248.0	69	60	250	110 ± 12	8.9	54	39	Na HCO_3	SUGW
NOTS 2	96.4 – 116.0	20	<5	13	40 ± 4.6	9.0	13	12	Na HCO_3	SCA
NOTS 3	110.0 – 129.0	1	<5	<1	0.6 ± 0.13	7.3	12	25	CaMg HCO_3	SUGW
	110.0 – 129.0	1	<5	<1	0.8 ± 0.16	7.3	12	25	CaMg HCO_3	SUGW
	155.4 – 174.4	23	5	1	29 ± 3.2	8.9	13	20	Na HCO_3	SUGW
NOTS 4	87.0 – 115.0	1	<5	<1	0.6 ± 0.14	7.7	5.8	4.2	CaMg HCO_3	SUGW
	142.2 – 170.2	2	<5	<1	0.9 ± 0.18	7.7	7.2	4.8	CaMg HCO_3	SUGW
	178.0 – 200.0	1	<5	<1	1.0 ± 0.20	7.8	5.1	17	CaMg HCO_3	SUGW
	243.5 – 271.5	1	8	<1	2.3 ± 0.34	7.7	9.3	6.9	CaMg HCO_3	SUGW
NOTS 5	48.0 – 76.0	1	<5	16	44 ± 4.8	7.5	31	34	Na HCO_3	SCA
	48.0 – 76.0	1	<5	18	42 ± 4.6	7.5	31	35	Na HCO_3	SCA
NOTS 6	96.4 – 116.8	1	<5	6	5.5 ± 0.81	7.5	9.9	18	CaNaMg HCO_3	SUGW
	121.4 – 160.5	1	<5	4	5.3 ± 0.82	7.4	11	18	CaMgNa HCO_3	SUGW
	161.2 – 200.3	2	20	3	7.0 ± 1.3	7.6	12	18	MgCaNa HCO_3	SUGW
	161.2 – 200.3	2	20	3	6.6 ± 1.5	7.6	12	13	MgCaNa HCO_3	SUGW
	203.2 – 242.3	2	20	2	7.0 ± 1.2	7.6	11	11	MgCaNa HCO_3	SUGW
	266.0 – 286.0	3	30	10	18 ± 2.5	8.0	11	14	NaCaMg HCO_3	SUGW
	286.0 – 306.4	1	20	3	14 ± 2.5	7.7	13	10	Na HCO_3	SUGW
	307.5 – 346.6	3	20	11	4.0 ± 0.56	8.0	11	9.9	Na HCO_3	DUGW
	456.0 – 494.2	65	40	380	320 ± 35	8.6	110	72	Na HCO_3Cl	DUGW
NOTS 7	229.2 – 276.2	33	<5	11	14* ± 4.1	9.6	16	44	Na HCO_3	SCGW
NOTS 7A	316.6 – 343.6	51	<5	93	35 ± 4.6	9.1	14	76	Na HCO_3	DCGW
	397.0 – 418.0	20	<5	19	5.4 ± 1.1	9.3	6.8	25	Na HCO_3	DCGW
	460.0 – 500.0	9	<5	3	5.8 ± 1.3	9.3	6.2	17	Na HCO_3	DCGW
	460.0 – 500.0	8	<5	3	--	9.3	8.2	18	Na HCO_3	DCGW

[1] Determined at sample site.

Chromium

Contingency-table statistics for historical chromium data (table 6) indicate that the proportion of analyses that exceeded the 1986 50-µg/L drinking-water standard was significantly different among the geohydrologic categories (*p*-value less than 0.001, null hypothesis rejected). Chromium concentrations exceeded the 50-µg/L standard in 9.4 percent of the 552 historical analyses. However, in the deep Garber-Wellington, 16 percent of the analyses from the unconfined zone, and 27.5 percent of analyses from the confined zone exceeded the standard. The only other geohydrologic category that exceeded the standard was the unconfined zone of the shallow Garber-Wellington where only 1.6 percent of analyses exceeded the standard. All five analyses from wells sampled for this study that exceeded the standard (table 3) were from the deep Garber-Wellington, two were from the unconfined zone, and three from the confined zone. These results indicate that chromium concentrations that exceed 50 µg/L are common in the confined zone of the deep Garber-Wellington, are less common in the unconfined zone, of the deep Garber-Wellington, are rare in the shallow Garber-Wellington, and are not present or are rare in the Chase-Admire category.

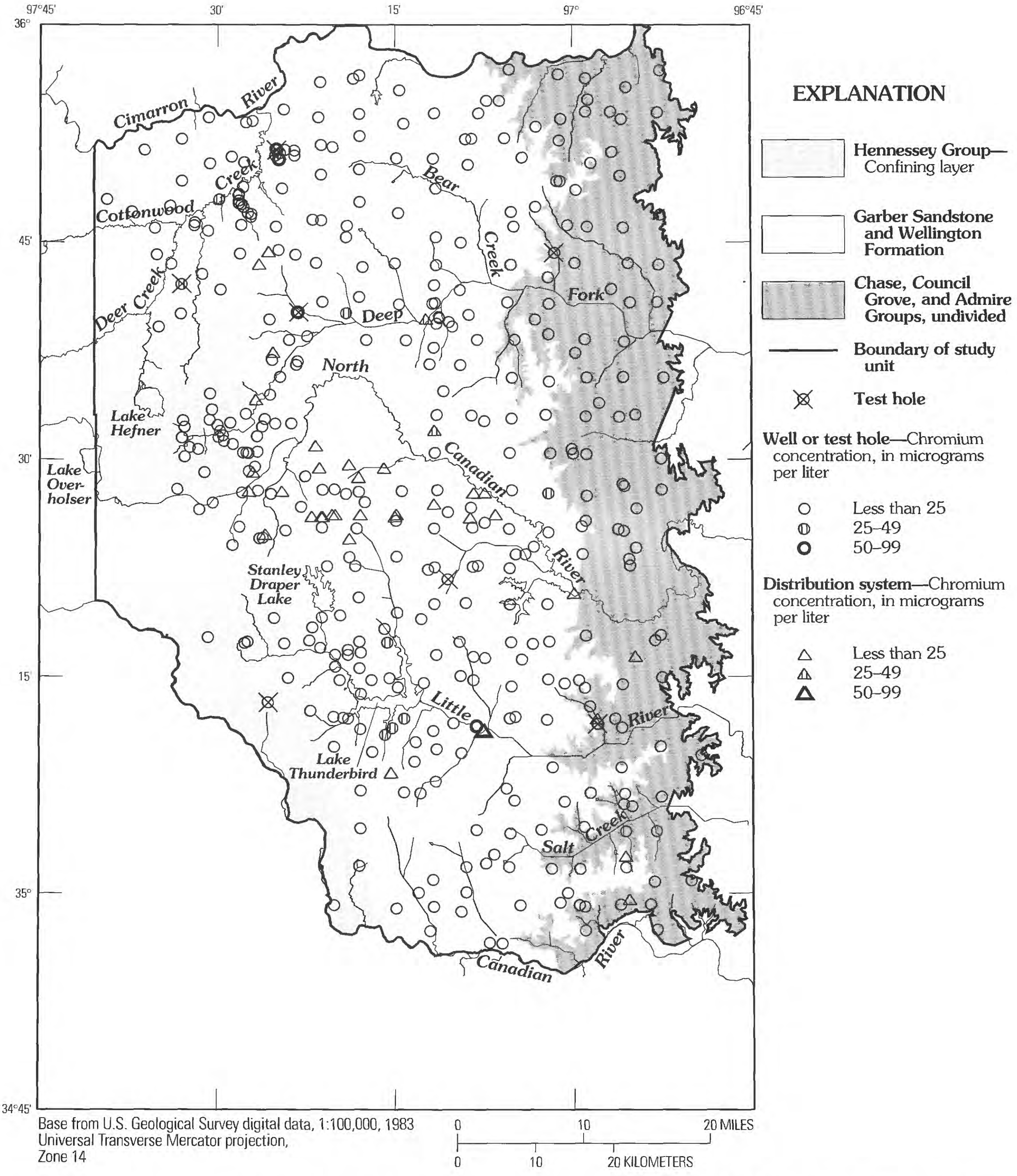
Fewer samples exceeded the 1991 100-µg/L chromium standard than exceeded the 1986 50-µg/L standard. Of the historical analyses, only 1.6 percent (nine analyses) exceeded 100 µg/L chromium, and all historical analyses that exceeded this concentration were from the deep Garber-Wellington. Three samples were from the unconfined zone, and six were from the confined zone. Similarly, only one sample collected for this study from the confined zone of the deep Garber-Wellington exceeded the proposed chromium standard.

The few shallow well samples that exceeded the 1986 50-µg/L chromium standard were from wells completed in the unconfined zone of the shallow Garber Sandstone in the northwestern part of the study unit or in the shallow Wellington Formation near Little River (fig. 10). These locations are within 2 mi of streams where the flow model indicates regional ground-water flow is discharging (fig. 5). Available chromium data for deep wells, distribution systems, and test holes are distributed spatially similar to deep arsenic data with a sparsity of data in the north and east. However, additional data are available for chromium in the south, clustered around Lake Thunderbird. Deep wells, distribution systems, and test holes that yielded water that exceeded the chromium drinking-water standard are located near the western boundary of the freshwater flow system, between major flowpaths to the north and south, in the geographic area near the headwaters of Deep Fork and Little River, and at locations

Table 6. Contingency table of chromium concentrations in the Central Oklahoma aquifer by geohydrologic category
[Data include historical filtered and unfiltered chromium analyses. Each analysis represents a distribution system, a well, or a geohydrologic category within a well. The four Garber-Wellington categories were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer; Chase-Admire, Chase, Council Grove, and Admire Groups, undivided; <, less than; ≥, greater than or equal to; µg/L, micrograms per liter]

Chromium concentration	Statistic	Geohydrologic category					Row totals
		Garber-Wellington				Chase-Admire	
		Shallow		Deep			
		Unconfined	Confined	Unconfined	Confined		
< 50 µg/L	Number of analyses	239	16	63	95	87	500
	Expected value	220	14.5	67.9	118.7	78.8	
	Cell chi square	1.6	.2	0.4	4.7	.9	
≥ 50 µg/L	Number of analyses	4	0	12	36	0	52
	Expected value	22.9	1.5	7.1	12.3	8.2	
	Percent ≥ 50 µg/L	1.6	0	16.0	27.5	0	9.4
	Cell chi square	15.6	1.5	3.4	45.4	8.2	
	Total number of analyses	243	16	75	131	87	552

Overall statistics: chi square 81.8; attained significance level less than 0.001; smallest expected value 1.5; degrees of freedom 4.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 10. Areal distribution of chromium concentrations in water from shallow (less than 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

where water is discharging from below the confining layer (fig. 11). The chromium concentration is greater than 25 µg/L in most wells completed in the confined zone of the deep Garber Sandstone and Wellington Formation. Only one deep well from historical data near the study unit center, where the flow model indicates water is recharging the confined part of the aquifer (area labeled “B” in fig. 11), exceeded the 1986 standard and the 1991 standard. This well is deep relative to other wells near it and may draw water from near the base of freshwater.

Analyses from the NOTS test holes (table 5) indicate no consistent vertical distribution of chromium concentration. Chromium concentrations only exceeded the 1986 50-µg/L standard in the two samples from test hole NOTS 1A. The higher dissolved chromium concentrations in test hole NOTS 6 were between 161 and 494 ft in depth. The highest concentration was in the deepest sample from that test hole, which is believed to be from near the base of freshwater. Altogether, the chromium data indicate that high chromium concentrations are present near the base of freshwater at some locations, in both confined and unconfined zones of the deep Garber Sandstone and Wellington Formation, and within 2 mi of streams where the flow model indicates regional ground-water flow discharges.

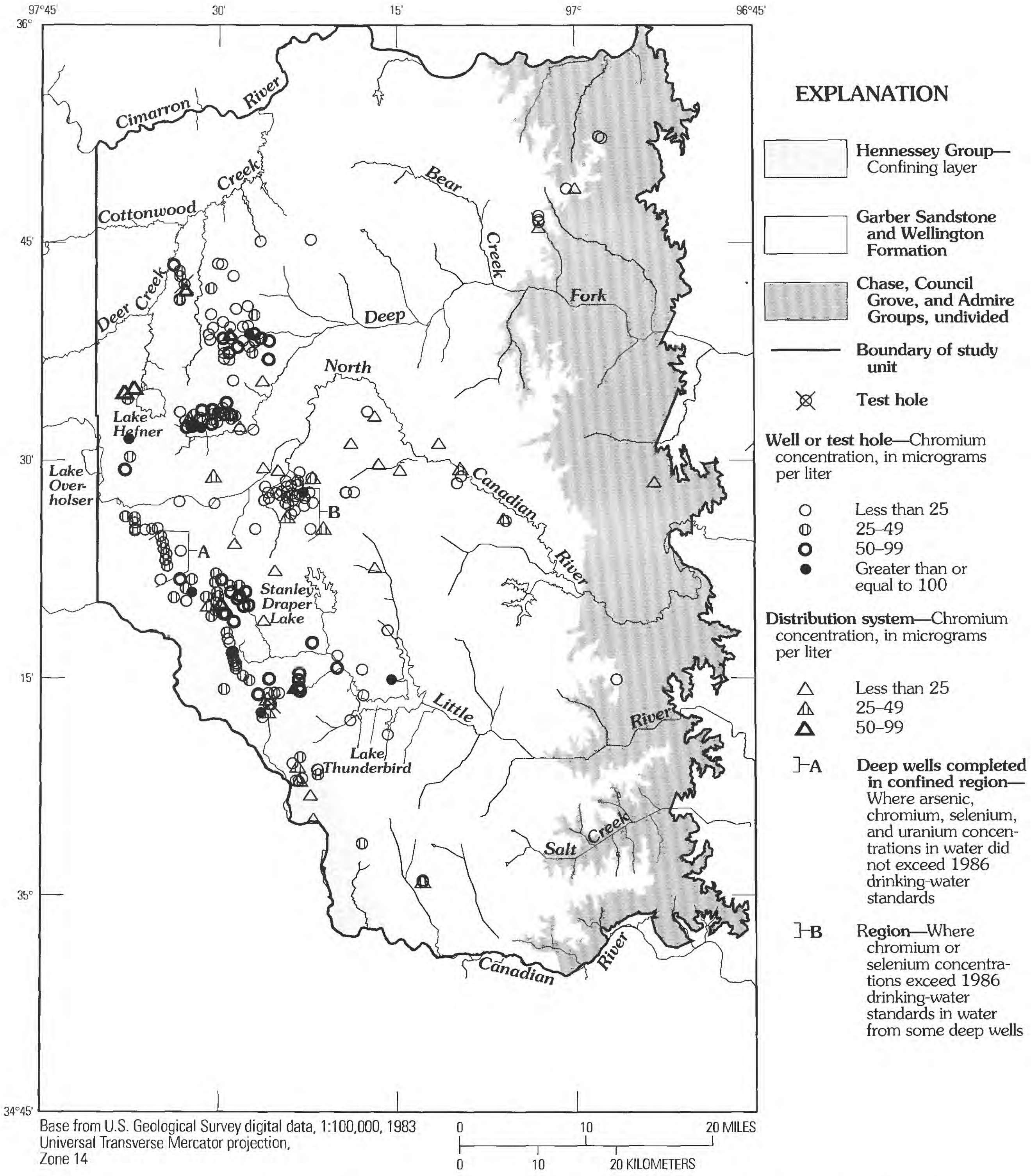
Selenium

Selenium concentrations exceeded the 1986 drinking-water standard in all geohydrologic categories. Contingency-table statistics for the historical data (table 7) indicate that the proportion of analyses that exceeded the 10-µg/L drinking-water standard was significantly different among the geohydrologic categories (*p*-value less than 0.001, null hypothesis rejected). Overall, 18.3 percent of the analyses exceeded the standard. Most analyses that exceeded the standard were from the deep Garber-Wellington, and more than 50 percent of analyses from the confined zone of the deep Garber-Wellington exceeded the standard. The numbers of analyses that exceeded the standard in the unconfined zone of the deep Garber-Wellington and the confined zone of the shallow Garber-Wellington were near the expected values for the geohydrologic category. Fewer analyses than expected exceeded the standard in the unconfined shallow Garber-Wellington and the Chase-Admire category. These data indicate that water with a selenium concentration that equals or exceeds 10 µg/L is common in the deep zones of the Garber-Wellington and is particularly abundant in the confined zone. Selenium concentrations that exceed the 1986 standard also are common in water from the confined zone of the shallow Garber-Wellington but are rare in water from the unconfined zone and in the Chase-Admire category.

These conclusions are supported partly by well data collected for this study, in that 11 of the 27 well-water analyses that exceeded the 1986 standard (table 3) were from the confined zone of the deep Garber-Wellington and analyses that exceeded the standard were found in all geohydrologic categories. However, 6 out of 27 analyses (22 percent) that exceeded the standard were from the Chase-Admire category, which is different from the proportion found in the historical data. A larger proportion (6 out of 25) of Chase-Admire category well-water analyses for this study, than for the historical data (4 out of 87), were from the deep zone of the groups, which might explain the difference. Four of the six well-water analyses from the Chase, Council Grove, and Admire Groups in the study data that exceeded the standard were from deep wells, indicating that selenium concentrations greater than 10 µg/L are more common in the deep Chase-Admire category than the shallow.

The 1991 50-µg/L selenium standard was exceeded by 5.2 percent of the historical analyses, and 82 percent of the analyses that exceeded the standard were from the deep Garber-Wellington (table 7). The 1991 standard was exceeded by 8.0 percent of analyses from the unconfined zone of the deep Garber-Wellington and 12.8 percent of analyses from the confined zone. Selenium concentrations exceeded 50 µg/L in 7.1 percent of the analyses for this study; 8 of the 10 analyses that exceeded the standard were from the deep Garber-Wellington. These results indicate that selenium concentrations exceeding 50 µg/L are common in the deep Garber-Wellington and are rare in the rest of the aquifer.

Shallow wells in the confined part of the Central Oklahoma aquifer that yield water exceeding the 1986 selenium standard are clustered in regions surrounding the headwaters of Deep Fork and Little River (fig. 12). These are regions where the confining layer is thin and may allow increased leakage of recharge to the aquifer. This possible relation between leakage through the confining layer and increased selenium concentrations in the shallow confined Garber Sandstone is supported by two selenium-standard-exceeding well-water sam-



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 11. Areal distribution of chromium concentrations in water from deep (greater than or equal to 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

ples collected for this study from the shallow confined Garber Sandstone that contained more than the 50th-percentile sulfate concentration (table 1). Shallow wells in the unconfined part of the aquifer that yield water exceeding the 10-µg/L selenium standard generally are clustered around the Deep Fork and Little River and their tributaries (fig. 12). Selenium concentrations also exceed the standard in shallow wells southeast of Cottonwood and Deer Creeks. These are areas where the flow model indicates regional ground-water discharge (fig. 5). This relation suggests that shallow occurrences of high selenium concentrations (equal to or greater than 10 µg/L) may be a result of regional discharge.

