

Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

By P.B. McMahon,¹ J.K. Böhlke,¹ and T.M. Lehman²

¹U.S. Geological Survey

²Texas Tech University, Lubbock, Texas

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Scientific Investigations Report 2004–5053

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
Charles G. Groat, Director

U.S. Geological Survey, Reston, Virginia: 2004
For sale by U.S. Geological Survey, Information Services

Box 25286, Denver Federal Center
Denver, CO 80225

For more information about the USGS and its products:
Telephone: 1-888-ASK-USGS
World Wide Web: <http://www.usgs.gov/>

Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained in this report.

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, multiscale 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, nongovernment organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

Contents

Foreword	iii
Abstract	1
Introduction	2
Purpose and Scope	2
Acknowledgments	2
Description of Study Area	2
Geohydrologic Setting	4
Land and Water Use	5
Study Methods	6
Vertical Changes in Lithology	9
Vertical Hydraulic Gradients	14
Vertical Gradients in Water Chemistry	16
Tritium	16
Dissolved Oxygen and Organic Carbon	16
Major Ions and Trace Elements	17
Nitrate	20
Pesticides	26
Vertical Gradients in Ground-Water Age	26
Mass-Balance Models	26
Radiocarbon Ages	28
Summary and Conclusions	34
References Cited	34
Appendix 1—Water-Quality Data from Monitoring Wells Screened in the Southern High Plains Aquifer and Dockum Group	41
Appendix 2—Calculated Phase Mass Transfers and Isotope Balances for Selected Pairs of Initial and Final Waters	47

Figures

1–5. Maps showing:	
1. Land-surface elevations and locations of the southern, central, and northern parts of the High Plains aquifer	3
2. Ground-water elevations in the southern High Plains aquifer and locations of monitoring wells	4
3. Geology underlying the southern High Plains aquifer and locations of monitoring wells	6
4. Saturated thickness of the southern High Plains aquifer and locations of monitoring wells	7
5. Land use overlying the southern High Plains aquifer and locations of monitoring wells	8
6. Natural gamma and resistivity logs for boreholes at the Castro and Hale County sites	10
7–13. Graphs showing:	
7. Water-level elevations and vertical hydraulic gradients in relation to time in nested wells at the Castro and Hale County sites	15
8. Concentration of selected dissolved constituents in relation to well-screen depth below the water table	18
9. (A) Bromide/chloride mole ratios in relation to concentration of dissolved chloride and (B) sulfate-sulfur isotopes in relation to concentration of dissolved sulfate	19
10. (A) Concentrations of dissolved sodium in relation to dissolved chloride, (B) concentrations of dissolved bicarbonate in relation to dissolved chloride, (C) concentrations of dissolved sodium in relation to dissolved bicarbonate, and (D) concentrations of dissolved calcium in relation to dissolved bicarbonate	20
11. Nitrogen isotope composition of nitrogen gas as a function of argon/nitrogen gas ratios	25

12. Median ground-water age as a function of well-screen depth below the water table	31
13. Stable isotope values for water from monitoring wells screened in the southern High Plains aquifer and Dockum Group.....	32

Tables

1. Construction information for monitoring wells.....	5
2. Lithologic description of drill cuttings and cores.....	11
3. Mineralogy in the Ogallala Formation.....	13
4. Carbon content of sediments.....	14
5. Isotope data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.....	16
6. Mineral-saturation indices for water from monitoring wells screened in the southern High Plains aquifer	21
7. Dissolved-gas and related data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.....	22
8. Additional water-quality data used in mass-balance models.....	27
9. Uncertainties assigned to measured isotope variables and isotope values assigned to unmeasured variables in PHREEQC simulations	27
10. Unadjusted radiocarbon ages of water from selected wells.....	29
11. Adjusted radiocarbon ages of water from selected wells.....	30
12. Estimated rates of dissolved-oxygen reduction and denitrification	33

CONVERSION FACTORS, DATUMS, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
acre	0.4047	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
milligrams per liter (mg/L)	1.0	parts per million
micrograms per liter (µg/L)	1.0	parts per billion
milligrams per liter as calcium	24.950	micromoles per liter
milligrams per liter as sodium	43.497	micromoles per liter
milligrams per liter as bicarbonate	16.389	micromoles per liter
milligrams per liter as nitrogen	71.378	micromoles per liter
milligrams per liter as dissolved oxygen	31.250	micromoles per liter

Temperature can be converted to degrees Celsius (°C) or degrees Fahrenheit (°F) by the equations:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32$$

Datums: Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29). Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Acronyms and Abbreviations

BP	before present
°C	degrees Celsius
¹⁴ C	carbon-14 or radiocarbon
cm ³	cubic centimeter
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
ft	feet
ft/d	feet per day
HPGW	High Plains Regional Ground-Water study
IAEA	International Atomic Energy Agency
in./yr	inches per year
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
mmol/kg	millimoles per kilogram
NAWQA	National Water-Quality Assessment
NBS	National Bureau of Standards (now NIST)
NIST	National Institute of Standards and Technology
pmc	percent modern carbon
PVC	polyvinyl chloride
SOC	sedimentary organic carbon
SLAP	Standard Light Antarctic Precipitation
TU	tritium units
USGS	U.S. Geological Survey
µg/L	micrograms per liter
µM	micromoles per liter
VCDT	Vienna Cañon Diablo troilite
VPDB	Vienna Peedee belemnite
VSMOW	Vienna Standard Mean Ocean Water
XRD	X-ray powder diffraction

Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

By P.B. McMahon, J.K. Böhlke, and T.M. Lehman

ABSTRACT

The southern High Plains aquifer is the primary source of water used for domestic, industrial, and irrigation purposes in parts of New Mexico and Texas. Despite the aquifer's importance to the overall economy of the southern High Plains, fundamental ground-water characteristics, such as vertical gradients in water chemistry and age, remain poorly defined. As part of the U.S. Geological Survey's National Water-Quality Assessment Program, water samples from nested, short-screen monitoring wells installed in the southern High Plains aquifer at two locations (Castro and Hale Counties, Texas) were analyzed for field parameters, major ions, nutrients, trace elements, dissolved organic carbon, pesticides, stable and radioactive isotopes, and dissolved gases to evaluate vertical gradients in water chemistry and age in the aquifer. Tritium measurements indicate that recent (post-1953) recharge was present near the water table and that deeper water was recharged before 1953. Concentrations of dissolved oxygen were largest (2.6 to 5.6 milligrams per liter) at the water table and decreased with depth below the water table. The smallest concentrations were less than 0.5 milligram per liter. The largest major-ion concentrations generally were detected at the water table because of the effects of overlying agricultural activities, as indicated by postbomb tritium concentrations and elevated nitrate and pesticide concentrations at the water table. Below the zone of agricultural influence, major-ion concentrations exhibited small increases with depth and distance along flow paths because of rock/water interactions and mixing with water from the underlying aquifer in rocks of Cretaceous age. The concentration increases primarily were accounted for by dissolved sodium, bicarbonate, chloride, and sulfate.

Nitrite plus nitrate concentrations at the water table were 2.0 to 6.1 milligrams per liter as nitrogen, and concentrations substantially decreased with depth in the aquifer to a maximum concentration of 0.55 milligram per liter as nitrogen. Dissolved-gas and nitrogen-isotope data from the deep wells in Castro County indicate that denitrification occurred in the aquifer, removing 74 to more than 97 percent of the nitrate originally present in recharge. There was no evidence of denitrification in the deep part of the aquifer in Hale County. After correcting for denitrification effects, the background concentration of nitrate

in water recharged before 1953 ranged from 0.4 to 3.2 milligrams per liter as nitrogen, with an average of 1.6 milligrams per liter as nitrogen. The $\delta^{15}\text{N}$ composition of background nitrate at the time of recharge was estimated to range from 9.6 to 12.3 per mil.

Mass-balance models indicate that the decreases in dissolved oxygen and nitrate concentrations and small increases in major-ion concentrations along flow paths can be accounted for by small amounts of silicate-mineral and calcite dissolution; SiO_2 , goethite, and clay-mineral precipitation; organic-carbon and pyrite oxidation; denitrification; and cation exchange. Mass-balance models for some wells also required mixing with water from the underlying aquifer in rocks of Cretaceous age to achieve mole and isotope balances. Carbon mass transfers identified in the models were used to adjust radiocarbon ages of water samples recharged before 1953. Adjusted radiocarbon ages ranged from less than 1,000 to 9,000 carbon-14 years before present. Radiocarbon ages were more sensitive to uncertainties in the carbon-14 content of recharge than uncertainties in carbon mass transfers, leading to 1-sigma uncertainties of about $\pm 2,000$ years in the adjusted ages. Despite these relatively large uncertainties in adjusted radiocarbon ages, it appears that deep water in the aquifer was considerably older (at least 1,000 years) than water near the water table.

There was essentially no change in ground-water age with depth in deeper parts of the aquifer, indicating that water in that part of the aquifer was vertically well mixed. Both sites are located in areas of intensive long-term irrigation; therefore, local irrigation pumping is the most likely explanation for vertical mixing. The absence of ground-water age gradients in the deep aquifer is an indication that pumping is likely to accelerate the downward movement of anthropogenic compounds like nitrate and pesticides from the water table to deeper parts of the aquifer. Denitrification rates for deeper parts of the aquifer estimated on the basis of nonatmospheric dissolved nitrogen gas concentrations and radiocarbon ages were slow, averaging about 3.5×10^{-4} milligram per liter per year as nitrogen. Considering these slow denitrification rates, this process may not attenuate nitrate that is transported deeper into the aquifer by processes like pumping.

INTRODUCTION

In 1991, the USGS 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 water quality (Gilliom and others, 1995). Understanding 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.

The High Plains Regional Ground-Water study, which began in June 1998, is one of more than 50 major river basins and aquifers being studied by the NAWQA Program. The High Plains aquifer is a nationally important water resource that underlies about 174,000 mi² in parts of eight States (fig. 1). In 1990, about 28 percent of all the ground water used for irrigation in the United States was pumped from this aquifer (Solley and others, 1993; McGuire and Sharpe, 1997). Due to the large areal extent of the High Plains aquifer, three geographic regions have been delineated for logistical purposes: northern High Plains (96,500 mi²), central High Plains (48,500 mi²), and southern High Plains (29,000 mi²). The southern High Plains aquifer is the focus of this report.

The southern High Plains aquifer is the primary source of water used for domestic, industrial, and irrigation purposes in parts of New Mexico and Texas. Despite the aquifer's importance to the overall economy of the southern High Plains, fundamental ground-water characteristics, such as vertical gradients in water chemistry and age, remain poorly defined. Understanding how water chemistry changes with depth in the aquifer is relevant because large water-level declines in some areas of the aquifer, primarily due to withdrawals for irrigation (McGuire and Sharpe, 1997), have increased the demand for water deeper in the aquifer. As of 1995, the saturated thickness of the southern High Plains aquifer in Texas had declined by 27 percent relative to the predevelopment saturated thickness (McGuire and Sharpe, 1997). Ground-water age distributions in aquifers also are relevant because, when combined with other hydrogeologic and geochemical information, they provide insights into recharge rates, an aquifer's susceptibility to contamination from sources at land surface, and biogeochemical reaction rates.

