

Vertical Gradients in Water Chemistry in the Central High Plains Aquifer, Southwestern Kansas and Oklahoma Panhandle, 1999

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (<http://water.usgs.gov/nawqa/nawqamap.html>). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings. (<http://water.usgs.gov/nawqa/natsyn.html>).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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ABBREVIATIONS USED IN THIS REPORT

ft ³ /s	cubic feet per second
DOC	dissolved organic carbon
MCL	maximum contaminant level
mg/L	milligrams per liter
mg/L as N	milligrams per liter as nitrogen
mg/L as P	milligrams per liter as phosphorus
mi ²	square miles
mL	milliliters
mm	millimeters
NAWQA	National Water-Quality Assessment
TU	tritium units
USGS	U.S. Geological Survey
USEPA	U.S. Environmental Protection Agency
µg/L	micrograms per liter
µm	micrometers

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.

Vertical Gradients in Water Chemistry in the Central High Plains Aquifer, Southwestern Kansas and Oklahoma Panhandle, 1999

By P.B. McMahon

Abstract

The central High Plains aquifer is the primary source of water for domestic, industrial, and irrigation uses in parts of Colorado, Kansas, New Mexico, Oklahoma, and Texas. Water-level declines of more than 100 feet in some areas of the aquifer have increased the demand for water deeper in the aquifer. The maximum saturated thickness of the aquifer ranged from 500 to 600 feet in 1999. As the demand for deeper water increases, it becomes increasingly important for resource managers to understand how the quality of water in the aquifer changes with depth. In 1998–99, 18 monitoring wells at nine sites in southwestern Kansas and the Oklahoma Panhandle were completed at various depths in the central High Plains aquifer, and one monitoring well was completed in sediments of Permian age underlying the aquifer. Water samples were collected once from each well in 1999 to measure vertical gradients in water chemistry in the aquifer.

Tritium concentrations measured in ground water indicate that water samples collected in the upper 30 feet of the aquifer were generally recharged within the last 50 years, whereas all of the water samples collected at depths more than 30 feet below the water table were recharged more than 50 years ago. Dissolved oxygen was present throughout the aquifer, with concentrations ranging from 1.7 to 8.4 mg/L.

Water in the central High Plains aquifer was predominantly a calcium-bicarbonate type that

exhibited little variability in concentrations of dissolved solids with depth (290 to 642 mg/L). Exceptions occurred in some areas where there had been upward movement of mineralized water from underlying sediments of Permian age and areas where there had been downward movement of mineralized Arkansas River water to the aquifer. Calcium-sulfate and sodium-chloride waters dominated and concentrations of dissolved solids were elevated (862 to 4,030 mg/L) near the base of the aquifer in the areas of upward leakage. Dissolution of gypsum or anhydrite and halite in sediments of Permian age by ground water was the likely source of calcium, sulfate, sodium, and chloride in those waters. Calcium-sodium-sulfate waters dominated, and concentrations of dissolved solids were as large as 4,916 mg/L near the water table in the area of downward leakage. Dissolution of minerals in sedimentary deposits of marine origin in upstream areas of the Arkansas River drainage were the likely sources of calcium, sodium, and sulfate in those waters.

Nitrate was detected throughout the aquifer and the background concentration was estimated to be 2.45 mg/L as N. The largest nitrate concentrations (8.28, 22, and 54.4 mg/L as N) occurred in recently recharged water collected adjacent to irrigated fields. Three pesticides (atrazine, metolachlor, simazine) and five pesticide degradation products (alachlor ethanesulfonic acid, alachlor oxanilic acid, deethylatrazine, metolachlor ethanesulfonic acid, metolachlor oxanilic acid) were detected in recently recharged water from six water-table wells. Five of the six wells were

adjacent to irrigated fields. These data indicate that concentrations of nitrate and pesticides increased over time in some areas of the aquifer as a result of agricultural activities.

Results from this study indicate that vertical gradients in water chemistry existed in the central High Plains aquifer. The chemical gradients resulted from chemical inputs to the aquifer from underlying sediments of Permian age, from the Arkansas River, and from agricultural activities. In areas where those chemical inputs occurred, water quality in the aquifer was impaired and may not have been suitable for some intended uses.

INTRODUCTION

Knowledge of the quality of the Nation's water resources is important because of the implications to human and aquatic health and because of the significant costs associated with decisions involving land and water management, conservation, and remediation. In 1991, the U.S. Geological Survey began full implementation of the National Water Quality Assessment (NAWQA) Program. The long-term goals of the NAWQA Program are to describe the status and trends in the quality of the Nation's surface- and ground-water resources and determine the natural and anthropogenic factors affecting the water quality (Gilliom and others, 1995).

The High Plains Regional Ground Water study began in June 1998 and represents a modification of the traditional NAWQA design in that the ground-water resource is the primary focus of this investigation. The High Plains aquifer is a nationally important water resource that underlies about 174,000 mi² in parts of eight States (fig. 1). About 20 percent of agricultural land in the United States is in the High Plains, and about 30 percent of all the ground water used for irrigation in the United States is pumped from this aquifer (Weeks and others, 1988). Due to the large areal extent of the High Plains aquifer, three geographic regions have been delineated for logistical purposes (fig. 1): northern High Plains (96,500 mi²); central High Plains (48,500 mi²); and southern High Plains (29,000 mi²).

The central High Plains aquifer is the focus of this investigation. The aquifer is the primary source of water used for domestic, industrial, and irrigation

purposes in parts of Colorado, Kansas, New Mexico, Oklahoma, and Texas. Water-level declines of more than 100 feet in some areas of the aquifer have increased the demand for water deeper in the aquifer. The maximum saturated thickness of the aquifer ranged from 500 to 600 feet in 1999. As the demand for water increases, it becomes increasingly important for resource managers to understand how the quality of water in the aquifer changes with depth. In previous studies, domestic, irrigation, and monitoring wells were sampled with the purpose of providing a broad areal assessment of water quality in the aquifer (Gutentag and others, 1981, 1984) or understanding specific water-quality problems like the intrusion of mineralized surface water into the aquifer (Whittemore, 1984). No studies had been designed specifically to document vertical changes in water chemistry in the aquifer. It is likely that vertical gradients in water chemistry exist in the central High Plains aquifer because of upward leakage of poor-quality water from underlying geologic units (Krothe and Oliver, 1982; Whittemore, 1984), infiltration of poor-quality surface water (Whittemore, 1984), and land-surface activities (McMahon, 2000).

Purpose and Scope

The purpose of this report is to describe vertical gradients in water chemistry in the central High Plains aquifer in southwestern Kansas and the Oklahoma Panhandle. In 1998–99, 18 monitoring wells at nine sites in southwestern Kansas and the Oklahoma Panhandle were completed in the aquifer and 1 monitoring well was completed in sediments of Permian age underlying the aquifer (fig. 2). The wells had single screens that were placed at various depths below the water table. In 1999, water samples were collected once from each well and analyzed for major ions, nutrients, trace elements, dissolved organic carbon (DOC), pesticides, and tritium. A water sample was collected from the Cimarron River and analyzed for major ions, trace elements, nutrients, and tritium during the same year.

Acknowledgments

The cooperation of landowners who agreed to the installation of monitoring wells on their property is

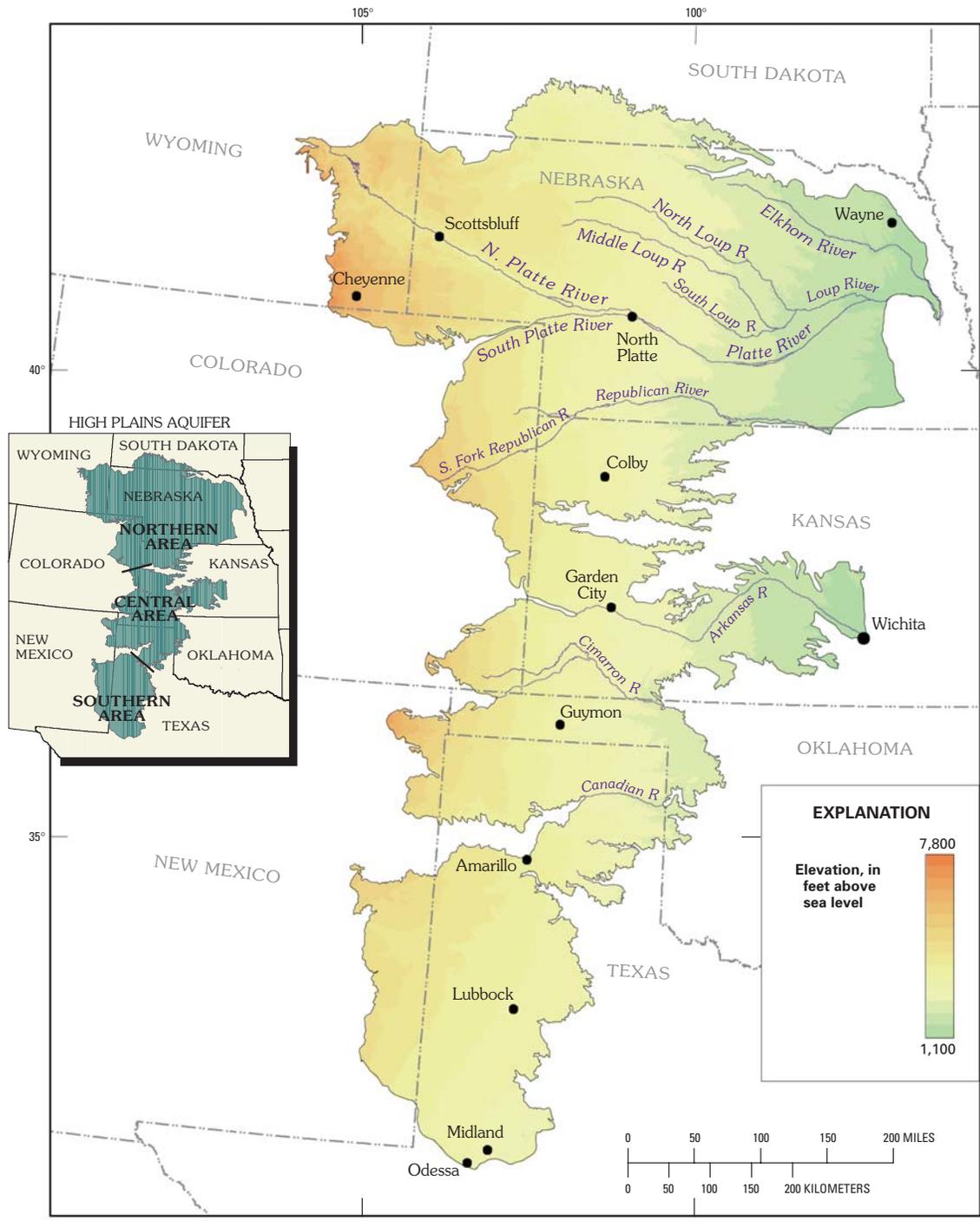


Figure 1. Land-surface elevations and locations of the southern, central, and northern parts of the High Plains aquife

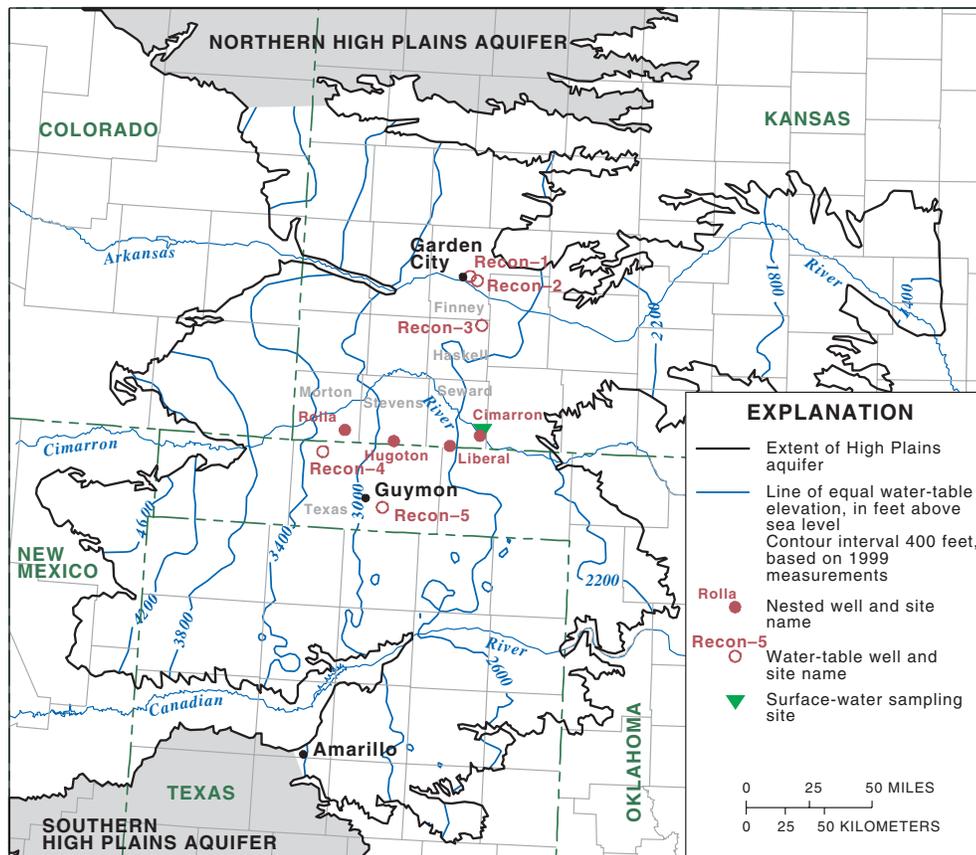


Figure 2. Ground-water elevations in the central High Plains aquifer and locations of monitoring wells. Elevations are based on 1999 measurements (V.L. McGuire, U.S. Geological Survey, written commun., 2000).

gratefully acknowledged. David Young, Kansas Geological Survey, provided the geophysical log of the Liberal borehole. Roy Glass (U.S. Geological Survey), Allen Macfarlane (Kansas Geological Survey), and Margaret Townsend (Kansas Geological Survey) provided technical reviews of the manuscript.

DESCRIPTION OF STUDY AREA

The study area includes parts of Finney, Haskell, Morton, Seward, and Stevens Counties in southwestern Kansas and Texas County in the Oklahoma Panhandle (fig. 2). The area is characterized by flat to rolling terrain, except in the Cimarron River valley in Seward County where the land-surface elevation drops 200 feet or more from the upland to the river. The study area is semiarid, receiving on average about 16 to 20 inches of precipitation annually (Weeks and

others, 1988). Natural vegetation is sparse and consists mostly of grasses. More detailed descriptions of the study area can be found in Smith (1940), Gutentag and others (1981, 1984), and Weeks and others (1988).

Geohydrologic Setting

The central High Plains aquifer consists of sediments of varying ages and compositions. The Ogallala Formation of Pliocene age is the largest geologic unit in the central High Plains aquifer (Smith, 1940; Gutentag and others, 1984). It consists primarily of unconsolidated clay, silt, sand, and gravel with scattered cemented zones consisting of calcium carbonate. The carbonate-cemented zones typically occur near the top of the formation. The sediments largely were deposited in a braided-stream environment. The thickness of the Ogallala Formation in the study area ranges

from 0 to about 500 feet. Younger sedimentary deposits that comprise a lesser proportion of the aquifer in the six-county study area include alluvial and windblown deposits of Pleistocene and Holocene age (Smith, 1940; Gutentag and others, 1981, 1984). The contact between the Ogallala Formation and younger deposits has not been mapped throughout the study area, and mapping that contact was beyond the scope of this project. A generalized section of the geologic units in southwestern Kansas and their relation to the central High Plains aquifer is shown in table 1.

The central High Plains aquifer in the study area is underlain by rocks ranging in age from Permian to Late Cretaceous (fig. 3). The Permian rocks consist of interbedded red shale, siltstone, sandstone, limestone, dolomite, gypsum, anhydrite, and halite (Gutentag and others, 1984). Dissolution of halite and gypsum/anhydrite in rocks of Permian age by ground water and subsequent discharge of this mineralized water to the aquifer is known to occur in Seward County (Gutentag and others, 1981; Whittemore, 1984).

The Arkansas and Cimarron Rivers (fig. 2) are the two principal drainages in the study area. Both rivers flow from west to east. Flow in the Arkansas River was intermittent before the late 1990's because of the large quantities of water directly diverted from the river and pumped from its alluvial aquifer for irrigation in Colorado and Kansas. Since the late 1990's, a reduction in pumping from the alluvial aquifer in Colorado has resulted in increased flow in the river in Kansas during the irrigation season, although flow in the river at Garden City during 2000 still was intermittent. The Arkansas River is a losing river in the study area and contains brackish water (Whittemore, 2000); therefore, infiltration of Arkansas River water impairs the water quality in the central High Plains aquifer. Flow in the Cimarron River is intermittent upstream from southeastern Seward County. Flow in the Cimarron River becomes perennial downstream from that area because of discharge from the central High Plains aquifer.

In 1999, the depth to water in the central High Plains aquifer ranged from about 50 to 300 feet below land surface and the saturated thickness ranged from 0 to about 600 feet (fig. 4). Declines of about 100 feet in the saturated thickness have occurred in some areas between the Arkansas and Cimarron Rivers since irrigation pumping began in the 1950's and 1960's (McGuire and Sharpe, 1997). In the areas of greatest

saturated thickness in Seward, Stevens, and Texas Counties, water-level declines have been less than 50 feet since pumping began (McGuire and Sharpe, 1997).

Hydraulic gradients in the central High Plains aquifer indicate that ground-water movement generally was from west to east (fig. 2). Gutentag and others (1984) estimated that water moved through the aquifer at an average rate of about 1 foot per day. However, directions and rates of ground-water movement in the aquifer were likely to vary areally depending on the intensity of well pumpage, sediment lithology, recharge and discharge rates, and other hydrologic factors.

Recharge to the central High Plains aquifer occurs by infiltration of irrigation water, areally diffuse infiltration of precipitation, infiltration of stormwater runoff through streambeds, and upward movement of water from underlying aquifers. Luckey and Becker (1999) estimated that mean recharge rates from precipitation ranged from 0.068 to 0.69 inch per year.

Discharge from the aquifer occurs by well pumping, discharge to streams and underlying aquifers, diffuse ground-water flow across the eastern boundary of the aquifer, and evapotranspiration. Pumping for irrigation accounted for about 95 percent of the discharge from the aquifer in 1997 (Luckey and Becker, 1999). Large-scale development of irrigated agriculture in the study area began in the 1950's and 1960's, and since that time a net depletion of water stored in the aquifer has occurred. The estimated decrease in volume of water stored in the High Plains aquifer in Kansas and Oklahoma between 1980 and 1995 was about 24 million acre-feet (McGuire and Sharpe, 1997). In Kansas and Oklahoma, about 84 and 90 percent of the predevelopment saturated thickness remained as of 1995 (McGuire and Sharpe, 1997).

Land and Water Use

Land in the study area is used primarily for grazing (rangeland) and the production of crops (irrigated and dryland cropland) (fig. 5). Wheat, corn, sorghum, and alfalfa are the main crops. Confined animal-feeding operations are an important industry in the study area, and many of the crops grown there are used for animal feed. The top five pesticides used in the study area (in terms of pounds applied) were atr

Table 1. Generalized section of the geologic units in southwestern Kansas and their relation to the central High Plains aquifer

[Modified from Gutentag and others, 1981, 1984; Macfarlane and others, 1993]

Era	System	Series	Geologic unit	Thickness, feet	Relation to central High Plains aquifer
Cenozoic	Quaternary	Pleistocene and Holocene	Alluvium	0–80	Forms part of the aquifer where hydraulically connected to underlying Quaternary and Tertiary deposits.
			Dune sand	0–75	Forms part of the aquifer where saturated.
			Loess	0–45	Generally lies above water table.
		Pleistocene	Undifferentiated deposits	0–550	Forms part of the aquifer where hydraulically connected to Tertiary deposits.
	Tertiary	Pliocene	Ogallala Formation	0–500	Primary geologic unit in the aquifer.
Mesozoic	Cretaceous	Upper Cretaceous	Niobrara Chalk	0–250	These geologic units generally are not considered part of the aquifer in southwestern Kansas.
			Carlile Shale	0–330	
			Greenhorn Limestone	0–200	
			Graneros Shale	0–130	
		Lower Cretaceous	Undifferentiated rocks	0–450	
	Triassic-Jurassic	Undifferentiated rocks	0–350		
Paleozoic	Permian	Upper Permian	Big Basin Formation	0–160	
			Day Creek Dolomite	0–80	
			Whitehorse Formation	100–350	
		Lower Permian	Dog Creek Formation	15–60	
			Blaine Formation	20–150	
			Flowerpot Shale	¹ --	
			Cedar Hills Sandstone	¹ --	

¹Not reported.