Available selenium data for deep wells, public drinking-water distribution systems, and test holes have spatial distribution similar to deep chromium data with a sparsity of data in the north and east. On the basis of these available data, deep wells that yield water exceeding the 1986 10-µg/L selenium standard are scattered throughout most of the confined part of the Garber Sandstone and Wellington Formation and the northern part of the Chase, Council Grove, and Admire Groups (fig. 13). Analyses from two deep wells from historical data near the study-unit center, where the flow model indicates water is recharging the confined part of the aquifer (area labeled "B" in fig. 13), exceeded the 1991 50-µg/L standard. These wells are deep relative to other nearby wells and may

Table 7. Contingency table of selenium concentrations in the Central Oklahoma aquifer by geohydrologic category

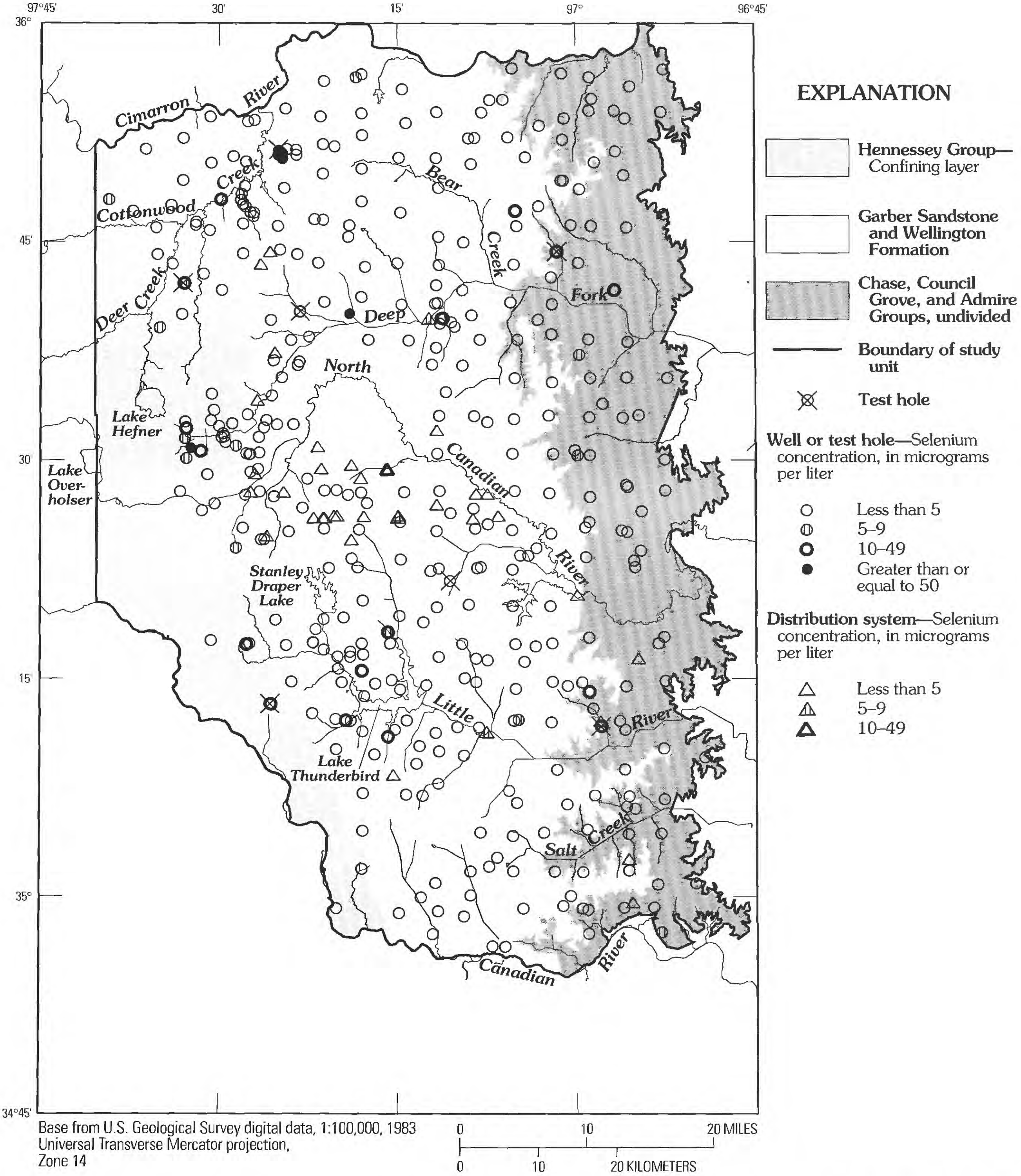
[Data include historical filtered and unfiltered selenium analyses. Each analysis represents a distribution system, a well, or a sample from a geohydrologic category within a well. The four Garber-Wellington categories were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer. Chase-Admire, Chase, Council Grove, and Admire Groups, undivided; <, less than; ≥, greater than or equal to; µg/L, micrograms per liter]

		Geohydrologic category					
		Garber-Wellington					
		Shallow		Deep			
Selenium concentration	Statistic	Unconfined	Confined	Unconfined	Confined	Chase-Admire	Row totals
< 10 µg/L	Number of analyses	233	14	58	69	85	549
	Expected value	198.5	13.1	61.3	115.2	71.1	
	Cell chi square	6.0	.1	.2	18.5	2.7	
≥ 10 µg/L	Number of analyses	10	2	17	72	2	103
	Expected value	44.5	2.9	13.7	25.8	15.9	
	Percent ≥ 10 µg/L	4.1	12.5	22.7	51.1	2.3	18.3
	Cell chi square	26.8	.3	.8	82.4	12.2	
	Total number of analyses	243	16	75	141	87	562

Overall statistics: chi square 150; attained significance level less than 0.001; smallest expected value of 2.9; degrees of freedom 4.

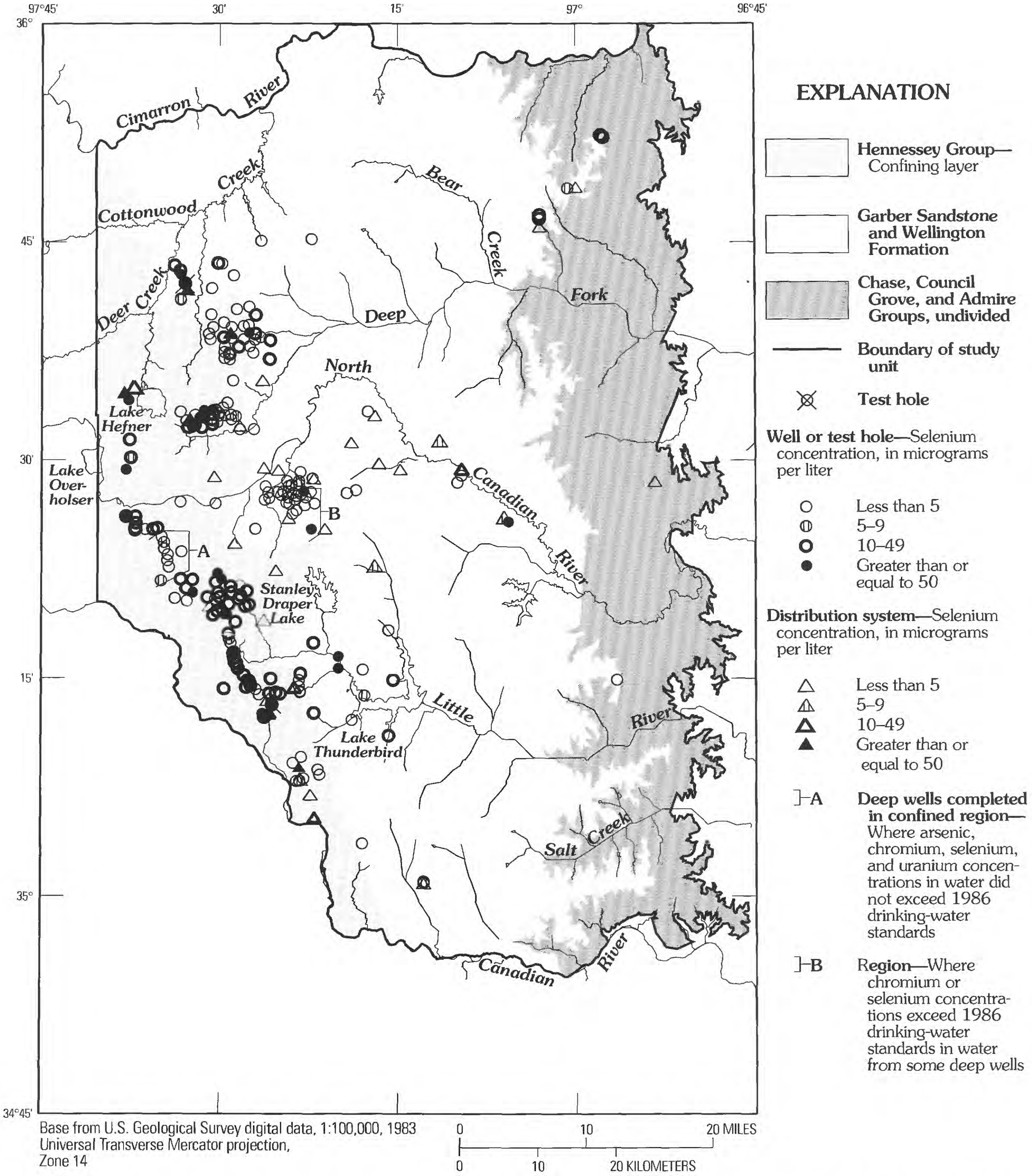
		Unconfined	Confined	Unconfined	Confined	Chase-Admire	Row totals
< 50 µg/L	Number of analyses	238	16	69	123	87	533
	Expected value	230.5	15.2	71.1	133.7	82.5	
	Cell chi square	.2	0	.1	.9	.2	
≥ 50 µg/L	Number of analyses	5	0	6	18	0	29
	Expected value	12.5	.8	3.9	7.3	4.5	
	Percent ≥ 50 µg/L	2.1	0	8.0	12.8	0	5.2
	Cell chi square	4.5	.8	1.2	15.8	4.5	
	Total number of analyses	243	16	75	141	87	562

Overall statistics: chi square 28.3; attained significance level less than 0.001; smallest expected value of 0.8; degrees of freedom 4.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 12. Areal distribution of selenium concentrations in water from shallow (less than 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection,
Zone 14

Figure 13. Areal distribution of selenium concentrations in water from deep (greater than or equal to 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

draw water from near the base of freshwater. Chloride or sulfate concentration cannot be used to determine proximity to the freshwater base in such deep wells because they are completed with long open intervals, and chloride and sulfate are diluted by borehole mixing of water from the well base with calcium magnesium bicarbonate water from the open interval.

Selenium concentrations exceeded the 1986 10-µg/L standard in samples from all but two of the NOTS test holes, NOTS 3 and 4 (table 5). Selenium concentrations generally increased with depth in test holes where it was detected, with the exception of test hole NOTS 7A. The highest selenium concentration in NOTS 7A was in the uppermost interval, about 130 ft below the base of the confining layer. Concentrations decreased below that interval. Samples from the shallow Chase, Council Grove, and Admire Groups (test holes NOTS 2 and 5) exceeded the 1986 standard but did not exceed the 1991 50-µg/L selenium standard. The highest selenium concentration in the test-hole samples was in the deepest sample from test hole NOTS 6 that is thought to have been collected near the base of freshwater. Selenium concentrations in test hole NOTS 6 varied with depth. One sample that exceeded the 1986 standard was from a sandstone layer located between other layers that yielded water with only 2 to 3 µg/L selenium.

In summary, selenium concentrations exceeding 10 µg/L are present at varying depths in the Central Oklahoma aquifer and in isolated lenses of water. Dissolved selenium concentrations exceeding either the 1986 or 1991 drinking-water standard can be present in a discrete sandstone layer within a column of the aquifer that yields water with generally low dissolved selenium concentrations. Altogether, the analyses indicate that concentrations of selenium that exceed the 1986 10-µg/L standard are present in all geohydrologic zones and typically are located in the upper part of the Garber Sandstone below the confining layer, at depth near the base of freshwater in the Garber Sandstone and Wellington Formation, near streams that receive discharge from regional ground-water flow in the unconfined part of the aquifer, and in the deep Chase, Chase Council Grove, and Admire Groups. Concentrations of selenium greater than 50 µg/L are present in the upper part of the Garber Sandstone below the confining layer and at depth and near the base of freshwater in the Garber Sandstone and Wellington Formation.

Uranium

Uranium, like selenium, exceeded the 1991 proposed 20-µg/L drinking-water standard in samples from all geohydrologic categories. Contingency-table statistics for historical uranium data (table 8) indicate that the proportion of analyses that exceeded the proposed 20-µg/L standard or exceeded 20 pCi/L uranium-alpha radioactivity was significantly different among the geohydrologic categories (p-value less than 0.001, null hypothesis rejected). A uranium-alpha radioactivity of 20 pCi/L was used in the contingency-table analyses and to prepare uranium distribution maps rather than the calculated-equivalent proposed standard of 30 pCi/L because uranium concentration at 20 µg/L is approximately equal to 20 pCi/L uranium-alpha radioactivity as picocuries per liter in the Central Oklahoma aquifer (table 9 and fig. 14). [This is a result of the variation in the activity ratio of uranium-234 to uranium-238 isotopes in the aquifer. Above 15-µg/L uranium, the uranium isotope activity ratio in the aquifer is consistently lower (less than 2.5) than the geometric mean ratio of 2.7 used by the EPA to calculate the 30-pCi/L value.] Sixteen percent of all historical analyses exceeded 20 µg/L or 20 pCi/L. However, all six analyses from the deep Chase-Admire category, more than 50 percent of analyses from the confined deep Garber-Wellington, and 40 percent of confined shallow Garber-Wellington analyses exceeded the proposed standard. Analyses that exceeded the proposed standard for unconfined deep Garber-Wellington and shallow Chase-Admire category analyses were near the expected proportion of 16 percent. Only 7 percent of the unconfined shallow Garber-Wellington analyses exceeded the proposed standard.

Samples collected for this study showed a greater overall proportion (21 percent) of well samples that exceeded the 1991 proposed standard (table 3) to the overall proportion of historical analyses (16 percent), and a different distribution between geohydrologic categories. Four out of six deep analyses and 26 percent of shallow analyses from the Chase-Admire category exceeded the proposed standard. Twenty-seven percent of confined shallow and 47 percent of confined deep Garber-Wellington analyses exceeded the proposed standard. Only 1 of the 17 unconfined deep Garber-Wellington and 4 of 61 unconfined shallow Garber-Wellington samples exceeded the proposed standard. Combined results for historical and current data show that uranium concentrations that exceed the

Table 8. Contingency table of uranium concentrations in the Central Oklahoma aquifer by geohydrologic category

[Data include historical filtered uranium concentrations in micrograms per liter and uranium-alpha radioactivity in picocuries per liter (pCi/L). The proposed drinking-water standard of 20 micrograms per liter (mg/L) and the typical uranium-alpha radioactivity emitted by that concentration in the Central Oklahoma aquifer (20 pCi/L) were used for comparison purposes in this contingency table. For Oklahoma Department of Health data, if gross-alpha activity was less than 15 pCi/L, then uranium-alpha activity was considered to be less than 20 pCi/L. Each analysis represents a distribution system, a well, or a geohydrologic category within a well. The four Garber-Wellington categories were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer. <, less than; , greater than or equal to]

Uranium concen-tration	Statistic	Geohydrologic category						Row totals
		Garber-Wellington				Chase- Admire		
		Shallow		Deep				
		Uncon-fined	Confined	Uncon-fined	Confined	Shallow	Deep	
< 20 μg/L or < 20 pCi/L	Number of analyses	172	6	15	10	65	0	268
	Expected value	155.4	8.4	15.1	18.5	65.5	5.0	
	Cell chi square	1.8	.7	0	3.9	0	5.0	
≥ 20 μg/L or ≥ 20 pCi/L	Number of analyses	13	4	3	12	13	6	51
	Expected value	29.6	1.6	2.9	3.5	12.5	1.0	
	Percent ≥ 20 μg/L or ≥ 20 pCi/L	7.0	40.0	16.7	54.5	16.7	100	16
	Cell chi square	9.3	3.6	0	20.5	0	26.5	
	Total number of analyses	185	10	18	22	78	6	319

Overall statistics: chi square 71.3; attained significance level less than 0.001; smallest expected value 0.96; degrees of freedom 5.

Table 9. Relation beween uranium concentration and uranium-alpha radioactivity in the Central Oklahoma aquifer

[Data include determinations from wells and test holes sampled for this study. The relation between uranium concentration and uranium-alpha radioactivity is variable below 15 micrograms per liter uranium. Above 15 micrograms per liter uranium, the 38 log-transformed values correlate well (r2= 0.96). Uranium concentration ± 20 percent can be predicted from measured uranium-alpha radioactivity by the formula:

$$U_{\mu g/L} = 10^{[1.21499 * \mathrm{LOG}_{10}(U_{pCi/L})] - 0.2988}$$

U, uranium; pCi/L, picocuries per liter; μg/L, micrograms per liter]

Measured uranium-alpha radioactivity (pCi/L as U)	Predicted uranium concentration (μg/L as U)	Measured uranium concentration (μg/L as U)
17.4	16 ± 3.1	18 ± 2.2
20.7	20 ± 4.0	20 ± 2.4
24.8	25 ± 5.0	25 ± 2.8
30.5	32 ± 6.4	37 ± 4.1
50.9	62 ± 12.3	67 ± 8.7
77.4	99 ± 20	100 ± 11
102	140 ± 27	130 ± 14
225	360 ± 72	320 ± 35

proposed 20-μg/L standard are abundant in the confined deep Garber-Wellington and the deep Chase-Admire category, common in the confined shallow Garber-Wellington and shallow Chase-Admire category, and rare in the unconfined Garber-Wellington.

Most shallow wells that yield water exceeding the 1991 proposed standard of 20 μg/L uranium are completed in: (1) the Garber Sandstone under the confining layer near the headwaters of Deep Fork, (2) the confined and unconfined Garber Sandstone and Wellington Formation north of Deep Fork, and (3) in the Chase, Council Grove, and Admire Groups along the eastern side of the study unit (fig. 15). Most shallow wells in the unconfined shallow Garber Sandstone and Wellington Formation with water exceeding the proposed standard are within 2 mi of streams where the flow model indicates regional ground-water flow discharges (similar to wells that exceed arsenic, chromium, and selenium standards). However, several wells and distribution systems that yield water with uranium exceeding 20 μg/L (or the equivalent 20 pCi/L uranium) are located on or near potentiometric highs where most water in the shallow ground-water column recently entered the aquifer (labeled "P" in figure 15).

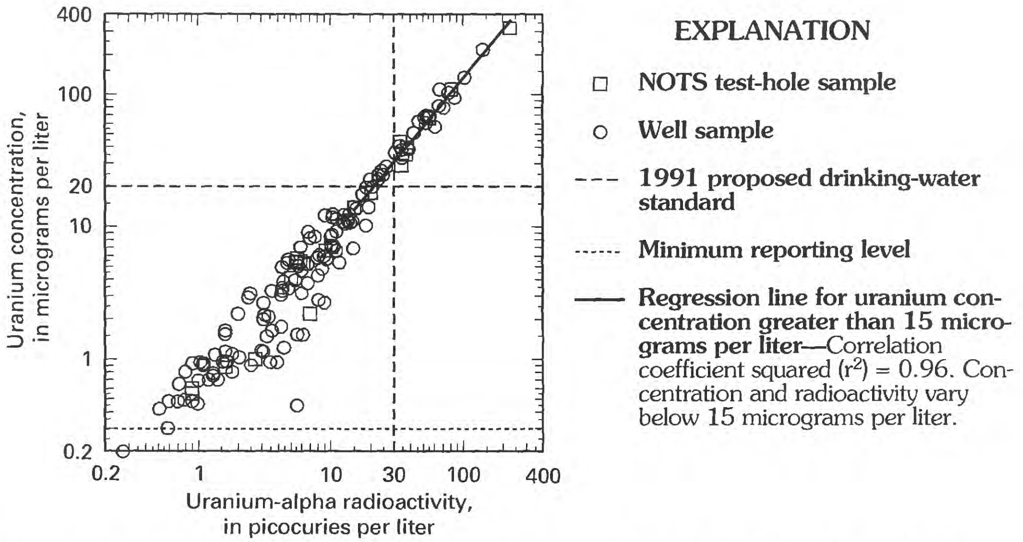


Figure 14. Relation of uranium concentrations to uranium-alpha radioactivity in the Central Oklahoma aquifer. Regression line is based on uranium concentrations greater than 15 micrograms per liter.

This suggests that uranium can accumulate to dissolved concentrations greater than 20 µg/L soon after water enters the aquifer. There is a sparsity of deep-well historical uranium data in most of the study unit, partly because most deep wells are public-supply wells; uranium is not monitored in such wells unless gross-alpha radioactivity exceeds 15 pCi/L. Additionally, deep-well data are sparse in the north, east, and south because the base of the aquifer is shallower in those regions and there is less urban development, thus fewer deep wells are either possible or required. On the basis of the limited data set, deep wells yielding water with concentrations that exceed the proposed standard are completed in the Garber Sandstone and Wellington Formation below the confining layer near the western limit of freshwater flow, to the east of Deer Creek where water discharges from below the confining layer, or are completed partly or entirely in the Chase, Council Grove, and Admire Groups, undivided (fig. 16).

Uranium concentration exceeded the 1991 proposed standard in at least one sample from all NOTS test holes except NOTS 4 (table 5). In the unconfined Garber Sandstone and Wellington Formation (test holes NOTS 1, 3, 4, and 6), uranium concentrations generally increased with depth. The highest concentration of uranium (320 µg/L) was in the deepest sample from test hole NOTS 6, which is thought to have been collected near the base of freshwater. The second highest uranium concentration was in the deepest sample from test hole NOTS 1A, a sample that contained 54 mg/L chloride, which may be from near the base of freshwater. The opposite depth relation was found in the confined Garber Sandstone in test hole NOTS 7A, where the highest concentration of uranium was in the uppermost sample collected 316 ft below the base of the confining layer. Samples collected from the Chase, Council Grove, and Admire Groups, undivided (test holes NOTS 2 and 5), exceeded 20 µg/L at depths less than 118 ft.