Several studies have examined water quality in the southern High Plains aquifer (Feder and Krothe, 1981; Nativ and Smith, 1987; Hopkins, 1993; Hudak, 2000; Mehta and others, 2000; Fryar and others, 2001). Most of those studies relied on water samples collected from relatively long-screened domestic, irrigation, or municipal wells to characterize water quality. Long-screened wells generally are not suitable for describing vertical water-chemistry gradients because water samples are a mix of water from the entire screened interval. Some studies have measured concentrations of age-dating tracers like tritium

and ¹⁴C in water collected from relatively long-screened wells and inferred approximate ground-water ages (Nativ and Smith, 1987; Dutton, 1995). Fryar and others (2001) measured concentrations of tritium and ¹⁴C in relatively short-screened wells, but most of those wells were screened near the water table or in perched-water zones. Thus, information on vertical gradients in ground-water age in the southern High Plains aquifer is lacking.

Purpose and Scope

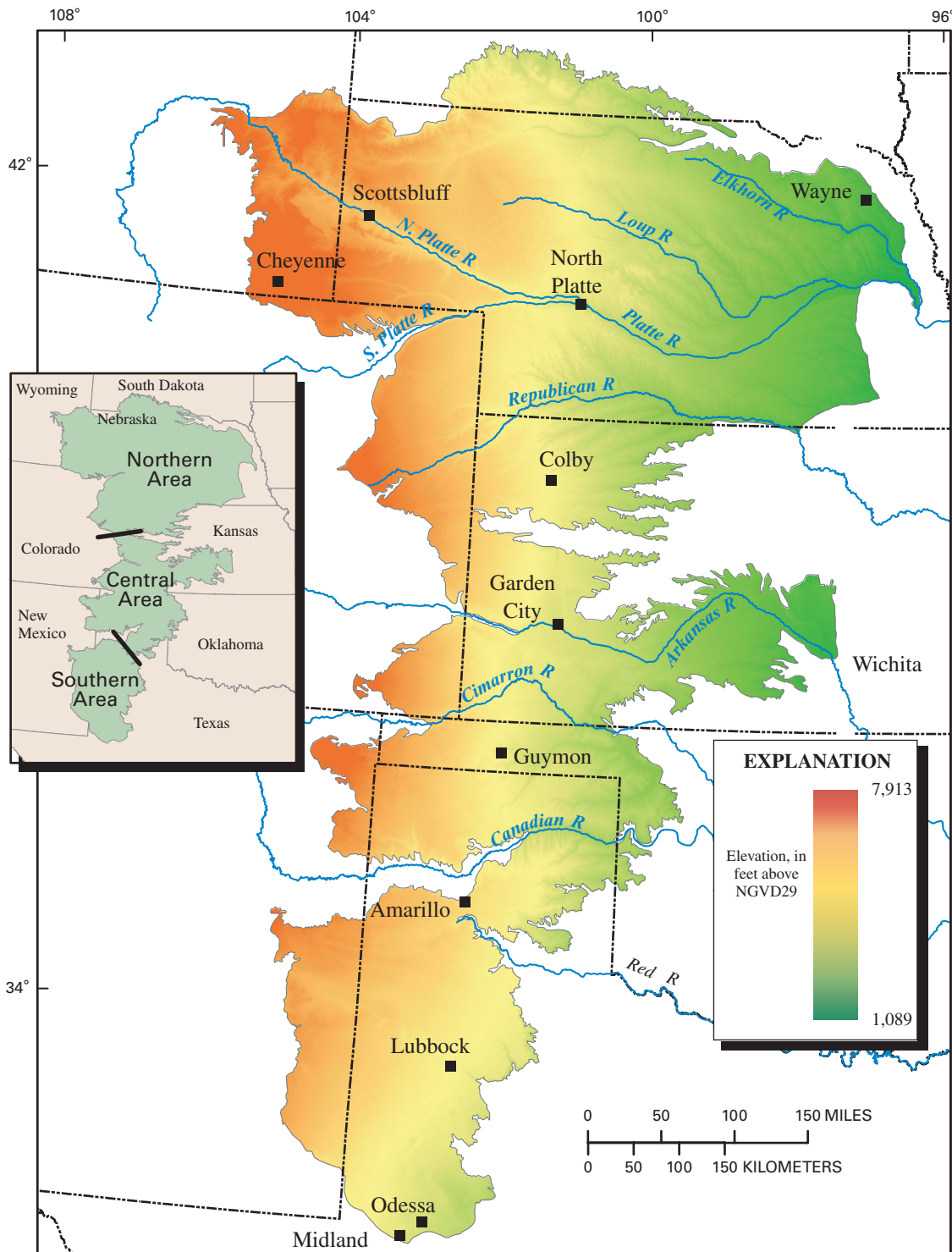
The purpose of this report is to describe vertical gradients in water chemistry and age in selected areas of the southern High Plains aquifer. In 2001, seven monitoring wells at two sites were completed in the aquifer and one monitoring well was completed in sediments of Triassic age underlying the aquifer (fig. 2 and table 1). The wells had single screens that were placed at various depths below the water table. In 2002, water samples were collected once from each well and analyzed for field parameters; major ions; nutrients; trace elements; dissolved organic carbon (DOC); pesticides; dissolved helium (He), methane (CH₄), neon (Ne), nitrogen (N₂), oxygen (O₂), and argon (Ar) gases; tritium (³H); stable isotopes of water ($\delta^2\text{H}[\text{H}_2\text{O}]$ and $\delta^{18}\text{O}[\text{H}_2\text{O}]$); stable nitrogen isotopes of dissolved nitrate ($\delta^{15}\text{N}[\text{NO}_3]$) and nitrogen gas ($\delta^{15}\text{N}[\text{N}_2]$); stable and radioactive isotopes of dissolved inorganic carbon ($\delta^{13}\text{C}[\text{DIC}]$ and ¹⁴C[DIC]); stable isotopes of dissolved sulfate ($\delta^{34}\text{S}[\text{SO}_4]$); and the dissolved strontium isotope ratio ⁸⁷Sr/⁸⁶Sr.

Acknowledgments

The cooperation of landowners who agreed to the installation of monitoring wells on their property is gratefully acknowledged. Alan Dutton (Texas Bureau of Economic Geology) and Lynne Fahlquist (U.S. Geological Survey, Texas) provided colleague reviews of this report.

DESCRIPTION OF STUDY AREA

The study area includes two sites with nested wells in parts of Castro and Hale Counties in northwest Texas (fig. 2). The area is characterized by generally flat terrain interrupted by numerous surface depressions referred to as playa basins. A summary of estimates of the number of playa basins in the southern High Plains ranged from 20,000 to 30,000 (Haukos and Smith, 1994). The study area is semiarid, receiving on average about 16 to 20 in. of precipitation annually (Gutentag and others, 1984). Natural vegetation is sparse and consists mostly of grasses. More detailed descriptions of the study area are in Seni (1980), Gutentag and others (1984), Nativ (1988), and Gustavson and others (1991).



Base information from U.S. Geological Survey digital data, 1:100,000
 Albers Equal-Area projection
 Standard Parallels 29°30' and 45°30', central meridian -96°

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

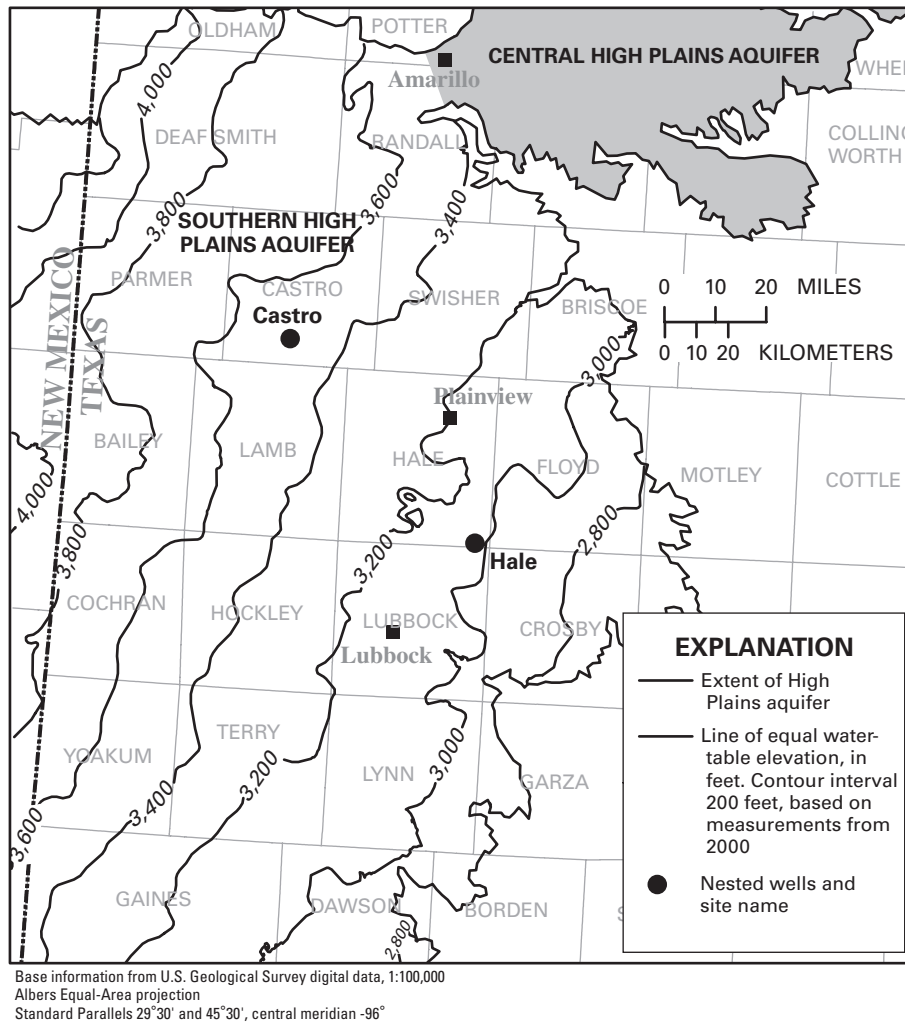


Figure 2. Ground-water elevations in the southern High Plains aquifer and locations of monitoring wells. Elevations are based on measurements made in 2000 (V.L. McGuire, U.S. Geological Survey, written commun., 2002).

Geohydrologic Setting

The southern High Plains aquifer consists of sediments of the Ogallala Formation and younger sedimentary deposits, primarily the Blackwater Draw Formation. The Ogallala Formation of Miocene-Pliocene age is the largest geologic unit in the southern High Plains aquifer. It contains coarse fluvial sands and gravels generally overlain by fine-grained eolian siltstone and clay (Seni, 1980; Nativ, 1988). A calcite, and sometimes silica, cemented zone, called the caprock caliche, lies near the top of the Ogallala Formation. Seni (1980) reported maximum total Ogallala thicknesses of 300 to 400 ft in the study area. The Ogallala Formation is overlain by younger sedimentary deposits, the most widespread of which is the Quaternary Blackwater Draw Formation. Sediments of the Blackwater Draw Formation were deposited in an eolian environment and range in texture from clay to silt to sand (Gustavson and others, 1991). The High

Plains aquifer consists of the Ogallala Formation at the nested-well locations.

The southern High Plains aquifer is underlain by rocks ranging in age from Triassic to Cretaceous (fig. 3). The nested-well locations are underlain by the Triassic Dockum Group. According to McGowen and others (1977), sediments of the Dockum Group were deposited in a variety of terrestrial environments and consist of clay, silt, and sand. Nativ (1988) reported that sandstone in the Upper Dockum Group may be in contact with basal sand and gravel in the Ogallala Formation in parts of Castro County, but hydraulic-head data indicate the direction of ground-water movement is from the aquifer to the Dockum Group in Castro and Hale Counties. Sediments of Cretaceous age consisting primarily of limestone directly underlie the aquifer in parts of southern Hale County (fig. 3). Hydraulic-head data reported by Nativ (1988) indicate a potential existed

Table 1. Construction information for monitoring wells.