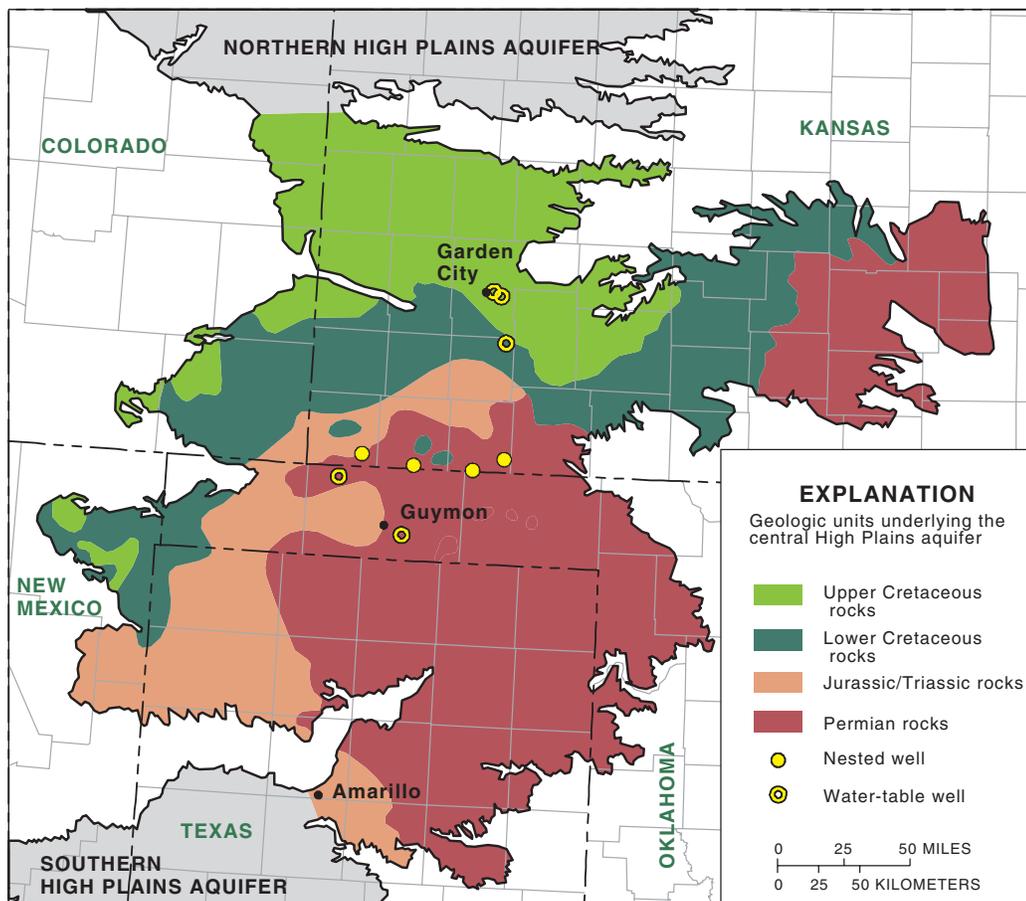


Figure 3. Geology underlying the central High Plains aquifer and locations of monitoring wells. Map modified from Gutentag and others (1984).

zine, 2,4-D, metolachlor, alachlor, and butylate (U.S. Department of Agriculture, 1999).

Irrigation is the primary use of ground water in the study area. Of the approximately 4.7 million acre-feet of water withdrawn from the High Plains aquifer in Kansas and Oklahoma in 1990, 96 percent was used for irrigation (McGuire and Sharpe, 1997). Pumping for irrigation in the central High Plains began in the 1940's, but it was not until the 1960's that the installation of irrigation wells proceeded at a rapid pace (Lucky and Becker, 1999).

METHODS OF INVESTIGATION

Monitoring wells sampled during this study were installed by the U.S. Geological Survey in 1998 and 1999. Water samples for chemical analysis were

collected from the wells by the U.S. Geological Survey in 1999. An additional sample was collected from one of the wells (Cimarron-436) in 2000 to verify the chemical analysis of the 1999 sample. The following section of the report describes the methods used in the well-site-selection process, well installation, geophysical logging, water-level measurements, sediment-sample collection, water-sample collection, methods of chemical analysis, and quality-control of the water-quality data.

Well-site selection. Nineteen monitoring wells were installed at nine sites for the collection of water levels and samples. A single water-table well was installed at each of five sites, and nested wells (wells screened at different depths below the water table) were installed at four sites (fig. 2). The well sites were selected based on the following criteria:

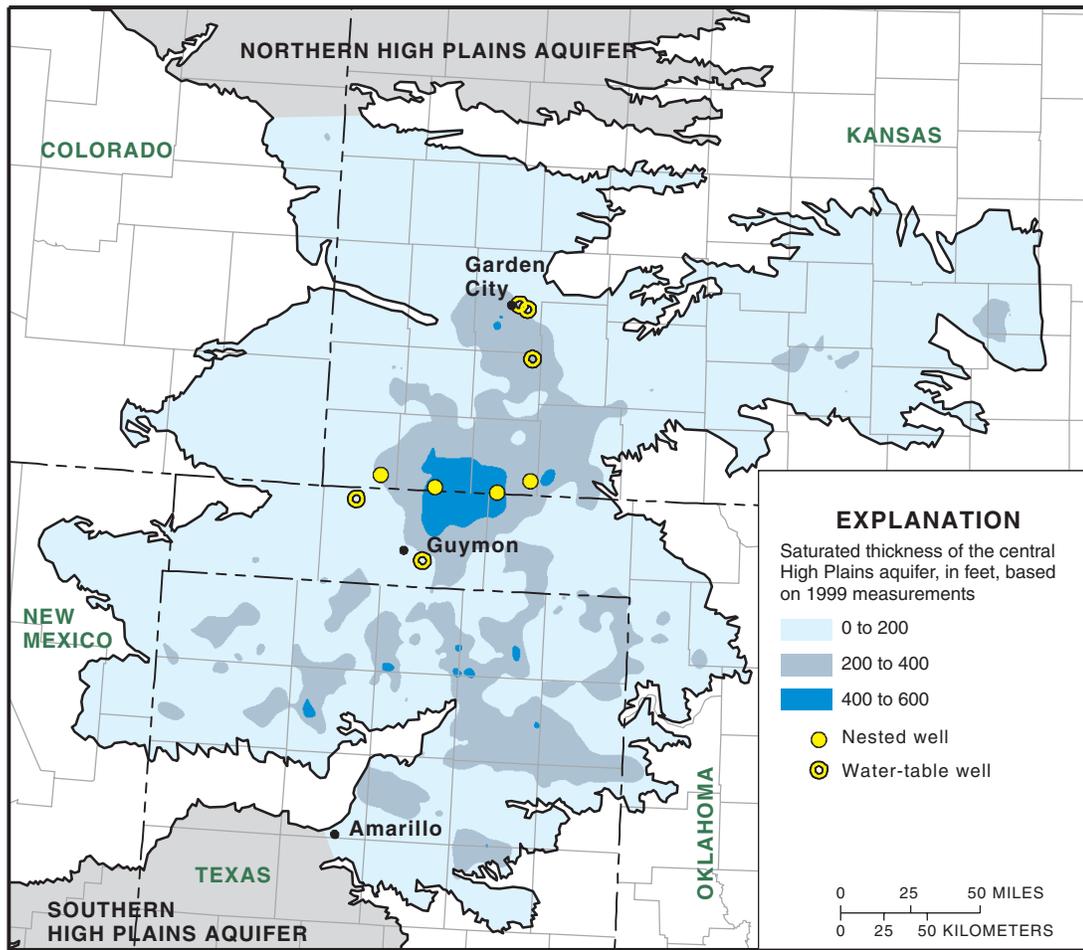


Figure 4. Saturated thickness of the central High Plains aquifer and locations of monitoring wells. Thicknesses based on 1999 water-level measurements and U.S. Geological Survey base-of-aquifer map (V.L. McGuire, U.S. Geological Survey, written commun., 2000; Gutentag and others, 1984).

1. Water-table wells were located adjacent to irrigated cropland (fig. 5 and table 2).
2. Nested wells were located in areas of the aquifer that overlie sediments of Permian age (fig. 3).
3. Nested wells were located in the thickest saturated section of the aquifer (fig. 4).

The water-table wells were located adjacent to irrigated cropland because water-table wells generally sample the most recently recharged ground water (McMahon, 2000) and because it was assumed that rates of water and agricultural-chemical application in that land-use setting would represent the maximum rates to be expected in most of the study area. Areas with the largest saturated thickness of the central High Plains aquifer were selected as nested-well sites because those areas may represent the most long-term ground-water supply in the study area. Those areas also overlie sediments of Permian age that contain mineralized water (Gutentag and others, 1981; Krothe and Oliver, 1982).

One surface-water sampling site was located on the Cimarron River (fig. 2). That site was located about 0.5 mile northeast of the Cimarron nested-well site. The land-surface elevation of the river site was about 75 feet lower than that at the nested-well site.

Well installation. Boreholes used for well installation were drilled in 1998–99 by the U.S. Geological Survey using a mud-rotary drill rig. Wells were installed using established well-installation protocols (Lapham and others, 1995). Generally, wells were installed by placing polyvinyl chloride (PVC) well screen and casing in the borehole after drilling to the target depth, placing a sand filter in the annular space around the well screen and a bentonite plug on top of the sand filter, and sealing the annular space from the top of the plug to land surface using a high-density bentonite grout. At the nested-well sites, two wells were placed in each borehole. The annular space between well screens was sealed with bentonite. The wells were developed by bailing and pumping

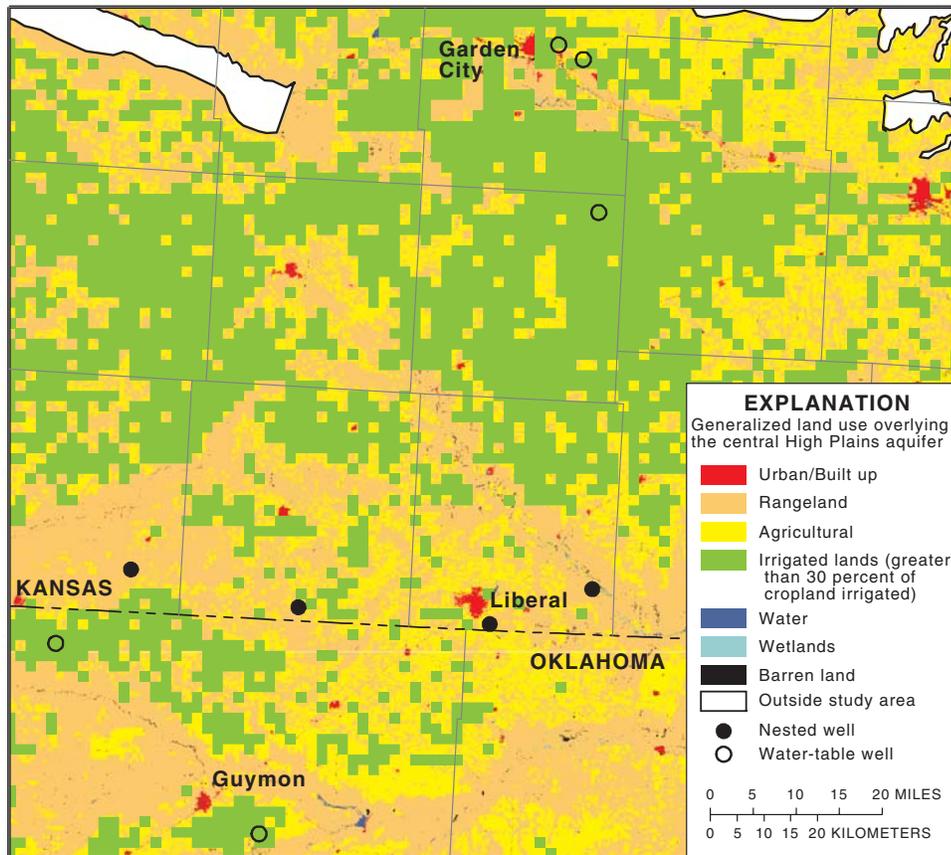


Figure 5. Land use overlying the central High Plains aquifer and locations of monitoring wells. Land-use data from Fegeas and others (1983). The data were collected from about 1977 to 1982.

(water-table wells) or by air lifting and pumping (wells screened beneath the water table) immediately after drilling and again at least one month before sample collection. During the second well-development period, the pH, temperature, specific conductance, and turbidity of the water were monitored to determine when the well began producing water representative of the aquifer. Water was considered to be representative of the aquifer after a minimum of five casing volumes of water had been pumped and the change in field-parameter values between three successive measurements (taken at 30-minute intervals) was less than 5 percent. Well construction details are listed in table 2.

Geophysical logging. Natural gamma and electrical resistivity logs were obtained for each borehole before the well casings were installed. Only the deepest borehole was logged at the nested-well sites. The borehole at the Liberal nested-well site was logged by the Kansas Geological Survey, Lawrence, Kansas. The boreholes at the Cimarron, Hugoton, and

Rolla nested-well sites were logged by Reeves Wireline, Inc., Liberal, Kansas. All other boreholes were logged by the U.S. Geological Survey.

Water-level measurement. Water levels in all of the wells were measured before water-sample collection by using an electric tape. Water levels were measured in the nested wells monthly for about 1 year.

Sediment-sample collection. Sediment samples were collected during drilling of the nested-well sites. Cuttings were collected from the drilling-mud return flow every 10 feet by using a wire mesh screen. The cuttings were rinsed in clean tap water to remove excess drilling mud and stored in sealed plastic bags after the lithology was determined. Cores of sediments of Permian age were collected from depths of 361 to 376 feet and from 421 to 425 feet below land surface at the Cimarron site. The 4-inch-diameter cores were wrapped in plastic and stored in cardboard boxes after the lithology was determined.

Table 2. Construction details for monitoring wells and generalized land use around each well

[All depths relative to land surface; n.d., not determined; Sch., Schedule; PVC, polyvinyl chloride; CRP, Conservation Reserve Program]

Site identification	Well name	Construction date	Elevation of land surface (feet above mean sea level)	Depth to base of central High Plains aquifer (feet)	Depth to water at time of construction (feet)	Total depth of well (feet)	Well diameter (inches)	Casing and screen material	Depth of open interval (feet)	Depth of screen midpoint below water table (feet)	General land use within 500-foot radius of well
Water-table well sites, central High Plains aquifer											
375855100484001	Recon-1	11/12/98	2,837	n.d.	72	94	2	Sch. 40 PVC	68 to 88	6	Irrigated cropland
375734100452301	Recon-2	11/13/98	2,904	n.d.	120	133	2	Sch. 40 PVC	107 to 127	-3	Irrigated cropland
374220100422501	Recon-3	11/14/98	2,801	n.d.	161	190	2	Sch. 40 PVC	164 to 184	13	Irrigated cropland
365610101484301	Recon-4	11/16/98	3,494	n.d.	274	300	2	Sch. 40 PVC	254 to 294	0	Irrigated cropland
363817101213101	Recon-5	11/18/98	3,032	n.d.	282	303	2	Sch. 40 PVC	277 to 297	5	Irrigated cropland
Nested-well sites, central High Plains aquifer											
370402101394402	Rolla-193	05/25/99	3,361	399	179	198	2.5	Sch. 80 PVC	173 to 193	4	Rangeland
370402101394401	Rolla-366	05/26/99	3,361	399	179	371	2.5	Sch. 80 PVC	356 to 366	182	Rangeland
370130101180904	Hugoton-140	06/19/99	3,112	635	126	145	2.5	Sch. 80 PVC	120 to 140	4	Irrigated cropland
370130101180903	Hugoton-313	06/18/99	3,112	635	127	318	2.5	Sch. 80 PVC	303 to 313	181	Irrigated cropland
370130101180902	Hugoton-495	06/15/99	3,112	635	126	500	2.5	Sch. 80 PVC	485 to 495	364	Irrigated cropland
370130101180901	Hugoton-617	06/14/99	3,112	635	128	627	2.5	Sch. 80 PVC	607 to 617	484	Irrigated cropland
370033100534204	Liberal-160	05/07/99	2,814	576	119	165	2.5	Sch. 80 PVC	140 to 160	31	CRP/cropland
370033100534203	Liberal-319	05/06/99	2,814	576	138	324	2.5	Sch. 80 PVC	309 to 319	176	CRP/cropland
370033100534202	Liberal-436	05/03/99	2,814	576	138	441	2.5	Sch. 80 PVC	426 to 436	293	CRP/cropland
370033100534201	Liberal-570	04/30/99	2,814	576	137	581	2.5	Sch. 80 PVC	560 to 570	428	CRP/cropland
370434100405204	Cimarron-65	05/23/99	2,444	345	58	70	2.5	Sch. 80 PVC	45 to 65	-3	Rangeland
370434100405203	Cimarron-210	05/20/99	2,444	345	53	215	2.5	Sch. 80 PVC	200 to 210	152	Rangeland
370434100405202	Cimarron-336	05/22/99	2,444	345	56	341	2.5	Sch. 80 PVC	326 to 336	275	Rangeland
Sediments of Permian age											
370434100405201	Cimarron-436	05/19/99	2,444	345	56	441	2.5	Sch. 80 PVC	396 to 436	360	Rangeland

Water-sample collection. A grab sample of water was collected from the right bank of the main channel of the Cimarron River near the Cimarron nested-well site (fig. 2) using clean 1-liter polypropylene bottles. The Cimarron River at that site occupied a broad valley, and the main channel, which was about 15 feet wide, flowed through a marshy area sustained by discharge from the central High Plains aquifer. The sample bottles containing river water were carried back to a mobile water-quality laboratory mounted on a truck for processing. Samples were processed for analyses of major ions, nutrients, trace elements, and tritium using the methods described below for the ground-water samples.

Ground-water samples were collected and processed in a mobile water-quality laboratory mounted on a truck. Water was pumped from the wells using a submersible piston-type pump made of stainless steel and Teflon. Sampling protocols used in this study are described in detail in Koterba and others (1995). To minimize the risk of sample contamination, all sample collection and preservation took place in dedicated environmental chambers consisting of clear polyethylene bags supported by tubular PVC frames. Sampling equipment was thoroughly decontaminated after sampling each well. Polyethylene bags forming the sample and preservation chambers were replaced after each sampling event.

Prior to sampling, wells were purged of stagnant water by pumping at least three casing volumes of water from the well. After the initial pumping period, field measurements of water temperature, specific conductance, pH, and dissolved oxygen were monitored every 5 minutes in a closed-cell, flow-through chamber until stable readings were obtained. Turbidity also was measured every 5 minutes using a portable turbidity meter. Once stable field measurements were obtained, water flow was redirected to the clean sampling chamber where water was immediately collected for analysis according to the NAWQA Program protocol (Koterba and others, 1995).

Water samples collected for the analysis of major cations and trace elements were filtered using a 0.45- μm disposable capsule filter and collected in precleaned plastic bottles that were rinsed with filtered ground water. Samples for major cations and trace elements were acidified to a pH of less than 2 using ultrapure nitric acid. Samples for major anions and nutrients were filtered using the capsule filter, collected in field-rinsed plastic bottles, and stored on ice with no other preservation. Additionally, a filtered

sample was collected for field titration of carbonate alkalinity. Unfiltered 1-liter water samples were collected in the sampling chamber in unrinsed plastic bottles and were capped leaving 2 mL of headspace for the analysis of tritium. The bottle caps were secured with electrical tape and stored at room temperature until delivered to the laboratory for analysis.