In summary, high uranium concentrations are present at shallow depths below the confining layer, near the base of freshwater, and at shallow depths in the Chase, Council Grove, and Admire Groups. Uranium concentrations greater than 20 µg/L are present in all geohydrologic zones but are found only in western, northern, and eastern parts of the Central Oklahoma aquifer. Uranium concentrations that exceed the 1991 proposed standard are rare in the unconfined deep or shallow Garber Sandstone and Wellington Formation south of Deep Fork.

Relations Among Arsenic, Chromium, Selenium, and Uranium Distribution

There are some similarities between the distributions of arsenic, chromium, selenium, and uranium throughout the Central Oklahoma aquifer (figs. 8 through 13, 15, and 16, table 5, and table 10). Concentrations that exceed the 1986 drinking-water standards

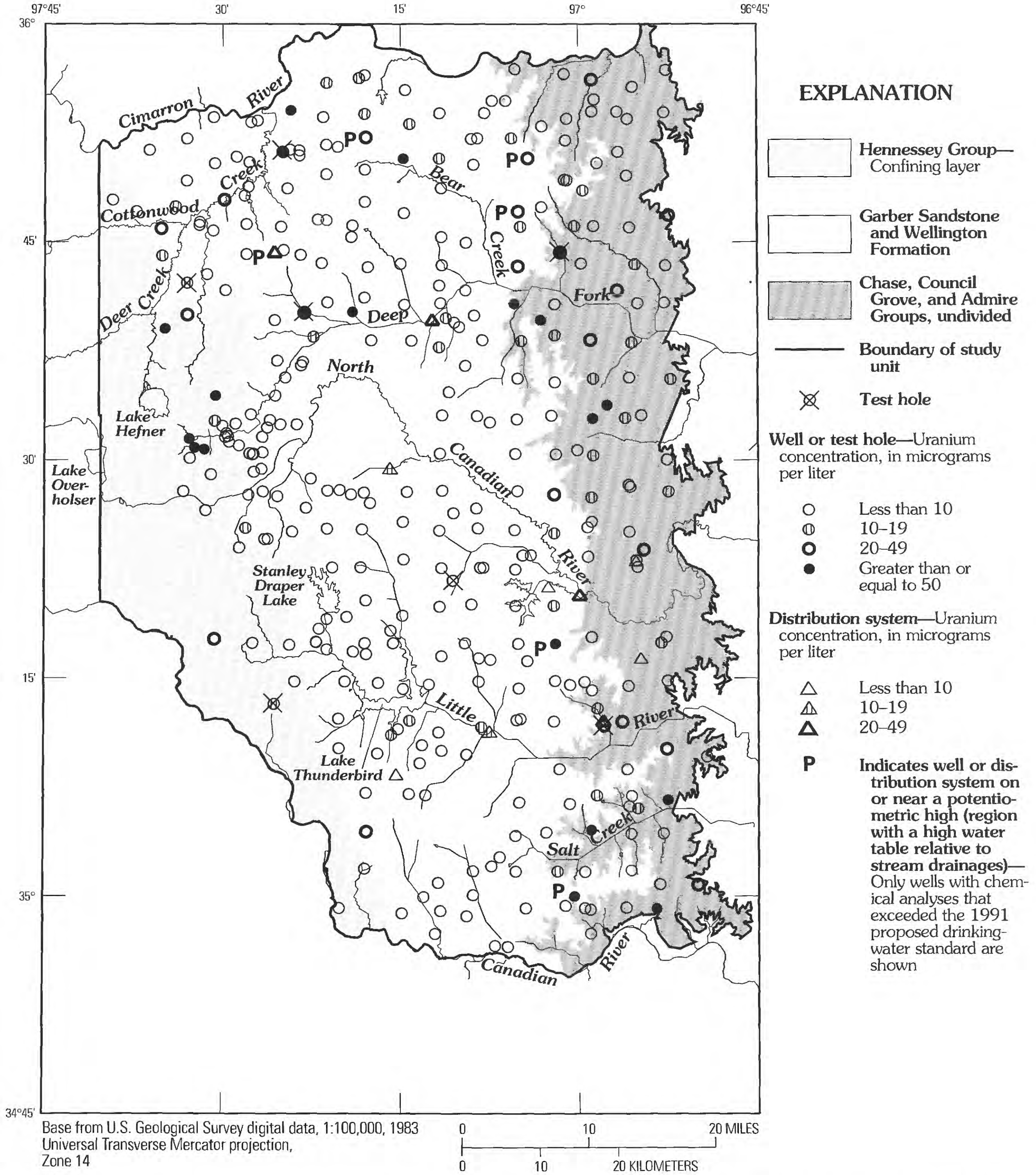


Figure 15. Areal distribution of uranium concentrations in water from shallow (less than 300 feet) wells, test holes, and distribution in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

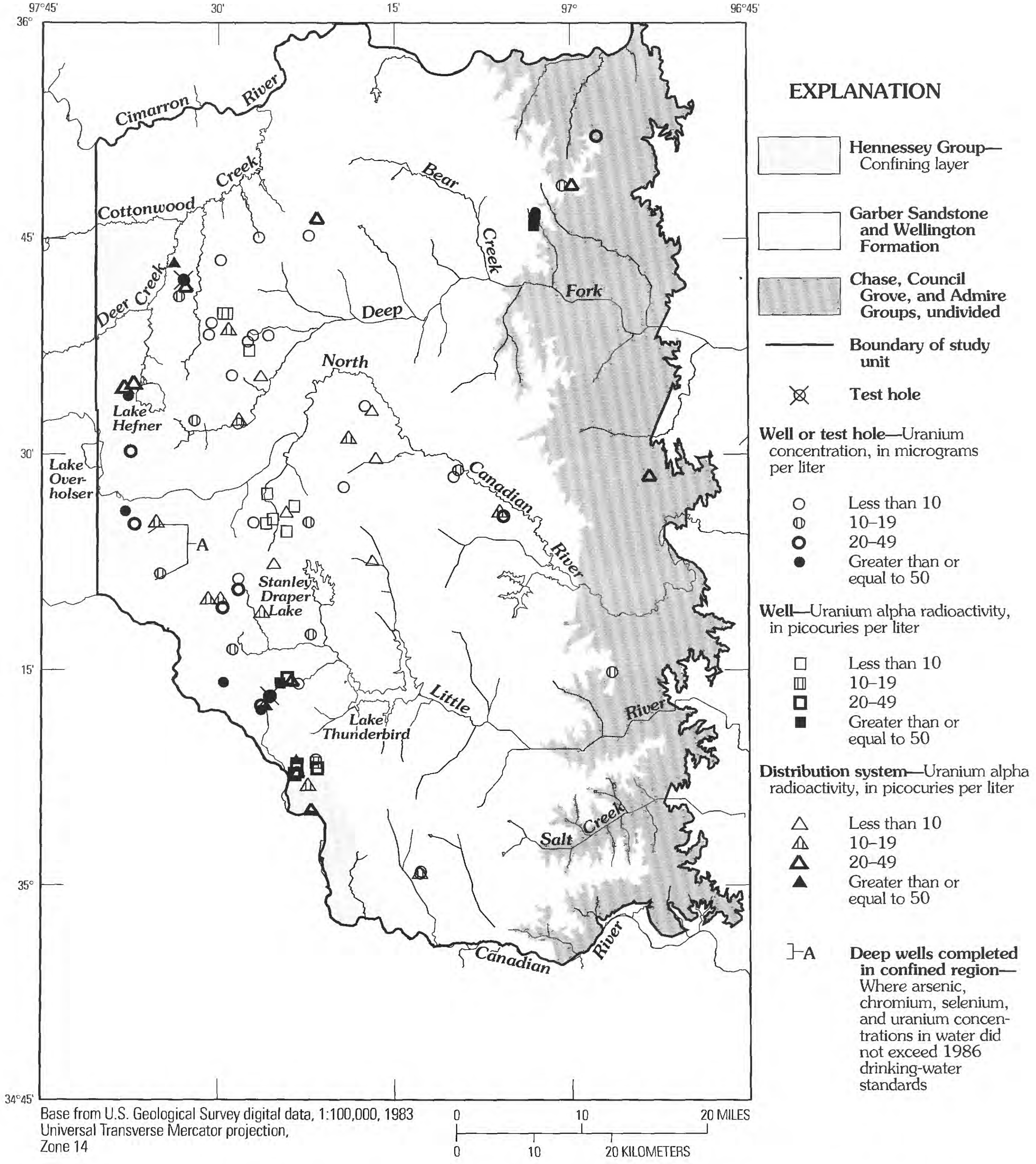


Figure 16. Areal distribution of uranium concentrations in water from deep (greater than or equal to 300 feet) wells, test holes, and distribution systems in the Central Oklahoma aquifer, based on historical data and data collected from 1987–90 as part of this study.

Table 10. Summary of dissolved arsenic, chromium, selenium, and uranium distribution in the Central Oklahoma aquifer

[The four Garber-Wellington zones were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer; Near stream, exceeded concentration within 2 miles of stream receiving regional discharge; ≥, greater than or equal to; μg/L, micrograms per liter; Rare, Less common, and Common indicate overall proportion of analyses that exceed concentration in either historical or study data sets. Rare, fewer than 10 percent exceeded concentration; Less common, fewer than 20 percent exceeded concentration; Common, 20 percent or more exceeded concentration; —, indicates no analyses from category exceeded concentration]

Element and concentration	Geohydrologic zone									
	Garber-Wellington								Near base of:	
	Shallow		Deep		Chase-Admire					
	Unconfined	Confined	Unconfined	Confined	Shallow	Deep	Near stream	Away from stream	Confining layer	Freshwater
Arsenic,										
≥ 50 μg/L	Rare	Rare	Rare	Common	—	—	Yes	—	Yes	Yes
Chromium,										
≥ 50 μg/L	Rare	—	Less common	Common	—	—	Yes	—	—	Yes
≥ 100 μg/L	—	—	Rare	Rare	—	—		—	—	Yes
Selenium,										
≥ 10 μg/L	Rare	Less common	Less common	Common	Rare	Common	Yes	—	Yes	Yes
≥ 50 μg/L	Rare	—	Rare	Common	—	—		—	Yes	Yes
Uranium,										
≥ 20 μg/L	Rare	Common	Rare	Common	Common	Common	Yes	Yes	Yes	Yes

for arsenic, chromium, or selenium or the 1991 proposed uranium standard are common under the confining layer in the deep zones of the aquifer. Samples from the confined part of the aquifer that exceed a standard or proposed standard generally are distant from recharge locations. The highest concentrations of the four elements generally are in deep wells in the far western part of the ground-water flow system, in distal parts of regional flowpaths, or near the base of the confining layer. However, deep in the western confined part of the aquifer, underlying an area that extends between 2 and 5 mi south of the North Canadian River (area labeled "A" in figs. 9, 11, 13, and 16), is a region where analyses have not exceeded any of the 1986 drinking-water standards nor the 1991 proposed uranium standard. This is an area of the confined zone of the deep Garber-Wellington where the flow model indicates some of the recharge to northern confined flowpaths is flowing west before turning to the north (fig. 5) and where sandstone distribution maps indicate the total thickness and percentage of sandstone are greater than surrounding deep regions (figs. 3 and 4). Deep wells completed under the confining layer to the south of this region commonly contain water that exceeds the 1986 arsenic, chromium, or selenium standards or the 1991 proposed uranium standard.

Arsenic and chromium typically are present only at low concentrations in the shallow zones of the Central Oklahoma aquifer. The few shallow wells that yield water that exceeds the 1986 arsenic or chromium standards are located in the Garber Sandstone or the Wellington Formation. Selenium and uranium, however, commonly exceed the 1986 10-μg/L selenium standard or the 1991 proposed uranium standard in the shallow zones of the aquifer. High selenium and uranium concentrations are present in the confined zone of the shallow Garber Sandstone near the headwaters of Deep Fork. Elsewhere in the confined shallow Garber Sandstone they are not found together at high concentrations. In the unconfined zone of the shallow Garber Sandstone and in the shallow Chase, Council Grove, and Admire Groups, undivided, however, high selenium concentration commonly is associated with high uranium concentration. Where both selenium and uranium data are available, most wells that exceed the proposed uranium standard also contain greater than 10 μg/L selenium.

Chromium and selenium concentrations that exceed the 1986 drinking-water standards are present in some deep wells in the unconfined part of the Central Oklahoma aquifer in regions west of Deep Fork and Little River and east of Deer Creek. These regions of high chromium and selenium concentrations typically are within 2 mi of streams that receive water discharging from beneath the confining layer (Parkhurst, Christenson, and Breit, 1993). Concentrations of both chromium and selenium are present in water from some deep wells in an area labeled "B" in figures 11 and 13. These wells are deep and are completed nearer the base of freshwater relative to other deep wells in the immediate area that have low chromium or selenium concentrations.

Shallow wells that exceed the 1986 arsenic, chromium, or selenium standards in the unconfined part of the Central Oklahoma aquifer are near major streams where the flow model indicates ground water from regional flowpaths discharges. This indicates that high concentrations develop along long flowpaths. Shallow wells that exceed the 1991 proposed uranium standard in the unconfined part of the aquifer, however, are not always near streams. High uranium concentrations are present in some shallow wells on or near potentiometric highs where most ground water has only recently entered the aquifer, as well as near streams that receive older ground-water discharging from regional sources. This suggests that some uranium may enter the ground water near the beginning of the water's path through the aquifer, in contrast to the other elements.

Water samples from the NOTS test holes provide additional information on the vertical distribution of arsenic, chromium, selenium, and uranium in the Central Oklahoma aquifer (table 5). Concentrations of the dissolved elements generally increase with depth in test holes in the unconfined part of the aquifer. Concentrations of the four elements are highest within test holes NOTS 1A and 6 in samples collected from the deepest intervals in unconfined Garber Sandstone. These samples also contain chloride at concentrations greater than the 75th percentile, indicating that the intervals are near the base of freshwater. The control well, test hole NOTS 4, yielded water with only low concentrations of the elements for the entire depth. In contrast, confined test holes NOTS 7 and 7a show higher concentrations near the top of the aquifer.

SOURCES OF ARSENIC, CHROMIUM, SELENIUM, AND URANIUM IN THE AQUIFER ROCK

Arsenic

Chemical and mineralogic analyses of rock core collected from the NOTS test holes revealed that the highest arsenic concentrations [as much as 62 µg/g] (Breit and others, 1990; Mosier and others, 1990) were found in sandstones containing abundant yellow-brown goethite grain coatings. These arsenic-enriched yellow-brown sandstone intervals were typically less than 0.5 ft thick and were most common in the Garber Sandstone. High arsenic concentrations also were present in some tightly cemented dolomite-nodule conglomerates. The tight cementation of the conglomerates indicates that they are relatively impermeable and not a likely arsenic source. No discrete arsenic-mineral phases were found, although two grains of pyrite (FeS_2) isolated by heavy-mineral separation did contain some arsenic.

Sequential extractions of samples with high concentrations of arsenic (Mosier, 1998) showed that most arsenic (as much as 77 percent) in the samples would dissolve in HCl, an extraction that dissolves iron oxides, some clay minerals, and dolomite. The arsenic extracted was not strongly associated with HCl-extracted iron in these samples (r^2=0.2, simple linear regression). This indicates that not all iron oxides are similarly enriched in arsenic. A substantial amount of arsenic (averaging 5.1 percent of total arsenic) is extractable using KH_2PO_4. This arsenic is probably adsorbed on mineral surfaces. Additional $NaHCO_3$ and $NaHCO_3$-NaOCl extractions—designed to mimic high pH and oxidizing conditions, respectively, that are present in some regions of the Central Oklahoma aquifer—also extracted a substantial percentage of the arsenic. These results indicate that a major source of dissolved arsenic in the aquifer is arsenic adsorbed on mineral surfaces, probably on goethite and hematite. A substantial amount of adsorbed arsenic can be transferred from rock to water by high pH or ligand exchange if arsenic is present as arsenic (V) species. Additional arsenic is mobilized by high pH oxidizing conditions indicating a reduced source in which arsenic is in a lower oxidation state. Ground water that is oxidizing and has a high pH can mobilize arsenic from the aquifer rock.

Chromium

The highest whole-rock concentration of chromium (170 µg/g) was found in a reduced zone near the base of the Garber Sandstone. Nonetheless, most Central Oklahoma aquifer sandstones, including the reduced zones, have low chromium concentrations. High chromium concentrations (40 to 140 µg/g) generally were in red mudstones. No discrete chromium-mineral phases were found in the chromium-enriched samples. Rare disseminated grains of chromite ($FeO \bullet Cr_2O_3$) were found in sandstone using a scanning electron microscope with electron dispersive spectroscopy (SEM-EDS). Chromite is resistant to dissolution, so it is not a likely source of dissolved chromium. A sample of a blue chromium-rich clay was collected from an outcrop of the base of the Hennessey Group. Chemical testing showed that the chromium in this sample was released only by strong acids that would destroy the silicate lattice, indicating this chromium clay is not a likely source of chromium. Sequential extraction analyses of test-hole core samples (Mosier, 1998) revealed most chromium in the aquifer is in an insoluble phase that can be dissolved only by destroying the crystal lattice with a multi-acid digestion. The rest of the chromium generally is extractable by HCl, thus indicating chromium may be included in some iron oxides or clay or may be protected from dissolution in the aquifer by a coating of dolomite. A substantial amount of chromium (as much as 66 percent of total chromium) was released from some samples by an oxidizing extraction using either HCl and $KClO_3$ or $NaHCO_3$-NaOCl. Most of these samples were from test holes NOTS 2 and 7 in the Chase-Admire and the Hennessey Group. None of these samples were from test holes that yielded water that exceeded the 1986 chromium standard. Where chromium is in water, accessible chromium in the rock has been oxidized; where chromium is not in water, an unoxidized source of chromium may be present in the rock. This indicates there may be a chromium-containing mineral present from which chromium is soluble once the chromium is oxidized. Oxidizing water with a high pH can mobilize chromium from some sources in the aquifer. Clay must be dissolved by aquifer water to release chromium from other sources such as clay minerals.

Selenium

The highest whole-rock selenium concentrations (as much as110 µg/g) were found in reduced zones and spots that also were enriched in uranium and vanadium. High selenium concentrations also were detected in some hematitic sandstones at concentrations of as much as 11 µg/g. Native selenium crystals, clausthalite (PbSe), and an unidentified copper-selenium-sulfur phase were found in reduced zones using SEM-EDS (Breit and others, 1990). These minerals contain selenium in reduced selenium (0) and selenide [selenium (–II)] valence states that form insoluble minerals (Balistrieri and Chao, 1990). Oxidation of selenium in these minerals to selenium (IV) or selenium (VI) is necessary before it would be soluble in the dissolved concentrations measured in the Central Oklahoma aquifer. The sequential extraction that dissolved the most selenium (an average of 52 percent) was the strongly oxidizing HCl-$KClO_3$ extraction. Small but substantial proportions of the selenium were released by the KCl, KH_2PO_4, $NaHCO_3$, and $NaHCO_3$-NaOCl extractions, particularly in test holes NOTS 2 and 7 in the Chase, Council Grove, and Admire Groups and the Hennessey Group. This readily extractable selenium indicates that some selenium is present in a readily mobilized state, possibly as selenium (IV) or selenium (VI) adsorbed on iron oxides or clay minerals (Chao and Sanzalone, 1989). These results indicate that oxidation is necessary to mobilize selenium that is present in clausthalite or native selenium. However, some selenium on mineral surfaces can be mobilized as a result of contact by aquifer water with adequate concentration of competing anions such as chloride, carbonate, or hydroxyl.

Uranium

The highest whole-rock uranium concentrations (as much as 123 µg/g) are in the reduced zones. Reduced zones with high uranium concentrations also have high vanadium concentrations. Meta-tyuyamunite [$Ca(U0_2)_2(V0_4)_2 \bullet 5H_2O$], small uranium-silicate spheres, and a uranium-titanium phase were found in reduced zones using SEM-EDS. Fission-track radiographs show that uranium is slightly enriched in some hematite cements. Most uranium was extracted in either the HCl extraction or the strong multi-acid digestion (Mosier, 1998), indicating that most uranium resides in iron oxides or clay or in insoluble accessory minerals such as zircon. An average of 11.3 percent of the uranium was extracted using the $NaHCO_3$ extraction, suggesting that a significant amount of oxidized uranium is adsorbed on clay or iron-oxide surfaces and can be readily mobilized by high-pH sodium bicarbonate water.