[All depths are in feet below land surface. Casing and screen for all wells are made of threaded, flush-joint, Schedule 80 polyvinyl chloride (PVC) with a diameter of 2.5 inches. Screen openings are 0.020 inch wide]

Site identification	Well name	Construction date	Elevation of land surface (feet above NGVD29)	Depth to base of southern High Plains aquifer (feet)	Depth to water at time of construction (feet)	Total depth of hole (feet)	Total depth of well (feet)	Depth of screened interval (feet)	Depth of screen midpoint below water table at time of sampling (feet)
Southern High Plains Aquifer									
342313102174404	Castro-241	04/28/01	3,716	430	228.14	390	246	231 to 241	5
342313102174403	Castro-330	04/24/01	3,716	430	228.14	497	335	320 to 330	94
342313102174402	Castro-380	04/27/01	3,716	430	228.14	390	385	370 to 380	144
342313102174401	Castro-427	04/23/01	3,716	430	228.14	497	432	417 to 427	191
335028101365004	Hale-255	05/14/01	3,226	410	229.22	409	260	245 to 255	12
335028101365003	Hale-340	05/03/01	3,226	410	229.22	498	345	330 to 340	96
335028101365002	Hale-400	05/13/01	3,226	410	229.22	409	405	390 to 400	156
Dockum Group									
335028101365001	Hale-490	05/02/01	3,226	410	229.22	498	495	460 to 490	237

for ground water to move from the aquifer in rocks of Cretaceous age to the High Plains aquifer.

In 2000, the average depth to water in the southern High Plains aquifer was about 125 ft below land surface and the average saturated thickness was about 59 ft (fig. 4) (V.L. McGuire, U.S. Geological Survey, written commun., 2002). Decreases in saturated thickness of more than 100 ft have occurred in some parts of the aquifer since irrigation pumping began in about the 1950s (Gutentag and others, 1984; McGuire and Sharpe, 1997). Hydraulic gradients in the aquifer indicate ground-water movement generally is from northwest to southeast (fig. 2). Nativ (1988) estimated ground-water velocities in the aquifer vary between about 0.05 and 5 ft/d based on measured values of hydraulic conductivity, hydraulic gradient, and porosity in the aquifer. The intensity and duration of well pumpage in the aquifer are likely to affect directions and rates of ground-water movement.

Recharge to the southern High Plains aquifer may occur by infiltration of irrigation water, aerially diffuse infiltration of precipitation, infiltration of stormwater runoff through streambeds, and leakage through the bottom of playa basins. Results of unsaturated-zone studies by Scanlon and Goldsmith (1997) indicate playas in the southern High Plains focused recharge to the aquifer, whereas little to no recharge occurred in undisturbed interplaya areas. They reported recharge rates of 2.4 to 4.7 in./yr beneath playas and rates less than 0.01 in./yr beneath interplaya areas. Wood and Sanford (1995) reported a similar recharge rate beneath one playa basin in the southern High Plains. They also used a mass-balance method based on dis-

solved chloride concentrations in ground water to estimate a composite recharge rate for the aquifer of 0.4 in./yr.

Discharge from the aquifer occurs through natural springs and seeps (especially along the eastern escarpment), leakage to underlying formations, evapotranspiration, and pumpage. Pumpage is the primary discharge mechanism in the aquifer (Luckey and others, 1986).

Land and Water Use

Land in the southern High Plains primarily was used for grazing (rangeland) and the production of crops (irrigated and dryland cropland) (fig. 5). In 1997, cotton (5,088,375 acres), wheat (2,505,565 acres), and corn (1,561,551 acres) were the primary crops grown in the study area in terms of acres planted (U.S. Department of Agriculture, 1999). 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) in 1997 were trifluralin, malathion, atrazine, 2,4-D, and pendimethalin (U.S. Department of Agriculture, 1999). Irrigation is the primary use of ground water in the study area. Of the approximately 4.8 million acre-ft of water withdrawn from the High Plains aquifer in Texas in 1990, 96 percent was used for irrigation (McGuire and Sharpe, 1997). In 1990, 11.4 percent of the southern High Plains area was irrigated (Qi and others, 2002). Irrigated corn was the primary crop grown in the vicinity of the Castro County site, and irrigated cotton was the primary crop grown in the vicinity of the Hale County site.

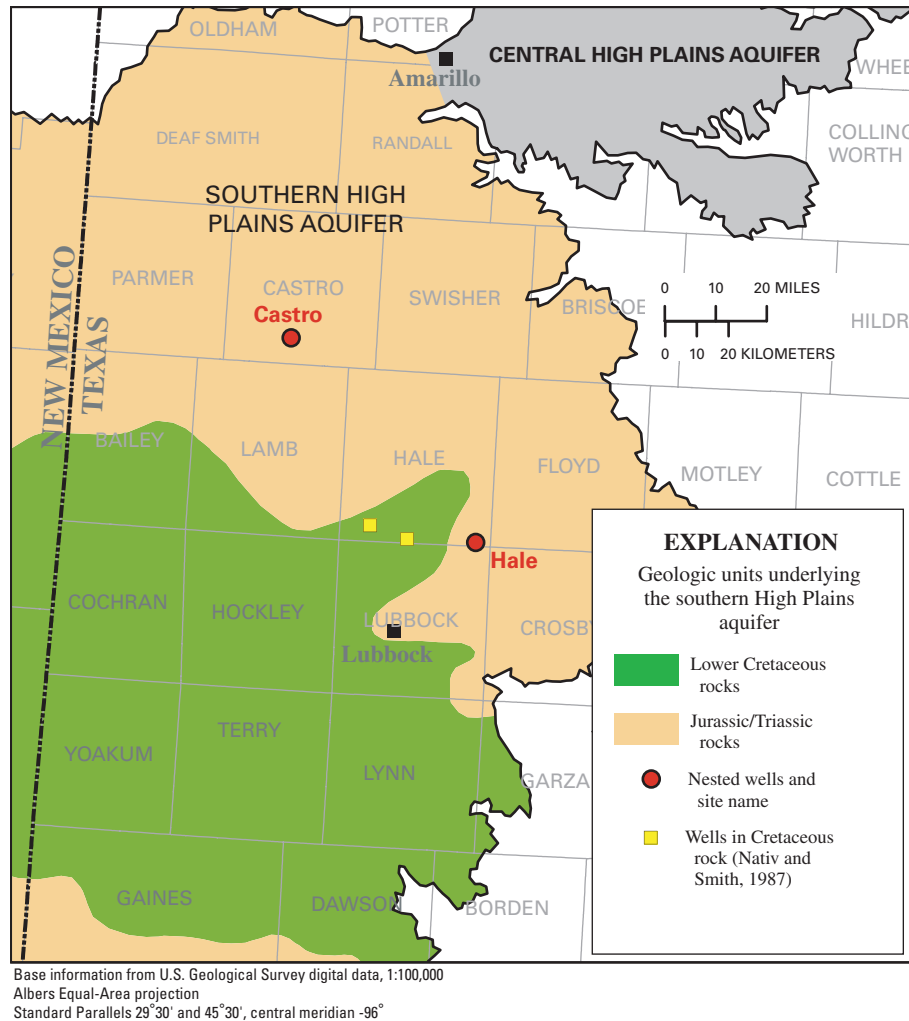


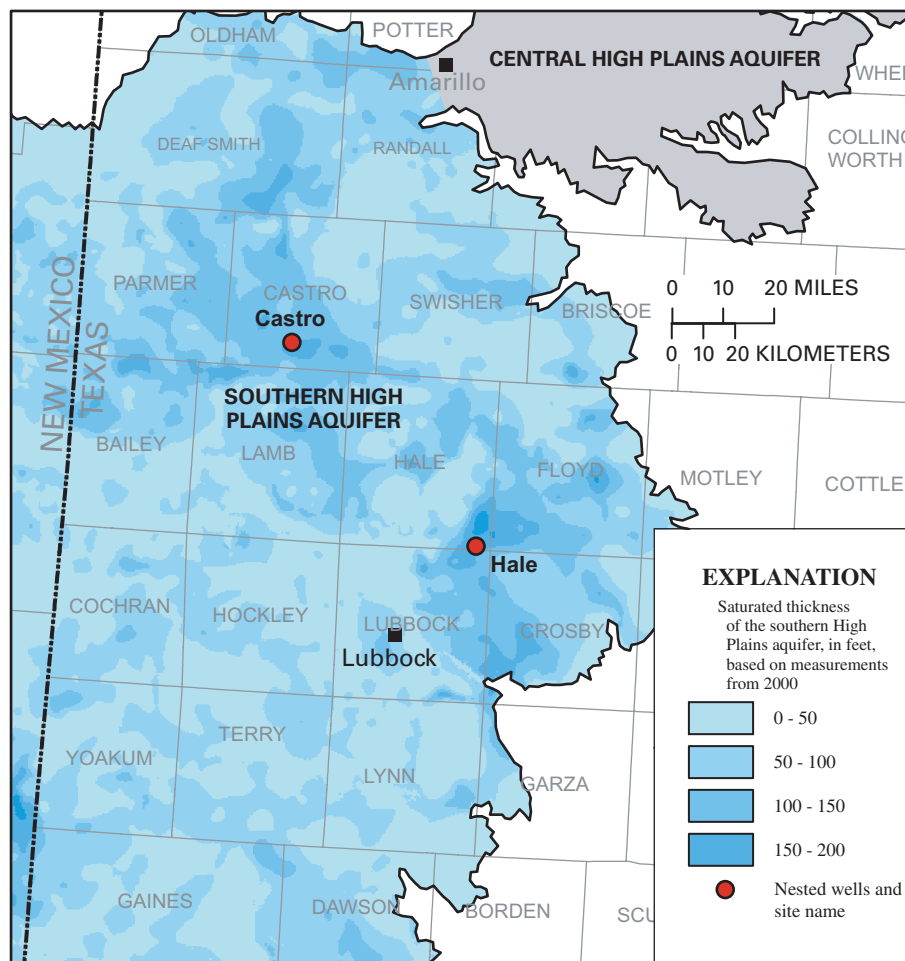
Figure 3. Geology underlying the southern High Plains aquifer and locations of monitoring wells. Map modified from Gutentag and others (1984). The well installed in bedrock for this study is located at the Hale County site. Wells in Cretaceous rock were not installed for this study and were sampled by Nativ and Smith (1987).

STUDY METHODS

In 2001, four nested monitoring wells were installed at each of the two sites for the collection of water levels and water samples for chemical analysis. The wells were located in some of the thickest saturated sections of the aquifer (fig. 4) because those areas may represent the best long-term ground-water supply in the study area. The Castro and Hale County sites are located along a regional hydraulic gradient from northwest to southeast in the aquifer (fig. 2). Water samples for chemical analysis were collected from the wells by the USGS in 2002. The following section of the report describes the methods used for the installation of monitoring wells, geophysical logging, water-level measurements, sediment-sample collection, water-sample collection, describing sediment mineralogy, chemical

analyses of sediment and water, and quality control of water-quality data.