Water samples collected for the analysis of pesticides and pesticide degradation products were passed through a methanol-rinsed stainless steel filter chamber containing a baked 0.7- μm glass fiber filter. Pesticide samples were collected in cleaned and baked amber-colored glass bottles and immediately chilled on ice until delivery to the laboratory for analysis. Samples for the analysis of DOC were passed through 0.45- μm silver filters, collected in baked amber glass bottles, and immediately chilled on ice until delivery to the laboratory for analysis.

Elemental and X-ray diffraction analysis of sediment samples. Selected subsamples of the sediment cuttings and core were analyzed for their carbonate and organic carbon contents and their bulk mineralogy. The sediments used for carbon measurements were dried, sieved to remove the fraction greater than 2 mm in diameter, and ground using a mortar and pestle. Carbonate and organic carbon contents were determined at Huffman Laboratories, Golden, Colo., by (a) directly measuring the total carbon content using a Leco Model CR12 carbon analyzer, (b) directly measuring the carbonate content using a UIC/Coulometrics System 140 carbonate carbon analyzer, and (c) calculating organic carbon content as the difference between total and carbonate contents.

Bulk mineralogy was qualitatively estimated by using X-ray powder diffraction analysis. Sediment samples were dried and ground to a fine powder prior to X-ray analysis. Each mineral type in the sediment samples was classified as comprising a major, minor, or trace portion of the bulk mineralogy based on the diffraction signal intensity.

Chemical analysis of water samples. Chemical analyses of water samples were performed at the USGS National Water-Quality Laboratory located in Lakewood, Colo., with the exception of the analyses for tritium (USGS Tritium Laboratory, Menlo Park, Calif.) and chloroacetanilide herbicide degradation products (USGS Pesticide Research Laboratory, Lawrence, Kan.). Table 3 lists references for the methods used for each chemical analysis.

Quality control of water-quality data. The quality of sample collection, processing, and analysis

Table 3. Methods used to analyze water samples

Constituent or constituent group	Analytical method	Reference
Pesticides and metabolites, National Water-Quality Laboratory	Solid phase extraction using a C-18 cartridge and capillary-column gas chromatography/mass spectrometry	Zaugg and others (1995)
Pesticide metabolites, Pesticide Research Laboratory	High performance liquid chromatography/mass spectrometry	Hostetler and Thurman (1999)
Dissolved organic carbon	Ultraviolet-light promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett (1993)
Major ions	Atomic absorption spectrometry	Fishman (1993)
Trace elements	Inductively coupled plasma-mass spectrometry	Faires (1993)
Nutrients	Various methods	Fishman (1993)
Tritium	Electrolytic enrichment with gas counting	Michel and Schroeder (1994)

was checked by collecting quality-control samples. The number of quality-control samples was approximately 30 percent of the number of environmental samples. Quality-control samples included field blanks, replicate environmental samples, and field matrix spike samples. Field blanks verified that decontamination procedures were adequate and that field and laboratory procedures did not contaminate samples. Replicate samples assessed the combined effects of field and laboratory procedures on measurement variability. Matrix spike samples assessed the recovery bias of analytes in the spike solution.

Blank samples were collected for major ions, nutrients, trace elements, DOC, and pesticides. The source solution for blank samples was specially prepared organic-free or inorganic-free water provided by the USGS for the NAWQA Program. Blank solution was passed through all sampling equipment, and then a sample of the blank solution was collected using the same procedures as for environmental samples.

Replicate samples were collected sequentially for all analyses except pesticides. Replication of pesticides was accomplished during the field matrix spiking process where replicate environmental samples were injected with known concentrations of selected pesticides.

VERTICAL CHANGES IN LITHOLOGY

Vertical changes in lithology in the central High Plains aquifer were determined from geophysical and lithologic logs (figs. 6 and 7; table 4). The general

lithologic descriptions were derived from examination of geophysical logs, cuttings, and cores and were supplemented by elemental carbon and X-ray diffraction analyses.

Geophysical and Lithologic Logs

Resistivity and natural-gamma logging tools record the electrical resistivity and natural gamma radioactivity of sediment, and the output from those logs can be used to evaluate lithologic variability in aquifers. Sands and gravels are resistive to the flow of electrical current used in resistivity logging; therefore, one can generally attribute the increase in resistivity in those logs to increased proportions of sand and gravel in the aquifer. However, other factors beside lithology can affect resistivity logs, including degree of water saturation, sediment mineralogy, and salinity of water. The presence of mineralized water in sandy deposits would produce small resistivities, possibly leading to the incorrect conclusion that the aquifer consisted of fine-grained material. Mineralized ground water affected the resistivity logs from the Recon-1 (below the 70-foot depth; fig. 6a), Recon-2 (below the 120-foot depth; fig. 6b), and Cimarron (below the 285-foot depth; fig. 7d) boreholes. Natural gamma logs record the gamma radioactivity emitted by naturally occurring radioactive elements in shale and clay. The increase in gamma activity recorded by natural gamma logs generally is attributed to increased proportions of clay in the aquifer or changes in clay mineralogy.

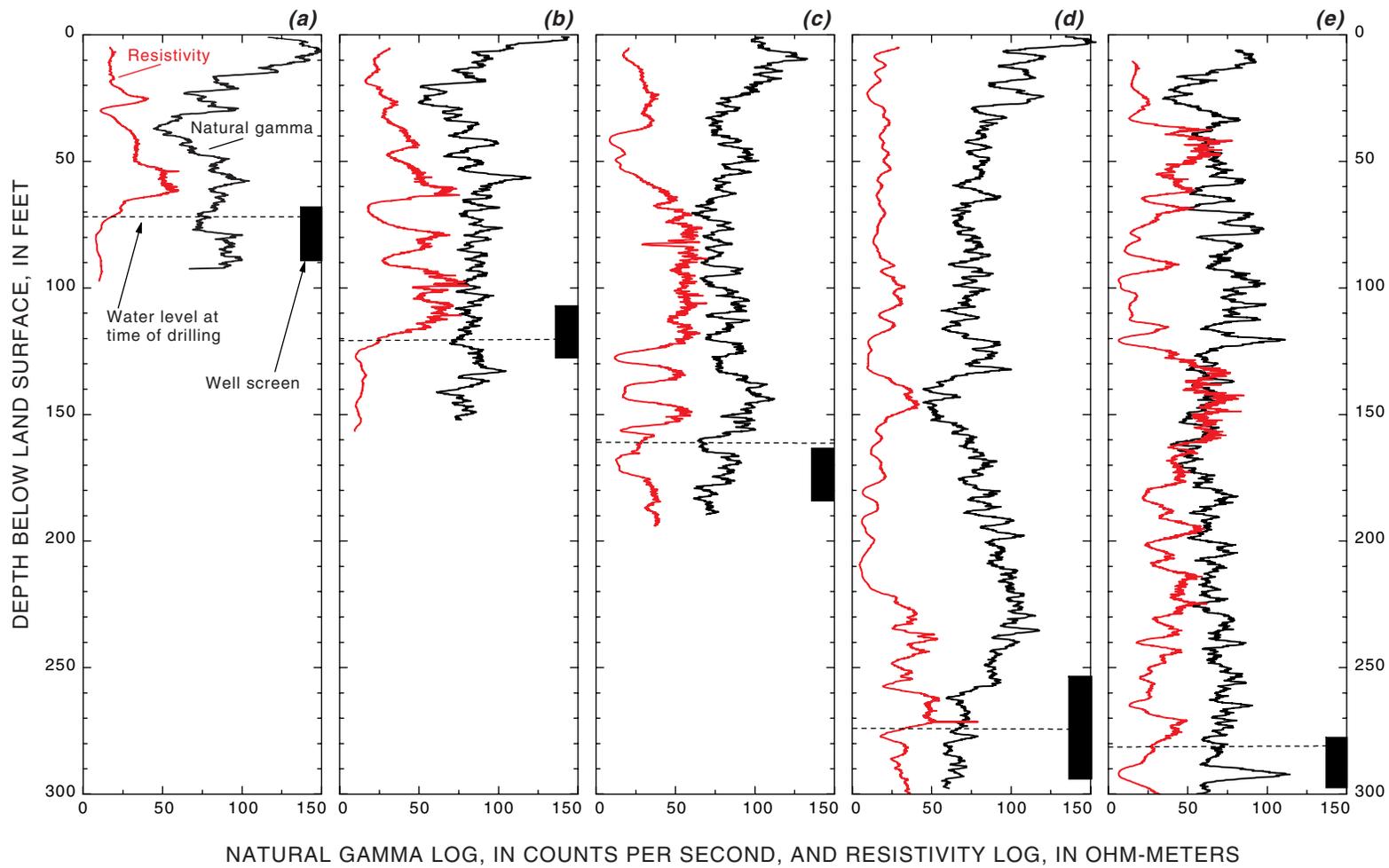


Figure 6. Natural gamma and resistivity logs for water-table-well boreholes (a) Recon-1, (b) Recon-2, (c) Recon-3, (d) Recon-4, and (e) Recon-5.

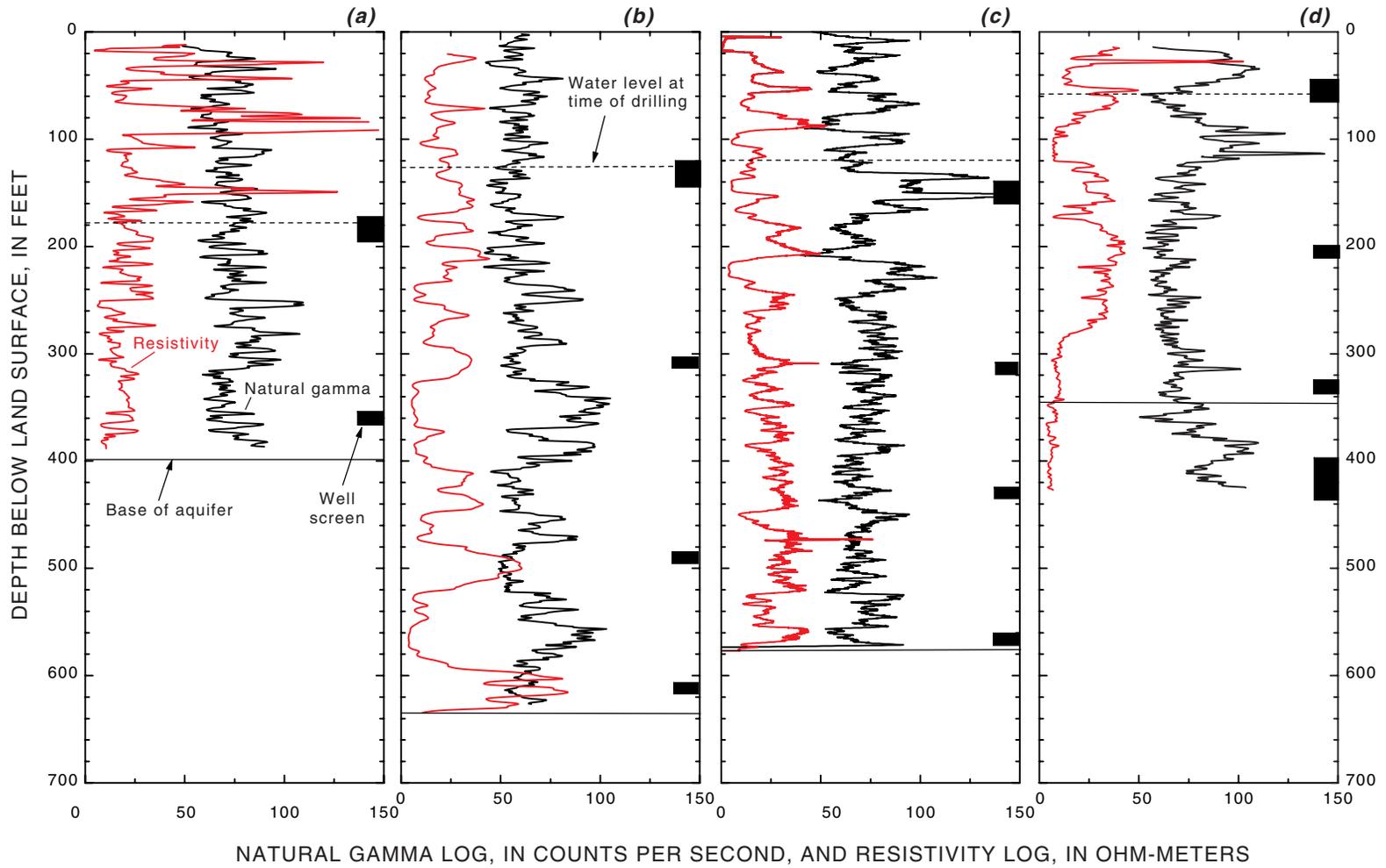


Figure 7. Natural gamma and resistivity logs for nested-well boreholes (a) Rolla, (b) Hugoton, (c) Liberal, and (d) Cimarron.

Table 4. Lithologic description of drill cuttings and core

[All depths relative to land surface; n.d., not determined]

Borehole name: Recon-1
Completion date: 11/12/98
Depth to base of aquifer (feet): n.d.
Depth to water at time of drilling (feet): 72
Total depth of borehole (feet): 101

Depth interval (feet below land surface)	Lithology
0-5	Silty sand, dark brown
5-10	Clayey silt, tan
10-15	Fine silty sand with some clay, tan
15-17	Fine sand, reddish brown
17-18	Clay, tan
18-30	Medium sand with some silt, tan
30-40	Sandy clay, light tan
40-50	Clayey sand, tan
50-55	Medium gravelly sand
55-70	Medium to coarse sand
70-75	Medium sand with some silt
75-101	Fine to medium silty sand

Borehole name: Recon-3
Completion date: 11/14/98
Depth to base of aquifer (feet): n.d.
Depth to water at time of drilling (feet): 161
Total depth of borehole (feet): 195

Depth interval (feet below land surface)	Lithology
0-10	Silty sand with some clay, dark brown
10-20	Light brown silty sand, light brown
20-35	Fine silty sand, tan
35-55	Fine to medium sand, tan
55-125	Medium to coarse sand, tan
125-130	Sandy clay
130-135	Medium to coarse sand
135-140	Sandy clay
140-165	Medium to coarse sand
165-175	Clayey sand
175-195	Fine to medium silty sand

Table 4.—Continued

Borehole name: Recon-4
Completion date: 11/16/98
Depth to base of aquifer (feet): n.d.
Depth to water at time of drilling (feet): 274
Total depth of borehole (feet): 305

Depth interval (feet below land surface)	Lithology
0-5	Clayey sand, dark reddish brown
5-30	Clayey sand, reddish brown
30-100	Silty sand, light reddish brown
100-130	Fine silty sand, tan
130-140	Fine silty sand with caliche, tan
140-160	Clayey sand, light tan
160-165	Clayey sand with caliche, light tan
165-180	Silty sand, light tan
180-210	Silty sand with caliche, light tan
210-220	Sand with caliche, light tan
220-240	Silty sand with clay, light tan
240-260	Silty sand, light tan
260-280	Medium sand
280-305	Silty sand

Borehole name: Recon-5
Completion date: 11/18/98
Depth to base of aquifer (feet): n.d.
Depth to water at time of drilling (feet): 282
Total depth of borehole (feet): 305

Depth interval (feet below land surface)	Lithology
0-5	Sandy clay, dark brown
5-10	Sandy clay, light brown
10-40	Caliche and sand, light brown
40-50	Fine sand with caliche stringers
50-60	Fine to medium sand
60-65	Medium sand
65-90	Sandy clay, light brown
90-100	Medium sand
100-145	Clay, light brown, with sand stringers
145-150	Sandy clay
150-170	Medium sand
170-180	Clay, light brown, with sand stringers
180-195	Sandy clay
195-215	Medium sand
215-220	Sandy clay
220-230	Medium sand
230-290	Sandy silty clay
290-295	Dense clay
295-305	Clayey sand

Table 4. Lithologic description of drill cuttings and core—Continued

[All depths relative to land surface; n.d., not determined]

Borehole name: Rolla Completion date: 05/26/99 Depth to base of aquifer (feet): 399 Depth to water at time of drilling (feet): 179 Total depth of borehole (feet): 400	
Depth interval (feet below land surface)	Lithology
0–30	Fine sand, red
30–40	Fine silty sand
40–50	Fine silty sand with gravel
50–70	Fine sand with caliche, light tan
70–90	Medium to coarse sand with gravel and caliche
90–100	Coarse sand and gravel
100–110	Sandy silt with clay, tan
110–140	Silty sand with caliche, light red
140–150	Coarse sand
150–210	Fine silty sand
210–230	Fine sand with caliche
230–240	Fine sand with clay stringers
240–250	Silty sand
250–260	Interbedded fine sand and clay
260–280	Interbedded sandy silt and clay
280–320	Silty sand
320–330	fine to medium sand
330–340	Fine to medium sand, light pinkish red
340–360	Fine sand, light pinkish red
360–390	Medium to coarse sand, light pinkish red
390–399	Medium sand, light pinkish red
399–400	Hard sandy clay, red and yellow

Table 4.—Continued

Borehole name: Hugoton Completion date: 06/14/99 Depth to base of aquifer (feet): 635 Depth to water at time of drilling (feet): 128 Total depth of borehole (feet): 640	
Depth interval (feet below land surface)	Lithology
0–10	Silty sand with clay, dark brown
10–30	Fine silty sand, light brown
30–50	Fine sand
50–100	Fine silty sand with caliche
100–110	Clay, brown
110–120	Silty clay, brown
120–140	Fine sand with caliche
140–180	Clay with caliche, brown
180–190	Sandy clay
190–200	Silty sand
200–230	Medium to coarse sand with clay stringers
230–240	Clayey sand
240–260	Sandy clay, brown
260–270	Silty sand with gravel
270–300	Fine to medium silty sand
300–310	Fine sand
310–325	Medium to coarse sand
325–370	Brown clay
370–375	Fine sand
375–390	Sandy clay
390–410	Fine silty sand with clay stringers
410–460	Medium to coarse sand with gravel
460–470	Sandy clay, brown
470–520	Medium to coarse sand
520–550	Clayey sand with caliche, brown and gray
550–580	Clay, blue/gray/brown
580–590	Medium clayey sand
590–600	Medium to coarse clayey sand
600–635	Fine to coarse sand with gravel near base
635–640	Medium sandy clay, red

Table 4. Lithologic description of drill cuttings and core—Continued

[All depths relative to land surface; n.d., not determined]

Borehole name: Liberal	
Completion date: 04/30/99	
Depth to base of aquifer (feet): 576	
Depth to water at time of drilling (feet): 137	
Total depth of borehole (feet): 583	
Depth interval (feet below land surface)	Lithology
0–5	Silty sand, dark brown
5–20	Fine sandy silt, brown
20–50	Fine sandy silt with caliche, tan
50–60	Fine silty sand, brown
60–80	Fine sandy silt, tan
80–95	Fine to medium sand
95–115	Clayey silt
115–130	Fine clayey sand
130–135	Clay, tan and white
135–150	Silty clay, tan and white
150–160	Clay and caliche, white
160–170	Brown clay
170–180	Fine silty sand
180–190	Fine to medium sand
190–240	Fine sand, silty near top, with caliche
240–260	Fine to medium sand, yellow
260–270	Fine to medium sand, brown
270–310	Fine clayey and silty sand
310–330	Fine to medium sand
330–350	Silty sand
350–360	Fine to medium sand
360–390	Medium to coarse sand with caliche
390–400	Silty sand
400–440	Medium to coarse sand
440–460	Siltstone, becoming sandier near bottom
460–470	Fine sand
470–480	Fine to medium sand
480–490	Siltstone
490–510	Medium sand
510–550	Interbedded sand and siltsone
550–560	Sand, yellow
560–570	Medium sand with 5 percent red clay
570–576	Medium sand and 40 percent red clay
576–582	More than 50 percent red clay, weathered red bed
582–583	Hard, dense red clay, unweathered red bed

Table 4.—Continued

Borehole name: Cimarron	
Completion date: 05/19/99	
Depth to base of aquifer (feet): 345	
Depth to water at time of drilling (feet): 56	
Total depth of borehole (feet): 441	
Depth interval (feet below land surface)	Lithology
0–15	Fine sand and silt, light red
15–30	Sandy clay, brown
30–50	Clay, brown
50–60	Sandy clay, brown, with gravel
60–70	Medium to coarse sand
70–90	Sandy clay, brown
90–120	Gray clay with some silt
120–130	Fine sandy clay, brown
130–140	Clayey sand, brown
140–160	Medium to coarse sand
160–170	Clayey sand, brown
170–290	Medium to coarse sand with some clay stringers
290–300	Silty sand with gravel
300–340	Sandy clay
340–345	Medium sand with red clay
345–360	Dense clay, clayey sand, silt, pink weathered redbed
360–362	Sandy silty clay, pink, with carbonate-filled fracture,
362–365	Dense clay, red, with gray reduced spots, unweathered red bed
365–375	Interbedded soft clay and hard claystone, carbonate-filled fractures, gray reduction spots, one fracture with slickensides
375–441	Interbedded clay and siltsone, red

The geophysical and lithologic logs indicate that the central High Plains aquifer at the well sites was a mix of clay, silt, sand, and gravel that was largely unconsolidated, except for cemented caliche layers that occurred in some places in the aquifer (table 4). There was no obvious trend in lithology toward finer or coarser grained material with depth in the aquifer. Fine to coarse sand was penetrated, however, at the base of the aquifer at the Rolla, Hugoton, and Liberal boreholes (table 4). The occurrence of basal sand and gravel also was reported in the southern High Plains aquifer (Seni, 1980). The geophysical and lithologic logs indicate that intervals of sand and gravel occurred at various depths in the unsaturated zone and aquifer. For example, several layers of medium to coarse sand were penetrated in the unsaturated zone at the Recon-3 site (table 4 and fig. 6c). Coarse-grained sediments under dry conditions in the unsaturated zone may actually inhibit the movement of water and solutes from land surface to the water table compared with fine-grained sediments. This is because the hydraulic conductivity of coarse-grained sediments may be smaller than that of finer grained sediments under dry conditions (Tindall and Kunkel, p. 189, 1999). Relatively thick layers of coarse-grained sediment were present below the water table in the Hugoton borehole at depths from about 290 to 330, 410 to 450, 470 to 520, and 600 to 635 feet below land surface (table 4 and fig. 7b). For the most part, the intervals of medium to coarse sand and gravel below the water table were less than 50 feet thick. One exception was a 120-foot-thick medium to coarse sand interval in the Cimarron borehole at the 170- to 290-foot depth interval. Those intervals of coarse-grained sediment are the principal water-bearing units in the aquifer at those sites.