Relation Among Sources and Dissolved Concentrations of Arsenic, Chromium, Selenium, and Uranium

Some water samples from sandstone in contact with arsenic-, chromium-, selenium- or uranium-enriched rocks did not exceed the 1986 standards or 1991 proposed standards. Most of this water was a different type (calcium magnesium bicarbonate rather than sodium bicarbonate) or had a lower pH than water that exceeded standards. Results of sequential extraction experiments indicate that water characteristics necessary to readily mobilize the elements are high pH, oxidizing ability, and certain anionic compositions such as high chloride, hydroxyl, or carbonate concentrations.

Arsenic-enriched yellow-brown rocks and the selenium- and uranium-enriched reduced zones generally are less than 0.5 ft thick and represent only a small volume of the Central Oklahoma aquifer. It is questionable whether these localized concentrations are the only source of these elements. Test-hole water samples that exceeded the 1986 standard for arsenic or exceeded the 1991 proposed standard for uranium were either within 15 ft of one of the thin enriched layers of rock or were from sandstones layers that contained concentrations within the top 25 percent of the element's distribution, as in an example from test hole NOTS 6 (fig. 17). Water samples that exceeded the 1991 standard for selenium generally were from sandstones only slightly enriched with selenium. However, water that exceeded the 1991 50-μg/L selenium standard was from sandstones containing rock lenses with selenium concentrations greater than the 75th percentile (0.8 μg/g) in test-hole cores. Some of these lenses were more than 0.5 ft thick. The abundance of element-enriched rock layers typically increased in the interval within 30 ft of water samples that exceeded the 1986 drinking-water standard for that element. These increases in enriched rocks are common near the base of freshwater flow. Water in such sampled intervals likely contacted some of these enriched rocks along its flowpath. Although the enriched rocks comprise only a small part of the total volume of the aquifer, they appear to be spatially concentrated in the vicinity of sandstones that yield water that exceeds drinking-water standards and likely are a major source of the elements in the water.

Another major source of arsenic, chromium, and uranium may be mudstone. Mudstone in the Central Oklahoma aquifer generally contains higher concentrations of arsenic, chromium, and uranium than sandstone, a significant proportion of which are extractable. Mudstone has a low permeability and is flushed by water more slowly than sandstone. The low permeability is consistent with a large remaining proportion of extractable arsenic, chromium, and uranium. The presence of the elements in the mudstone indicates mudstone may be a long-term source of the elements, but the low permeability suggests that transport of the elements from mudstone may be insignificant relative to transport from sandstone.

EFFECT OF REDOX CONDITIONS IN THE AQUIFER ON MOBILITY OF ARSENIC, CHROMIUM, SELENIUM, AND URANIUM

Results of sequential extractions indicate that oxidizing conditions are necessary to allow arsenic, chromium, selenium, and uranium to be mobile in the Central Oklahoma aquifer. Detectable dissolved oxygen (greater than 1 mg/L) is present in most water in the aquifer, indicating an oxic environment (Berner, 1981). This is consistent with abundant ferric minerals and the general lack of organic matter and ferrous sulfides in the aquifer rock. Measurable dissolved oxygen was found in some water that entered the aquifer tens of thousands of years ago and is now deep below the confining layer (Parkhurst, Christenson, and Breit, 1993).

Some water lacks measurable dissolved oxygen in parts of the Central Oklahoma aquifer that are recharged through clay-rich soils, such as those developed over the confining layer and the Chase-Admire, and thus is considered to be post-oxic (Berner, 1981). Clay-rich soils favor development of reducing conditions (Chapelle, 1993). This could account for the lack of oxygen. Water in the aquifer with less than 1 mg/L dissolved oxygen commonly contains greater than 1 μg/L selenium or uranium, which generally are soluble in oxic and some post-oxic environments and are

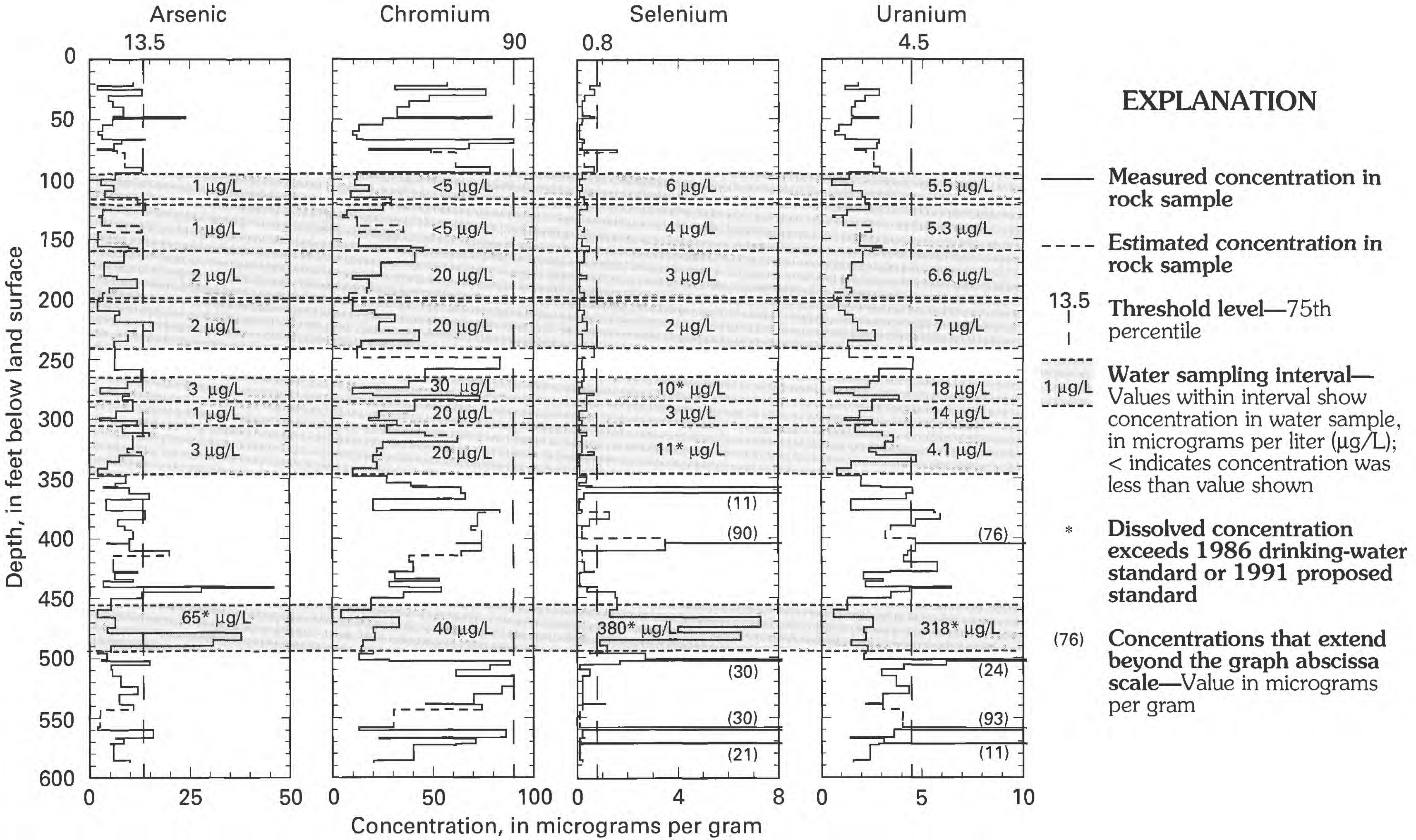


Figure 17. Distribution of arsenic, chromium, selenium, and uranium concentrations in rock and water samples from test hole NOTS 6 in the Central Oklahoma aquifer. Estimated rock concentrations for missing core were assumed to equal that of the next deepest sample.

not mobile in sulfidic and methanic environments. The presence of selenium and uranium in the oxygen-depleted water, therefore, suggests that this water represents post-oxic conditions and that sulfidic and methanic environments apparently are not present in the aquifer. Arsenic, chromium, and selenium in this oxygen-depleted water and in oxic water are present as arsenic (V), chromium (VI), and selenium (VI) (Schlottmann and Funkhouser, 1991), their highest oxidation states. These oxidation states are stable in all oxic and some post-oxic conditions (fig. 18). Chromium (VI) and selenium (VI) require a higher redox potential (Eh) at a given pH to be stable than do arsenic (V) or uranium (VI). The presence of dissolved oxygen and arsenic (V), chromium (VI), and selenium (VI) indicate that uranium also should be in its highest oxidation state [uranium (VI)]. The presence of detectable concentrations of chromium (VI) and selenium (VI) in some post-oxic water further suggests that the water retains a relatively high redox potential, which approaches oxic conditions.

Parkhurst, Christenson, and Breit (1993) divided the 141 wells sampled for this study into oxic and post-oxic categories. Oxic wells contain: (1) detectable dissolved oxygen (greater than or equal to 1 mg/L), (2) less than 500 µg/L iron, and (3) detectable nitrate if ammonium is present. Twenty-two wells not meeting all three of these criteria were classified as post oxic. Most post-oxic wells were completed in the confined shallow Garber Sandstone or in the Chase, Council Grove, and Admire Groups, undivided, locations where some recharge may be through clay-rich soils. Sulfidic and methanic classifications were not used because dissolved sulfide and sulfide minerals that characterize these environments are rare in the aquifer. These oxic criteria were used to classify the redox environment of water that exceeds the 1986 drinking-water standards. Four of the five wells that yielded water that exceeded the arsenic standard were oxic, and all five wells that yielded water that exceeded the chromium standard were oxic (table 11). Twenty-two of the 27 wells that yielded water that exceeded the selenium standard were oxic, and only 19 of the 29 wells that yielded water that exceeded the 1991 proposed uranium standard were oxic. These results suggest that a greater Eh is required for chromium than for arsenic, selenium, and uranium to be dissolved. Dissolved chromium concentrations that exceed the standard are restricted to more oxidizing parts of the aquifer, whereas arsenic, selenium, and uranium also may be present in less oxidizing post-oxic environments.

Table 11. Redox conditions in study wells in the Central Oklahoma aquifer that exceeded existing or proposed drinking-water standards

[--, indicates standard not available for element]

Element	Number of wells that exceeded existing standard	Number of oxic wells	Number of post-oxic wells	Number of wells that exceeded proposed or 1991 standard	Number of oxic wells	Number of post-oxic wells
Arsenic	5	4	1	--	--	--
Chromium	5	5	0	1	1	0
Selenium	27	22	5	10	9	1
Uranium	--	--	--	29	19	10

Six of seven samples that exceeded the 1991 proposed uranium standard but contain only small amounts of selenium (less than 3 µg/L) were post oxic. Because selenium is generally associated with uranium in the Central Oklahoma aquifer rock, this may indicate that most water containing only uranium may have an Eh too low to oxidize selenium (fig. 18). Results of these redox investigations indicate all sampled water had adequate Eh to oxidize arsenic and uranium to mobile arsenic (V) and uranium (VI). Most, but not all, sampled water was adequately oxidizing to oxidize chromium and selenium to mobile chromium (VI) and selenium (VI). Thus, redox conditions in the aquifer will not limit arsenic and uranium mobility but may limit chromium and selenium mobility in areas recharged through clay-rich soils.

RELATION OF MUDSTONE DISTRIBUTION TO WATER CHEMISTRY AND ARSENIC, CHROMIUM, SELENIUM, AND URANIUM DISTRIBUTION

The relative abundance of mudstone in the Central Oklahoma aquifer affects water chemistry by directly affecting cation-exchange reactions, permeability, and redox conditions. These conditions directly affect the distribution of dissolved arsenic, chromium, selenium, and uranium.

Clay minerals, which are abundant in mudstone, control cation exchange in the Central Oklahoma aquifer. Whole-rock X-ray diffraction (XRD) (Breit and

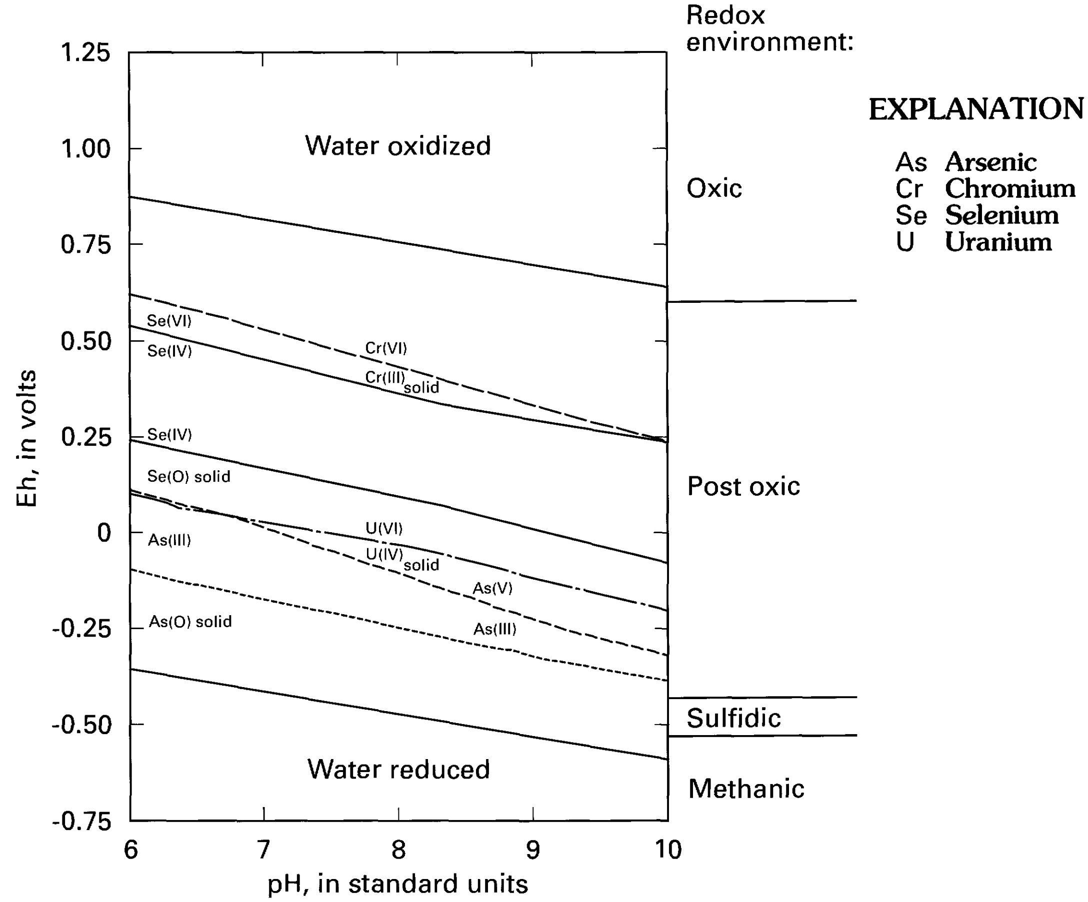


Figure 18. Generalized relation of arsenic, chromium, selenium, and uranium species to Eh and pH at 25 degrees Celsius and 1 atmosphere pressure. Activity of arsenic species 0.67 μ*M* (micromolal), carbon species 6 m*M* (millimolal), chromium species 1 μM, iron species 1 μ*M*, phosphorus species 0.5 μ*M*, sulfur species 0.5 μ*M*, selenium species 0.63 μ*M*, and uranium species 0.1 μ*M*. Sources of thermodynamic data used to construct the diagram: arsenic (Wagman and others, 1968; Barton and Skinner, 1979); chromium (Schmidt, 1984; Rai, Sass, and Moore, 1987); iron (Wagman and others, 1968; Nordstrom and others, 1990); selenium (Wagman and others, 1968; Vaughn and Craig, 1978); uranium (Langmuir, 1978).

others, 1990) determined that sandstones interbedded with mudstones in the clay-rich Chase, Council Grove, and Admire Groups, undivided, in the east, just below the confining layer, and at depth in the Garber Sandstone and Wellington Formation contain more clay than sandstones in the sand-rich part of the aquifer. Analyses of cation-exchange capacity of clay-size separates indicate that mudstones contain 31 to 88 meq/100 g of exchangeable cations, dominantly calcium and magnesium, with 3.5 to 20 percent sodium (Parkhurst, Christenson, and Breit, 1993). Sodium is the dominant exchangeable cation on one mudstone below the base of freshwater. Clay-size separates from sandstones in the aquifer contain 22 to 40 meq/100 g exchangeable cations with 0.25 to 10 percent sodium. The lowest percentages of exchangeable sodium were found in samples from the sand-rich part of the aquifer. Mixed-layer illite-smectite is the dominant ion exchanger (Schlottmann and Breit, 1992). In clay-rich parts of the aquifer in the east and at depth, the exchange of sodium$^+$ bound to mixed-layer clays for dissolved calcium^{2+} and magnesium^{2+} allows dolomite to dissolve, although dolomite is at saturation in most aquifer water (Parkhurst, Christenson, and Breit, 1993). The combined effects of cation exchange and dolomite dissolution increase pH and alkalinity in the clay-rich parts.

The overall permeability of rocks in clay-rich parts of the Central Oklahoma aquifer is lower than in sand-rich parts. This reduced permeability causes ground water to flow more slowly in clay-rich than in sand-rich parts so that a smaller volume of water moves through the clay-rich parts per unit time, assuming potentiometric gradients are equal. The reduced flow slows the removal of soluble constituents from the rocks so that potentially soluble constituents such as exchangeable sodium, dolomite, gypsum, arsenic, chromium, selenium, or uranium can be retained in the rock even at shallow depth. In addition, sodium and chloride from brine that once filled the aquifer are retained. Conversely, flushing of soluble constituents is likely in shallow, more permeable, sand-rich parts. This relation between low permeability and corresponding occurrence of soluble constituents is shown by the distribution of major ions in the aquifer. Shallow ground water from less-flushed clay-rich rocks of the Chase-Admire commonly contains higher chloride and sulfate concentrations than shallow ground water from the sand-rich part of the aquifer (Parkhurst, Christenson, and Schlottmann, 1989). Clay-rich rocks near the base of freshwater yield water with chloride and rocks that receive some recharge through the gypsum-bearing clay-rich Hennessey Group contain increased sulfate.

Residual soils that developed over mudstone in the Chase, Council Grove, and Admire Groups and over parts of the confining layer are poorly drained because of their high clay content. The resulting reducing environment, commonly developed in poorly drained soils or confining layers (Chapelle, 1993), removes oxygen from the water as it recharges the Central Oklahoma aquifer in clay-rich regions. Eleven out of 22 wells classified as post oxic by Parkhurst, Christenson, and Breit (1993) were completed in the shallow zone of the Chase, Council Grove, and Admire Groups. That represents nearly half of the shallow wells sampled in these groups, suggesting that post-oxic conditions are common in the region. Selenium and uranium concentrations that exceed the 1986 10-μg/L selenium standard or the 1991 proposed 20-μg/L uranium standard are common in water in the shallow Chase-Admire, but the dissolved selenium concentration is less than 50 μg/L although the uranium concentration is as high as 220 μg/L. Uranium commonly is present at high concentrations in water with only low concentrations of selenium, suggesting that selenium mobility is restricted in these groups, perhaps because of inadequate redox potential. The highest chromium concentration in water from shallow wells in these groups was 7 μg/L, and only two samples contained detectable chromium concentrations at a reporting level of 5 μg/L. The low chromium and selenium concentrations suggest that most water in the groups is not adequately oxidizing to mobilize chromium and selenium.

Arsenic, chromium, and selenium concentrations that exceed the 1986 drinking-water standards and uranium concentrations that exceed the 1991 proposed standard have been found just below the base of the confining layer or just above the base of freshwater. Selenium also exceeds the standard, and uranium exceeds the proposed standard in water in the clay-rich Chase-Admire. All of these are regions where mudstone interbeds are abundant relative to the rest of the aquifer. This association probably is related to a source of the elements in clay-rich rocks, the reduced amount of flushing in these regions (as evidenced by residual concentrations of chloride or sulfate greater than the aquifer 75th percentile), and a difference in water chemistry at these locations related to cation-exchange processes. The lack of dissolved chromium and the selenium concentrations consistently below 50 μg/L in the Chase-Admire, although oxidizable and soluble chromium and selenium are most available in these groups (Mosier and others, 1991), further indicate that recharge through clay-rich soils results in shallow ground water depleted in dissolved oxygen and inadequately oxidizing to oxidize chromium and selenium.