Well installation. In 2001, the USGS used a mud-rotary drill rig to drill boreholes used for well installation. Two boreholes were drilled at each site, and two wells were placed in each borehole 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, then sealing the annular space from the top of the plug to the bottom of the next screened interval using a high-density bentonite grout. Well screen and casing for the shallower well then were placed in the borehole, followed by a sand filter around the well screen, bentonite plug on top of the sand filter, and bentonite grout from the top of the plug to land surface. At each site, the shallowest well was installed at the



Base information from U.S. Geological Survey digital data, 1:100,000
 Albers Equal-Area projection
 Standard Parallels 29°30' and 45°30', central meridian -96°

Figure 4. Saturated thickness of the southern High Plains aquifer and locations of monitoring wells. Thicknesses based on water-level measurements made in 2000 and U.S. Geological Survey base-of-aquifer map (V.L. McGuire, U.S. Geological Survey, written commun., 2002; Gutentag and others, 1984).

water table. The wells were developed by bailing and pumping (water-table wells) or by air lifting and pumping (wells screened beneath the water table) immediately after installation and again at least 1 month before sample collection. During the second well-development period, 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 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 information is listed in table 1. The well name includes site and well-depth information. For example, Castro-241 refers to a well at the Castro County site with a maximum depth of the screened interval of 241 ft below land surface.

Geophysical logging. Natural gamma and electrical resistivity logs were obtained for the open boreholes. Only the deepest borehole at each site was logged. The boreholes were logged by Century Geophysical, Inc., Tulsa, Okla.

Water-level measurements. Water levels in all wells were measured before water-sample collection by using an electric tape. In addition, water levels were measured monthly for 15 months. The latitude and longitude of the well locations were determined by using a Global Positioning System (GPS) with a precision of about ± 20 ft. The vertical position of the measuring point for each well was determined relative to a local datum (land surface) using a transit level and rod with an accuracy of ± 0.01 ft. The elevation of the land surface was determined from the USGS National Elevation Dataset (U.S. Geological Survey, 1999).

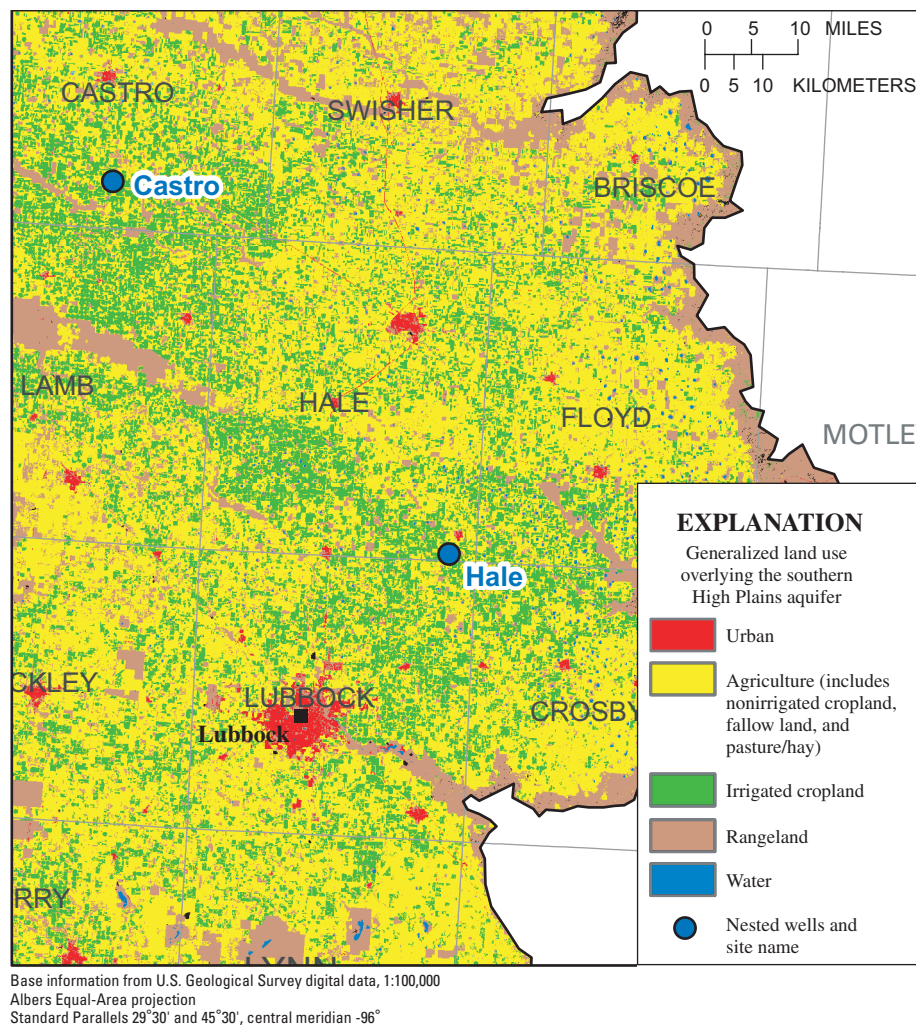


Figure 5. Land use overlying the southern High Plains aquifer and locations of monitoring wells. Land-use data from Feagas and others (1983). The data were collected from about 1977 to 1982.

Sediment-sample collection. Cuttings were collected from the drilling-mud return flow every 10 ft 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 from the Dockum Group were collected from depths of 491 to 497 ft below land surface at the Castro County site and from depths of 495 to 500 ft below land surface at the Hale County site.

Water-sample collection. Ground-water samples were collected and processed in a mobile water-quality laboratory using methods described by Koterba and others (1995), McMahon (2001), and McMahon and others (in press). Water was pumped from the wells by using a submersible piston-type pump made of stainless steel and Teflon. To minimize the risk of sample contamination, sample collection and preservation took place in dedicated environmental chambers consisting of clear polyethylene bags supported by tubular PVC frames. Sampling equipment was thoroughly cleaned after sampling each well. Polyethylene bags containing the sample and preser-

vation chambers were replaced after each sampling event. Measurements of field parameters (pH, water temperature, specific conductance, turbidity, dissolved oxygen, and alkalinity) were made using the techniques described in U.S. Geological Survey field manual (1998). Dissolved hydrogen sulfide (H_2S) also was measured in the field using a portable spectrophotometer and the methylene blue method (Hach Company, 1989).

Mineralogy of sediment samples. Mineralogy of selected sediment samples was estimated by examination of thin sections under a petrographic microscope and XRD analysis at Texas Tech University in Lubbock, Tex. Twenty-two thin sections were examined and four mudstone samples were used for XRD analysis. Mineral percentages in thin sections are visual estimates and are not based on point counts. Percentages for XRD analyses are based on relative peak area/intensities and are semiquantitative.

Chemical analysis of sediment and water. Chemical analyses for major ions, nutrients, trace elements, DOC, and pesticides were done at the USGS National Water-Quality

Laboratory in Lakewood, Colo. (Fishman, 1993; Zaugg and others, 1995). The charge balance of analyses (calculated relative to the sum of the equivalents of cations and anions) ranged from -3.2 to 0.8 percent, with an average absolute value of 1.5 percent.

Analyses of dissolved CH₄, N₂, O₂, and Ar were done at the USGS Chlorofluorocarbon Laboratory in Reston, Va. (Busenberg and others, 1993; <http://water.usgs.gov/lab/dissolved-gas/>, accessed on 12/3/2003). Analyses of dissolved He and Ne were done at the Lamont-Doherty Earth Observatory, Noble Gas Laboratory in Palisades, N.Y. (Ludin and others, 1998).

Analyses of $\delta^2\text{H}[\text{H}_2\text{O}]$, $\delta^{18}\text{O}[\text{H}_2\text{O}]$, $\delta^{15}\text{N}[\text{NO}_3]$, $\delta^{15}\text{N}[\text{N}_2]$, and $\delta^{34}\text{S}[\text{SO}_4]$ were done at the USGS Stable Isotope Laboratory in Reston, Va. (Coplen and others, 1991; Epstein and Mayeda, 1953; Böhlke and Denver, 1995; Böhlke and others, 2002; Carmody and others, 1997). Values of $\delta^2\text{H}[\text{H}_2\text{O}]$ and $\delta^{18}\text{O}[\text{H}_2\text{O}]$ are reported in per mil relative to Vienna Standard Mean Ocean Water (VSMOW), normalized to VSMOW of Standard Light Antarctic Precipitation (SLAP) (Coplen, 1988). The 2-sigma uncertainties of hydrogen (H) and oxygen (O) isotopic results are 2 and 0.2 per mil, respectively. Values of $\delta^{15}\text{N}[\text{NO}_3]$ are reported with respect to atmospheric N₂ and were calibrated by analyses of aqueous nitrate laboratory standards prepared as samples and normalized to values of +0.4 and +180.0 per mil for International Atomic Energy Agency (IAEA)-N1 and USGS-32, respectively (Böhlke and Coplen, 1995). Values of $\delta^{15}\text{N}[\text{N}_2]$ are reported with respect to atmospheric N₂ and were calibrated by analyses of air (0 per mil). The procedures were verified by analyses of air-saturated water samples that were collected at 16°C under controlled laboratory conditions, prepared as samples, and yielded $\delta^{15}\text{N}[\text{N}_2]$ values equal to $+0.72 \pm 0.03$ per mil consistent with air-water equilibrium (Klots and Benson, 1963; Hübner, 1986). Values of $\delta^{34}\text{S}[\text{SO}_4]$ are reported in per mil relative to Vienna Cañon Diablo troilite (VCDT), defined by assigning a value of -0.3 per mil exactly (Coplen and Krouse, 1998) to IAEA-S-1 Ag₂S. Analyses of IAEA-SO-5, IAEA-SO-6, and National Bureau of Standards (NBS) 127 BaSO₄ reference materials in this laboratory yield +0.5, -34.05, and +21.10 per mil, respectively. The 2-sigma uncertainty of sulfur (S) isotopic results is 0.4 per mil. Analyses of tritium (³H) were done at the USGS Tritium Laboratory in Menlo Park, Calif. (Thatcher and others, 1977). The average 2-sigma precision of the analyses was 0.3 tritium unit (TU). Measurements of $\delta^{13}\text{C}[\text{DIC}]$, reported relative to Vienna Pee Dee belemnite (VPDB), and ¹⁴C[DIC] sample preparation were done at the University of Waterloo in Ontario, Canada. Measurements of ¹⁴C[DIC] were done at the IsoTrace Radiocarbon Laboratory Accelerator Mass Spectrometry facility in Toronto, Canada, using accelerator mass spectrometry. Reported ¹⁴C values (in pmc) are not adjusted for the difference between -25 per mil and the $\delta^{13}\text{C}$ value of the sample. Strontium isotope analyses were done at the USGS Solid-Source Mass Spectrometry Laboratory in Menlo Park, Calif. Ratios of ⁸⁷Sr/⁸⁶Sr were analyzed by the positive ion thermal mass spectrometry method with a precision of 0.00002.

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

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. 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. The quality-control data are available online at <http://co.water.usgs.gov/nawqa/hpgw/dataprep/Toc.html> (accessed on 06/30/04).