Thick clay layers were penetrated during drilling at most sites. In the unsaturated zone at the Recon-5 site, sandy clay and clay were penetrated from 65 to 90 and 100 to 145 feet below land surface (table 4 and fig. 6e). In the Hugoton borehole, a brown clay was penetrated below the water table in the 325 to 370 foot depth interval (table 4 and fig. 7b). A tan and white silty clay was penetrated in the 130- to 150-foot depth interval in the Liberal borehole (table 4 and fig. 6c). Water-level data indicate that clay intervals such as those created locally confined conditions in the aquifer (see discussion in the section "Vertical Hydraulic Gradients").

The Cimarron borehole was the only one that penetrated the unweathered sediments directly below the aquifer to any appreciable depth, approximately 80 feet. Cuttings and cores were available for that site. Limited lithologic information from cuttings was available for the sediments underlying the aquifer at the Rolla, Hugoton, and Liberal boreholes. Sediments underlying the aquifer in those locations are Permian in age (fig. 3; Macfarlane and others, 1993). Sediment retrieved from the drill bit at the bottom of the Liberal borehole indicated that the unweathered sediments of Permian age at that site consisted of hard, dense, red clay with no evidence of fractures. About 6 feet of weathered sediment of Permian age overlies the unweathered sediment. The unweathered sediments of Permian age at the Cimarron borehole were quite variable lithologically, ranging from dense clay to fractured siltstone (table 4). The numerous fractures in the unweathered sediment were either lined or completely filled with carbonate cement. The presence of secondary cement in the fractures indicates that water had moved through the fractures.

Elemental and X-Ray Diffraction Analyses

Measured amounts of carbonate and organic carbon in the sediments ranged from less than 0.02 to 3.22 and less than 0.05 to 0.60 weight percent, respectively (table 5). Carbonate carbon in the aquifer occurred as caliche layers and cemented nodules, whereas carbonate in the sediments of Permian age occurred as pore- and fracture-filling cements and as fine-grained matrix material. The carbonate carbon in the aquifer and in the cements in sediments of Permian age was calcite. The fine-grained carbonate carbon matrix in sediments of Permian age was dolomite. The largest measured organic carbon content, 0.60 weight percent, occurred in a sandy brown clay from the Cimarron borehole. However, the five other fine-grained sediments that were measured contained less than 0.25 weight percent organic carbon. Organic carbon tends to be concentrated in fine-grained sediments; therefore, sand and gravel in the aquifer also probably contained less than 0.25 weight percent organic carbon. The one medium to coarse sand sample analyzed for organic carbon contained less than 0.05 weight percent (table 5). The general lack of organic carbon in the aquifer probably limits the amount of natural microbial activity in the aquifer that could affect water quality.

Table 5. Results of elemental and X-ray diffraction analyses

[--, not measured; <, less than indicated value]

Borehole	Depth (feet below land surface)	Lithology	X-ray diffraction results		Carbon content (weight percent)		
			Mineral phase	Relative abundance	Carbonate	Organic	
Rolla	360	Medium to coarse sand, light pinkish red	Quartz	Major	--	--	
			Potassium feldspar	Major	--	--	
			Albite	Minor	--	--	
			Calcite	Minor	--	--	
			Muscovite	Trace	--	--	
			Montmorillonite	Trace	--	--	
Hugoton	200	Medium to coarse sand with clay stringers	--	--	3.22	<0.05	
	240	Sandy clay, brown	--	--	1.77	0.06	
	380	Sandy clay	--	--	0.68	0.12	
	610	Fine to coarse sand	Quartz	Major	--	--	
Anorthoclase			Major	--	--		
Calcite			Minor	--	--		
Albite			Minor	--	--		
Liberal	430	Medium to coarse sand	Quartz	Major	--	--	
			Potassium feldspar	Major	--	--	
			Albite	Minor	--	--	
			Muscovite	Trace	--	--	
	520	Siltstone	--	--	<0.02	<0.05	
Cimarron	80	Sandy clay, brown	--	--	1.71	0.60	
	160	Clayey sand, brown	--	--	0.65	0.21	
	200	Medium to coarse sand	Quartz	Major	--	--	
Potassium feldspar			Major	--	--		
Albite			Minor	--	--		
Calcite			Trace	--	--		
Muscovite			Trace	--	--		
361			Sandy, silty clay	Quartz	Major	0.19	<0.05
				Microcline	Minor	--	--
				Montmorillonite	Minor	--	--
				Muscovite	Minor	--	--
				Albite	Minor	--	--
361	Carbonate-filled fracture	Hematite	Trace	--	--		
		Chlorite	Trace	--	--		
		Kaolinite	Trace	--	--		
		Calcite	Major	--	--		
		Quartz	Minor	--	--		
422	Siltstone, red	Microcline	Minor	--	--		
		Muscovite	Trace	--	--		
		Albite	Trace	--	--		
		Quartz	Major	0.74	0.07		
		Dolomite	Minor	--	--		
		Orthoclase	Minor	--	--		
		Albite	Minor	--	--		
Muscovite	Minor	--	--				
			Montmorillonite	Minor	--	--	
			Kaolinite	Trace	--	--	

Quartz was the major mineral detected by X-ray diffraction analysis of the aquifer sediments (table 5). Various feldspar minerals were next largest in abundance after quartz. Less abundant minerals in the aquifer included calcite, muscovite, and montmorillonite. Quartz also was the major mineral detected in the detrital sediments of Permian age. However, calcite was the major authigenic mineral in the fracture-filling cement. Neither halite, anhydrite, nor gypsum was detected in the sediments of Permian age using X-ray diffraction analysis. Those minerals are known to occur in the sediments of Permian age and may occur in sediments at the base of the Ogallala Formation (Smith, 1940; Gutentag and others, 1981).

VERTICAL HYDRAULIC GRADIENTS

The potential for upward or downward water movement at any given location in an aquifer can be determined by measuring water-surface elevations in wells screened at different depths in the aquifer at that location. Those measured water-surface elevations are referred to as “hydraulic heads.” Ground water moves from areas of high hydraulic head to areas of low hydraulic head. The vertical hydraulic gradient in an aquifer is defined as the difference in hydraulic head divided by the distance between screened intervals in two wells screened at different depths in the aquifer. The potential for upward or downward water movement in an aquifer is directly proportional to the hydraulic gradient.

Vertical hydraulic gradients in the central High Plains aquifer varied spatially and temporally in the aquifer (fig. 8) and were affected by lithology and pumping in nearby wells. A large downward gradient that existed between the shallowest well and the three deeper wells at the Liberal site probably was created by pumping from the nearby City of Liberal well field, which lowered heads in the deep part of the aquifer where those supply wells were screened. A clay layer at a depth of 130 to 170 feet (table 4, fig. 7c) isolated the shallow part of the aquifer from the pumping effects (fig. 8c). The downward gradient at that site probably persisted over time because the municipal wells pumped throughout the year. Superimposed on the drawdown caused by pumping at the municipal well field was seasonal pumping of irrigation wells, which produced additional drawdowns during the summers of 1999 and 2000.

Seasonal pumping of a nearby irrigation well produced downward hydraulic gradients between the shallowest well and the three deeper wells at the Hugoton site that did not persist throughout the year (fig. 8b). An irrigation well was located about 0.3 mile from the nested wells and was screened in the bottom 250 feet of the aquifer. Pumping of that well during the 1999 and 2000 irrigation seasons (typically from about the end of May through the middle of September) caused water levels in the three deep monitoring wells to drop from about 20 to 60 feet relative to the water level in the shallow well. The water levels in the deeper monitoring wells recovered to within 1 foot of the shallow water level after the irrigation season ended in 1999 (fig. 8b). Clay layers at depths of 180 to 190, 240 to 260, and 325 to 370 feet (table 4) probably helped to isolate the shallow monitoring well from the effects of pumping deeper in the aquifer.

The water-level data from the Liberal and Hugoton sites indicate that clay layers in the aquifer caused local confinement of the deep ground water. That local confinement may help protect deep water in the aquifer from the downward movement of contaminants. However, in the absence of clay layers, pumping could draw more water, as well as more contaminants, deeper into the aquifer. The lowering of heads that was produced by pumping deep in the aquifer could also have induced the upward migration of mineralized water into the aquifer from underlying geologic units.

Unlike the Liberal and Hugoton sites, where the hydraulic gradients were downward, the hydraulic gradients at the Cimarron site were upward from the two deeper wells screened in the aquifer to the water-table well (fig. 8d). The apparent difference in hydraulic head between the two deep wells was less than 1 foot, whereas the head difference between the two deep wells and the water-table well was about 2 to 2.5 feet. On the basis of the depth of the water table below land surface in Cimarron-65 (about 55 feet) and the land-surface elevation difference between the river and Cimarron-65 (about 75 feet), it is likely that there also was an upward hydraulic gradient between the aquifer and the river at that site. The Cimarron River was located about 0.5 mile northeast of the Cimarron well site. The hydraulic-head and elevation data indicate that there was potential for deep water in the aquifer to discharge to the river in the vicinity of the Cimarron well site. A seepage run conducted on the

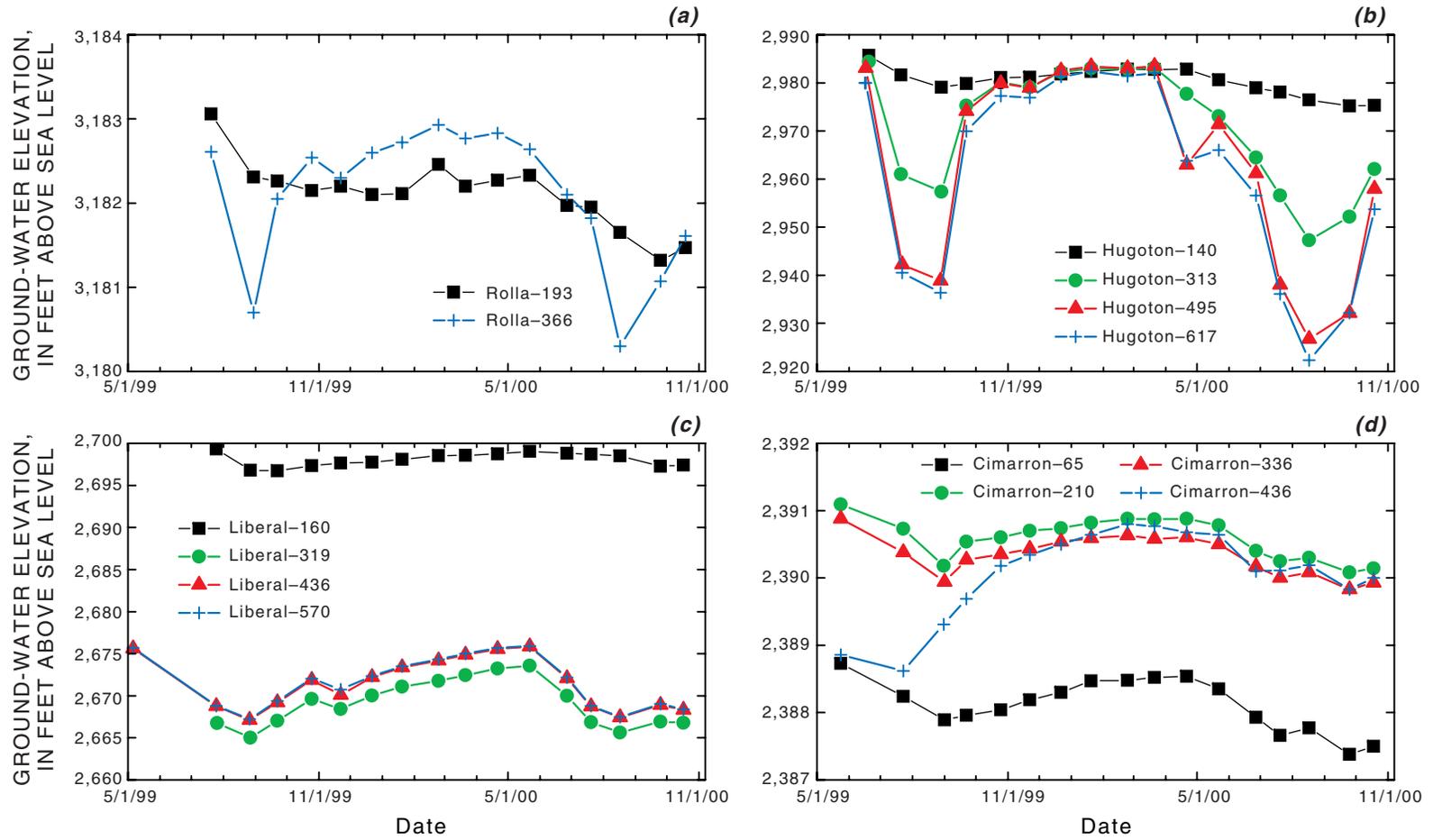


Figure 8. Ground-water elevations at the nested-well sites (a) Rolla, (b) Hugoton, (c) Liberal, and (d) Cimarron. Well Cimarron-436 was screened in sediments of Permian age. All other wells were screened in the central High Plains aquifer.

Cimarron River near the Cimarron site by Gutentag and others (1981) indicated that ground-water discharge from the aquifer contributed flow to the river at a rate of about 1.7 ft³/s per mile of stream channel. It is likely that the rate of ground-water discharge decreased since those measurements were taken because of water-level declines in the aquifer. Nevertheless, the upward hydraulic gradient at the Cimarron site and the observed perennial flow in the Cimarron River near the Cimarron site indicate that water in the central High Plains aquifer still discharged to the river in 1999.

Some hydraulic heads in the aquifer at the Cimarron site were lower than the heads in the underlying sediments of Permian age (fig. 8*d*). Thus, there was an upward gradient directed from the sediments of Permian age to the aquifer. Estimating the magnitude of the upward gradient and the amount of upward flow was hampered because water in the sediments of Permian age was more dense than freshwater in the aquifer. The density of the water in the sediments of Permian age was 1.012 grams per cubic centimeter. For comparison, the densities of freshwater and seawater are 1 and 1.023 grams per cubic centimeter, respectively. Although it is possible to calculate an equivalent freshwater head for the deep Cimarron well, that freshwater head could be used to calculate the hydraulic gradient between that and another well only if the two wells were screened at the same elevation (Reilly, 1993). Nevertheless, the uncorrected head data and chemical data (discussed in the following sections) indicate that there was diffusion or advective movement of mineralized water from the sediments of Permian age to the aquifer.

VERTICAL GRADIENTS IN WATER CHEMISTRY

Concentrations of tritium, major ions, nitrate, arsenic, and pesticides varied with depth in the central High Plains aquifer. Some of those chemical gradients were the result of chemical inputs from the land surface, upward leakage of mineralized water from the underlying sediments of Permian age, and recharge of mineralized water from the Arkansas River. This section presents the chemical data and discusses processes that could explain the observed vertical gradients in water chemistry.

Tritium

Determining the apparent age of ground water is important because it can be indicative of an aquifer's vulnerability to contamination from sources at the land surface. Aquifers that contain recently recharged water are more vulnerable to contamination originating at land surface than are aquifers containing no recently recharged water. Several methods are available for age-dating ground water, although the suitability of the methods differs depending on various factors including the recharge age of the water and the thickness of the unsaturated zone. Results of a tritium method of age-dating are discussed in this section. Tritium is a radioactive isotope of hydrogen that is present in some water molecules. Tritium in ground water of the central High Plains aquifer ultimately came from precipitation that recharged the aquifer. Because tritium is radioactive, with a half-life of 12.43 years, its concentration in water decreases over time due to radioactive decay. Before the onset of atmospheric testing of nuclear weapons in the early 1950's, the tritium content of precipitation in the study area was probably on the order of 8 TU (Thatcher, 1962). Therefore, ground water totally derived from precipitation that fell before the early 1950's would contain less than 0.5 TU in 1999. The tritium content of precipitation increased substantially after the onset of atmospheric nuclear weapons testing but has slowly decreased since its peak in the early 1960's. For example, the tritium content of precipitation at a measurement site in Albuquerque, New Mexico, the closest tritium measurement site to the study area, peaked at about 2,000 to 4,500 TU in 1963–64, whereas the tritium content in precipitation ranged from about 6 to 10 TU in 1991 (the most recent data) (International Atomic Energy Agency/World Meteorological Organization, 1998). Even with the variability in the tritium content of precipitation over time, ground water totally derived from precipitation that fell since the early 1950's would contain more than 0.5 TU in 1999.