CHANGES IN MAJOR-ELEMENT GROUND-WATER CHEMISTRY ALONG FLOWPATHS RELATED TO MOBILIZATION OF ARSENIC, CHROMIUM, SELENIUM, AND URANIUM

Mass-balance geochemical modeling results (Parkhurst, Christenson, and Breit, 1993) show that the major reactions controlling water chemistry in the Central Oklahoma aquifer are uptake of carbon dioxide gas, dolomite dissolution, and cation exchange. The extent to which these reactions occur in various parts of the aquifer directly affect the water's ability to mobilize arsenic, chromium, selenium, and uranium. Water in the unconfined sand-rich part of the aquifer generally is calcium magnesium bicarbonate type water with detectable dissolved oxygen, a pH near neutral, and little sodium. When water enters the sand-rich part of the aquifer, it takes up carbon dioxide gas in the vadose zone and, as it moves through the aquifer, equilibrates with dolomite. As water moves into either the confined or clay-rich part of the aquifer, interaction with sodium-rich mixed-layer clays results in the exchange of some of the dissolved calcium and magnesium for sodium in the clays. The resulting depletion of calcium and magnesium in the water allows more dolomite to dissolve. Deep in the aquifer where the water is isolated from vadose-zone carbon dioxide, dolomite dissolution causes an increase in pH from near-neutral to values as great as 9.6. The amount of pH increase may be limited by the availability of clay and exchangeable sodium in the clay. Contingency-table analysis of samples collected for this study (table 12) indicates high pH water is common in the deep, confined zone of the Garber-Wellington and deep zone of the Chase-Admire. High pH water is less common in the deep, unconfined zone of the Garber-Wellington and clay-rich shallow zone of the Chase-Admire and is rare in the shallow zones of the Garber-Wellington.

Where cation exchange and dolomite dissolution occur in the vadose zone, carbon dioxide gas is available, and uptake of carbon dioxide buffers the pH to near neutral. Without the cation exchange the alkalinity would be controlled only by dolomite saturation and the partial pressure of carbon dioxide gas. The extent of the reactions is controlled by availability of exchangeable sodium and residence time of the water in the vadose zone. The abundant clay in the sandstones in regions of the study unit where mudstone is the dominant lithology provides exchangeable sodium, and the low transmissivity increases residence time. High alkalinities [300 to 650 mg/L as calcium carbonate ($CaCO_3$)] are common in these regions, and pH is near neutral. This high alkalinity results in a high carbonate-ion (CO_3^{2-}) activity relative to other water with the same pH. Water type in these regions is generally sodium calcium magnesium bicarbonate, with approximately equal milliequivalents of each cation. As the water moves deeper into the Central Oklahoma aquifer, cation exchange and dolomite dissolution continue in the absence of carbon dioxide, and pH increases.

Water Chemistry Associated with Arsenic, Chromium, Selenium, and Uranium

Data collected for this study show general relations between concentrations of dissolved arsenic, chromium, selenium, and uranium and sodium water types, high pH, carbonate-ion activity, water age, gross-alpha radioactivity, vanadium, and boron. In general, high arsenic and chromium concentrations are in older water with high pH. High chromium concentrations also are in water with detectable dissolved oxygen. High arsenic concentrations are in water with high vanadium concentrations. High uranium concentrations are in water with high gross-alpha radioactivity and boron concentrations. High arsenic and selenium concentrations typically are related to high uranium concentrations. This section describes the relations and the processes causing these relations.

Table 12. Contingency table of pH values in the Central Oklahoma aquifer by geohydrologic category

[Data include analyses determined at the sample site for water from wells and test holes sampled for this study. Each analysis represents a well or a depth interval within a test hole. The four Garber-Wellington categories were defined on the basis of well depth (or sampling depth if available) and by confined condition: Shallow, less than 300 feet; Deep, greater than or equal to 300 feet; Unconfined, outside confined part of the aquifer; Confined, within confined part of the aquifer. <, less than; ≥, greater than or equal to]

pH, standard units	Statistic	Geohydrologic category						Row totals
		Garber-Wellington				Chase-Admire		
		Shallow		Deep				
		Unconfined	Confined	Unconfined	Confined	Shallow	Deep	
< 8.5	Number of analyses	47	14	5	45	17	2	130
	Expected value	40.7	12.0	4.8	51.8	16.7	4.0	
	Cell chi square	1.0	.3	0	.9	0	1.0	
≥ 8.5	Number of analyses	4	1	1	20	4	3	33
	Expected value	10.3	3.0	1.2	13.2	4.3	1.0	
	Percent ≥ 8.5	7.8	6.7	17	31	19	60	20
	Cell chi square	3.9	1.4	0	3.6	0	3.9	
	Total number of analyses	51	15	6	65	21	5	163

Overall statistics: chi square 16.0; attained significance level 0.007; smallest expected value 1.0; degrees of freedom 5.

Relation of Sodium Water Types to Trace-Element Concentrations

Piper diagrams (Piper, 1944) were used to illustrate the relation between water type and arsenic, chromium, selenium, and uranium concentrations that exceed the 1986 or the 1991 proposed drinking-water standards. These diagrams show the relative percentages of the major cations and anions in the triangular plots and the overall chemical character in the central diamond-shaped plot. Water type can be interpreted from these plots. Water in which one cation or anion constitutes 50 percent or more of the total is identified by the dominant cation and anion. Water of intermediate cation or anion composition is that which contains more than 25 percent of two or three principal cations or anions. The ions in intermediate water types are listed in order of decreasing percentage, such as sodium calcium magnesium bicarbonate.

The variety of water types found in the 141 wells and the 8 test holes sampled for this study are shown in figure 19. Water compositions vary from calcium magnesium bicarbonate water type (in the left part of the central diamond) to sodium bicarbonate (at the bottom center). Addition of chloride from mixing with residual brine or sulfate from gypsum dissolution shifts water types to the upper right of the diamond diagram.

Sodium is the dominant cation in most water that exceeds a 1986 drinking-water standard or 1991 proposed standard (fig. 20). Dissolved arsenic concentration exceeded 50 µg/L only in sodium bicarbonate water. Chromium exceeded 50 µg/L in sodium bicarbonate water and one sodium chloride bicarbonate water. Water that contains greater than or equal to 10 µg/L selenium or 20 µg/L uranium has a wide cation and anion compositional range, although most is bicarbonate rich. Sodium percentage exceeds relative calcium and magnesium percentage in all but two of the water samples that exceed the selenium standard and in all but one of the water samples that exceed the proposed uranium standard. One sample that exceeded the selenium standard was a calcium magnesium bicarbonate water and plots in the left corner of the diamond diagram. This water was from a shallow well in the unconfined part of the Garber-Wellington and had a pH of 7.5. That pH is uncommonly high for shallow calcium magnesium bicarbonate water in the Central Oklahoma aquifer, suggesting that the water has dissolved some dolomite in the absence of carbon dioxide gas; however, little cation exchange has occurred. Several wells with high concentrations of selenium or uranium contain a substantial percentage of chloride or sulfate.

Water that contained greater than 50 µg/L chromium and in which sodium was less than 85 percent of the total cations contained an excess of magnesium over calcium. Most water in the Central Oklahoma aquifer either contains equal percentages of calcium and magnesium, or calcium exceeds magnesium. This reversed calcium-magnesium relation is consistent with dissolution of magnesium-rich clay and suggests that the water that contains high dissolved chromium concentrations may indicate magnesium-rich clay dissolution.

The sodium dominance in this water also is seen in the relation between sodium concentration and arsenic, chromium, selenium, and uranium (fig. 21). All four elements generally increase in concentration with increasing sodium. Concentrations of arsenic exceeded the 1986 standard only in water with more than 120 mg/L sodium; chromium in water with more than 85 mg/L sodium; and uranium in water with more than 65 mg/L sodium. Selenium commonly exceeded the 1986 standard in water with more than 60 mg/L sodium but also exceeded the standard in three samples with lower sodium concentrations, reflecting the wider range of water types in which selenium is found. Sodium concentrations in most samples that exceeded the 1986 standards or 1991 proposed standards were greater than the median sodium concentration of 49 mg/L.

The relation of arsenic, chromium, selenium, and uranium concentration to sodium- and bicarbonate-dominant water types supports relations between dissolved arsenic, chromium, selenium, and uranium and cation-exchange processes in clay-rich parts of the Central Oklahoma aquifer. The presence of chloride and sulfate ions further supports indications that much of the dissolved arsenic, chromium, selenium, and uranium are from less-flushed, clay-rich parts.

Effect of pH on Trace-Element Concentrations

High arsenic concentrations (50 to 110 µg/L) are present only in water with a pH greater than or equal to 8.5 (fig. 22). High chromium concentrations (50 to 100 µg/L) are present only in water with a pH greater than or equal to 8.3. Selenium and uranium exceeded 10 and 20 µg/L, respectively, in some water with pH values greater than or equal to 7.0, but about two-thirds of the samples with a pH greater than 8 exceed these values. The relation to pH is attributed to adsorption

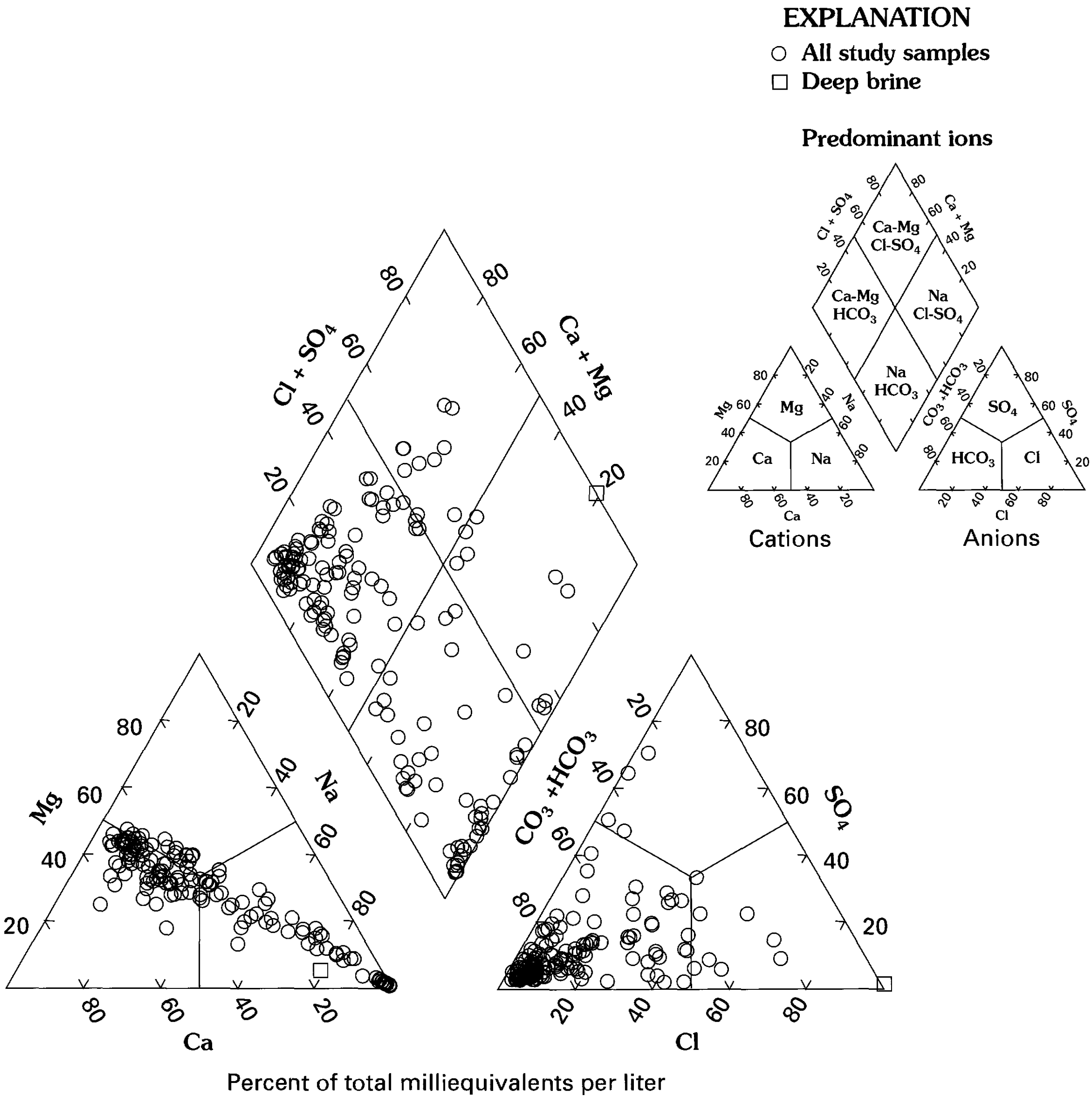


Figure 19. Piper diagram showing water types for all samples collected for this study of the Central Oklahoma aquifer, 1987–90.

processes that control mobility of the arsenic (V), chromium (VI), selenium (VI), and uranium (VI) valence species on the basis of results of the sequential extraction experiments. The adsorption of these species is related to the formation of arsenic, selenium, chromium, and uranium oxyions and uranium-carbonate complexes.

Arsenic (V) forms the oxyanions $H_2AsO_4^-$ and $HAsO_4^{2-}$ in water (fig. 23). Arsenic (V) is generally soluble, although the mobility is limited at low pH (less than 7.5) in the presence of iron oxides because of adsorption on iron-oxide surfaces (Welch, Lico, and Hughes, 1988). Arsenic (V) oxyanions form an inner sphere complex with the iron-oxide surface, so water containing an abundance of phosphate ions or with a pH from 7.5 to 11 is necessary to mobilize it (Davis and Kent, 1990). A pH of 8.5 or greater is necessary for arsenic (V) concentrations to exceed 50 µg/L in the Central Oklahoma aquifer (fig. 22). Other valence species of arsenic oxidize to arsenic (V) at a lower Eh than the other elements studied (fig. 18).

Chromium (VI) is present as the oxyanions $HCrO_4^-$ and CrO_4^{2-} in water (fig. 23). Selenium (VI) forms the SeO_4^{2-} oxyanion in water (fig. 23). These oxyanions tend to form outer sphere complexes with iron-oxide surfaces and are only weakly adsorbed. Increasing pH, increasing ionic strength, or the presence of competing ions such as sulfate, chloride, or carbonate will enhance the desorption of these oxyanions (Davis and Kent, 1990). Laboratory adsorption

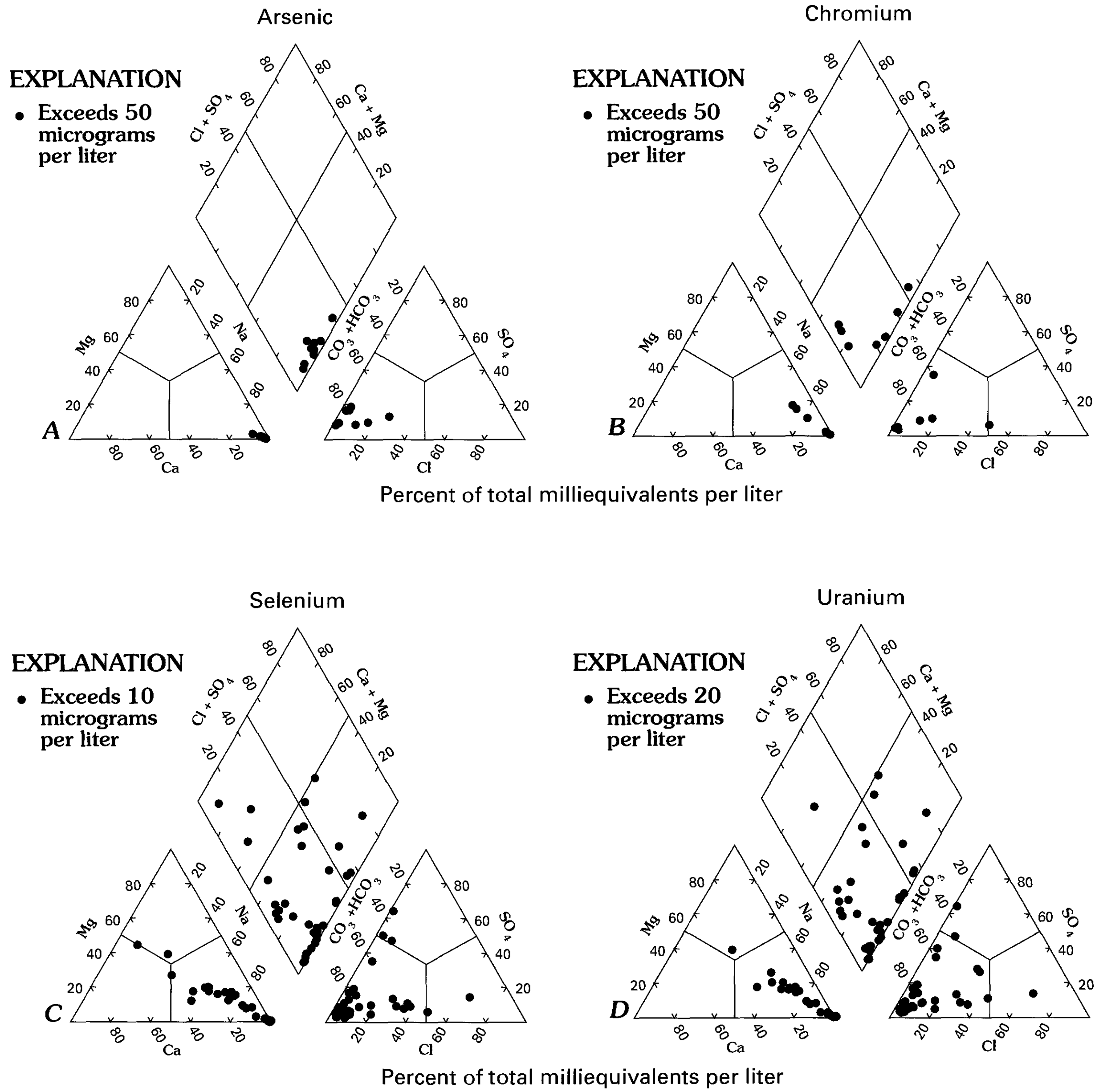


Figure 20. Piper diagrams showing water types for all samples collected for this study of the Central Oklahoma aquifer that exceeded a 1996 Federal drinking-water standard for arsenic, chromium, and selenium or the 1991 proposed standard for uranium.

experiments indicate chromium (VI) tends to desorb from iron oxyhydroxides at a higher pH (7.0 to 8.5) than selenium (VI) (pH 5 to 7) (Zachara and others, 1987; Balistrieri and Chao, 1990; Davis and Kent, 1990). This difference can be seen in the plots of the elements concentrations by pH in the Central Oklahoma aquifer (fig. 22). Selenium exceeds 10 and even 50 µg/L at a pH near 7, though chromium does not exceed 50 µg/L until a pH of 8.3. Chromium (III) and selenium (IV) require a much higher Eh than arsenic (III) to be oxidized to chromium (VI) and selenium (VI), so dissolved concentrations are limited in post-oxic conditions even where pH is high.