VERTICAL CHANGES IN LITHOLOGY

Lithologic variability in the aquifer may affect water chemistry and ground-water-age distributions because of its effect on rock/water interactions and rates of ground-water movement. Therefore, vertical changes in lithology in the southern High Plains aquifer were examined using geophysical (gamma and resistivity) and lithologic logs, thin sections, XRD analyses of sediments, and elemental carbon analyses. Gamma logs record the natural gamma radiation emitted by radioactive elements in sediment (Keys, 1990). Shale and clay tend to have larger proportions of these radioactive elements than sand; therefore, an increase in gamma activity recorded by gamma logs generally is attributed to increased proportions of clay in the aquifer or changes in clay mineralogy. Resistivity logs record the electrical conductivity or resistivity of the rocks and water surrounding the borehole. Electrical conductivity and resistivity are affected by the porosity, permeability, and clay content of the rocks and by the dissolved-solids concentration of the water within the rocks. In freshwater aquifers, decreasing resistivity readings normally indicate increasing clay content of the formation. The presence of mineralized water in sandy deposits, however, also would produce small resistivities, possibly leading to the incorrect interpretation that the formation consisted of fine-grained material. Mineralized water in the Dockum Group may have affected the resistivity log at the Hale County site (fig. 6).

The southern High Plains aquifer at the Castro and Hale County sites is underlain by sediments of the Dockum Group (fig. 6 and table 2). Sediments of the Dockum Group generally consisted of mudstone near the contact with the Ogallala Formation and graded downward into very fine- to medium-grained sandstone. The presence of mudstone at the top of the

10 Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

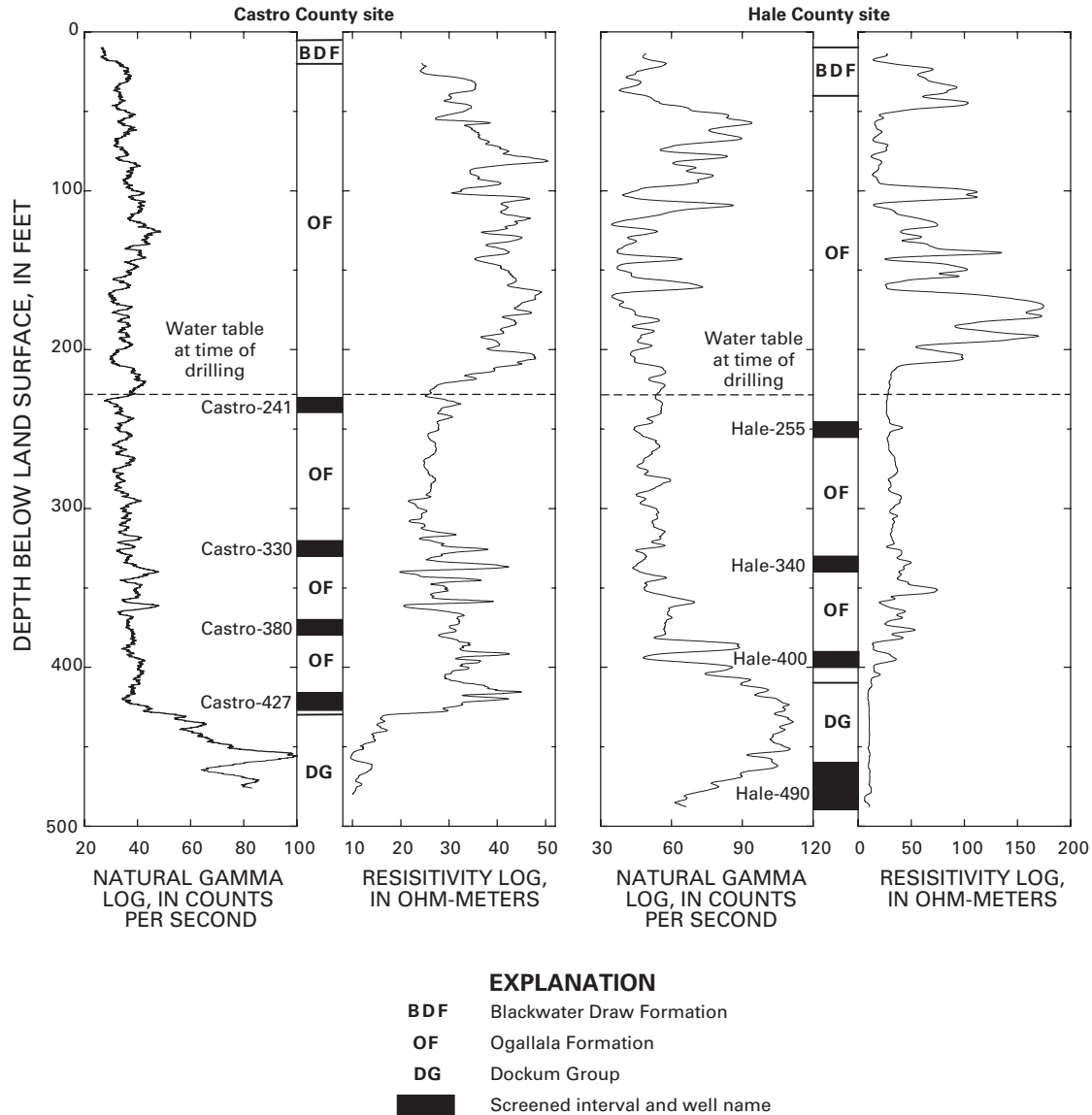


Figure 6. Natural gamma and resistivity logs for boreholes at the Castro and Hale County sites.

Dockum Group resulted in poor hydraulic connection of water-bearing units in the Dockum Group with the High Plains aquifer (see the section “Vertical Hydraulic Gradients”).

The aquifer at the Castro and Hale County sites primarily consisted of medium- to coarse-grained sandstone of the Ogallala Formation, occasionally interbedded with thin mudstone layers (fig. 6 and table 2). The absence of thick, confining mudstone layers in the aquifer at these locations indicates that water-table drawdowns caused by pumping large-capacity wells (McGuire and Sharpe, 1997) could draw anthropogenic contaminants near the water table deeper into the aquifer. Bruce and Oelsner (2001) proposed this mechanism to explain the more frequent occurrence of recent recharge and pesticides in water from large-capacity public supply wells compared to domestic wells in the central High Plains aquifer.

The Ogallala Formation above the water table generally consisted of fine- to medium-grained sandstone capped by a caliche layer that was about 10 ft thick (table 2). A portion of this sediment probably was saturated prior to the onset of widespread irrigation pumping in the area. The generally fining upward sedimentary sequence in the Ogallala Formation at the Castro and Hale County sites is indicative of their locations along the channel axis of a major wet alluvial-fan depositional system (Seni, 1980). At both locations, the Ogallala Formation was overlain by sediments of the Blackwater Draw Formation. These sediments consisted of very fine- to fine-grained sandstone with some caliche (table 2).

Quartz was the primary detrital mineral in the aquifer (Ogallala Formation) at the Castro and Hale County sites (table 3). Quartz is a relatively stable mineral phase that is not readily dissolved in water; therefore, quartz dissolution is not a

Table 2. Lithologic description of drill cuttings and cores.

Geologic unit	Depth, in feet below land surface	Color	Lithology
Castro County Site			
Surface deposits	0–5	Dark yellowish brown	Sandy mud/muddy, very fine sand.
Blackwater Draw Formation	5–10	Pale brown	Very fine quartzose sand, small soft caliche nodules.
Ogallala Formation	10–20	Very pale brown	Very fine sandy caliche.
	20–30	Moderate brown	Hard sandy caliche in very fine/fine sandstone.
	30–50	Light brown	Fine/medium-grained sandstone (weakly cemented with calcite, sublithic, some sandy caliche).
	50–240	Light brown	Fine/medium-grained sandstone (weakly cemented with calcite, sublithic).
	240–280	Pale brown	Fine/medium-grained sublithic sandstone (weakly indurated) with sparse granule gravel (clasts are primarily chert, quartzite, sandstone).
	280–310	Pale brown	Medium/coarse-grained sublithic sandstone (well indurated with calcite).
	310–320	Pale brown	As above, but including cuttings of reddish brown mudstone - probably thin mudstone beds in this interval.
	320–330	Pale brown	Fine/medium-grained sublithic sandstone (weakly indurated) with sparse granule gravel (clasts are primarily chert, quartzite, sandstone).
	330–410	Pale brown	Medium/coarse-grained sublithic sandstone and granule gravel (clasts are primarily chert, quartzite, sandstone, abundant limestone, shells, some igneous and metamorphic rocks).
	410–430	Pale brown	As above, but with some coarser (small pebble) gravel.
Dockum Group	430–440	Pale yellowish brown	Mudstone.
	440–450	Pale yellowish brown	Mudstone with mottles of moderate brown.
	450–491	Moderate brown	Unstructured mudstone.
	491–494	Moderate brown	Massive slickensided mudstone with micaceous laminated siltstone.
	494–495	Grayish green	Micaceous siltstone/very fine-grained sandstone (lithic, calcite cemented).
Hale County Site			
Surface deposits	0–5	Pale yellowish brown	Sandy mud/muddy, very fine/fine sand with small caliche nodules and iron-oxide nodules.
	5–10	Very pale yellowish brown	Muddy, very fine/fine sand with small soft caliche nodules.
Blackwater Draw Formation	10–15	Light brown	Very fine/fine sand (quartzose).
	15–20	Light brown	Very fine/fine sand with small soft caliche nodules and clay/iron oxide grain coatings.
	20–40	Light brown	Soft sandy caliche in very fine/fine sand.
Ogallala Formation	40–50	Light brown	Hard laminated and massive caliche.
Hale County Site—Continued			
Ogallala Formation—Continued	50–60	Moderate reddish brown	Massive silty claystone with manganese-oxide coatings on joint surfaces and small caliche nodules.
	60–100	Moderate reddish brown	Weakly indurated siltstone/very fine sandstone with some claystone beds.

Table 2. Lithologic description of drill cuttings and cores.—Continued

Geologic unit	Depth, in feet below land surface	Color	Lithology
	100–140	Moderate to light brown	Fine/medium-grained sandstone (weakly indurated, sublithic).
	140–160	Moderate to light brown	Medium-grained sandstone (weakly indurated, sublithic).
	160–190	Light brown	Medium/very coarse-grained sublithic sandstone with granule gravel (clasts primarily chert, quartzite).
	190–210	Light brown	Medium/very coarse-grained sublithic sandstone with granule/small pebble gravel (clasts primarily chert, quartzite with some schist, gneiss, porphyritic igneous rocks).
	210–240	Pale brown	Medium-grained sublithic sandstone (well indurated with calcite) and sparse granule/small pebble gravel (clasts primarily chert, quartzite, sandstone, some limestone).
	240–280	Pale brown	Medium-grained sublithic sandstone (well indurated with calcite) and sparse granule/small pebble gravel (clasts primarily chert, quartzite, sandstone, abundant limestone).
	280–360	Pale brown	Medium/coarse-grained sublithic sandstone (well indurated with calcite) and sparse granule/small pebble gravel (clasts primarily chert, quartzite, sandstone, abundant limestone).
	360–380	Pale brown	As above, but including cuttings of reddish brown sandy mudstone—probably thin mudstone beds in this interval.
	380–410	Pale brown	Medium/coarse-grained sublithic sandstone (well indurated with calcite) and granule/small pebble gravel (clasts primarily limestone, chert, quartzite, sandstone), cuttings of reddish brown sandy mudstone.
Dockum Group	410–450	Moderate brown	Unstructured mudstone.
	450–490	Moderate brown	As above, but with greenish gray reduction spots.
	490–495	Greenish gray	Unstructured mudstone.
	495–500	Greenish gray	Crudely bedded micaceous lithic medium-grained sandstone (weakly cemented with calcite).

Table 3. Mineralogy in the Ogallala Formation.