At the time of sampling in 1999, all of the water samples collected from more than 30 feet below the water table contained less than 0.5 TU of tritium (table 6 and fig. 9), indicating that water was recharged by precipitation that fell before the early 1950's. In contrast, all but two of the water samples collected from less than 30 feet below the water table contained more than 0.5 TU (fig. 9), indicating that

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Sample date	Depth to water (feet below land surface)	Depth of screen midpoint below water table (feet)	Specific conductance ($\mu\text{S}/\text{cm}$)	pH, whole water, field (standard units)	Temperature ($^{\circ}\text{C}$)	Oxygen, dissolved (mg/L)
370434100405205	Cimarron River	09/01/99	--	--	1,044	8.04	--	--
Water-table well sites, central High Plains aquifer								
375855100484001	Recon-1	02/03/99	70	8	5,130	6.96	11.5	4.7
375734100452301	Recon-2	02/02/99	121	-4	1,635	7.00	12.1	6.5
374220100422501	Recon-3	02/04/99	161	13	1,001	7.19	11.7	8.1
365610101484301	Recon-4	02/05/99	273	1	632	7.69	16.7	8.3
363817101213101	Recon-5	02/17/99	279	8	619	7.73	17.9	--
Nested-well sites, central High Plains aquifer								
370402101394402	Rolla-193	08/30/99	179	4	459	7.70	22.7	8.4
370402101394401	Rolla-366	08/30/99	180	181	1,136	7.47	19.3	5.8
370130101180904	Hugoton-140	08/29/99	133	-3	704	7.65	23.8	--
370130101180903	Hugoton-313	08/29/99	154	154	602	7.50	19.2	5.9
370130101180902	Hugoton-495	08/28/99	172	318	560	7.66	20.6	5.6
370130101180901	Hugoton-617	08/28/99	175	437	578	7.64	20.6	6.0
370033100534204	Liberal-160	08/27/99	117	33	540	7.65	23.6	6.5
370033100534203	Liberal-319	08/27/99	149	165	513	7.72	18.5	3.5
370033100534202	Liberal-436	08/26/99	147	284	504	7.59	22.9	3.2
370033100534201	Liberal-570	08/26/99	147	418	583	7.47	20.8	1.7
370434100405204	Cimarron-65	09/01/99	56	-1	645	7.59	18.1	7.0
370434100405203	Cimarron-210	08/31/99	54	151	671	7.50	18.6	7.0
370434100405202	Cimarron-336	09/01/99	54	277	6,360	7.13	19.0	2.0
Sediments of Permian age								
370434100405201	Cimarron-436	08/31/99	55	361	23,200	7.15	20.0	0.5
		10/18/00	55	361	22,700	7.30	19.6	0.3

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Alkalinity, filtered, field (mg/L as CaCO_3)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)
370434100405205	Cimarron River	--	81.4	27.7	87.9	6.69	118	144
Water-table well sites, central High Plains aquifer								
375855100484001	Recon-1	290	486	260	525	17.2	246	2,642
375734100452301	Recon-2	340	145	69.6	81.6	8.89	101	163
374220100422501	Recon-3	240	113	17.0	73.5	3.95	44.3	80.0
365610101484301	Recon-4	142	36.3	30.7	47.5	6.07	29.1	73.1
363817101213101	Recon-5	168	44.2	31.5	26.5	6.79	16.9	89.0
Nested-well sites, central High Plains aquifer								
370402101394402	Rolla-193	174	42.8	6.52	42.5	4.21	10.8	23.5
370402101394401	Rolla-366	144	133	41.6	47.9	3.60	15.6	432
370130101180904	Hugoton-140	206	39.1	11.7	74.3	8.32	21.4	60.6
370130101180903	Hugoton-313	149	70.5	21.5	19.8	3.42	12.0	122
370130101180902	Hugoton-495	162	63.7	18.9	19.7	3.32	12.0	105
370130101180901	Hugoton-617	160	66.9	19.3	20.2	3.29	12.6	117
370033100534204	Liberal-160	208	38.6	34.6	17.9	3.49	20.0	21.4
370033100534203	Liberal-319	174	44.2	23.7	25.2	3.48	9.22	61.0
370033100534202	Liberal-436	162	41.8	22.5	26.5	3.78	9.79	59.5
370033100534201	Liberal-570	182	46.7	24.1	36.1	3.88	12.7	87.4
370434100405204	Cimarron-65	157	54.4	14.1	48.8	4.66	71.4	36.7
370434100405203	Cimarron-210	162	67.1	18.8	41.8	3.67	52.5	76.5
370434100405202	Cimarron-336	144	300	148	761	10.7	1,861	261
Sediments of Permian age								
370434100405201	Cimarron-436	88	776	431	3,836	17.7	7,615	1,269
		92	749	431	4,051	20.0	7,811	1,277

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Bromide, dissolved (mg/L as Br)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Ammonium, dissolved (mg/L as N)	Nitrite, dissolved (mg/L as N)	Ammonium plus organic nitrogen, dissolved (mg/L as N)
370434100405205	Cimarron River	0.13	0.76	24.8	0.02	0.01	0.26
Water-table well sites, central High Plains aquifer							
375855100484001	Recon-1	1.48	0.61	39.6	0.04	<0.01	0.18
375734100452301	Recon-2	0.25	0.69	46.8	<0.02	<0.01	0.65
374220100422501	Recon-3	0.26	0.28	24.5	<0.02	<0.01	0.15
365610101484301	Recon-4	0.27	1.8	23.5	<0.02	<0.01	<0.1
363817101213101	Recon-5	0.14	1.9	29.4	<0.02	<0.01	<0.1
Nested-well sites, central High Plains aquifer							
370402101394402	Rolla-193	0.07	0.18	29.4	0.25	0.13	0.21
370402101394401	Rolla-366	0.16	0.27	30.3	<0.02	<0.01	<0.1
370130101180904	Hugoton-140	0.13	0.49	34.1	1.07	0.04	0.88
370130101180903	Hugoton-313	0.14	0.33	31.8	<0.02	<0.01	<0.1
370130101180902	Hugoton-495	0.13	0.34	30.0	<0.02	<0.01	<0.1
370130101180901	Hugoton-617	0.13	0.34	30.5	<0.02	<0.01	<0.1
370033100534204	Liberal-160	0.10	3.5	54.3	<0.02	<0.01	<0.1
370033100534203	Liberal-319	0.11	0.84	31.4	<0.02	<0.01	<0.1
370033100534202	Liberal-436	0.11	0.55	28.7	<0.02	<0.01	<0.1
370033100534201	Liberal-570	0.09	0.57	27.4	<0.02	<0.01	<0.1
370434100405204	Cimarron-65	0.08	0.88	22.9	0.18	0.01	0.23
370434100405203	Cimarron-210	0.14	0.55	26.9	<0.02	<0.01	<0.1
370434100405202	Cimarron-336	0.42	0.47	26.9	<0.02	<0.01	<0.1
Sediments of Permian age							
370434100405201	Cimarron-436	0.26	0.26	38.4	<0.02	<0.01	<0.1
		1.36	0.25	36.1	0.05	<0.01	<0.1

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Nitrite plus nitrate, dissolved (mg/L as N)	Orthophosphate, dissolved (mg/L as P)	Phosphorus, dissolved (mg/L as P)	Organic carbon, dissolved (mg/L as C)	Solids, residue at 180°C , dissolved (mg/L)	Aluminum, dissolved ($\mu\text{g}/\text{L}$ as Al)
370434100405205	Cimarron River	0.79	0.04	0.058	--	642	<1
Water-table well sites, central High Plains aquifer							
375855100484001	Recon-1	8.28	0.03	0.023	--	4,916	--
375734100452301	Recon-2	54.4	0.02	0.009	--	1,058	--
374220100422501	Recon-3	22.0	0.02	0.007	--	642	--
365610101484301	Recon-4	3.38	0.02	0.013	--	379	--
363817101213101	Recon-5	3.80	<0.01	0.005	--	390	--
Nested-well sites, central High Plains aquifer							
370402101394402	Rolla-193	5.71	<0.01	0.009	--	290	1.2
370402101394401	Rolla-366	2.40	<0.01	0.004	0.5	862	1.2
370130101180904	Hugoton-140	2.24	<0.01	0.01	1.6	372	<1
370130101180903	Hugoton-313	2.56	<0.01	0.004	1.5	397	1.3
370130101180902	Hugoton-495	2.50	<0.01	<0.004	0.3	366	<1
370130101180901	Hugoton-617	2.30	<0.01	<0.004	0.4	381	<1
370033100534204	Liberal-160	1.90	<0.01	0.004	0.5	331	<1
370033100534203	Liberal-319	3.15	<0.01	0.008	0.4	311	1.3
370033100534202	Liberal-436	3.06	<0.01	0.009	0.4	309	<1
370033100534201	Liberal-570	2.36	<0.01	0.007	0.5	364	<1
370434100405204	Cimarron-65	2.06	<0.01	0.007	0.4	370	<1
370434100405203	Cimarron-210	3.06	<0.01	0.008	0.3	414	<1
370434100405202	Cimarron-336	2.30	<0.01	<0.004	0.3	4,030	<3
Sediments of Permian age							
370434100405201	Cimarron-436	0.39	<0.01	0.008	<0.1	15,430	<10
		0.32	0.01	0.006	--	15,430	<10

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued

[$\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g/L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Antimony, dissolved ($\mu\text{g/L}$ as Sb)	Arsenic, dissolved ($\mu\text{g/L}$ as As)	Barium, dissolved ($\mu\text{g/L}$ as Ba)	Beryllium, dissolved ($\mu\text{g/L}$ as Be)	Cadmium, dissolved ($\mu\text{g/L}$ as Cd)	Chromium, dissolved ($\mu\text{g/L}$ as Cr)	Cobalt, dissolved ($\mu\text{g/L}$ as Co)
370434100405205	Cimarron River	<1	1.5	103	<1	<1	<1	<1
Water-table well sites, central High Plains aquifer								
375855100484001	Recon-1	--	--	--	--	--	--	--
375734100452301	Recon-2	--	--	--	--	--	--	--
374220100422501	Recon-3	--	--	--	--	--	--	--
365610101484301	Recon-4	--	--	--	--	--	--	--
363817101213101	Recon-5	--	--	--	--	--	--	--
Nested-well sites, central High Plains aquifer								
370402101394402	Rolla-193	<1	2.3	78	<1	<1	<1	<1
370402101394401	Rolla-366	<1	1.8	15	<1	<1	1.8	<1
370130101180904	Hugoton-140	<1	3.7	38	<1	<1	2.2	<1
370130101180903	Hugoton-313	<1	2.0	31	<1	<1	2.3	<1
370130101180902	Hugoton-495	<1	1.7	30	<1	<1	2.4	<1
370130101180901	Hugoton-617	<1	1.6	29	<1	<1	1.9	<1
370033100534204	Liberal-160	<1	4.6	108	<1	<1	2.6	<1
370033100534203	Liberal-319	<1	1.7	53	<1	<1	3.2	<1
370033100534202	Liberal-436	<1	3.6	52	<1	<1	3.6	<1
370033100534201	Liberal-570	<1	2.6	39	<1	<1	1.8	<1
370434100405204	Cimarron-65	<1	<1.0	99	<1	<1	1	<1
370434100405203	Cimarron-210	<1	1.0	43	<1	<1	1.9	<1
370434100405202	Cimarron-336	<3	<1.0	48	<3	<3	<1	<3
Sediments of Permian age								
370434100405201	Cimarron-436	<10	12	32	<10	<10	<1	<10
		<10	9.4	27	<10	<10	8.3	2

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Copper, dissolved ($\mu\text{g}/\text{L}$ as Cu)	Iron, dissolved ($\mu\text{g}/\text{L}$ as Fe)	Lead, dissolved ($\mu\text{g}/\text{L}$ as Pb)	Manganese, dissolved ($\mu\text{g}/\text{L}$ as Mn)	Molybdenum, dissolved ($\mu\text{g}/\text{L}$ as Mo)	Nickel, dissolved ($\mu\text{g}/\text{L}$ as Ni)	Selenium, dissolved ($\mu\text{g}/\text{L}$ as Se)
370434100405205	Cimarron River	<1	<10	<1	26	9.2	2.6	3.6
Water-table well sites, central High Plains aquifer								
375855100484001	Recon-1	--	<30	--	<12	--	--	--
375734100452301	Recon-2	--	<10	--	<3	--	--	--
374220100422501	Recon-3	--	<10	--	<3	--	--	--
365610101484301	Recon-4	--	<10	--	<3	--	--	--
363817101213101	Recon-5	--	<10	--	8.0	--	--	--
Nested-well sites, central High Plains aquifer								
370402101394402	Rolla-193	<1	<10	<1	24	4.1	2.0	1.3
370402101394401	Rolla-366	1.4	<10	<1	<3	1.1	3.2	4.0
370130101180904	Hugoton-140	<1	<10	<1	6.7	12	1.2	3.5
370130101180903	Hugoton-313	<1	<10	<1	<3	1.8	1.9	3.2
370130101180902	Hugoton-495	<1	<10	<1	<3	1.8	1.4	4.2
370130101180901	Hugoton-617	<1	<10	<1	<3	1.8	1.5	3.9
370033100534204	Liberal-160	<1	<10	<1	<3	3.0	1.1	2.7
370033100534203	Liberal-319	<1	<10	<1	<3	3.7	<1	5.7
370033100534202	Liberal-436	<1	<10	<1	<3	4.3	<1	6.3
370033100534201	Liberal-570	<1	<10	<1	7.8	5.4	<1	6.4
370434100405204	Cimarron-65	<1	<10	<1	4.9	5.8	1.7	2.5
370434100405203	Cimarron-210	<1	<10	<1	<3	2.5	1.8	3.7
370434100405202	Cimarron-336	<3	<50	<3	130	3.4	8.2	4.0
Sediments of Permian age								
370434100405201	Cimarron-436	<10	<200	<10	111	11	21	<1
		5.1	<120	<10	68	11	7.0	<1

Table 6. Physical properties and concentrations of major ions, nutrients, trace elements, and tritium in water from the Cimarron River and sampled wells in the central High Plains aquifer and sediments of Permian age—Continued

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $^{\circ}\text{C}$, Celsius; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed or not applicable]

Station identification	Well name	Silver, dissolved ($\mu\text{g}/\text{L}$ as Ag)	Uranium, dissolved ($\mu\text{g}/\text{L}$ as U)	Zinc, dissolved ($\mu\text{g}/\text{L}$ as Zn)	Tritium (tritium units)
370434100405205	Cimarron River	<1	6.6	<1	0.9
Water-table well sites, central High Plains aquifer					
375855100484001	Recon-1	--	--	--	8.7
375734100452301	Recon-2	--	--	--	4.9
374220100422501	Recon-3	--	--	--	5.8
365610101484301	Recon-4	--	--	--	0.9
363817101213101	Recon-5	--	--	--	<0.3
Nested-well sites, central High Plains aquifer					
370402101394402	Rolla-193	<1	2.5	<1	0.3
370402101394401	Rolla-366	<1	7.4	1.1	<0.3
370130101180904	Hugoton-140	<1	6.3	2.5	12.3
370130101180903	Hugoton-313	<1	4.7	<1	<0.3
370130101180902	Hugoton-495	<1	4.7	1.1	<0.3
370130101180901	Hugoton-617	<1	4.5	2.0	<0.3
370033100534204	Liberal-160	<1	8.3	3.4	<0.3
370033100534203	Liberal-319	<1	6.8	1.7	<0.3
370033100534202	Liberal-436	<1	8.0	1.0	<0.3
370033100534201	Liberal-570	<1	9.6	3.2	<0.3
370434100405204	Cimarron-65	<1	5.2	1.1	4.4
370434100405203	Cimarron-210	<1	4.8	1.8	<0.3
370434100405202	Cimarron-336	<3	11.0	<3	<0.3
Sediments of Permian age					
370434100405201	Cimarron-436	<10	<10	<10	<0.3
		<10	8.4	<10	--

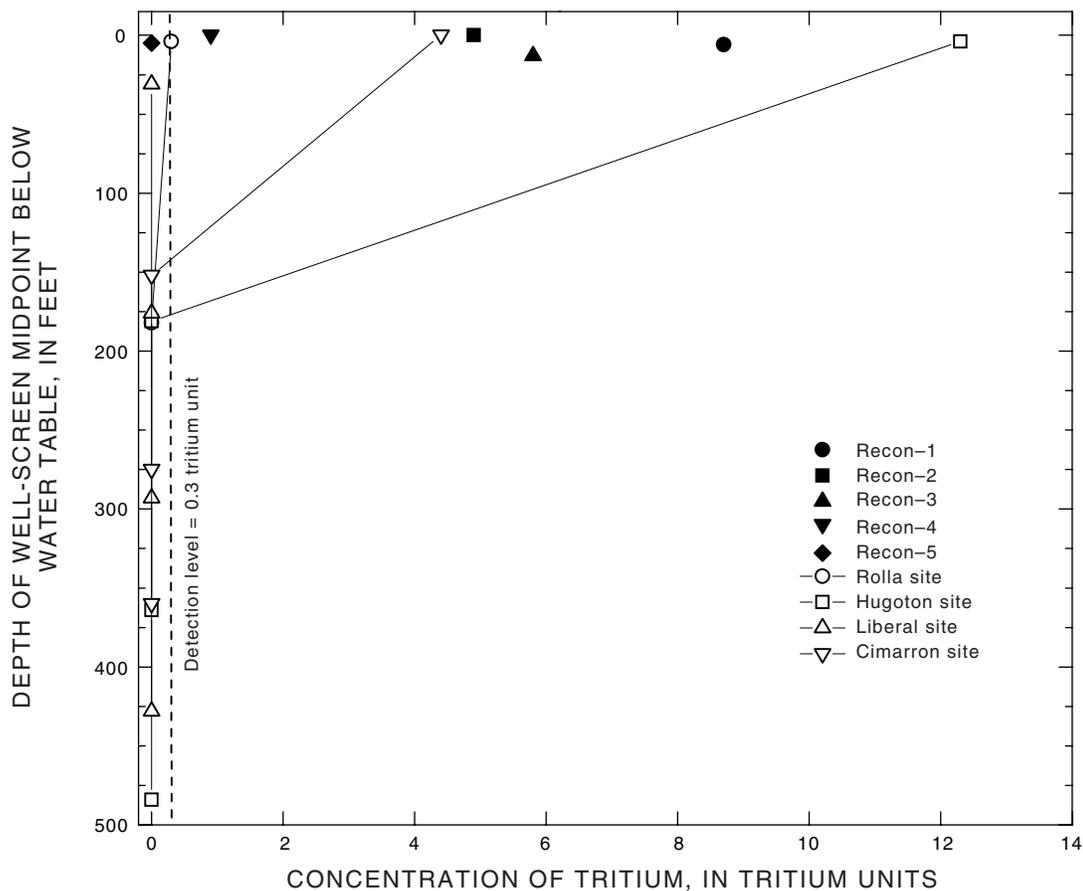


Figure 9. Relation between tritium concentrations and depth of the well-screen midpoint below the water table. Concentrations of tritium less than 0.3 tritium unit were set to zero.

those samples contained at least a portion of water recharged less than 50 years ago. The two water-table wells that produced water with less than 0.5 TU tritium had relatively large depths to water of 179 and 279 feet below land surface (Rolla-193 and Recon-5; table 6).

The tritium data indicate a vertical gradient in ground-water ages exists in the aquifer at the sampling sites. Most of the water at the water table was recharged less than 50 years ago, whereas all of the deep water was recharged more than 50 years ago. Better definition of the age gradient below the water table will require the use of other techniques and will be the subject of future investigations. Shallow ground water at most of the sampling sites was recharged since the onset of widespread irrigated agriculture in the 1950's and 1960's; therefore, that water could be susceptible to contamination from agricultural chemicals. The lack of recently recharged water at depth below the water table probably was the result of

various factors that limited the amount of recharge to the aquifer, including the relatively large depths to water (median depth of 147 feet below land surface at the time of sampling), the semiarid climate, and the presence of thick clay layers in some areas which isolate shallow from deep zones in the aquifer.

Water from the Cimarron River, which was collected during base-flow conditions in the late summer of 1999, contained 0.9 TU of tritium (table 6). In comparison, the tritium concentrations in water from the nearby Cimarron nested wells were 4.4 TU in the water-table well and less than 0.3 TU in the deeper wells. Those data indicate that ground water discharging to the river at that site was a mixture of relatively old (deep) water having little or no tritium and recently recharged (shallow) water. It is unlikely that the tritium content of Cimarron River water was substantially affected by isotopic exchange with water vapor in the atmosphere because that exchange process is slow relative to the residence time of most

river water (Michel and Schroeder, 1994). Thus, the tritium concentration in the river under base-flow conditions should have been controlled primarily by the tritium concentration in ground-water discharge.