Unlike the other elements studied here, uranium (VI) forms an oxycation, the uranyl ion (UO_2^{2+}), in water. Uranium is oxidized to uranium (VI) at an Eh slightly higher than that required to oxidize arsenic (III) to arsenic (V). The oxycation adsorbs on

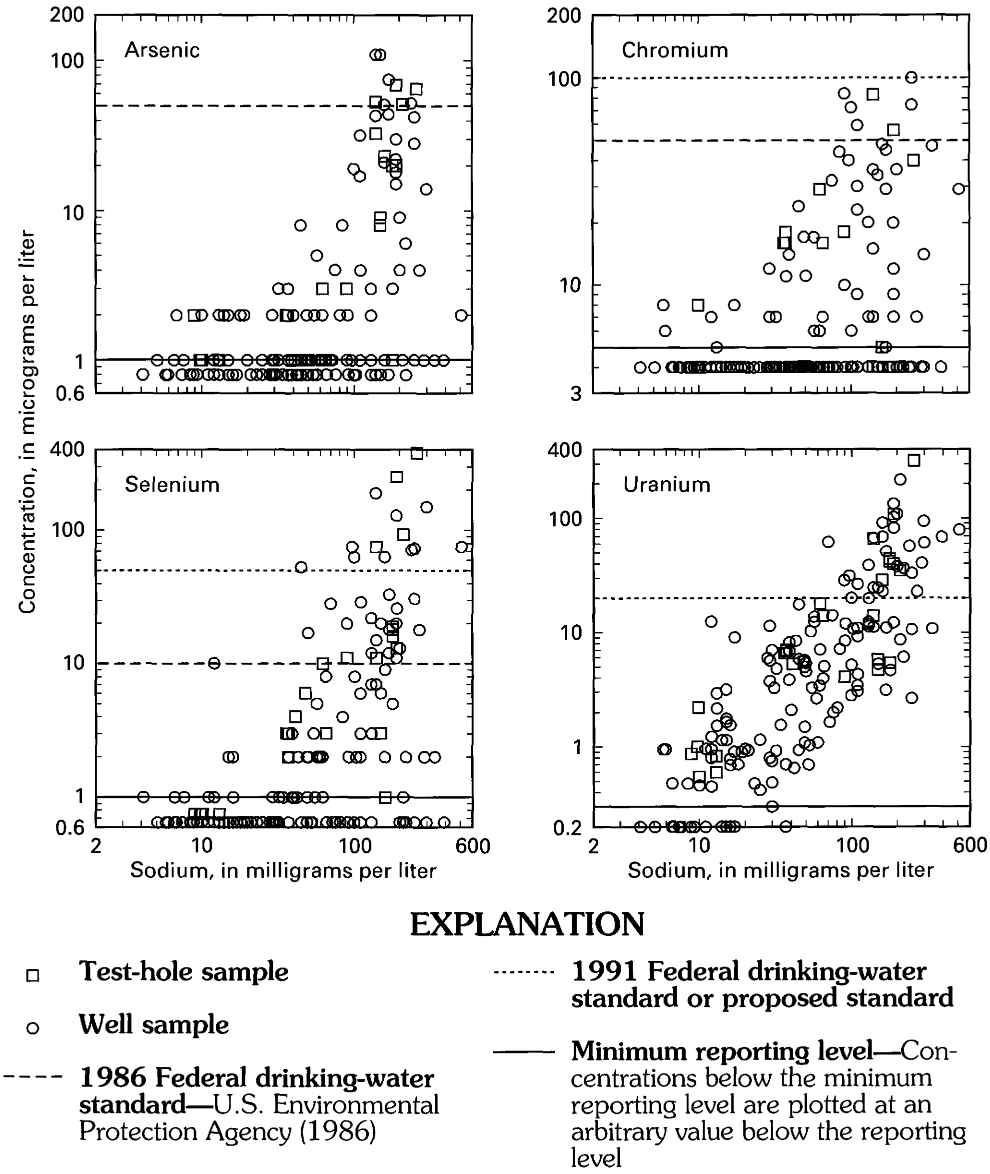
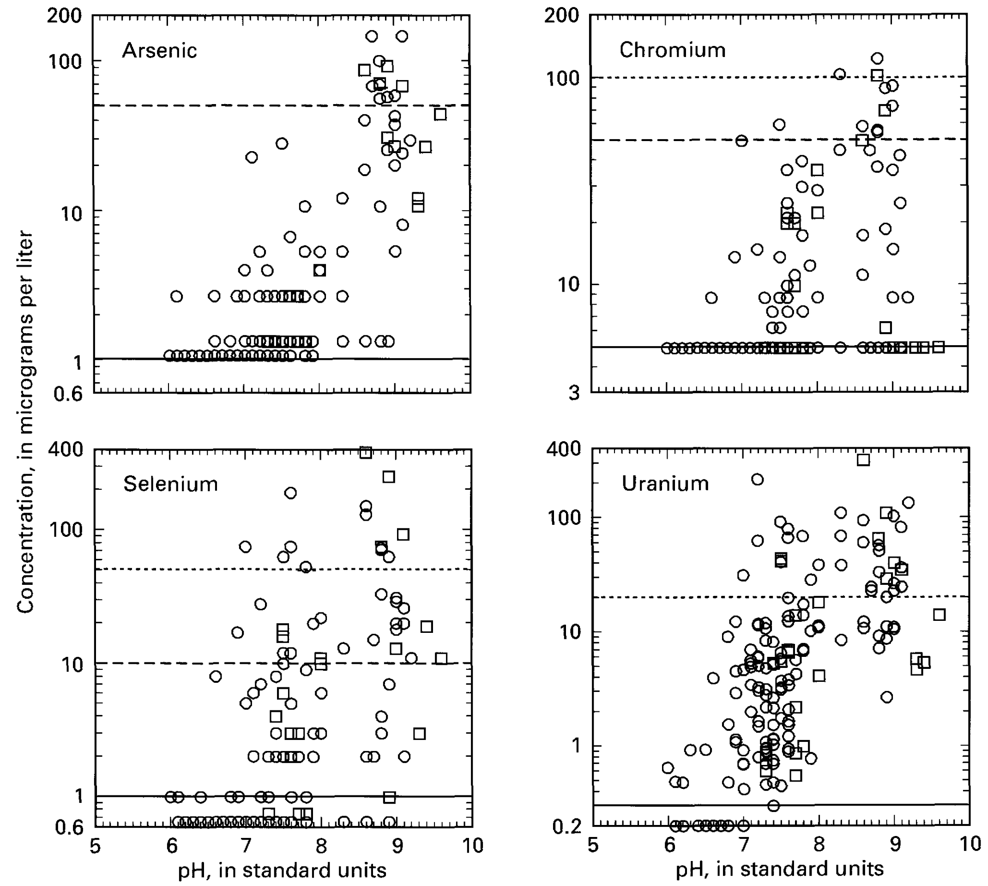


Figure 21. Relation of arsenic, chromium, selenium, and uranium concentrations to sodium concentrations in the Central Oklahoma aquifer.

iron-oxide minerals with increasing pH if no ions are available to form a complex. Within the pH range of the Central Oklahoma aquifer, uranium (VI) mobility can be enhanced by the presence of phosphate or carbonate ions (Langmuir, 1978; Hsi and Langmuir, 1985). Uranium (VI) forms a neutral or anionic complex with these ions that does not tend to adsorb on the iron-oxide surface at high pH (greater than 8.0). In water with a small phosphate-ion activity relative to carbonate-ion activity $[(PO_4^{3-})_T/(CO_3^{2-})_T$ less than $10^{-3}]$, uranyl-carbonate complexes predominate (Sandino and Bruno, 1992). In the Central Oklahoma aquifer, the maximum $(PO_4^{3-})_T/(CO_3^{2-})_T$ is $10^{-5.2}$, thus phosphate complexes are unlikely, and uranyl-carbonate complexes will dominate (fig. 23). Additionally, in bicarbonate type water, carbonate-ion activity increases with pH, which enhances uranium mobility. This effect is seen in the general increase in uranium concentration with pH (fig. 22).

Effect of Carbonate-Ion Activity on Uranium Concentration

Eleven samples between pH 7 and 8 contained high uranium concentrations. These samples are from shallow wells (less than 300 ft) completed either in the Garber Sandstone just below the base of the Hennessey Group or in the Chase, Council Grove, and Admire Groups, undivided. All but one sample contained less



EXPLANATION

□ **Test-hole sample**

○ **Well sample**

---- **1986 Federal drinking-water standard**—U.S. Environmental Protection Agency (1986)

········ **1991 Federal drinking-water standard or proposed standard**

—— **Minimum reporting level**—Concentrations below the minimum reporting level are plotted at an arbitrary value below the reporting level

Figure 22. Relation of arsenic, chromium, selenium, and uranium concentrations to pH in the Central Oklahoma aquifer.

than 0.01 mol/L dissolved inorganic carbon, which means the ground water does not contain an unusual carbon concentration for the Central Oklahoma aquifer. Alkalinity of these samples ranged from 172 to 646 mg/L; however, all but two samples contained less than 400 mg/L alkalinity. Uranium might be expected to remain adsorbed on iron-oxide surfaces or be present at low dissolved concentrations under these conditions (Hsi and Langmuir, 1985). A plot of pH versus carbonate-ion activity (fig. 24) calculated using PHREEQE (Parkhurst, Thorstenson, and Plummer, 1980) shows that the high uranium concentrations (greater than or equal to 20 µg/L) typically are present in samples that plot to the right of samples with less uranium. In the pH range from 7 to 8, high uranium concentrations are to the right of the median carbonate-ion activity for each pH. This indicates that for a given pH, increased carbonate-ion activity enhances uranium mobilization. This effect is even apparent at pH values greater than 8, where high uranium concentrations still tend to lie to the right of low concentrations on the plot. The elevated relative carbonate-ion activity is thought to be due to high alkalinities (300 to 650 mg/L as $CaCO_3$) generated in water recharged through a clay-rich vadose zone with abundant exchangeable sodium and dolomite. Two samples with high uranium plot to the

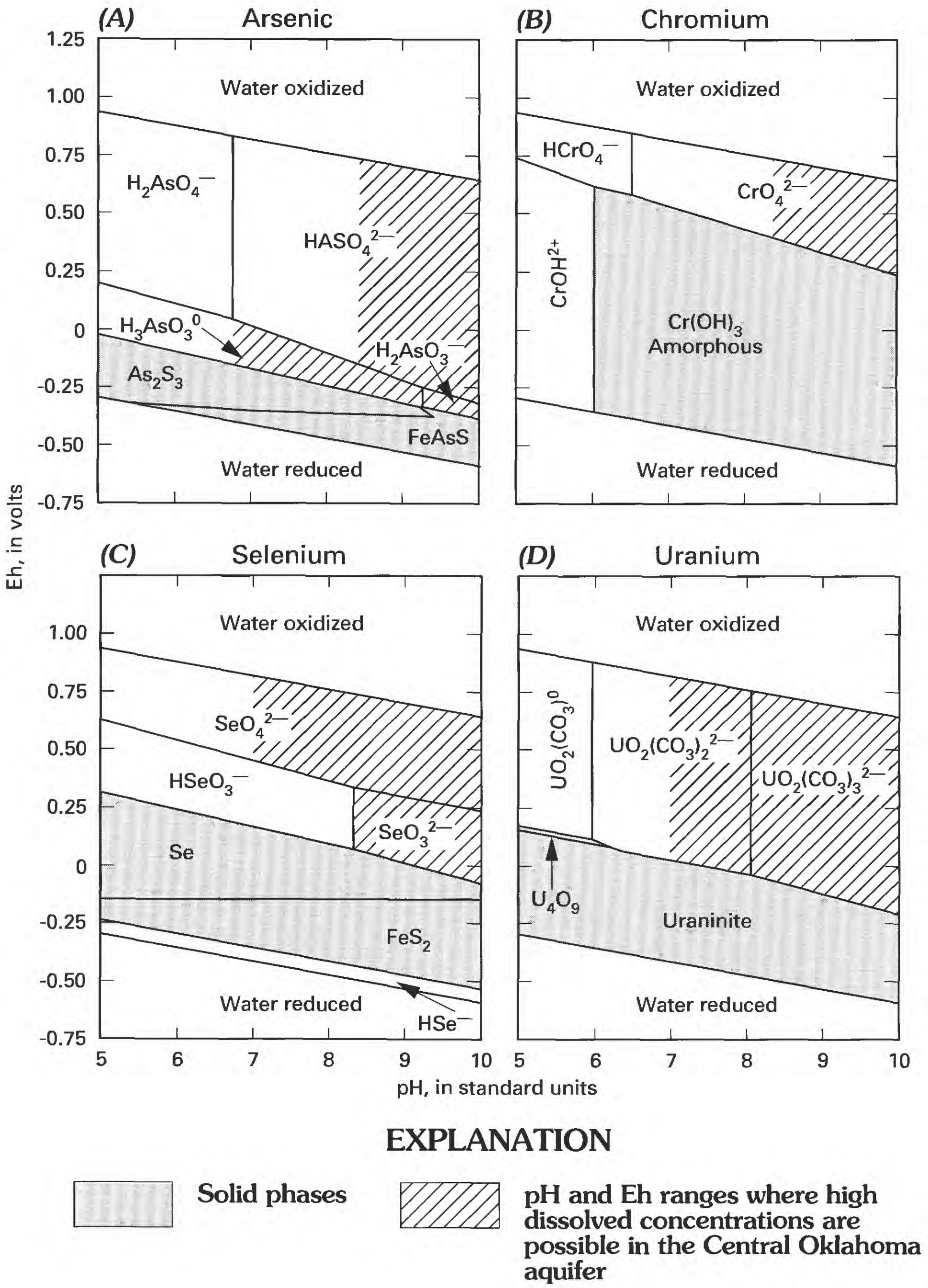


Figure 23. Fields of stability for solid and dissolved forms of arsenic, chromium, selenium and uranium as a function of Eh and pH at 25 degrees Celsius and 1 atmosphere pressure. (A), arsenic-sulfur-iron water system. Activity of dissolved arsenic = $10^{-6.17}$ *M* (molal) and iron = 10^{-6} *M* and sulfur = $10^{-3.3}$ *M*. (B), chromium water system. Activity of dissolved chromium = 10^{-6} *M*. (C), selenium-sulfur- iron water system. Activity of dissolved selenium = $10^{-6.2}$ *m*, iron and sulfur activity as in (A). (D), uranium-carbon-phosphorous water system. Dissolved uranium activity = 10^{-7} *M*, carbon = $10^{-2.2}$ *M*, phosphorous = $10^{-6.3}$ *M*. Sources of thermodynamic data used to construct diagrams: arsenic (Wagman and others, 1968; Barton and Skinner, 1979); chromium (Schmidt, 1984; Rai, Sass, and Moore, 1987); iron (Wagman and others 1968; Nordstrom and others, 1990); selenium (Wagman and others, 1968; Vaughn and Craig, 1978); and uranium (Langmuir, 1978).

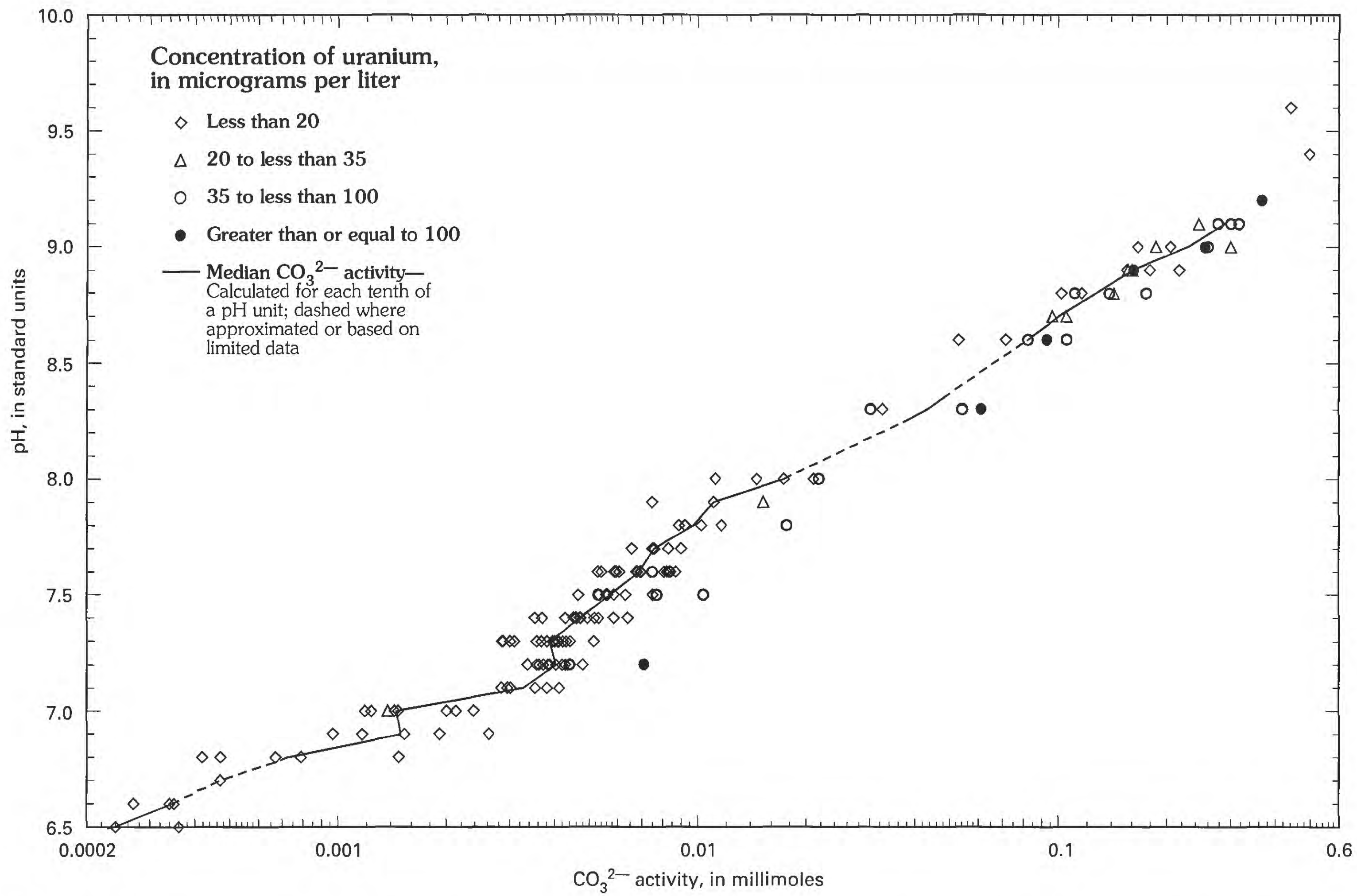


Figure 24. Relation of uranium concentrations to pH and carbonate-ion activity in the Central Oklahoma aquifer. Samples with the highest uranium concentrations tend to plot to the right of the median carbonate-ion activity.

left of the median carbonate-ion activity at pH 7.0 and 7.5. These samples are from deep wells, and it is suspected that the apparent low relative carbonate-ion activity results from borehole mixing of high uranium and high relative carbonate-ion activity water with water having low uranium concentration, relatively low pH, and low alkalinity. Water that plots to the right of the median alkalinity but does not contain high uranium concentrations may have recharged in a region where uranium was not available in the rock.

When uranium concentration is plotted with pH and alkalinity (fig. 25), it is apparent that high uranium concentrations are present in samples with alkalinity greater than the median alkalinity for a pH less than 8 except in the two deep wells where borehole mixing may have reduced the apparent alkalinity. Although the data in this plot scatter widely, the plot may be useful for determining the potential of a given water to exceed the 1991 proposed uranium standard. Alkalinity fluctuates as pH increases in the Central Oklahoma aquifer, so at a given pH an alkalinity of 300 mg/L may be high, medium, or low relative to other water with the same pH. If pH and alkalinity measured at the sampling site plot on or to the right of the median alkalinity curve, the water is likely to contain more dissolved uranium than other water (*p*-value = 0.0004, Mann-Whitney uranium test; P-STAT, 1989). This relation is consistent with laboratory studies of adsorption of UO_2^{2+} on iron oxides and iron oxyhydroxides in solutions with varying dissolved inorganic carbon concentration (Hsi and Langmuir, 1985). The percentage of uranium adsorbed at a given pH decreased with increasing carbon.

Water Age

The relation between δD, which indicates water age, and concentrations of dissolved arsenic, chromium, selenium, and uranium are shown in figure 26. Parkhurst, Christenson, and Breit (1993) determined that δD decreases with water age in the Central Oklahoma aquifer. Very old water (more than 20,000 years old) has low δD (less than -40 per mil) because it entered the aquifer when the Earth's atmosphere was colder as a result of the last ice age. Warming of the atmosphere since the last ice age resulted in the gradual increase in δD of recharge water from -40 to -34 per mil. Young water, with a δD of -34 to -27 per mil relative to standard mean ocean water, generally entered the aquifer less than 5,000 years ago.

Concentrations of arsenic, chromium, selenium, and uranium generally increase with water age. Dissolved arsenic concentration exceeds the 1986 standard only in water with a δD value less than -34 per mil, indicating it is in moderately old (more than 5,000 years) to very old water (more than 20,000 years). Chromium exceeds the 1986 standard in water with a δD value of less than -37 per mil, indicating it is only in old water. Some very old water contained no detectable chromium, indicating that not all old water is enriched with chromium, possibly because the water is not capable of mobilizing chromium because of low redox or pH or because soluble chromium was not present in the rock along the flowpath. Selenium and uranium are present at high concentrations in most very old water but also are present in some young water with a δD value as great as -31 per mil. This indicates that abundant selenium and uranium are dissolved soon after the water enters the ground, whereas arsenic and chromium require more time to reach high concentrations. Arsenic and chromium may require more time to reach high concentrations because (1) their sources have low concentrations and are disseminated through the aquifer, (2) the source requires more time to oxidize, or (3) the source is limited in accessibility to ground water as with arsenic and chromium in mudstones. The relation between old water and high arsenic, chromium, selenium, and uranium concentrations in wells near streams receiving regional discharge indicates that high concentrations of the elements at these locations are in water from regional flow rather than from local recharge.

Gross-Alpha Radioactivity

Gross-alpha radioactivity increases with uranium concentration in samples collected for this study ($r^2 = 0.95$, linear regression). Alpha radioactivity is emitted by many radioactive elements, but only a few occur naturally in ground water—polonium, radium, radon, thorium, and uranium (isotopes uranium-234, uranium-235, and uranium-238). Gross-alpha radioactivity is a measure of alpha radioactivity emitted by naturally occurring uranium, radium, thorium, and polonium but excludes radon. Radon is assumed to outgas or decay from the samples by the time the samples are analyzed.