Lithology	Description
GRAVEL/CONGLOMERATE	<p><u>QUARTZITE</u> - sutured polycrystalline quartz grains with some included muscovite and microcline crystals.</p> <p><u>SANDSTONE</u> - reworked fragments of quartzose sandstone, at least three types: (1) with calcite cement, (2) with iron-oxide cement, and (3) with siderite cement.</p> <p><u>LIMESTONE</u> - reworked fragments of limestone, all composed primarily of calcite (no dolomite), at least four types: (1) microcrystalline caliche, some with spar-filled cracks; (2) coarse skeletal limestone with sparry calcite cement and minor authigenic pyrite (mostly altered to iron oxides); (3) foliated calcite shell fragments (mostly ostreid bivalves); and (4) sandy phosphatic limestone with quartz silt/sand grains.</p> <p><u>MICROCLINE</u> - large monocrystalline and polycrystalline grains.</p> <p><u>VOLCANIC/PLUTONIC ROCKS</u> - fragments of fine-textured igneous rocks, some with orthoclase phenocrysts; groundmass of altered microcrystalline feldspar, quartz, and iron oxides.</p> <p><u>CHERT</u> - microcrystalline quartz with tiny amorphous iron-oxide inclusions.</p> <p><u>SHALE</u> - laminated cherty phosphatic shale, possibly with sponge spicules.</p>
SAND/SANDSTONE (detrital mineralogy)	<p><u>QUARTZ</u> (80–90 percent) - mostly monocrystalline plutonic and metamorphic quartz types; many grains are reworked sedimentary grains with abraded quartz overgrowths, minor number of chert grains.</p> <p><u>FELDSPAR</u> (5–10 percent) - mostly microcline (75 percent), minor plagioclase (15 percent), and orthoclase (10 percent); most grains are relatively fresh in appearance, except many orthoclase grains are partly sericitized (possibly during pre-depositional hydrothermal alteration).</p> <p><u>ALTERED VOLCANIC ROCK FRAGMENTS</u> (1–5 percent) - altered grains of groundmass from fine-textured volcanic or shallow plutonic rocks, silicic to intermediate composition; grains consist of microcrystalline mixtures of quartz, feldspar, and iron oxides (little or no remaining unaltered glass).</p> <p><u>CALCITE</u> (1–5 percent) - grains of caliche (microcrystalline calcite), limestone, reworked shell fragments and foraminifera, abraded spar crystals.</p> <p><u>ACCESSORY MINERALS</u> (less than 1 percent) - very small amounts of iron oxides (altered and pseudomorphic replacement of magnetite/ilmenite and/or pyrite), a few grains of muscovite, biotite, hornblende, zircon, tourmaline, apatite.</p>
SAND/SANDSTONE (authigenic mineralogy)	<p><u>CALCITE</u> - cementing agent is exclusively calcite, mostly microcrystalline, with some coarsely crystalline sparry calcite in lower part of the Ogallala Formation (Castro County, 290–300 feet and Hale County, 280–290 feet); in well-indurated sandstone the grains exhibit “super loose” packing and calcite cement comprises as much as 30–40 percent of the rock volume (an indication of early cementation at shallow depth - probably as pedogenic caliche).</p>
MUDSTONE (paired Ogallala and Dockum mudrock samples)	<p><u>COARSE FRACTION</u> - 35–50 percent quartz, 2–10 percent plagioclase, 1–8 percent calcite, 0–1 percent potassium feldspar.</p> <p><u>CLAY MINERALS</u> - 30–40 percent smectite, 5–12 percent illite (+ mica), 5–10 percent kaolinite.</p>

14 Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

substantial source of dissolved solids in ground water. Calcite and feldspars were less abundant than quartz in the aquifer, but both are relatively reactive mineral phases. Dissolution of these minerals can be a source of dissolved calcium, potassium, sodium, bicarbonate, and silica. Detrital calcite occurred in various forms, including pore-filling cements in sandstone rock fragments, reworked limestone and shell fragments, and caliche. Calcite was the only authigenic cementing agent observed in thin sections. Smectite was the primary clay mineral detected in mudstone samples from near the Ogallala/Dockum contact (table 3). Illite and kaolinite also were detected in lesser amounts in the mudstone. Fryar and others (2001) reported similar relative abundances of these clay minerals in the High Plains aquifer near Amarillo, Tex. Smectite has a relatively large cation exchange capacity, and cation exchange can be an important process affecting ground-water chemistry.

The Ogallala Formation at the Hale County site contained very little sedimentary organic carbon (table 4). The small amounts of organic carbon that were present mostly were in mudstone. The largest measured concentration of organic carbon was in a sample of the Randall Clay recovered from a playa floor near Lubbock, Tex. Most recharge to the aquifer is thought to occur through the bottom of playa basins (Wood and Sanford, 1995; Scanlon and Goldsmith, 1997), so it is possible that organic-carbon-enriched playa sediments could be a source of organic carbon to the aquifer.

VERTICAL HYDRAULIC GRADIENTS

Water-level data were collected from the nested wells at the Castro and Hale County sites on about a monthly basis from

April 2001 through September 2002 (figs. 7A and 7B). Water levels at both sites declined during the 2001 and 2002 irrigation seasons that extended from about April through September. For example, water levels declined by about 3 ft from April to September 2002 at the Castro County site. During the same time period at the Hale County site, the water-level decline was about 11 ft. Water levels dropped below the bottom of the screen in the water-table well (Hale-255) at the Hale County site during the 2001 and 2002 irrigation seasons; however, water levels rose above the bottom of the screen during the intervening winter months.

The water-level response during the winter of 2001–02 was very different at the two sites. At the Castro County site, wintertime water levels did not recover to levels measured at the start of the 2001 irrigation season (fig. 7A). In fact, water levels declined by about 0.4 ft from September to April. Wintertime water levels at the Hale County site recovered about 15 to 20 ft (fig. 7B) but did not recover to levels measured at the start of the 2001 irrigation season. These data indicate a net water-level decline occurred at both sites during the period of measurement.

Vertical hydraulic gradients indicate the direction of water movement in the aquifer. Downward gradients indicate the potential for contaminants that enter the aquifer from land surface to move deeper into the aquifer. Upward gradients likewise indicate the potential for contaminants that enter the aquifer from underlying geologic units to move upward into the aquifer. Almost all of the measured vertical gradients between adjacent wells in the aquifer at the Castro County site were downward (fig. 7C), and the median gradient at that site was 0.0013. In contrast, more than one-half the measured vertical gradients between adjacent wells in the aquifer at the Hale County site were upward (fig. 7D), and the median gradient at that site was

Table 4. Carbon content of sediments.

[Carbon contents are for the size fraction less than 2 millimeters; All values are estimated, so the total carbon content may not equal the sum of inorganic plus organic carbon; depths are in feet below land surface; g/kg, grams of carbon per kilogram of dry sediment; <, less than]

Site	Depth (feet)	Geologic unit	Lithology	Total carbon (g/kg)	Inorganic carbon (g/kg)	Organic carbon (g/kg)
Hale County	10–15	Blackwater Draw Formation	Red/brown very fine clayey sand.	23.21	21.30	1.91
	40–50	Ogallala Formation	Caliche.	72.64	71.90	.74
	50–60	Ogallala Formation	Upper fine-grained interval, red/brown mudstone.	41.67	39.70	1.97
	90–100	Ogallala Formation	Fine-grained sandstone.	36.41	36.40	< .20
	140–150	Ogallala Formation	Medium-grained sandstone.	5.28	5.50	< .20
	410–420	Ogallala/Dockum contact	Dockum mudstone and Ogallala gravel.	48.12	46.60	1.52
	470–480	Dockum Group	Red mudstone.	11.70	11.80	< .20
	490–480	Dockum Group	Green mudstone.	11.98	11.90	< .20
Playa lake near Lubbock, Texas	surface	Randall Clay soil	Clay.	4.17	< .20	4.14

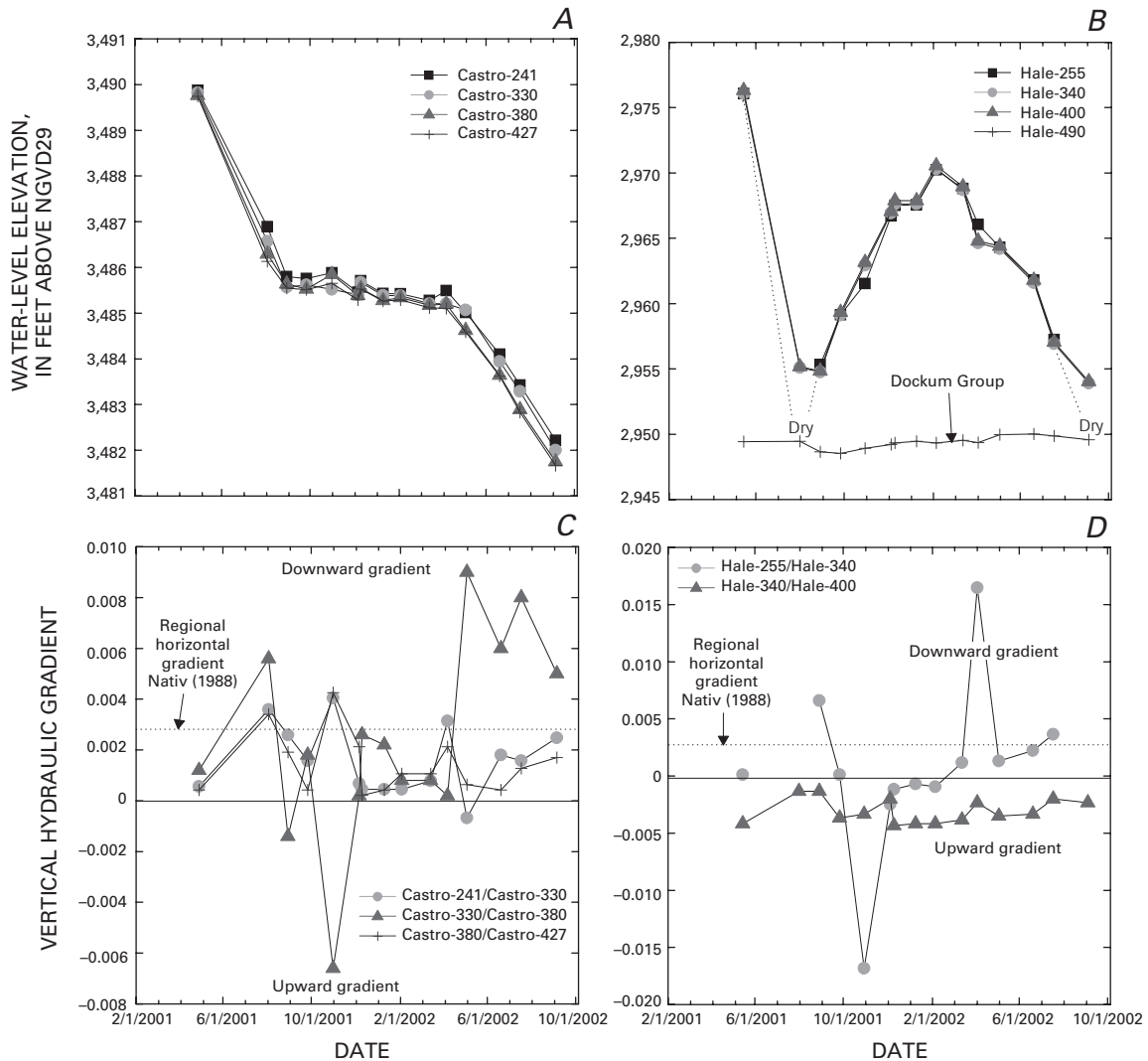


Figure 7. Water-level elevations and vertical hydraulic gradients in relation to time in nested wells at the Castro and Hale County sites.