Dissolved Oxygen and Organic Carbon

Several chemicals of environmental concern in the central High Plains aquifer may be used by naturally occurring microorganisms under anoxic conditions, including nitrate, arsenate, and sulfate. In the absence of dissolved oxygen, microbes may reduce dissolved nitrate, arsenate (the primary form of arsenic in oxygenated ground water), and sulfate to less oxidized forms (Chapelle, 1993). Microbial reduction of those chemicals is beneficial because it lowers their concentration in water by converting them into less soluble or less toxic forms. In oxygenated ground water, microbes may oxidize other chemicals of environmental concern in the aquifer, such as atrazine, to carbon dioxide (McMahon and others, 1992). The role of dissolved oxygen in microbial processes makes measuring its distribution in ground water important if the fate of potentially harmful chemicals is to be understood.

Dissolved oxygen is readily removed from ground water by microbes if suitable electron donors are available. Typically, those electron donors are DOC in ground water or solid organic carbon in the aquifer sediments. Concentrations of DOC in the aquifer were relatively small (table 6 and fig. 10a), ranging from 0.3 to 1.6 mg/L, with a median concentration of 0.4 mg/L. The single measured value of DOC in the sediments of Permian age was less than 0.1 mg/L. For comparison, Thurman (1985) reported a median DOC concentration of 0.7 mg/L for ground water from several other aquifers. Concentrations of solid organic carbon in the aquifer also were relatively small (median concentration was 0.06 weight percent, table 5). Sediments that are enriched in organic carbon typically contain more than about 0.2 percent organic carbon by weight (McMahon and others, 1999). Only two samples of clay contained more than 0.2 percent organic carbon by weight (table 5). The data indicate that the supply of DOC and solid organic carbon to support microbial oxygen reduction in the aquifer was limited; therefore, dissolved oxygen in the aquifer was likely to persist.

Dissolved oxygen was detected in water throughout the aquifer, as well as in water from the

sediments of Permian age (table 6 and fig. 10b). Concentrations of dissolved oxygen in the aquifer ranged from 1.7 to 8.4 mg/L. The general trend of decreasing dissolved oxygen concentrations with increasing depth below the water table at three of the four nested-well sites indicates that some oxygen reduction probably occurred along flow paths in the aquifer. However, the reduction rate was not fast enough to use all of the oxygen. The presence of dissolved oxygen throughout the aquifer indicates that chemicals like sulfate, nitrate, and arsenate would not be reduced by microbes to any significant extent; therefore, those chemicals would persist in the aquifer. The lack of a vertical gradient in dissolved oxygen concentrations at the Hugoton site probably was caused by vertical mixing of ground water during pumping of the nearby irrigation well that was screened in the lower one-half of the aquifer.

Major Ions

Calcium and bicarbonate were commonly the most abundant dissolved major ions in the aquifer (fig. 11), which reflects the dissolution of calcite (CaCO_3) in the aquifer. Calcite was not a major mineral phase in the aquifer in terms of abundance (table 5), but it is readily soluble in water compared to more abundant minerals in the aquifer like quartz and feldspars. Calcite dissolution apparently occurred during the movement of water through the unsaturated zone, or very shallow in the flow system, because water throughout the aquifer was in thermodynamic equilibrium with respect to calcite (fig. 12). The saturation index (SI) is defined as:

$$SI = \log(IAP/K_T)$$

where

IAP is the ion activity product of the components of the mineral phase (dissolved calcium and carbonate in the case of calcite), and K_T is the solid phase solubility equilibrium product at the specified water temperature. If $SI = 0$, water is at equilibrium with respect to the mineral phase; if $SI < 0$, water is undersaturated with respect to the mineral phase, and the mineral has the potential to dissolve; if $SI > 0$, water is supersaturated with respect to the mineral phase, and the mineral has the potential to precipitate.

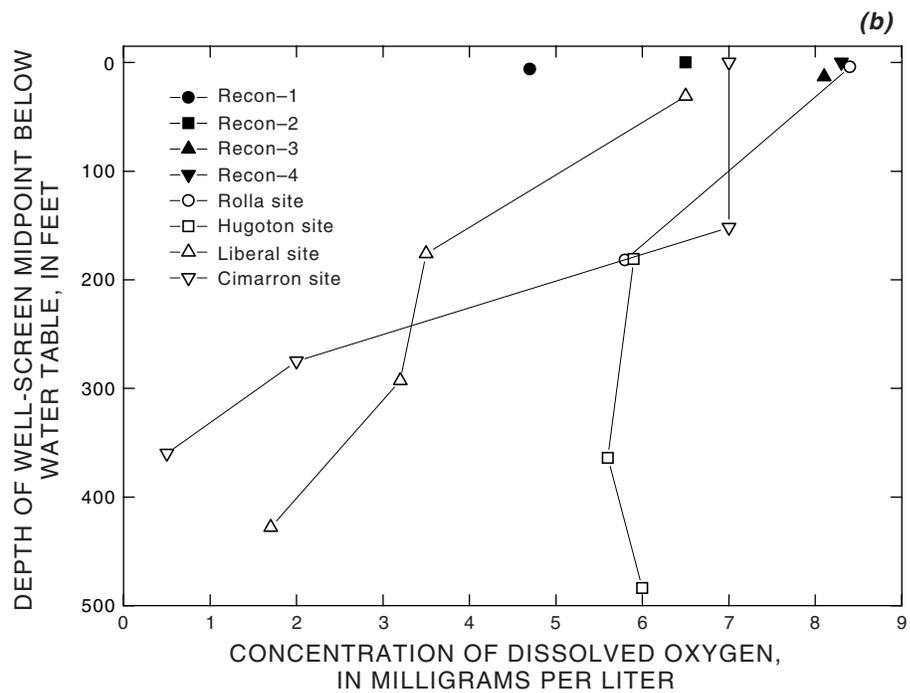
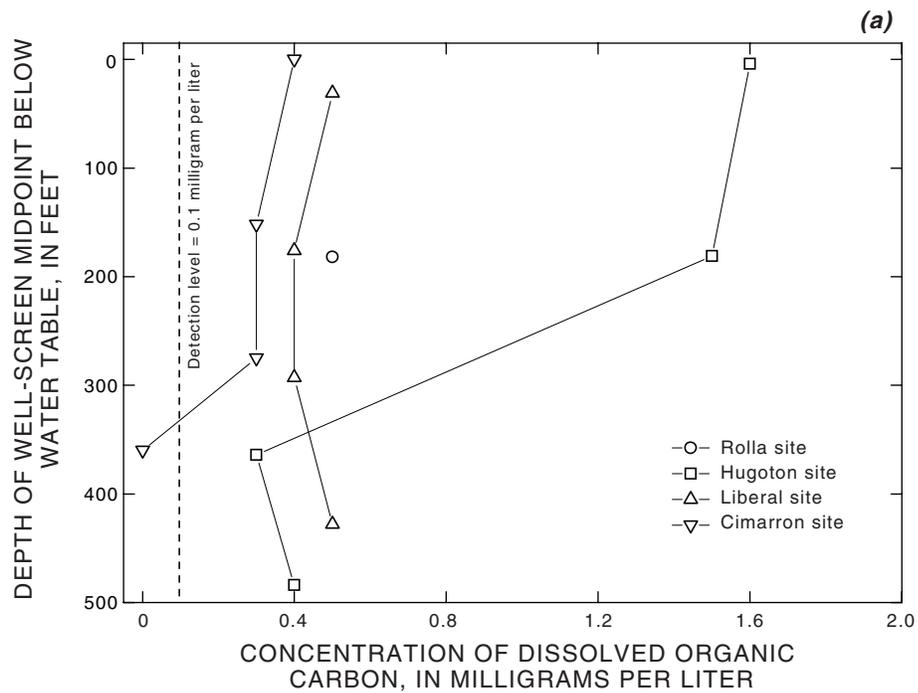


Figure 10. Relation between dissolved (a) organic carbon and (b) oxygen concentrations and depth of the well-screen midpoint below the water table. Concentrations of dissolved organic carbon less than 0.1 milligram per liter were set to zero.

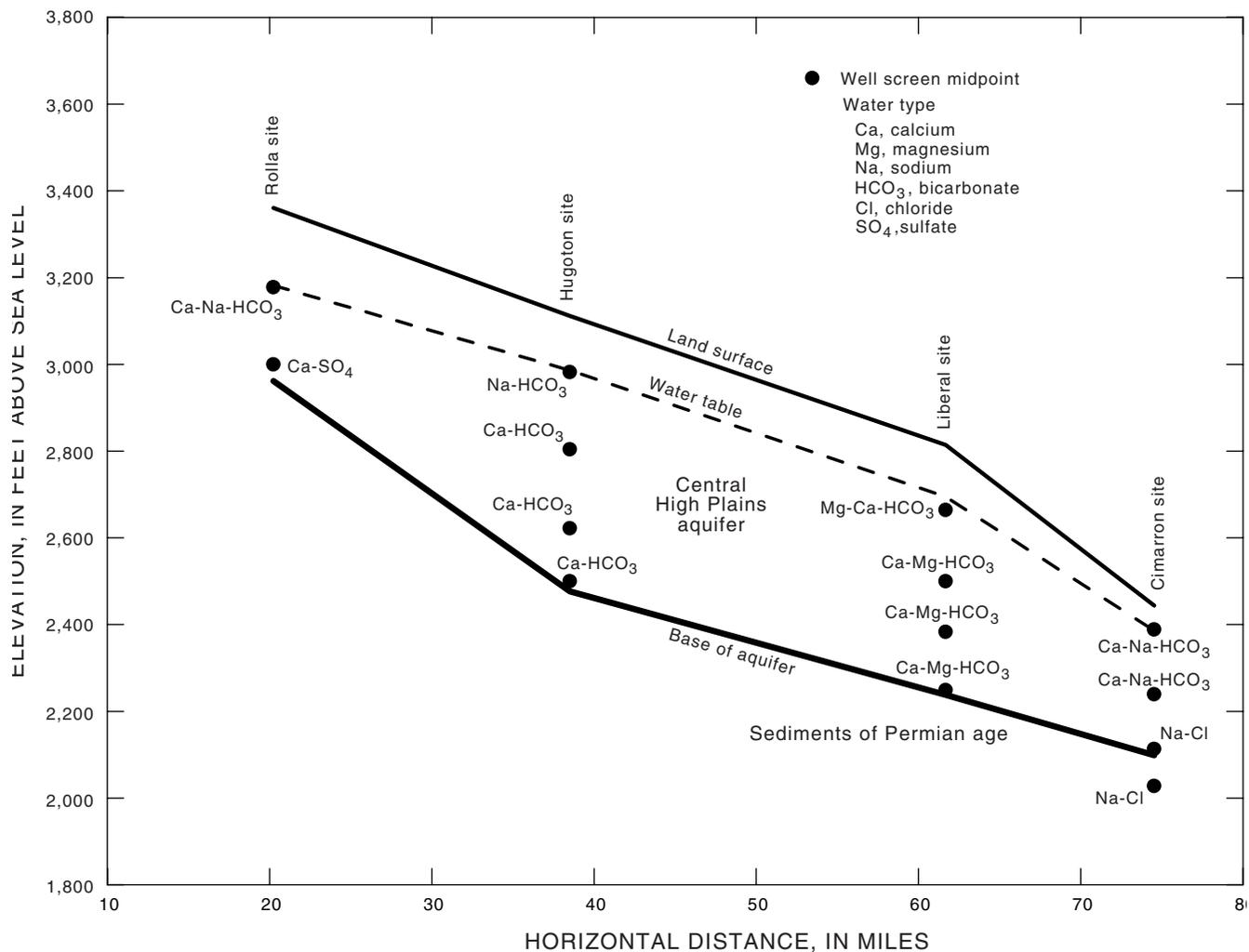


Figure 11. Horizontal and vertical distribution of water types at the nested-well sites. Water types were based on relative percentages of the major-ion concentrations expressed in milliequivalents per liter.

The SI values in figure 12 were calculated using the WATEQFP speciation model in the computer program NETPATH (Plummer and others, 1994). Because of the salinity of water from Cimarron-436, the computer program PHRQPITZ (Plummer and others, 1988), a computer program for calculating geochemical reactions in brines, was used to calculate the calcite SI for that sample. Calcite SI values within ± 0.25 of the zero value were assumed to indicate that water was in equilibrium with respect to calcite due to uncertainties in the water-temperature measurements. Caliche, a calcite-bearing deposit, was detected in the unsaturated zone at many of the drill sites and is one possible source of the dissolved calcium and bicarbonate. If the dissolved major ions in the aquifer were largely derived from the unsaturated zone or shallow

part of the flow system, then there should have been very little change in the concentrations of dissolved solids with depth in the aquifer. The concentrations of dissolved solids in water samples from the Hugoton and Liberal nested-well sites did exhibit very little variability with depth (fig. 13). However, that was not the case at the Rolla or Cimarron sites.

Concentrations of dissolved solids at the Rolla and Cimarron sites increased from 290 and 370 mg/L near the water table to 862 and 4,030 mg/L at the bottom of the aquifer (fig. 13 and table 6). In addition, the relative proportions of major ions at the top and bottom of the aquifer at those sites changed. At the Rolla site, the water type changed from calcium-sodium-bicarbonate at the top to calcium-sulfate at the bottom. At the Cimarron site, the water type changed

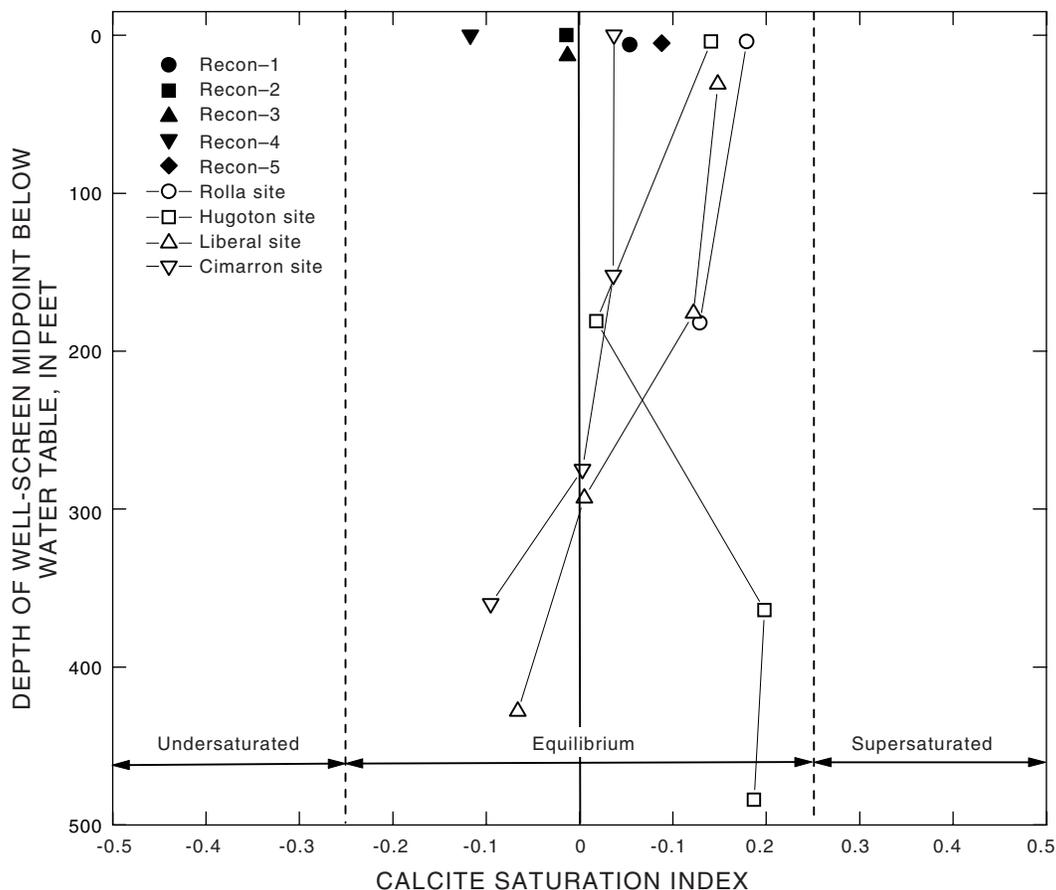


Figure 12. Relation between calcite saturation indices and depth of the well-screen midpoint below the water table. Water samples with saturation indices within ± 0.25 of the zero value were considered to be in equilibrium with respect to calcite due to uncertainties in the measurement of water temperatures.

from calcium-sodium-bicarbonate at the top to sodium-chloride at the bottom. The vertical changes in dissolved solids and water type at those sites could be the result of the dissolution of a different mineral assemblage at the bottom of the aquifer or from the upward movement of mineralized water from underlying geologic units. For example, the calcium-sulfate and sodium-chloride waters at those sites could have been derived from the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and halite (NaCl). Neither of those minerals was detected in sediments at the bottom of the aquifer using X-ray diffraction analysis (table 5); however, it is possible that small amounts of gypsum in reworked sediments of Permian age could exist at the base of the aquifer (Smith, 1940). It is unlikely that small amounts of halite, which is very soluble, would persist in the aquifer. Therefore, the change in dissolved solids and water types with depth at those sites probably resulted from a combination of the dissolution of reworked Permian sediments near the

base of the aquifer and the upward movement of mineralized water from sediments underlying the central High Plains aquifer.

The central High Plains aquifer at the Rolla site was underlain by sediments of Permian age younger than the Cedar Hills Sandstone (table 1), on the basis of the elevation of the aquifer base (table 2) and the elevations of the tops of the bedrock units underlying the aquifer near that site (Macfarlane and others, 1993). It was beyond the scope of this project to determine which of those Permian units were actually present at the Rolla site; however, several of them contain gypsum and anhydrite (Day Creek Dolomite, Dog Creek Formation, Blaine Formation, Flowerpot Shale) and halite (Blaine Formation, Flowerpot Shale) (Gutentag and others, 1981; Macfarlane and others, 1993). The Day Creek Dolomite in Morton County is reported to contain elevated concentrations of dissolved calcium and sulfate (Gutentag and others, 1981). The calcium-sulfate-bearing mineral phases

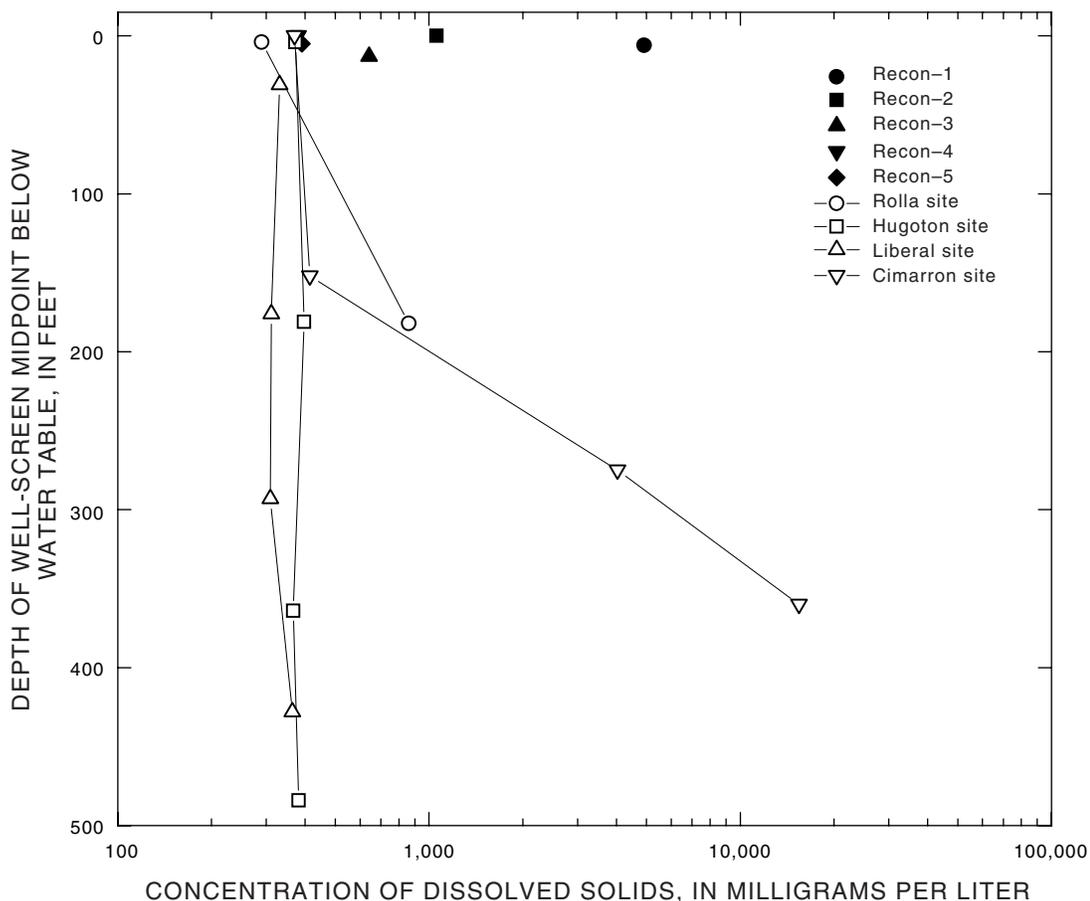


Figure 13. Relation between concentrations of dissolved solids and depth of the well-screen midpoint below the water table.