Gross-alpha radioactivity is not regulated in drinking water. However, a 15-pCi/L drinking-water standard exists for residual-alpha radioactivity, which is the gross-alpha radioactivity minus the uranium alpha radioactivity (U.S. Environmental Protection Agency, 1986). A substantial number of historical analyses in

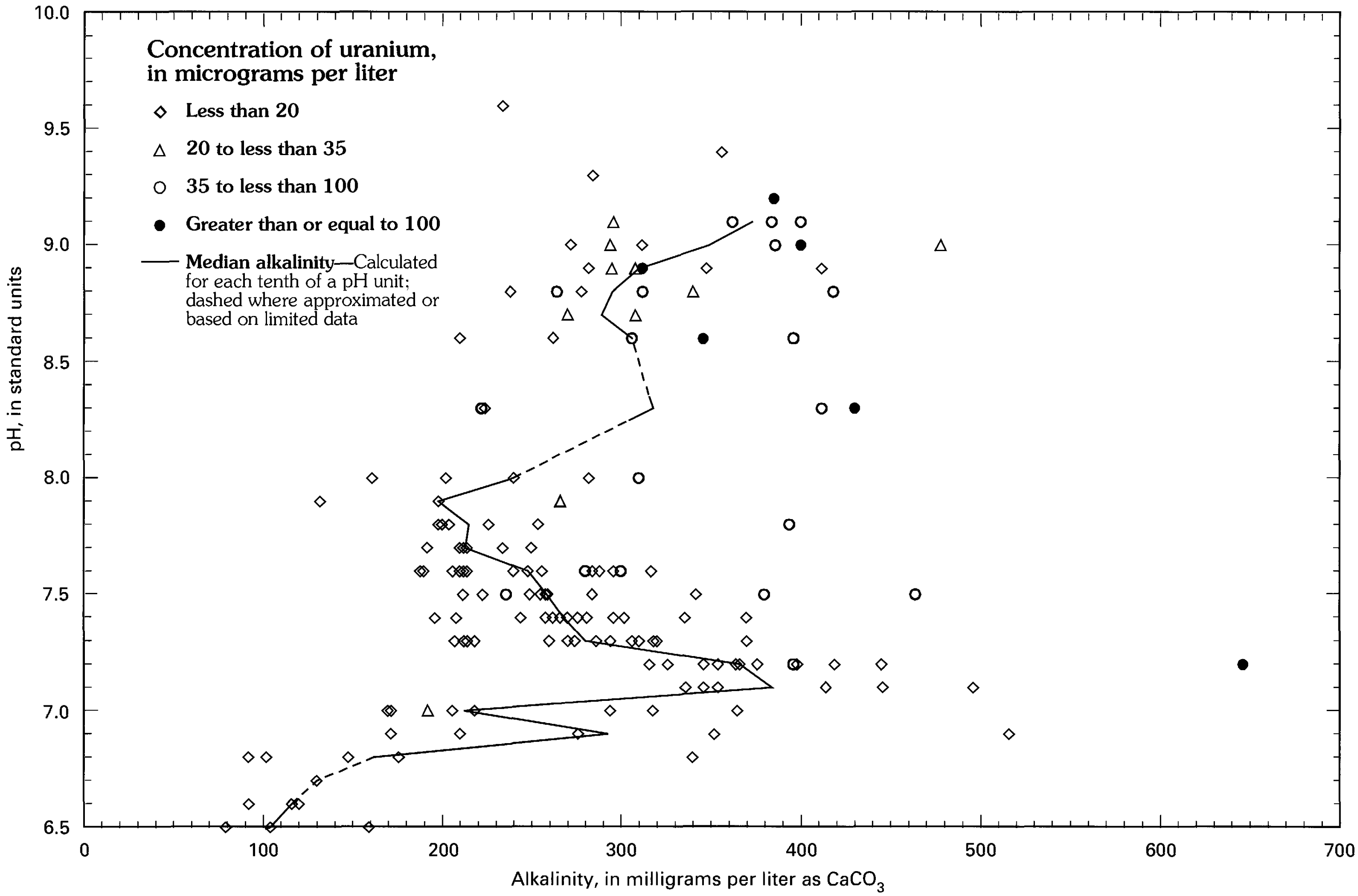


Figure 25. Relation of uranium concentrations to pH and alkalinity in the Central Oklahoma aquifer. Samples with the highest uranium concentrations tend to plot to the right of the median alkalinity.

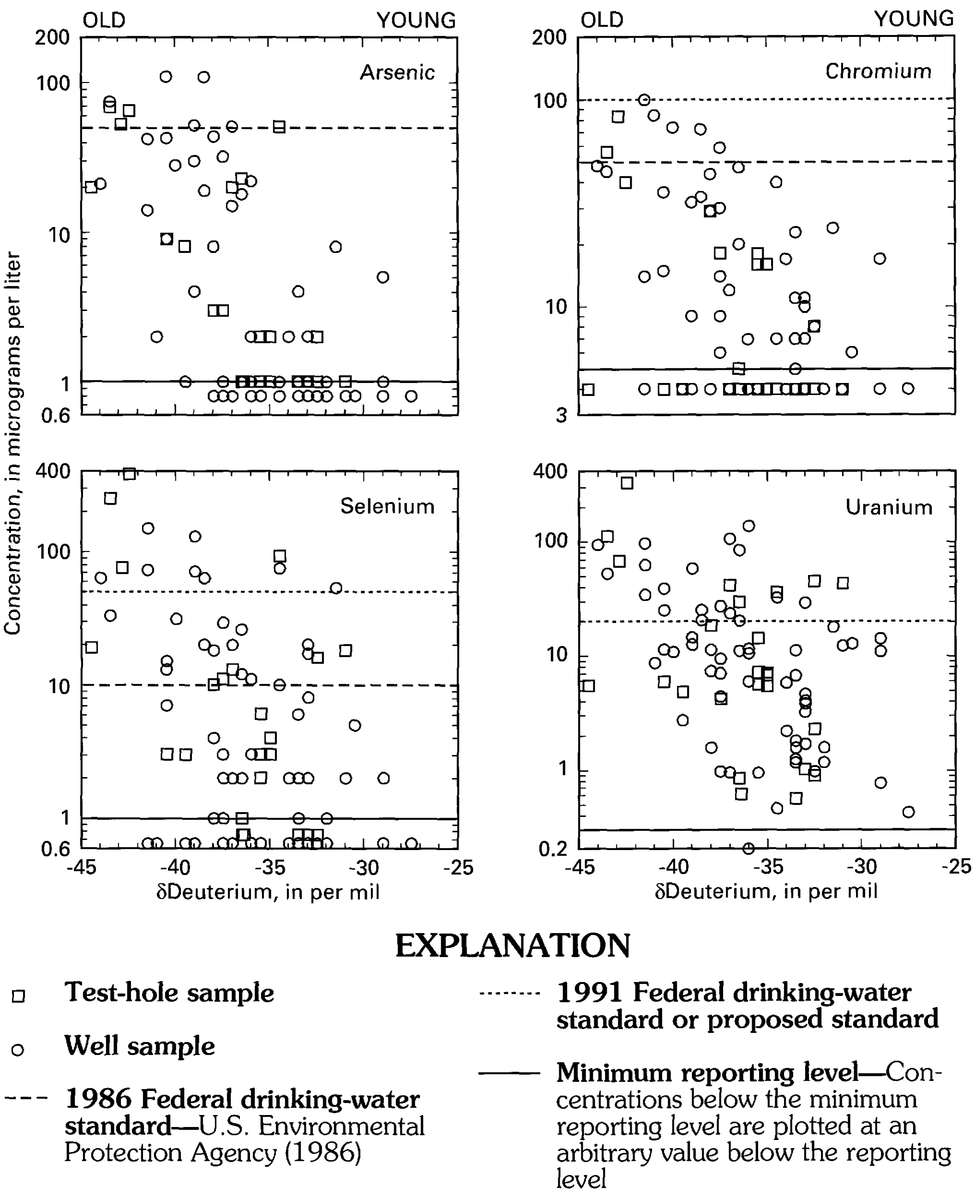


Figure 26. Relation of arsenic, chromium, selenium, and uranium concentrations to water age in the Central Oklahoma aquifer, as represented by δDeuterium per mil relative to Standard Mean Ocean Water.

the Central Oklahoma aquifer exceeded the 1986 residual-alpha standard (Parkhurst, Christenson, and Schlottmann, 1989).

Because residual-alpha radioactivity is a water-quality problem in the Central Oklahoma aquifer, this study investigated the source of the residual-alpha radioactivity. Radium-226, thorium-230, thorium-232, and polonium-210 alpha radioactivities were measured in samples from seven wells with previously measured residual-alpha radioactivity greater than 15 pCi/L. Alpha radioactivity for all of these isotopes totaled less than 2.5 pCi/L. All seven samples contained greater than 50 µg/L uranium. The lack of a source of the alpha radioactivity other than uranium and the strong correlation between gross-alpha radioactivity and dissolved uranium suggest that the residual-alpha radioactivity measured in samples collected for this study results from a systematic error in the gross-alpha measurement in samples with high uranium concentrations.

Vanadium and Boron

Most water in the Central Oklahoma aquifer that exceeds a 1986 drinking-water standard or 1991 proposed standard for arsenic, chromium, selenium, or uranium contains detectable vanadium and a high boron concentration. Known geochemical behavior of vanadium and boron in various water types and redox conditions can be used to determine why these elements are present in water with high arsenic, chromium, selenium, or uranium concentrations and is further evidence of the sources of and processes mobilizing the four elements.

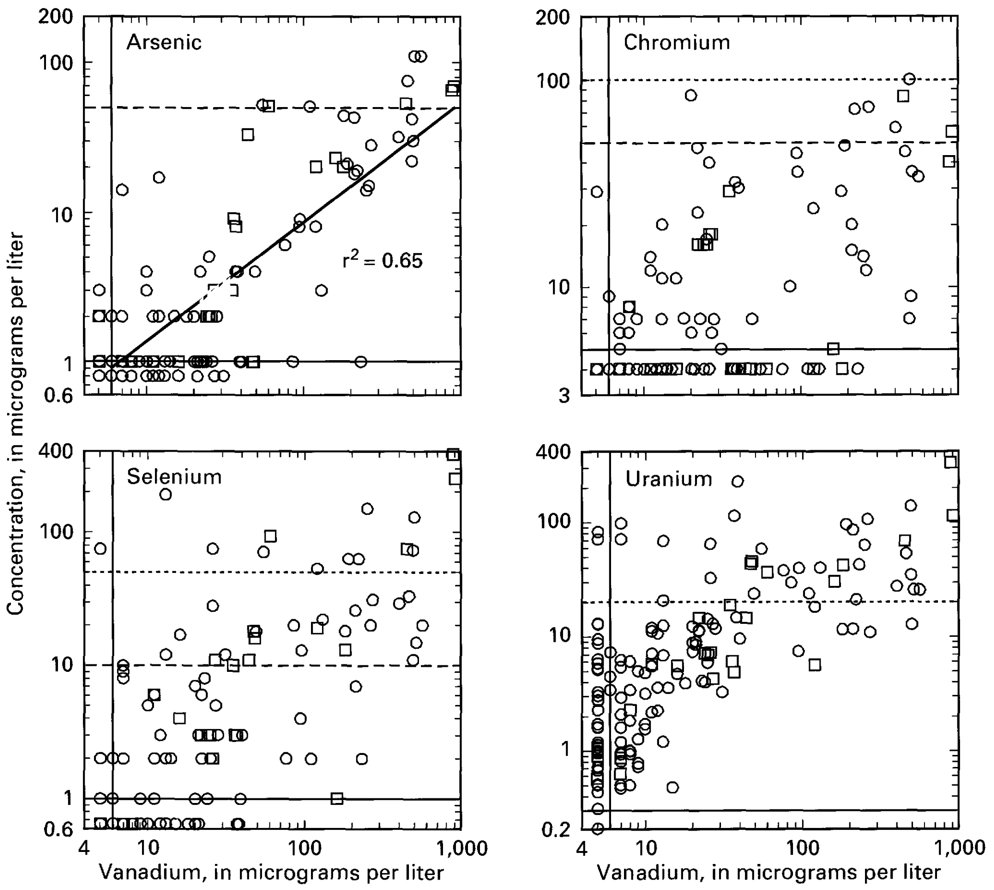
Vanadium concentration ranged from less than 6 to 910 µg/L, with a median value of 10 µg/L, in 172 samples from the 141 wells and 8 test holes sampled for this study. The geochemical behavior of vanadium is similar to that of arsenic. It is oxidized to mobile pentavalent vanadium [vanadium (V)] at an Eh slightly lower than that required to oxidize arsenic. Vanadium (V) is strongly adsorbed on iron oxides in the lower part of the pH range of the aquifer and desorbs at high pH. Arsenic concentration shows the strongest relation to vanadium (r^2=0.68, linear regression on log-transformed data) of the four elements because both arsenic and vanadium desorb from iron oxides at about the same pH in the aquifer (fig. 27). Uranium concentration increases with vanadium in most samples because they are from the same sources (reduced zones and iron-oxide surfaces) and because carbonate-ion activity increases with pH in bicarbonate type water. Vanadium is present only at low concentrations (less than 50 µg/L vanadium) in the low pH (less than 7.8) water that has high selenium or uranium concentrations.

Boron concentration ranged from 20 to 8,000 µg/L, with a median value of 225 µg/L, in 172 analyses from the wells and test holes sampled for this study. Arsenic, chromium, and selenium do not show strong relations to boron, although they generally increase with boron concentration and exceed the 1986 standards only in water with a high boron concentration (fig. 28). Arsenic exceeded 50 µg/L only in water with more than 1,000 µg/L boron, chromium in water with more than 400 µg/L boron, and selenium exceeded 10 µg/L only in water with 140 µg/L or more boron. Selenium only exceeded the 1991 selenium standard of 50 µg/L in water with more than 400 µg/L boron. Uranium showed a strong relation to boron (r^2=0.80, linear regression on log-transformed data). This relation is thought to be the result of interaction of fresh dilute water with clay in the aquifer. Boron adsorbs on clay from saline pore water and tends to desorb when the clay is subsequently exposed to low ionic strength water (Keren and O'Connor, 1982; Goldberg and Glaubig, 1985, 1986; Bloesch, Bell and Hughes, 1987), which happens when the base of freshwater gradually displaces underlying brine. As the aquifer is flushed, boron desorption tends to occur concurrently with the cation-exchange processes that increase alkalinity and enhance uranium mobility. Uranium exceeded the 1991 proposed standard of 20 µg/L only in water with a boron concentration greater than 400 µg/L. The relation between elevated boron concentrations and high concentrations of arsenic, chromium, selenium, and uranium further indicates that the source of the elements are in less-flushed clay-rich parts of the aquifer near the base of freshwater, just below the confining layer, and in the Chase-Admire.

Relations Among Arsenic, Chromium, Selenium, and Uranium

High concentrations of dissolved arsenic, chromium, selenium, and uranium commonly are present together in some regions of the Central Oklahoma aquifer. The combinations of elements that occur together appear to follow the order in which they are oxidized in increasingly oxidizing conditions: arsenic–uranium–selenium–chromium (table 13). In samples collected for this study, water that exceeded the 1986 standards for arsenic and chromium also exceeded the 1991 proposed uranium standard and the 1986 selenium standard (table 13). Water that exceeded selenium and arsenic standards, but not the chromium standard, exceeded the proposed uranium standard. Water that exceeded the proposed uranium standard and the chromium standard, but not the arsenic standard, exceeded the selenium standard. The interrelation of these elements provides clues to the source of the elements and the processes mobilizing them.

All samples that exceeded the 1986 standard for arsenic also exceeded the 1991 proposed standard for uranium (table 13). This is because arsenic and uranium are oxidized in similar redox conditions and because both are mobile in high-pH sodium bicarbonate type water. That they are present together in the water implies that sources of both elements are present in the rock the water has moved through, although rock investigations indicated that the highest concentrations of arsenic and uranium are present in different rock



EXPLANATION

□ **Test-hole sample**

○ **Well sample**

---- **1986 Federal drinking-water standard**—U.S. Environmental Protection Agency (1986)

········ **1991 Federal drinking-water standard or proposed standard**

—— **Minimum reporting level**—Concentrations below the minimum reporting level are plotted at an arbitrary value below the reporting level

—— **Arsenic-vanadium regression line**—r^2 value indicates the square of the correlation coefficient for the regression

Figure 27. Relation of arsenic, chromium, selenium, and uranium concentrations to vanadium concentrations in the Central Oklahoma aquifer.

types. Arsenic is in yellow-brown iron-oxide cemented rock, and uranium is in reduced zones.

Six of seven well or test-hole samples that exceeded the 1986 chromium standard also exceeded the 1986 selenium standard, and five exceeded the 1991 proposed uranium standard (table 13). Chromium, selenium, and uranium all are mobile in high-pH, oxic environments. In most regions where chromium is mobile, selenium and uranium are present and also are mobile. One sample exceeded only the chromium standard and only had low concentrations of arsenic (2 µg/L), selenium (less than 1 µg/L), and uranium (8.5 µg/L). This indicates that there may be regions where only chromium is available in the rock.

Most samples (86 percent) that exceeded the 1991 50-µg/L standard for selenium also exceeded the 1991 proposed standard for uranium. All but two samples that exceeded the 1986 selenium standard of 10 µg/L contained more than 3.8 µg/L uranium (the median uranium concentration for 141 wells sampled for this study), and more than 75 percent exceeded the 1991 proposed uranium standard. Selenium and uranium

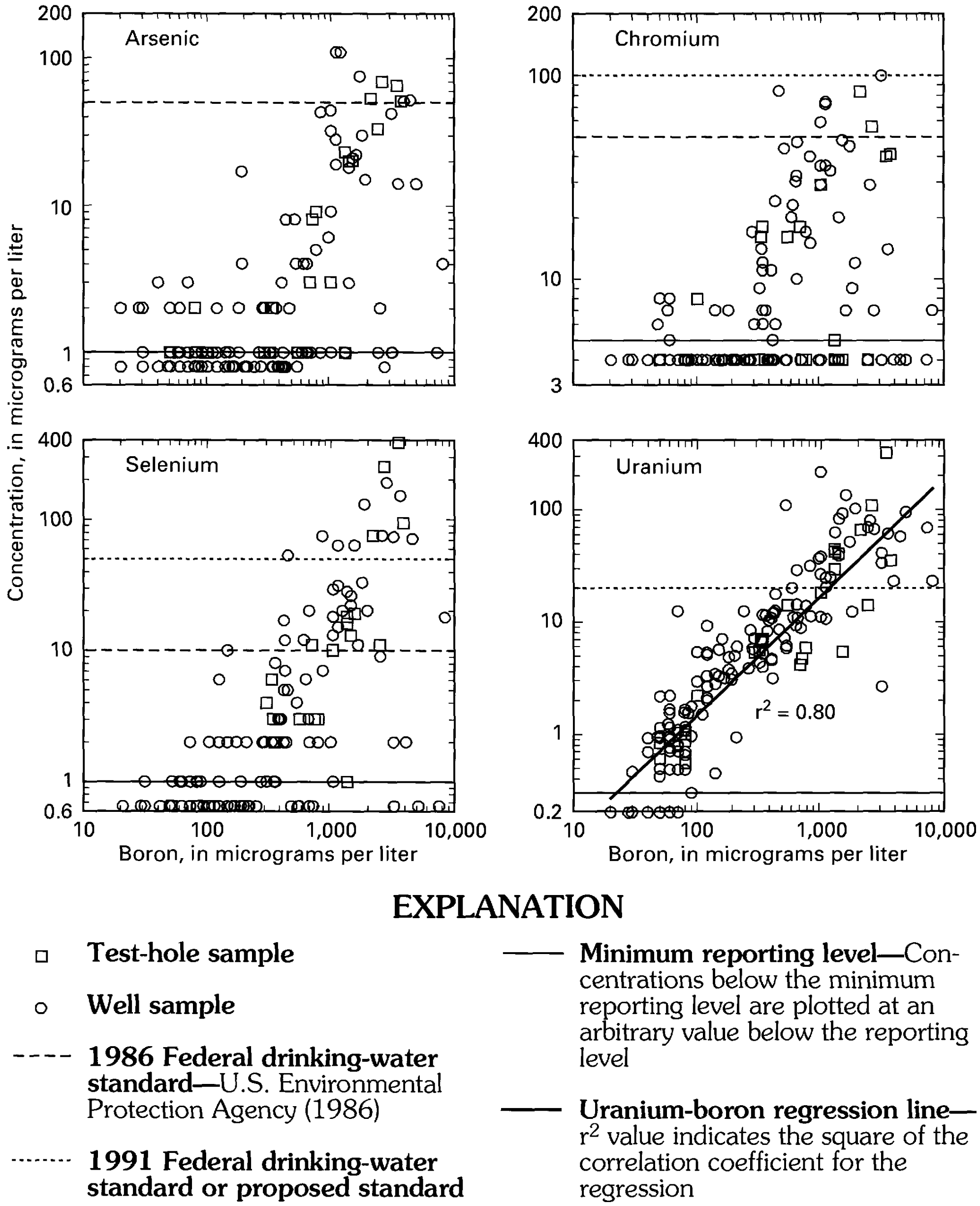


Figure 28. Relation of arsenic, chromium, selenium, and uranium concentrations to boron concentrations in the Central Oklahoma aquifer.

both are mobile more than a wide pH range, and mobilization of both is enhanced by increasing activity of carbonate ion. Additionally, both elements are found together in reduced zones, so both elements have sources in the same rock. Eight samples exceeded only the selenium standard, probably because of the low 1986 10-µg/L drinking-water standard for selenium relative to higher standards for the other elements. Selenium concentrations in these eight samples were less than 20 µg/L.