-0.0022. The more frequent occurrence of upward gradients at the Hale County site compared to the Castro County site may be due, in part, to the proximity of the Hale County site to the regional discharge area along the eastern aquifer boundary (fig. 2).

The median gradient at the Castro County site (0.0013) was about one-half the value of the regional horizontal gradient (0.0028) reported by Nativ (1988). These values indicate that there was a greater potential for horizontal water movement in the aquifer at that site than vertical movement, which is expected in a semiarid environment in which recharge rates are slow. The actual horizontal and vertical components of water flux depend on the horizontal and vertical hydraulic conductivities of the sediment as well as the gradients. The median gradient at the Hale County site (-0.0022) was similar to that of the regional horizontal gradient, but opposite in sign, indicating

approximately equal potentials for horizontal and upward water movement existed at that site.

The vertical hydraulic gradient between Hale-400 and Hale-490 was downward with a median gradient (0.16) at least 10 times larger than most other measured gradients, indicating a strong potential for water in the aquifer to move into the underlying Dockum Group. This finding is important because water in the Dockum Group at this location was relatively mineralized compared to water in the aquifer, and the strong downward gradient indicates that little potential existed for that mineralized water to enter the High Plains aquifer. If the net water-level decline in the aquifer continues, however, it is possible that the hydraulic gradient between the aquifer and Dockum Group would be reversed, resulting in movement of mineralized water from the Dockum Group to the aquifer. A gradient reversal is most likely to occur during the irrigation season when water levels in the aquifer are low (fig. 7B).

VERTICAL GRADIENTS IN WATER CHEMISTRY

Concentrations of dissolved constituents varied with depth in the southern High Plains aquifer. Some of those variations were the result of inputs from sources at the land surface, and possibly underlying aquifers, and others were the result of chemical reactions along flow paths in the aquifer. This section presents chemical data and discusses processes that might account for the observed vertical gradients in water chemistry.

Tritium

Tritium is a radioactive isotope of hydrogen with a half-life of about 12.3 years. It is an excellent tracer of water movement because it substitutes for stable hydrogen isotopes in the water molecule. Because tritium is radioactive, its concentration in ground water decreases over time due to radioactive decay. In general, tritium in ground water originates from precipitation. Before the onset of atmospheric testing of nuclear weapons in 1953 (prebomb), the tritium content of precipitation in the study area probably was about 8 TU (Thatcher, 1962). As

a result of radioactive decay, ground water derived from precipitation that fell before 1953 contained less than 0.5 TU in 2002. The tritium content of precipitation increased substantially after the onset of atmospheric nuclear weapons testing but has slowly decreased from its peak in the early 1960s. Even with the variability in tritium content of precipitation over time, ground water totally derived from precipitation that fell since 1953 (postbomb) contained more than 0.5 TU in 2002. Water from the water-table wells (Castro-241 and Hale-255) contained more than 0.5 TU tritium at the time of sampling in 2002 (table 5), indicating that at least some of the water from those wells was derived from post-1953 recharge. The tritium concentrations in water from all the deeper wells were less than 0.3 TU, indicating that water from those wells was recharged before 1953.

Dissolved Oxygen and Organic Carbon

Some chemicals of environmental concern in the aquifer may be reduced to less oxidized forms by naturally occurring microorganisms under anoxic conditions, such as nitrate, selenate (the primary form of selenium in oxygenated ground water), uranium, and sulfate. Microbial reduction of these

Table 5. Isotope data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.

[Multiple entries indicate replicate samples or measurements; TU, tritium units; pmc, percent modern carbon; <, less than; --, no data]

Isotope	Well name and sampling date							
	Castro-241	Castro-330	Castro-380	Castro-427	Hale-255	Hale-340	Hale-400	Hale-490
	04-07-02	04-08-02	04-08-02	04-09-02	04-04-02	04-05-02	04-05-02	04-06-02
Tritium, in TU	1.3	< 0.3	< 0.3	< 0.3	5.7	< 0.3	< 0.3	< 0.3
$\delta^{18}\text{O}[\text{H}_2\text{O}]$, in per mil	-6.04	-7.65	-8.16	-8.22	-5.04	-6.71	-6.77	-7.96
$\delta^2\text{H}[\text{H}_2\text{O}]$, in per mil	-44.2	-52.9	-57.3	-58.0	-35.5	-48.1	-45.8	-54.6
$\delta^{13}\text{C}[\text{DIC}]$, in per mil	-9.47	-6.26 -4.25	-6.41	-6.16 -6.39	-7.30	-6.49	-6.15	-12.07 -12.14
$^{14}\text{C}[\text{DIC}]$, in pmc	67.03	21.98 22.36	22.05	20.36 21.42	50.54	34.55	31.38	48.08 47.68
$\delta^{15}\text{N}[\text{NO}_3]$, -in per mil	12.98	--	--	14.02 14.30	11.26	--	--	--
$\delta^{15}\text{N}[\text{N}_2]$, in per mil	0.68 0.80	1.51 1.54 1.53	1.61 1.75	1.65 1.75 1.72 1.75	0.55 0.50	0.96	0.93 0.89	1.02 1.58 1.05 1.40
$\delta^{34}\text{S}[\text{SO}_4]$, in per mil	3.58	1.95	0.43	0.16	5.45	2.84	3.05	9.84 9.87
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70900	0.70902	0.70898	0.70894 0.70893	0.70870	0.70893	0.70890	0.70902 0.70900

chemicals is beneficial because it may convert the chemicals into less soluble or less toxic forms. Reducing conditions, however, also may lead to the mobilization of toxic elements like arsenic. In oxygenated ground water, microorganisms may oxidize some chemicals, such as atrazine, ultimately to carbon dioxide (CO₂) (McMahon and others, 1992). The role of dissolved O₂ in microbial processes makes measuring its distribution in ground water important if the fate of potentially harmful chemicals is to be understood.

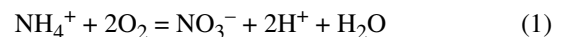
Concentrations of O₂ in the aquifer at the two sites ranged from less than 0.5 to 5.6 mg/L (Appendix 1). The largest concentrations occurred in water from the wells screened closest to the water table. At the Castro County site, concentrations of O₂ in water from the three deepest wells were less than 0.5 mg/L. There are two possible explanations for the small O₂ concentrations deeper in the aquifer at the Castro County site. The first possibility is that water from those wells was recharged with small O₂ concentrations. The second possibility is that the water from those wells was recharged with O₂ but subsequently lost the O₂ through biogeochemical reactions along flow paths in the aquifer. Determining which of these possibilities is correct has some importance with respect to interpreting other chemical data from the wells. Given that water from both water-table wells sampled in this study and 27 of 29 water-table wells sampled in another study of the southern High Plains aquifer (Lynne Fahlquist, U.S. Geological Survey, written commun., 2003) had O₂ concentrations larger than 2.5 mg/L, it is likely that water from deeper wells at the Castro County site contained O₂ at the time of recharge but subsequently lost the O₂ through biogeochemical reactions along flow paths in the aquifer. Concentrations of O₂ in water from the Hale County wells also decreased with depth below the water table, although O₂ concentrations in water from the deep Hale County wells were larger than the concentrations in water from the deep Castro County wells. The concentration of O₂ in water from the well screened in the Dockum Group (Hale-490) was less than 0.5 mg/L (Appendix 1).

Dissolved O₂ is readily reduced by microorganisms if suitable electron donors are available. Typical electron donors in aquifers are DOC, sedimentary organic carbon (SOC), and sulfide minerals. Concentrations of DOC in the aquifer were relatively small compared with DOC concentrations in the Dockum Group at the Hale County site (Appendix 1). The downward hydraulic gradient at the Hale County site precluded advective transport of DOC from the Dockum Group to the aquifer. However, it is possible that diffusive transport of DOC from the Dockum Group to the base of the aquifer occurred. Upward diffusive transport of DOC could have enhanced O₂ reduction near the base of the aquifer. Reduction of O₂ in the aquifer farther above its base may have been focused near contacts with fine-grained sediments that contained larger SOC concentrations (table 4) or at other locations in the aquifer containing electron donors such as sulfide minerals. Pyrite, mostly altered to iron oxides, was observed in gravel-sized rock fragments and in sand-sized grains in the aquifer (table 3).

Major Ions and Trace Elements

Water samples collected from the southern High Plains aquifer were of a mixed cation-bicarbonate type, indicating that no single major cation accounted for more than 50 percent of the cations and that bicarbonate accounted for more than 50 percent of the anions in the water. This water type is in agreement with the water types reported for this part of the aquifer by Nativ and Smith (1987). The sole exception to the mixed cation-bicarbonate water type was the water from Hale-255, which was of a mixed cation-mixed anion type. The water from Hale-490, screened in the Dockum Group, was of a sodium-chloride type.

Dissolved-solids concentrations in undisturbed aquifers usually increase with depth below the water table as the residence time of ground water increases and rock/water reactions progress. In this study, the largest concentrations of dissolved solids measured in the aquifer occurred at the water table (fig. 8A), which is a condition that has been observed in aquifers affected by agricultural recharge (Böhlke, 2002). Major ions that consistently exhibited elevated concentrations at the water table relative to deeper water included magnesium, sodium, chloride, and sulfate (Appendix 1 and fig. 8). The concentration of bicarbonate was larger at the water table at the Castro County site but not at the Hale County site. The opposite was true for potassium. Böhlke (2002) described several processes that can result in elevated concentrations of inorganic constituents in recharge under agricultural areas. Nitrogen in the fertilizer and manure applied to fields commonly is in a reduced form such as ammonium. Microbial oxidation of ammonium to nitrate produces acidity (eq. 1) that can result in dissolution of calcite (eq. 2) that is abundant in the unsaturated zone in the southern High Plains.



Dissolved calcium produced by equation 2 can exchange with sodium adsorbed to clay minerals, resulting in a net loss of dissolved calcium and a net gain in dissolved sodium (eq. 3).



Fryar and others (2001) concluded that cation exchange was an important process affecting the chemical composition of recharge in the southern High Plains aquifer. They also noted that recently recharged water in the aquifer near Amarillo, Tex., contained elevated chloride concentrations and attributed the chloride to human activities. Potassium chloride applied to fields as fertilizer might contribute to the elevated chloride concentrations at the water table, and calcium sulfate applied to fields as a soil amendment might contribute to elevated sulfate concentrations. Other evidence for the occurrence of recent recharge at the water table included postbomb tritium concentrations and pesticide detections (table 5 and Appendix 1).