(and possibly water) in sediments of Permian age at the Rolla site are possible sources of the elevated concentrations of dissolved calcium and sulfate at the base of the aquifer. Water-level data for the sediments of Permian age were not available in the vicinity of the Rolla nested-well site; therefore, the hydraulic gradient across the Permian/High Plains-aquifer contact was not known. However, water-level data from the Rolla nested wells indicate that water levels at the base of the aquifer declined during the irrigation season (fig. 8a), which might have induced the upward movement of water from the sediments of Permian age to the aquifer.

At the Cimarron site, water-quality data from the well screened in sediments of Permian age indicate the presence of a sodium-chloride water in those sediments (table 6). Furthermore, the water-level data indicate that the hydraulic gradient at that site was directed upward from the sediments of Permian age to the aquifer during at least part of the measurement period

(fig. 8d). Thus, the chemical and water-level data demonstrate that the sodium-chloride water at the base of the aquifer could have come from the underlying sediments of Permian age.

Bromide/chloride mass ratios are useful for understanding the origin of saline waters (Whittemore, 1995). Bromide/chloride mass ratios were plotted for water from the central High Plains aquifer, water from well Cimarron-436 (screened in sediments of Permian age), halite-dissolution brines in sediments of Permian age in south-central Kansas (Whittemore, 1993), and oil brines in southwestern Kansas (Whittemore, 1984) to further aid in the identification of possible sources of salinity in wells Cimarron-336 and Cimarron-436 (fig. 14). All but one of the water samples from the aquifer plotted in the mixing zone defined by freshwater and halite-dissolution brine, thus indicating that water from well Cimarron-336 was derived from the mixing of freshwater and halite-dissolution brine from the Permian section. Calculations indicate that mixing

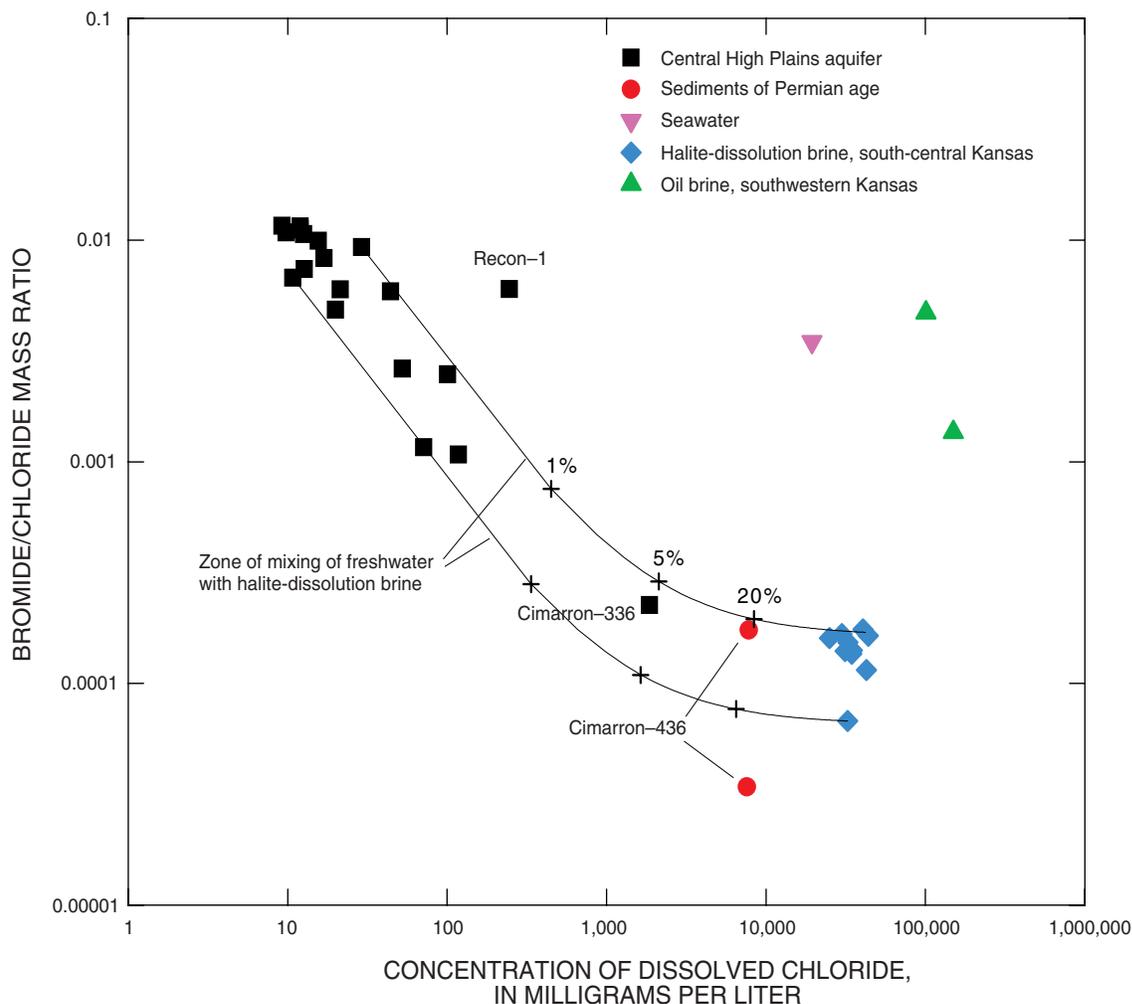


Figure 14. Relation between bromide/chloride mass ratios and concentrations of dissolved chloride in water samples from the central High Plains aquifer and sediments of Permian age. For comparison, bromide/chloride mass ratios were plotted for halite-dissolution brines in sediments of Permian age from south-central Kansas (Whittemore, 1993), seawater, and oil brines in southwestern Kansas (Whittemore, 1984). The solid lines define a zone of mixing of freshwater in the aquifer and halite-dissolution brine. The percentages refer to the amount of halite-dissolution brine in the mixture.

of about 5 percent halite-dissolution brine with freshwater would produce water with the chloride concentration and bromide/chloride ratio measured in water from well Cimarron-336. Whittemore (1995) and Mehta and others (2000) also concluded that upward movement of halite-dissolution brine was an important mechanism for salinization of water in the High Plains aquifer of Kansas, Oklahoma, and Texas. Whittemore (1984) proposed that dissolution of halite beds in the Lower Permian Blaine Formation was the source of sodium chloride water in Seward County, Kansas, the location of the Cimarron nested-well site.

The bromide/chloride ratio measured in water collected from Cimarron-436 in August 1999 plotted below the zone of mixing of freshwater and halite-

dissolution brine shown in figure 14. However, Cimarron-436 was resampled in October 2000 to check that earlier measurement. The bromide/chloride ratio measured in water collected from Cimarron-436 in October 2000 plotted within the mixing zone. Calculations indicate that mixing of about 20 percent halite-dissolution brine with freshwater would produce water with the chloride concentration and bromide/chloride ratio measured in water collected from well Cimarron-436 in October 2000.

Calcium-sulfate or sodium-chloride waters were not detected at the base of the aquifer at the Hugoton or Liberal nested-well sites, even though sediments of Permian age underlie both sites (fig. 3) and well pumping lowered water levels in the deeper part of the

aquifer (figs. 8b and 8c), increasing the potential for upward movement of water. Those findings indicate that sediments at the top of the Permian section at those sites probably had small hydraulic conductivities, which limited the upward movement of mineralized water. The sample of sediment of Permian age retrieved from the Liberal borehole consisted of dense red clay (table 4), which likely did have a small hydraulic conductivity. Another possibility is that the hydraulic gradient between the aquifer and sediments of Permian age was horizontal or directed downward at the Hugoton and Liberal sites.

Sediments of Permian age were not the only source of mineralized water in the aquifer. The water sample from well Recon-1 also had a large concentration of dissolved solids, with the dominant ions being calcium-sodium-sulfate. However, the bromide/chloride ratio in water from Recon-1 lies above the zone of mixing of freshwater and halite-dissolution brine shown in figure 14, indicating that halite-dissolution brine was not the source of mineralized water in Recon-1. Recon-1 was screened at the water table and was located about 2.5 miles north of the Arkansas River, which contains large concentrations of calcium-sodium-sulfate water (Whittemore, 2000). Whittemore proposed that the source of dissolved solids in Arkansas River water was the dissolution of minerals in marine shales in southeastern Colorado by irrigation water. In fact, the bromide/chloride ratio in water from Recon-1 is intermediate in value to the ratios for freshwater and seawater (fig. 14). Leakage of Arkansas River water into the underlying central High Plains aquifer has occurred since the 1970's (Whittemore, 2000). The similarity in chemical compositions between water from Recon-1 and the Arkansas River, their proximity to each other, and the presence of a hydraulic gradient directed from the river toward the aquifer indicate that the Arkansas River is the source of the mineralized water in well Recon-1. Whittemore (2000) also concluded that the Arkansas River is a source of mineralized water in the central High Plains aquifer in the study area. In summary, the data presented in this section indicate that there are chemically distinct sources of mineralized water above and below the aquifer that produced vertical gradients in dissolved solids and water types in the aquifer.

Nitrate

Nitrogen occurs naturally in relatively small concentrations in rocks, soils, organic material, and the water that comes in contact with them (Holloway and Dahlgren, 1999). It also occurs in relatively large concentrations in animal manure and fertilizers and in treated sewage effluent from municipalities. Nitrate, the most commonly occurring form of nitrogen in ground water, is of environmental concern because its discharge to surface water can support eutrophication. Nitrate is a health concern because ingestion of large concentrations of nitrate in drinking water by infants can cause low levels of oxygen in the blood (Fan and Steinberg, 1996). For this reason, the USEPA established an MCL of 10 mg/L as N in drinking water (U.S. Environmental Protection Agency, 2001a). Other adverse health effects from the ingestion of nitrate might include spontaneous abortion among some women (Centers for Disease Control and Prevention, 1996) and increased risk of non-Hodgkins lymphoma (Ward and others, 1996).

Concentrations of dissolved nitrate in water from the aquifer ranged from 1.90 to 54.4 mg/L as N, and the water samples from the sediments of Permian age contained from 0.32 to 0.39 mg/L as N (table 6 and fig. 15). Only 2 of the 20 samples had nitrate concentrations greater than the MCL. The median concentration of nitrate in the 10 samples from the aquifer that contained no measurable tritium was 2.45 mg/L as N. That nitrate concentration might be representative of the background nitrate concentration in the aquifer in the study area because ground water represented by those samples was recharged before the onset of modern (post-1950's) anthropogenic activity in the study area.

The three largest nitrate concentrations occurred in water samples that were collected at the water table beneath irrigated fields. Those samples also contained pesticides, indicating that the nitrate probably was derived from agricultural activities. In contrast to those shallow samples, water samples collected from farther below the water table generally contained less nitrate and no detectable tritium. McMahon and others (2000) concluded that concentrations of dissolved nitrate in recently recharged water were significantly larger than the concentrations in older water in the aquifer, on the basis of 123 analyses of ground water collected in 1999. In addition, they concluded that the smaller nitrate concentrations in older water were not

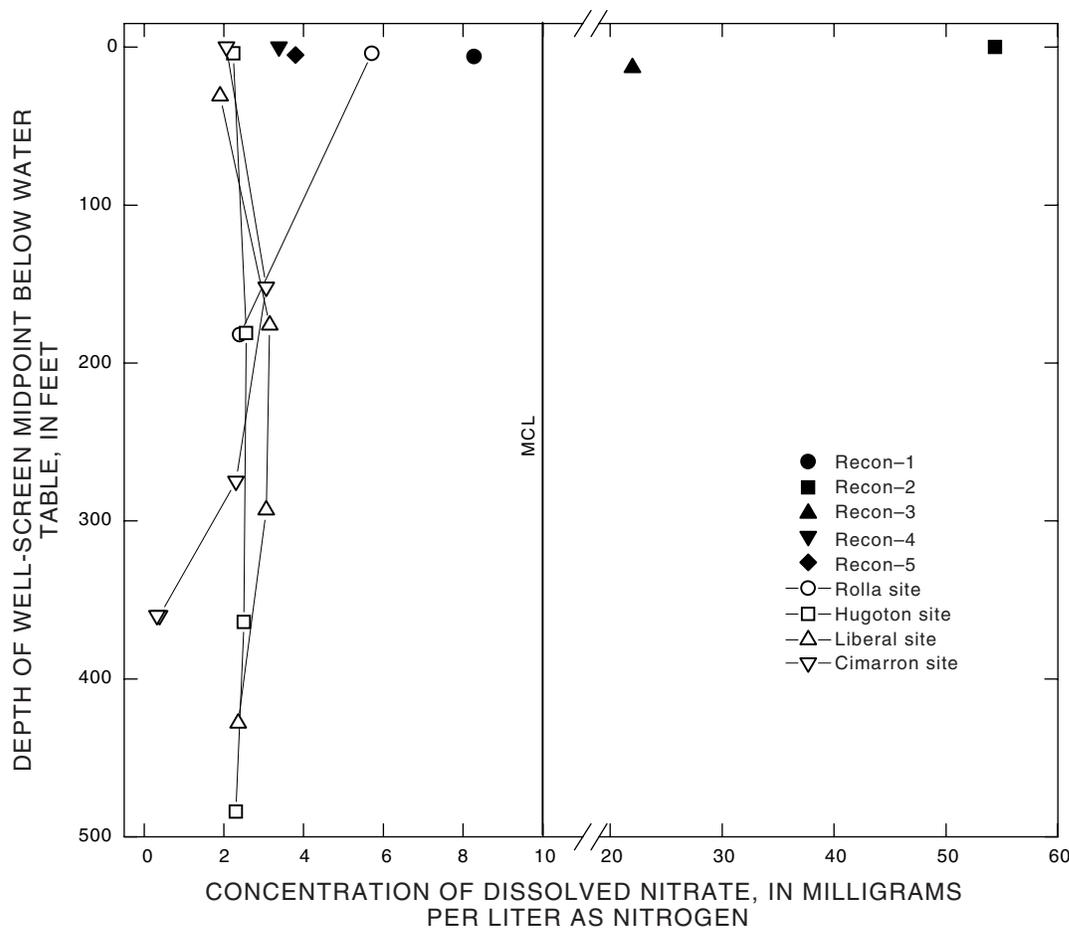


Figure 15. Relation between concentrations of dissolved nitrate and depth of the well-screen midpoint below the water table. MCL refers to the maximum contaminant level permitted in drinking water, as established by the U.S. Environmental Protection Agency (2001a).

the result of extensive denitrifying activity at depth in the aquifer because of the generally oxidizing conditions present in the aquifer. The implications of the findings from this study and that of McMahon and others (2000) are that (a) anthropogenic activity in the study area during the last 50 years has resulted in an increase in nitrate concentrations in the aquifer and (b) nitrate in the aquifer is likely to persist because geochemical conditions in the aquifer are not conducive to extensive denitrification, which would substantially decrease nitrate concentrations.

Not all of the water samples collected at the water table near irrigated fields contained elevated nitrate concentrations. Samples from wells Recon-4, Recon-5, and Hugoton-140 contained from 2.20 to 3.80 mg/L as N of nitrate, even though all three wells

were screened at the water table below irrigated fields. Two of the wells, Recon-4 and Recon-5, had depths to water greater than 250 feet and produced water that contained little or no tritium; therefore, those samples may have predated significant agricultural activity in the study area. It is unclear why water from Hugoton-140 only contained 2.20 mg/L as N of nitrate, given that the depth to water was only 133 feet and the water contained 12.3 TU of tritium. One possibility is that the amount of nitrogen applied to cropland at the Hugoton-140 site was much less, or was not applied until more recently, than the nitrogen applied at the three irrigated sites having larger nitrate concentrations at the water table. Records of nitrogen applications at those sites are needed to evaluate that possibility.

Arsenic

Arsenic occurs naturally in rocks, soils, and the water that comes in contact with them. It also occurs in anthropogenic products such as wood preservatives and herbicides. Long-term exposure to small concentrations of arsenic in drinking water can lead to skin, bladder, lung, and prostate cancer. Other effects of ingesting arsenic at low levels include cardiovascular disease, diabetes, and anemia, as well as reproductive and developmental, immunological, and neurological effects. The U.S. Environmental Protection Agency may lower the MCL for arsenic from 50 to 10 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2001b).

None of the water samples collected from the central High Plains aquifer exceeded the proposed MCL of 10 $\mu\text{g/L}$ for arsenic (table 6). A water sample collected from sediments of Permian age contained

12 $\mu\text{g/L}$ arsenic, but the elevated dissolved-solids concentration of that water made it unsuitable for human consumption anyway. Based on the hydraulic-head and arsenic data (figs. 8d and 16), water relatively enriched in arsenic had the potential to move upward from the sediments of Permian age to the aquifer in the area of the Cimarron nested-well site. However, the arsenic concentration in water from Cimarron-336 (less than 1 $\mu\text{g/L}$), the well screened just above the High Plains/Permian contact, did not indicate that water with elevated arsenic concentrations was entering the aquifer. At least two mechanisms could attenuate arsenic concentrations in water from the sediments of Permian age—dilution and adsorption. The median arsenic concentration in water from the aquifer (1.8 $\mu\text{g/L}$) was smaller than the concentration in water from the sediments of Permian age; therefore, mixing

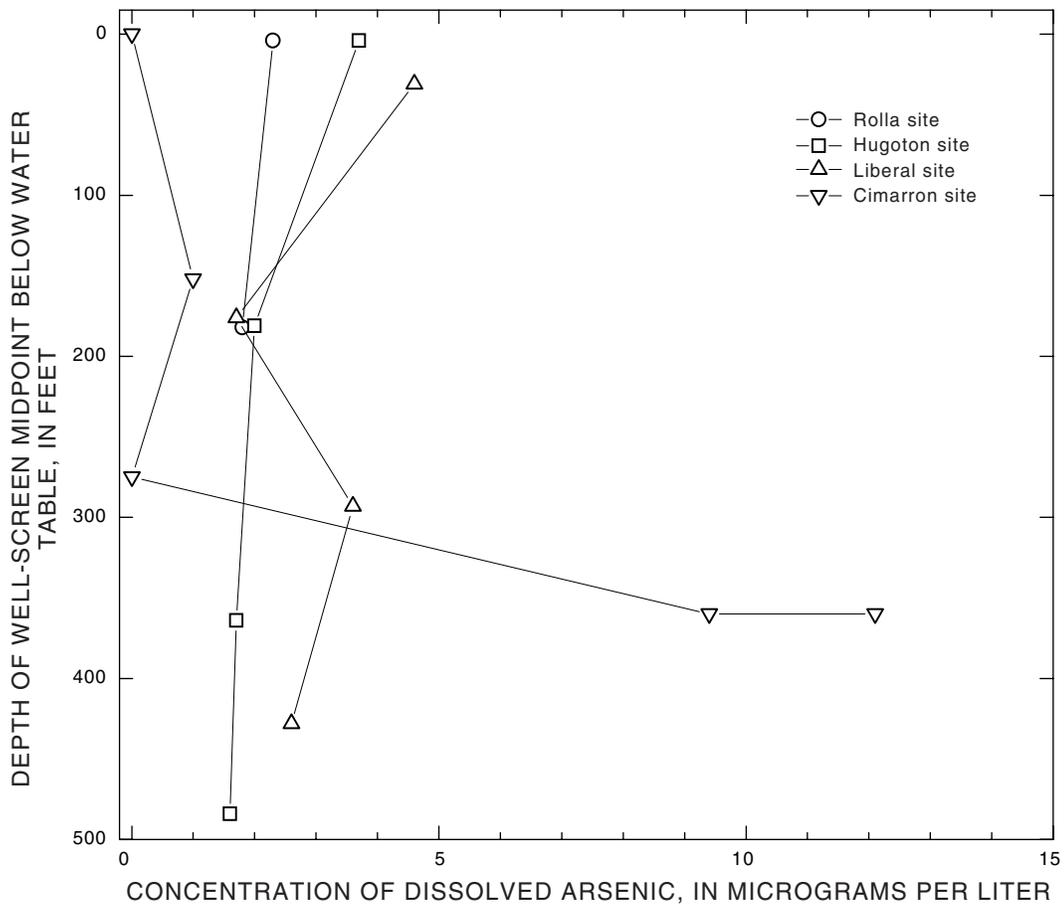


Figure 16. Relation between concentrations of dissolved arsenic and depth of the well-screen midpoint below the water table.

of those waters would reduce the arsenic concentration in the upwelling water. Interestingly, the arsenic concentration in Cimarron-336 was smaller than the median concentration in the aquifer, indicating that dilution was not the only mechanism attenuating arsenic concentrations in the upwelling water. Adsorption of arsenate in oxygenated water onto ferric iron- and manganese-oxide grain coatings is an important mechanism in some hydrologic settings (Welch and Lico, 1998) and may be responsible for further reducing the concentration of arsenic in water entering the aquifer from underlying sediments. Other trace elements that had relatively elevated concentrations in water from the sediments of Permian age included

chromium, copper, manganese, molybdenum, and nickel (table 6).