The reverse of the uranium association with arsenic, chromium, and selenium concentrations that exceed 1986 drinking-water standards is not true; samples that exceeded the 1991 proposed uranium standard generally did not contain high concentrations of arsenic, 86 percent did not exceed the chromium standard, and 24 percent did not exceed the selenium

Table 13. Summary table of samples collected for the present study of the Central Oklahoma aquifer that exceeded established or proposed drinking-water standards, sorted by geohydrologic zone

[Shaded areas indicate determinations that exceed established or proposed drinking-water standards; deg, degrees; min, minutes; sec, seconds; µg/L, micrograms per liter; As, arsenic; U, uranium; Se, selenium; Cr, chromium; <, indicates concentration is less than specified value; Geohydrologic zones: SUGW; shallow (less than 300 feet) unconfined Garber-Wellington; DUGW, deep (greater than 300 feet) unconfined Garber-Wellington; SCGW, shallow confined Garber-Wellington; DCGW, deep confined Garber-Wellington; SCA, shallow Chase-Admire; DCA, deep Chase-Admire. All samples analyzed by the National Water-Quality Laboratory of the U.S. Geological Survey unless otherwise noted]

Geohydrologic zone	Location		pH[1], standard units	Arsenic, (µg/L as As)	Uranium, (µg/L as U)	Selenium, (µg/L as Se)	Chromium, (µg/L as Cr)
	Latitude (deg min sec)	Longitude (deg min sec)					
			Well samples				
SUGW	35 39 47	97 11 15	7.6	1	20 ± 2.4	12	20
SUGW	35 18 17	97 15 52	7.5	<1	0.4 ± 0.1	10	7
SUGW	35 40 08	97 19 09	7.6	2	80 ± 9.3	75	29
SUGW	35 47 06	97 05 10	9.0	4	23 ± 2.6	18	7
SUGW	35 47 58	97 29 52	8.3	9	38 ± 4.2	13	37
SUGW	35 50 49	97 04 14	7.5	1	41 ± 4.5	2	<5
SCGW	35 30 42	97 31 38	7.2	1	62 ± 7.9	28	<5
SCGW	35 30 51	97 32 20	7.6	<1	67 ± 8.7	190	7
SCGW	35 31 31	97 32 54	7.8	1	69 ± 8.9	9	<5
DUGW	35 14 09	97 23 18	8.3	2	8.5 ± 1.4	<1	84
DUGW	35 17 29	97 22 13	9.0	28	11 ± 1.2	31	74
DUGW	35 25 50	97 05 54	7.0	1	31 ± 3.3	75	40
DUGW	35 25 19	97 22 25	7.8	8	18 ± 2.2	53	24
DCGW	35 07 56	97 23 20	8.7	51	23 ± 2.7	2	<5
DCGW	35 12 19	97 26 23	8.6	14	61 ± 7.1	150	14
DCGW	35 12 36	97 26 28	8.8	42	33 ± 3.7	73	100
DCGW	35 13 14	97 25 47	8.8	52	57 ± 7.5	71	<5
DCGW	35 14 14	97 29 39	8.6	14	94 ± 12	<1	<1
DCGW	35 16 27	97 28 51	9.0	44	11 ± 1.8	18	29
DCGW	35 19 26	97 29 40	8.9	19	20 ± 2.9	63	72
DCGW	35 20 43	97 28 20	9.0	32	27 ± 3.2	29	59
DCGW	35 25 15	97 37 08	9.1	110	25 ± 2.8	20	34
DCGW	35 25 50	97 05 54	7.0	<1	4.5 ± 0.6	17	11
DCGW	35 26 05	97 37 57	8.8	75	51 ± 6.9	33	45
DCGW	35 30 13	97 37 33	8.7	110	25 ± 3.4	15	36
DCGW	35 32 23	97 32 05	8.6	30	12 ± 1.3	130	9
DCGW	35 34 11	97 37 45	7.5	21	92 ± 9.2	63	48
SCA	35 00 03	97 00 33	8.3	4	110 ± 12	<1	<5
SCA	35 14 11	96 59 00	7.5	<1	3.1 ± 0.4	12	5
SCA	35 23 51	96 54 40	9.1	6	37 ± 4.1	2	<5
SCA	35 33 51	96 57 46	7.2	1	220 ± 25	1	<5
SCA	35 39 38	97 03 11	8.3	1	69 ± 7.7	<1	<5
SCA	35 41 43	96 56 43	8.0	3	39 ± 4.3	22	<5
DCA	35 46 33	97 03 08	9.1	18	82 ± 7.9	26	20
DCA	35 46 37	97 03 08	9.2	22	130 ± 14	11	7
DCA	35 46 54	97 03 08	9.0	15	100 ± 11	20	12
DCA	35 52 14	96 57 48	7.9	1	29 ± 2.8	20	10
			NOTS test-hole samples				
SUGW	35 40 12	97 23 10	8.9	23	29 ± 3.2	1	5
SUGW	35 51 18	97 25 00	8.8	53	66 ± 10	75	80
SUGW	35 51 18	97 25 00	8.9	69	110 ± 12	250	60
SUGW	35 42 08	97 33 02	8.0	3	18 ± 2.5	10	30
SUGW	35 42 08	97 33 02	8.0	3	4.1 ± .6	11	20
DUGW	35 42 08	97 33 02	8.6	65	320 ± 35	380	40
DCGW	35 13 15	97 25 43	9.6	33	14 ± 4.1	11	<5
DCGW	35 13 15	97 25 42	9.1	51	35 ± 4.6	93	<5
DCGW	35 13 15	97 25 42	9.3	20	5.4 ± 1.1	19	<5
SCA	35 11 42	96 58 01	7.5	1	44 ± 4.8	16	<5
SCA	35 11 42	96 58 01	7.5	1	42 ± 4.6	18	<5
SCA	35 44 18	97 01 35	9.0	20	40 ± 4.6	13	<5

[1] Determined at sample site.

standard. In some regions the pH is too low to mobilize arsenic and chromium, and redox conditions are not adequate to oxidize chromium and selenium to mobile chromium (VI) and selenium (VI)

CONSIDERATIONS FOR GROUND-WATER DEVELOPMENT

In addition to information about the distribution of dissolved arsenic, chromium, selenium, and uranium in the Central Oklahoma aquifer, several important water and rock characteristics related to the occurrence of high arsenic, chromium, selenium, and uranium concentrations were determined in this study. This information can be used to improve the prospects of completing wells that yield acceptable drinking water.

Results of this study indicate that high concentrations of dissolved arsenic, chromium, selenium, and uranium are present in specific regions of the Central Oklahoma aquifer (figs. 8 through 13, 15 and 16 and table 10). These elements do not tend to be present in regions of the aquifer below recharge areas or in the shallow unconfined zones of the sand-rich part of the aquifer. They do tend to be found in "old" water near the base of the aquifer, in the distal parts of long flowpaths below the confining layer, and in regions of the shallow zones within 2 mi of streams that receive discharge from below the confining layer. High concentrations of selenium and uranium also tend to be present in shallow, clay-rich parts in the Chase-Admire, just below the base of the confining layer, and north of Deep Fork.

When developing water resources where high concentrations of the toxic elements are known to be present or data are sparse, careful investigation and additional testing will be needed prior to well installation to avoid completion of wells that yield water that exceeds a drinking-water standard. The first step in such an investigation would be to review any available well-completion data, geophysical logs, or water-quality data for wells nearest the proposed well sites. A comparison of mudstone distribution in nearby wells, based on geophysical logs, to water quality for wells with various completion depths may indicate sandstone intervals in the area that are likely to yield water with high concentrations of arsenic, chromium, selenium, or uranium.

Because few data are available for several regions in the Central Oklahoma aquifer, additional testing in these regions is needed before developing a water supply. These regions dominantly are in the north- and south-central parts of the study unit and between clusters of data presented on the maps in figures 8 through 13, 15 and 16. Test holes or test wells could be installed prior to locating a well field in such a region in order to determine which sandstone layers yield water with high concentrations of arsenic, chromium, selenium, or uranium.

Test-hole results showed that concentrations of dissolved arsenic, chromium, selenium, and uranium vary between sandstone layers. This variation results from differences in the water and rock chemistry. In sandstone layers, where the water has a chemical composition that favors dissolution of the elements and the rock contains the elements in a form available for solution, the occurrence of high concentrations of the elements is likely. Where the water does not have high pH, dissolved oxygen, or a high relative carbonate-ion activity (all of which tend to mobilize the elements), dissolved arsenic, chromium, selenium, and uranium will not be present at high concentrations. Likewise, where the rocks do not contain the elements in a form available for mobilization, the elements will not be present even if the water has the necessary characteristics to favor transfer from rock to water.

Observation of cuttings during the drilling process is not likely to be a good indicator of the probability of a well yielding water with high arsenic, chromium, selenium, or uranium concentrations. Rocks, such as yellow-brown sandstones, greenish-gray reduced zones in sandstones, and interbedded mudstones, that are known to be associated with high concentrations of the elements do not always contain high concentrations. Water samples collected from isolated sandstone layers before well completion are a better indication of whether the elements are in the water.

In regions where high concentrations of dissolved arsenic, chromium, selenium, and uranium are known to be present, sampling of water from individual sandstone layers prior to well completion also will identify intervals that yield water that is not of adequate drinking-water quality. Onsite analysis of pH, alkalinity, dissolved oxygen, and sodium with well-calibrated meters can help identify sand layers that may yield water with high arsenic, chromium, selenium, or uranium concentrations; this information is useful for isolating sandstone layers from production zones in the well that yield water with low concentrations of the elements. However, onsite analyses cannot be used as a substitute for laboratory analyses of arsenic, chromium, selenium, and uranium. Without laboratory analyses, sandstone layers that contain water with little arsenic, chromium, selenium, and uranium but with high pH, high dissolved-oxygen concentration, and high relative alkalinity could be excluded inadvertently.

SUMMARY

Concentrations of dissolved arsenic, chromium, selenium, and uranium in confined and deep zones of the Central Oklahoma aquifer commonly exceed the 1986 Federal drinking-water standards of 50 µg/L arsenic, 50 µg/L chromium, 10 µg/L selenium, and the 1991 proposed standard of 20 µg/L uranium. Dissolved selenium and uranium concentrations commonly exceed 10 µg/L and 20 µg/L in unconfined zones of the aquifer. The distribution of the four elements in water and rock in the aquifer, the water and rock characteristics associated with high dissolved concentrations of the elements, and the processes that transfer the elements from the rock into the water were investigated. Historical water analyses, analyses of water samples collected from 141 wells and from varying depth intervals in 8 test holes along with rock core from the 8 test holes were used.

The high concentrations of dissolved arsenic, chromium, selenium, and uranium were found to be a function of: (1) the distribution of the elements in the solid phases, (2) the redox conditions, (3) the distribution of mudstone, and (4) changes in water chemistry as the water flows through the aquifer, primarily increases in pH and carbonate-ion activity.

Permian geologic units in the Central Oklahoma aquifer include the Garber Sandstone, the Wellington Formation, and undivided rocks of the Chase, Council Grove, and Admire Groups. The western one-third of the aquifer is confined by the Permian Hennessey Group. The aquifer is composed primarily of sandstone, lenticularly interbedded with mudstone. Authigenic minerals that affect water chemistry include hematite, goethite, gypsum, dolomite, and illite-smectite.

A flow model developed for the aquifer as part of an earlier investigation indicates that precipitation recharges the Central Oklahoma aquifer. Discharge is mainly into nearby streams within years to thousands of years. A small percentage of the recharge flows west into the confined part of the aquifer. The ground water then flows along long regional flowpaths to the north and south under the confining layer and discharges into streams.

Dominant water types in the Central Oklahoma aquifer vary from calcium magnesium bicarbonate with pH 6.0 to 7.8 to sodium bicarbonate with pH 8.3 to 9.6. Calcium magnesium bicarbonate water types are most common in shallow (less than 300 ft) and sand-rich parts of the aquifer, and sodium bicarbonate type water is in deep and confined zones of the aquifer. Dissolved chloride concentration is generally high near the base of freshwater and in clay-rich regions in the eastern part of the study unit. High sulfate is present near the base of the confining layer, near the base of freshwater, and where gypsum is dissolving in the southeastern part of the study unit. The Central Oklahoma aquifer can be divided into six geohydrologic zones related to major element chemistry on the basis of depth, geology, and confined or unconfined conditions including: the shallow unconfined Garber-Wellington, the deep (greater than or equal to 300 ft deep) unconfined Garber-Wellington, the shallow confined Garber-Wellington, the deep confined Garber-Wellington, the shallow Chase-Admire, and the deep Chase-Admire.

Fewer than 4 percent of the wells sampled for this study yielded water that exceeded the 1986 arsenic or chromium standards. The 1986 selenium standard was exceeded in 19 percent, and the 1991 proposed uranium standard was exceeded in 21 percent. When concentrations of all four elements are considered, water from 26 percent of the wells in this study exceeded at least one standard or proposed standard.

High dissolved concentrations of arsenic, chromium, selenium, and uranium are in specific regions of the Central Oklahoma aquifer. Dissolved arsenic and chromium concentrations typically are low in the shallow zones of the aquifer, whereas the 1986 selenium standard and the 1991 proposed uranium standard commonly are exceeded in shallow zones of the aquifer. The few shallow wells that yield water with arsenic or chromium concentrations that exceed the respective 1986 standards are completed in regions of the Garber Sandstone or the Wellington Formation that have water with high pH. The selenium standard and the proposed uranium standard are exceeded in shallow wells in regions where a decrease in freshwater flushing resulting from abundant mudstone interbeds has slowed the removal of soluble forms of these elements. Shallow wells in the unconfined part of the aquifer that yield water that exceeds the arsenic, chromium, or selenium standards are close to major streams where long regional flowpaths discharge. The high concentrations of arsenic, chromium, selenium, and uranium developed along the long flowpaths. High concentrations of uranium also are found in water from some shallow wells located on or near potentiometric highs where most ground water has only recently entered the aquifer (fig. 15), which indicates that high uranium concentrations can develop along short flowpaths.

High concentrations of all four of the elements are common in the deep confined Garber-Wellington geohydrologic zone; high chromium, selenium, and uranium concentrations are common in the deep unconfined Garber-Wellington; and only selenium and uranium are present at high concentrations in the deep Chase-Admire. The 1986 arsenic standard is exceeded by water in the Garber Sandstone in some sandstone layers near the base of the confining layer in the westernmost part of the aquifer and locally near the base of freshwater in the unconfined part of the Garber Sandstone. These are regions where sodium bicarbonate water with pH greater than 8.5 are common. Chromium concentrations are high near the base of freshwater at some locations and in both confined and unconfined zones of the deep Garber-Wellington where both high pH and oxic conditions are available. Selenium concentrations that exceed the 1986 10-µg/L standard are common in all deep geohydrologic zones. Selenium concentrations exceed 50 µg/L at depth and near the base of freshwater in the Garber-Wellington but not in the deep Chase-Admire. Uranium concentrations also exceed the 1991 proposed 20-µg/L standard near the base of freshwater. Ground water with uranium concentrations that exceed 20 µg/L is common in all deep geohydrologic zones but is located only in western, northern, and eastern regions of the aquifer where mudstone abundance increases.

Dissolved concentrations of the elements generally increase with depth in the unconfined part of the Central Oklahoma aquifer. The highest concentrations were detected in test-hole samples that were collected near the base of freshwater. In contrast, in the confined part of the aquifer, high concentrations are near the top of the aquifer. However, the distribution is heterogeneous, some high dissolved concentrations of arsenic, selenium, and uranium were collected from a sandstone layer between layers that yielded water with lower concentrations of the elements. Thus, an individual sandstone layer can yield water that exceeds drinking-water standards.

Regions of the aquifer with high arsenic, chromium, selenium, or uranium concentrations in ground water also have high concentrations of these elements in nearby rock. Results of sequential extraction experiments on rock samples indicate that water characteristics necessary to mobilize the elements are oxidizing capacity, high pH, and high chloride or carbonate-ion concentrations.

The abundance of clay-rich mudstone exerts a key effect on the mobilization of these elements in the Central Oklahoma aquifer because it affects cation-exchange ability, permeability, and redox conditions. Cation-exchange reactions between water and clay minerals increase dissolved sodium and decrease dissolved calcium and magnesium concentrations. This causes dolomite to dissolve, which raises pH and alkalinity. The increased pH and carbonate-ion activity enhance mobility of oxidized arsenic, chromium, selenium, and uranium. Increased interbedding of mudstone near the base of the confining layer, near the base of the aquifer, and in the Chase, Council Grove, and Admire Groups results in low transmissivity in those regions so that they tend to be poorly flushed by freshwater. Regions of the aquifer poorly flushed by freshwater have higher concentrations of dissolved and solid-phase arsenic, chromium, selenium, and uranium than do well-flushed regions. Sodium also remains in mixed-layer clays for cation exchange because it has not yet been removed by abundant flushing.

Recharge to most of the Central Oklahoma aquifer is through sandy soils that do not deplete dissolved oxygen. This results in oxic conditions in most of the aquifer in which arsenic, chromium, selenium, and uranium are stable in their greatest valence state and should be soluble. Recharge through poorly drained clay-rich soils, where abundant mudstone crops out, results in depletion of oxygen in recharge at those locations such as in the Chase, Council Grove, and Admire Groups and below the confining layer. The resulting lower redox potential apparently decreases the mobility of chromium and selenium in those locations.

In shallow zones of the aquifer where abundant mudstone crops out, cation exchange coupled with dolomite and carbon dioxide gas dissolution in the clay-rich vadose zone results in sodium calcium magnesium bicarbonate type shallow ground water with pH near neutral and a high relative carbonate-ion activity. Deep in the aquifer, away from available soil carbon dioxide gas, cation exchange coupled with dolomite dissolution results in sodium bicarbonate type water with a pH as high as 9.6 and slightly increased alkalinity. High pH enhances desorption of oxidized arsenic, chromium, selenium, and uranium from iron-oxide surfaces, and increased alkalinity enhances uranium solubility. These effects are apparent in the association of high concentrations of dissolved arsenic, chromium, selenium, and uranium with sodium water types, high pH, and relatively high carbonate-ion activity.

High concentrations of dissolved arsenic, chromium, selenium, and uranium commonly occur together in the same water, partly because their release from rocks is controlled by oxidation. The order of increasing redox potential required to oxidize each element (arsenic–uranium–selenium–chromium) indicates the order in which the elements occur together, with adjacent elements present together at high concentrations and combinations ranging from all four elements to a single element present at high concentrations. However, all samples that exceeded the 1986 arsenic standard also exceeded the 1991 proposed uranium standard.

High dissolved boron and vanadium concentrations are associated with high concentrations of arsenic, chromium, selenium, and particularly uranium. The boron is thought to be desorbing from clay surfaces as they are exposed to fresh ground water. The relation between boron and arsenic, chromium, selenium, and uranium further indicates that the element sources are in less flushed clay-rich parts of the aquifer. Vanadium concentration increases with arsenic concentration because the geochemistry of the elements is similar.

In the regions of the Central Oklahoma aquifer where high concentrations of dissolved arsenic, chromium, selenium, and uranium are common, abundance of the dissolved elements varies with depth and between sandstone layers. When exploring for a drinking-water supply in these regions, sampling of water from packer-isolated sandstone layers in test holes prior to well completion may provide locations of sandstone layers that yield water with high concentrations of the elements. These layers could then be isolated from those that yield water with low concentrations in the completed well, reducing the probability that the well will yield water that exceeds a drinking-water standard. Observations of test-hole drill cuttings and onsite measurement of sodium concentration, pH, and alkalinity may provide a quick onsite prediction of which sand layers are likely to yield water that will exceed a drinking-water standard.

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