Pesticides

Of the 53 compounds analyzed for in the water samples (table 7), 3 pesticides (atrazine, metolachlor, and simazine) and 5 pesticide degradation products (alachlor ethanesulfonic acid, alachlor oxanilic acid, deethylatrazine, metolachlor ethanesulfonic acid, and metolachlor oxanilic acid) were detected in samples from six water-table wells (table 8). Five of the six wells were adjacent to irrigated fields. The frequency of detection of the compounds that were measured in all samples was, in order of decreasing frequency;

Table 7. Pesticides and pesticide degradation products analyzed in water from sampled wells in the central High Plains aquifer and sediments of Permian age

[*, only analyzed in water samples from Recon wells; µg/L, micrograms per liter]

Constituent	Analytical method reporting limit (µg/L)	Constituent	Analytical method reporting limit (µg/L)
2,6-diethylaniline	0.003	Acetochlor	0.002
Acetochlor ethanesulfonic acid*	0.050	Acetochlor oxanilic acid*	0.050
Alachlor	0.002	Alachlor ethanesulfonic acid*	0.050
Alachlor oxanilic acid*	0.050	Atrazine	0.001
Azinphos-methyl	0.001	Benfluralin	0.002
Butylate	0.002	Carbaryl	0.003
Carbofuran	0.003	Chlorpyrifos	0.004
Cyanazine	0.004	DCEPA	0.002
Deethylatrazine	0.002	Diazinon	0.002
Dieldrin	0.001	Disulfoton	0.017
EPTC	0.002	Ethalfuralin	0.004
Ethoprophos	0.003	Fonofos	0.003
Lindane	0.004	Linuron	0.002
Malathion	0.005	Metolachlor	0.002
Metolachlor ethanesulfonic acid*	0.050	Metolachlor oxanilic acid*	0.050
Metribuzin	0.004	Molinate	0.004
Napropamide	0.003	Parathion	0.004
Parathion-methyl	0.006	Pebulate	0.004
Pendimethalin	0.004	Phorate	0.002
Prometon	0.018	Propachlor	0.007
Propanil	0.004	Propargite	0.013
Propyzamide	0.003	Simazine	0.005
Tebuthiuron	0.010	Terbacil	0.007
Terbufos	0.013	Thiobencarb	0.002
Triallate	0.001	Trifluralin	0.002
alpha-HCH	0.002	cis-Permethrin	0.005
p,p'-DDE	0.006		

Table 8. Pesticide usage in the study area and concentrations of pesticides and pesticide degradation products detected in water from sampled wells in the central High Plains aquifer and sediments of Permian age

[µg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; E, estimated concentration; <, less than indicated concentration; --, not analyzed or not applicable]

Station identification	Well name	Sample date	Depth to water (feet below land surface)	Depth of screen midpoint below water table (feet)	Alachlor, dissolved (µg/L)	Alachlor ESA, dissolved (µg/L)	Alachlor OA, dissolved (µg/L)
Pesticide usage, ranked according to pounds of active ingredient applied in the study area ¹		--	--	--	4	--	--
Water-table well sites, central High Plains aquifer							
375855100484001	Recon-1	02/03/99	70	8	<0.002	0.44	<0.05
375734100452301	Recon-2	02/02/99	121	-4	<0.002	<0.05	<0.05
374220100422501	Recon-3	02/04/99	161	13	<0.002	1.5	0.08
365610101484301	Recon-4	02/05/99	273	1	<0.002	0.12	<0.05
363817101213101	Recon-5	02/17/99	279	8	<0.002	<0.05	<0.05
Nested-well sites, central High Plains aquifer							
370402101394402	Rolla-193	08/30/99	179	4	<0.002	--	--
370402101394401	Rolla-366	08/30/99	180	181	<0.002	--	--
370130101180904	Hugoton-140	08/29/99	133	-3	<0.002	--	--
370130101180903	Hugoton-313	08/29/99	154	154	<0.002	--	--
370130101180902	Hugoton-495	08/28/99	172	318	<0.002	--	--
370130101180901	Hugoton-617	08/28/99	175	437	<0.002	--	--
370033100534204	Liberal-160	08/27/99	117	33	<0.002	--	--
370033100534203	Liberal-319	08/27/00	149	165	<0.002	--	--
370033100534202	Liberal-436	08/26/99	147	284	<0.002	--	--
370033100534201	Liberal-570	08/26/99	147	418	<0.002	--	--
370434100405204	Cimarron-65	09/01/99	56	-1	<0.002	--	--
370434100405203	Cimarron-210	08/31/99	54	151	<0.002	--	--
370434100405202	Cimarron-336	09/01/99	54	277	<0.002	--	--
Sediments of Permian age							
370434100405201	Cimarron-436	08/31/99	55	361	<0.002	--	--

Table 8. Pesticide usage in the study area and concentrations of pesticides and pesticide degradation products detected in water from sampled wells in the central High Plains aquifer and sediments of Permian age—Continued

[µg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; E, estimated concentration; <, less than indicated concentration; --, not analyzed or not applicable]

Station identification	Well name	Atrazine, dissolved (µg/L)	Deethylatrazine, dissolved (µg/L)	Metolachlor, dissolved (µg/L)	Metolachlor ESA, dissolved (µg/L)	Metolachlor OA, dissolved (µg/L)	Simazine, dissolved (µg/L)
Pesticide usage, ranked according to pounds of active ingredient applied in the study area ¹		1	--	3	--	--	67
Water-table well sites, central High Plains aquifer							
375855100484001	Recon-1	0.006	² 0.014 E	<0.002	<0.05	<0.05	<0.005
375734100452301	Recon-2	5.0	1.7 E	0.096	2.8	1.2	0.038
374220100422501	Recon-3	1.2	0.60 E	<0.002	<0.05	<0.05	0.029
365610101484301	Recon-4	0.40	0.12 E	<0.002	<0.05	<0.05	<0.005
363817101213101	Recon-5	<0.001	<0.002	<0.002	<0.05	<0.05	<0.005
Nested-well sites, central High Plains aquifer							
370402101394402	Rolla-193	0.007	0.002 E	<0.002	--	--	<0.005
370402101394401	Rolla-366	<0.001	<0.002	<0.002	--	--	<0.005
370130101180904	Hugoton-140	0.072	0.009 E	<0.002	--	--	<0.005
370130101180903	Hugoton-313	<0.001	<0.002	<0.002	--	--	<0.005
370130101180902	Hugoton-495	<0.001	<0.002	<0.002	--	--	<0.005
370130101180901	Hugoton-617	<0.001	<0.002	<0.002	--	--	<0.005
370033100534204	Liberal-160	<0.001	<0.002	<0.002	--	--	<0.005
370033100534203	Liberal-319	<0.001	<0.002	<0.002	--	--	<0.005
370033100534202	Liberal-436	<0.001	<0.002	<0.002	--	--	<0.005
370033100534201	Liberal-570	<0.001	<0.002	<0.002	--	--	<0.005
370434100405204	Cimarron-65	<0.001	<0.002	<0.002	--	--	<0.005
370434100405203	Cimarron-210	<0.001	<0.002	<0.002	--	--	<0.005
370434100405202	Cimarron-336	<0.001	<0.002	<0.002	--	--	<0.005
Sediments of Permian age							
370434100405201	Cimarron-436	<0.001	<0.002	<0.002	--	--	<0.005

¹Data from U.S. Department of Agriculture, 1999.²Concentrations of deethylatrazine are estimated because of their poor recoveries from the water samples (see text).

atrazine = deethylatrazine > simazine > metolachlor. The median concentration for the compounds that were detected was 0.12 µg/L. The reported concentrations of deethylatrazine probably underestimated the actual concentrations because recoveries of deethylatrazine in water samples spiked with known concentrations of deethylatrazine only averaged 59 percent. Recoveries for the other spiked compounds were 106 percent for simazine, 89 percent for atrazine, 86 percent for alachlor, and 84 percent for metolachlor. Only the water sample from Recon-2 contained a pesticide concentration (atrazine at 5.0 µg/L) that exceeded an MCL (3 µg/L for atrazine) (U.S. Environmental Protection Agency, 2001a). The monitoring wells are not water-supply wells, but the aquifer is an important source of water to domestic and public-supply wells in the central High Plains.

The pesticide data indicate that the degradation products are an important component of the pesticide mass balance in the aquifer. For example, 12 of the 21 detections were of pesticide degradation products. The mass ratio of parent compound/degradation product ranged from 0 to 0.024 for alachlor and metolachlor, indicating that the mass of degradates far outweighed the masses of alachlor and metolachlor. The atrazine/deethylatrazine ratio was greater than 1, but that ratio probably was affected by the relatively poor recovery of deethylatrazine from the water samples compared with atrazine. These results indicate that measurement of pesticide degradation products is necessary in order to accurately assess the effects of pesticides on water quality in the aquifer. Similar conclusions were reached in other studies of pesticide occurrences in ground water in the Midwestern United States (Kolpin and others, 1996; Kalkhoff and others, 1998).

Application of synthetic organic pesticides to cropland in the United States largely began after World War II (Barbash and Resek, 1996). Because of the relatively recent introduction of pesticides to the environment, pesticide detections can be used as an indicator of ground water that contains at least a component of recently recharged water. The top five pesticides used in the study area, in terms of pounds of active ingredient applied and listed in order of decreasing usage, are atrazine > 2,4-D > metolachlor > alachlor > butylate (U.S. Department of Agriculture, 1999). The list of pesticides analyzed for in this study includes all of the top five pesticides used in the study area except 2,4-D (table 7). Three of the top five pesticides used in the study area, or their degradation products, were detected in the water samples (table 8).

Pesticides, or their degradation products, were only detected in water samples collected from wells screened near the water table (fig. 17), similar to the distribution of tritium (fig. 9), providing additional evidence that recently recharged water probably did not penetrate deeply into the aquifer at the well sites. The lack of pesticide detections at depth in the aquifer at the well sites might indicate that clay/silt layers in the aquifer inhibited the downward movement of contaminants. Other studies of the central High Plains aquifer have reported pesticide detections in water samples from domestic and public-supply wells that were screened as much as 160 feet below the water table (M.F. Becker, U.S. Geological Survey, written commun., 1999; B.W. Bruce, U.S. Geological Survey, written commun., 1999). Thus, it appears that in some areas of the aquifer, pesticides penetrated to greater depths than those observed in this study.

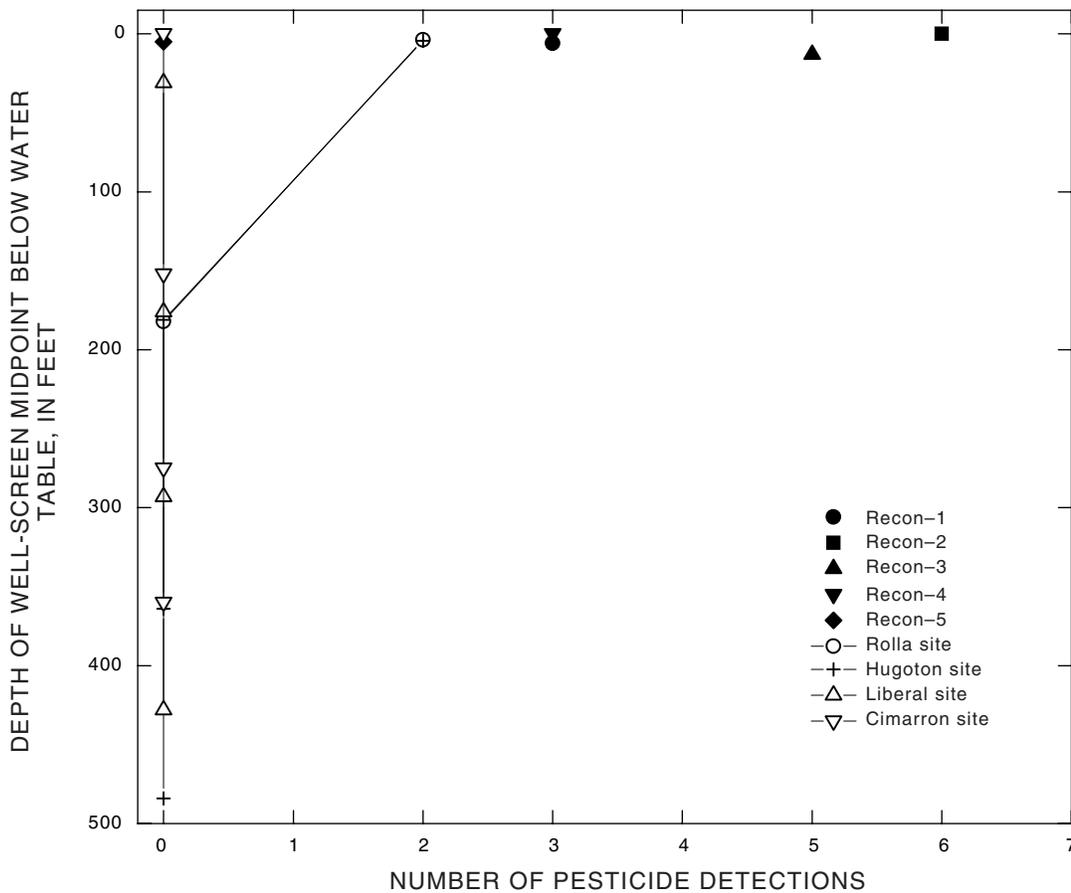


Figure 17. Relation between number of pesticide detections and depth of the well-screen midpoint below the water table.

SUMMARY AND CONCLUSIONS

The central High Plains aquifer is the primary source of water for domestic, industrial, and irrigation uses in parts of Colorado, Kansas, New Mexico, Oklahoma, and Texas. Water levels have declined in some areas, increasing the demand for water deeper in the aquifer. The maximum saturated thickness of the aquifer ranged from about 500 to 600 feet in 1999. As the demand for water builds, it becomes increasingly important for resource managers to understand how the quality of water in the aquifer changes with depth. In 1998–99, 18 monitoring wells at nine sites in southwestern Kansas and the Oklahoma Panhandle were completed at various depths in the central High Plains aquifer, and 1 monitoring well was completed in sediments of Permian age underlying the aquifer. Water samples were collected once from each well in 1999 to measure vertical gradients in water chemistry in the central High Plains aquifer.

Geophysical and lithologic logs indicate that the aquifer largely consists of unconsolidated clay, silt, sand, gravel, and caliche. There was no apparent trend in grain size with depth in the aquifer. Relatively thick intervals of clay/silt and sand/gravel were penetrated in the unsaturated and saturated zones at several sites. Quartz and feldspars were the major minerals identified in the aquifer, and calcite was observed in trace amounts except in caliche beds, in which case it was the major mineral phase.

Water-level data indicate that vertical hydraulic gradients varied spatially and temporally in the aquifer and were affected by pumping in nearby wells and lithology. Seasonal irrigation pumping caused water-level declines of 20 to 60 feet in deep monitoring wells at the Hugoton site. However, the water levels recovered to within 1 foot of prepumping levels after the irrigation season. Clay layers in the aquifer caused local confinement of the deep ground water and may help protect deep ground water from the downward

movement of contaminants. In the absence of clay layers, pumping could draw contaminants deeper into the aquifer. Pumping in the aquifer could also induce the upward migration of mineralized water from underlying geologic units.

Vertical gradients in ground-water age were present in the aquifer. Most of the water samples collected from the upper 30 feet of the aquifer were recharged in the last 50 years, whereas all of the water samples collected from depths more than 30 feet below the water table were recharged more than 50 years ago, on the basis of tritium concentrations measured in ground water. Despite the presence of relatively old water at depth in the aquifer, dissolved oxygen was present throughout the thickness of the aquifer, with concentrations ranging from 1.7 to 8.4 mg/L. The presence of dissolved oxygen throughout the aquifer indicates that some redox-sensitive chemicals of environmental concern (nitrate, arsenic, sulfate) had the potential to persist in the ground water.

Major-ion data indicate that water in the aquifer was predominantly a calcium-bicarbonate type that showed little variability in concentrations of dissolved solids with depth (290 to 642 mg/L). Exceptions included two areas (Rolla and Cimarron) of the aquifer where there had been upward movement of mineralized water from underlying sediments of Permian age and one area (near Garden City, Kansas) where there had been downward movement of mineralized Arkansas River water. In the areas of upward leakage, calcium-sulfate and sodium-chloride waters dominated and concentrations of dissolved solids were elevated at the base of the aquifer (862 to 4,030 mg/L). Dissolution of gypsum or anhydrite and halite in sediments of Permian age by ground water were the likely sources of calcium, sulfate, sodium, and chloride in these areas.

Poor-quality Arkansas River water infiltrated the aquifer near Garden City, Kansas (Recon-1), calcium-sodium-sulfate waters dominated, and concentrations of dissolved solids near the water table were as large as 4,916 mg/L. Dissolution of minerals in sedimentary deposits of marine origin in upstream areas of the Arkansas River drainage were the likely sources of calcium, sodium, and sulfate in this area.

Nitrate was detected throughout the aquifer, and the background concentration was estimated to be 2.45 mg/L as N. The largest concentrations (8.28, 22.0, and 54.4 mg/L as N) occurred in recently

recharged water collected adjacent to irrigated fields. These data indicate that concentrations of nitrate increased over time in some areas of the aquifer as a result of agricultural activities. The pesticide data also indicate that agricultural activity has affected water quality in the aquifer. Three pesticides (atrazine, metolachlor, simazine) and five pesticide degradation products (alachlor ethanesulfonic acid,alachlor oxanilic acid, deethylatrazine, metolachlor ethanesulfonic acid, and metolachlor oxanilic acid) were detected in water samples from six water-table wells. Five of the six wells were adjacent to irrigated fields. Three of the top five pesticides used in the study area (in terms of pounds applied), or their degradation products, were detected in the water samples. Atrazine was present in water from one of the water-table wells at a concentration of 5 µg/L, which exceeded the 3-µg/L MCL.

Results from this study indicate that vertical gradients in water chemistry existed in the central High Plains aquifer. The chemical gradients were the result of chemical inputs to the aquifer from underlying sediments of Permian age, from the Arkansas River, and from agricultural activities. In areas where those chemical inputs occurred, water quality in the aquifer was impaired and may not have been suitable for some intended uses.

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