18 Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

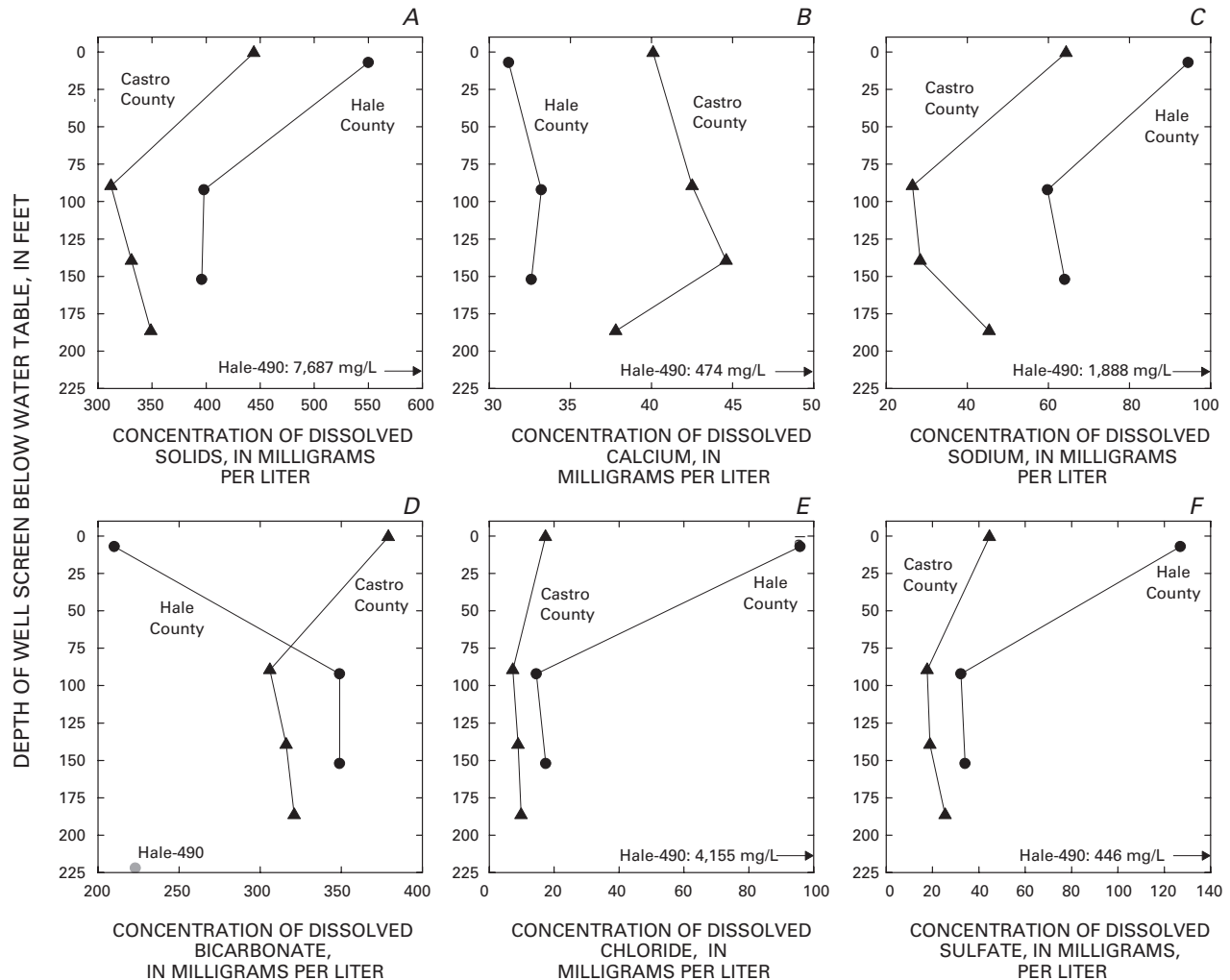


Figure 8. Concentration of selected dissolved constituents in relation to well-screen depth below the water table.

Prebomb tritium concentrations in water from the deeper wells indicate that those waters were recharged prior to the early 1950s and large-scale development of irrigated agriculture in the southern High Plains. Thus, the major-ion chemistry of water from the deeper wells could not have evolved from the water chemistry measured at the water table in 2002. The maximum measured dissolved-solids concentration in water from the deeper High Plains aquifer wells was 398 mg/L in Hale-340, indicating that deep water in the aquifer was dilute relative to the water table. In the deeper wells, the small increases in dissolved-solids concentrations with depth and distance along the regional hydraulic gradient from the Castro to Hale County sites primarily can be attributed to increases in concentrations of dissolved sodium, bicarbonate, chloride, and sulfate (fig. 8). The small increase in chloride concentrations with depth at the Castro County site (about 2.5 mg/L) may reflect temporal or spatial variability in chloride concentrations in recharge to the three deeper wells because there are no apparent chloride sources in the aquifer in that area. Chloride concentrations exhibited a larger increase (about 4.7 to 10.1 mg/L) along the

regional hydraulic gradient from the Castro to Hale County sites and could result from upward discharge of water from the underlying aquifer in rocks of Cretaceous age in addition to chemical variability in recharge. Nativ and Smith (1987) reported that the aquifer in rocks of Cretaceous age subcropping between the Castro and Hale County sites (fig. 3) discharged to the southern High Plains aquifer. Discharge from that aquifer could be lateral as well as vertical because of relief on Cretaceous erosional remnants (Seni, 1980). A cross plot of bromide/chloride mole ratios and chloride concentrations (fig. 9A) shows that water from the Hale County wells generally plot along mixing lines between water from the Castro County wells and from wells screened in the aquifer in rocks of Cretaceous age (Nativ and Smith, 1987). Water samples from the Hale County wells could contain 10 to 20 percent water from the aquifer in rocks of Cretaceous age based on their positions along the mixing lines. Data from the water-table wells were excluded from the cross plots because they are not considered to be upgradient equivalents of water from the deeper wells. Data from Hale-490 also were excluded from the cross plots because the Dockum

Group in which that well is screened is considered to be part of a separate flow system.

The increase in sulfate concentrations with depth at the Castro County site was inversely related to the $\delta^{34}\text{S}[\text{SO}_4]$ values (fig. 9B). This trend indicates that the sulfate-concentration increase might be related to oxidation of small amounts of pyrite, a source of ^{34}S -depleted sulfur, in the aquifer. Pyrite, mostly oxidized to iron oxides, was observed in thin sections of sediments from this site (table 3). Sulfate concentrations also increased along the regional hydraulic gradient from the Castro to Hale County sites, but this concentration increase was directly related to $\delta^{34}\text{S}[\text{SO}_4]$ values (fig. 9B). This trend might be explained by ^{34}S -enriched dissolved sulfate from the underlying aquifer in rocks of Cretaceous age (fig. 9B) entering the southern High Plains aquifer between the Castro and Hale County sites. The presence of an upward hydraulic gradient between the southern High Plains aquifer and the aquifer in rocks of Cretaceous age (Nativ and Smith, 1987) indicates that the potential existed for water to move from that aquifer at least to the base of the southern High Plains aquifer. Water at the

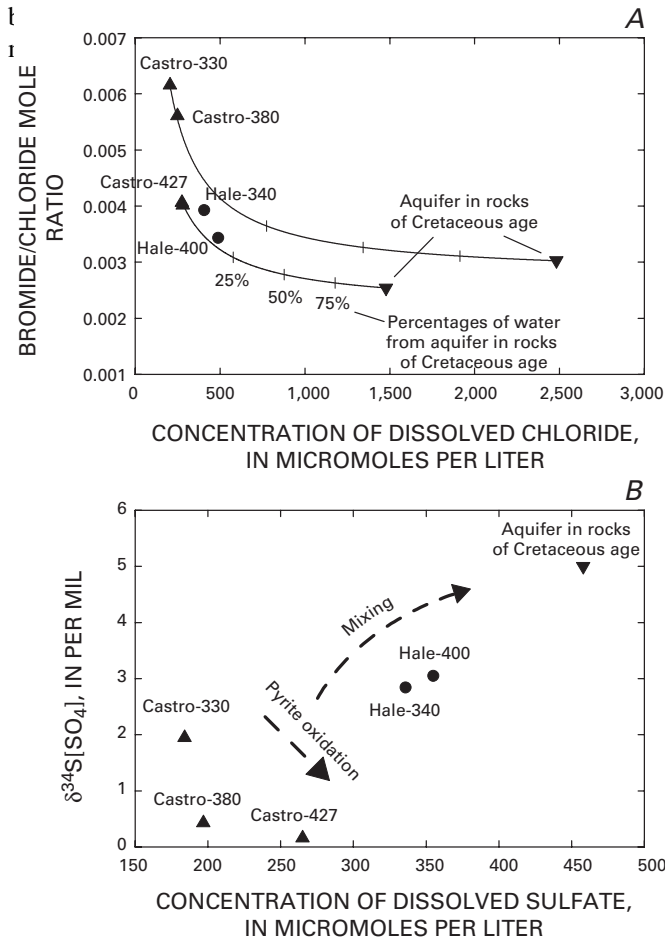
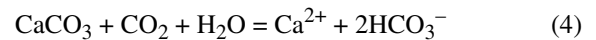


Figure 9. (A) Bromide/chloride mole ratios in relation to concentration of dissolved chloride and (B) sulfate-sulfur isotopes in relation to concentration of dissolved sulfate. Chemical and isotope data for water from the aquifer in rocks of Cretaceous age from Nativ and Smith, 1987. Dashed lines indicate approximate trends.

pumping in this area of intensive irrigation (fig. 5). Vertical mixing is discussed further in the section “Radiocarbon Ages.”

Cross plots of chloride concentrations compared to sodium and bicarbonate concentrations indicate that mixing with water from the aquifer in rocks of Cretaceous age cannot fully account for observed increases in concentrations of these constituents with depth and distance along the regional hydraulic gradient (figs. 10A and 10B). Data from the southern High Plains aquifer plot above the general trend lines for mixing, indicating that the sodium and bicarbonate concentration increases are in excess of what could be produced by mixing. Cross plots of sodium and bicarbonate and calcium and bicarbonate concentrations indicate that the coupled processes of calcite dissolution and cation exchange also might contribute to observed sodium and bicarbonate increases in the aquifer (eqs. 2 and 3; fig. 10C). The net result of equations 2 and 3 would be an increase in sodium and bicarbonate concentrations in a 2:1 ratio. A line with a slope of 2.2 was obtained from a linear regression least-squares fit to the data in figure 10C. Pyrite oxidation might be one source of acidity to cause calcite dissolution. Carbon dioxide produced from the oxidation of organic matter coupled to O_2 reduction (discussed in the section “Dissolved Oxygen and Organic Carbon”) and denitrification (discussed in the section “Nitrate”) also could dissolve calcite, as shown in equation 4.



The net result of equations 3 and 4 would be an increase in sodium and bicarbonate concentrations in a 1:1 ratio. The measured slope of 2.2 in figure 10C is more indicative of equations 2 and 3; however, the data in figure 10C also could reflect variable recharge compositions as well as mixing with water from the aquifer in rocks of Cretaceous age. The apparent state of equilibrium between ground water and calcite based on saturation indices (table 6) indicates that oxidation-reduction reactions and cation exchange were required to cause small amounts of calcite dissolution in the southern High Plains aquifer.

Concentrations of dissolved trace elements in the southern High Plains aquifer generally were small (Appendix 1) and did not exceed primary drinking-water standards (U.S. Environmental Protection Agency, 2003b). Manganese concentrations in water from three wells at the Castro County site did, however, exceed the secondary drinking-water standard of 50 $\mu\text{g}/\text{L}$ (U.S. Environmental Protection Agency, 2003b). Two of these relatively large manganese concentrations occurred in anoxic water and probably are the products of microbially mediated manganese reduction. The largest measured manganese and iron concentrations, 471 and 1,062 $\mu\text{g}/\text{L}$, were in water from Hale-490, screened in the Dockum Group. These large concentrations indicate more extensive manganese and iron reduction occurred in the Dockum Group sediments than in the aquifer, probably supported by the large DOC concentrations in water from the Dockum Group (Appendix 1). Other evidence of

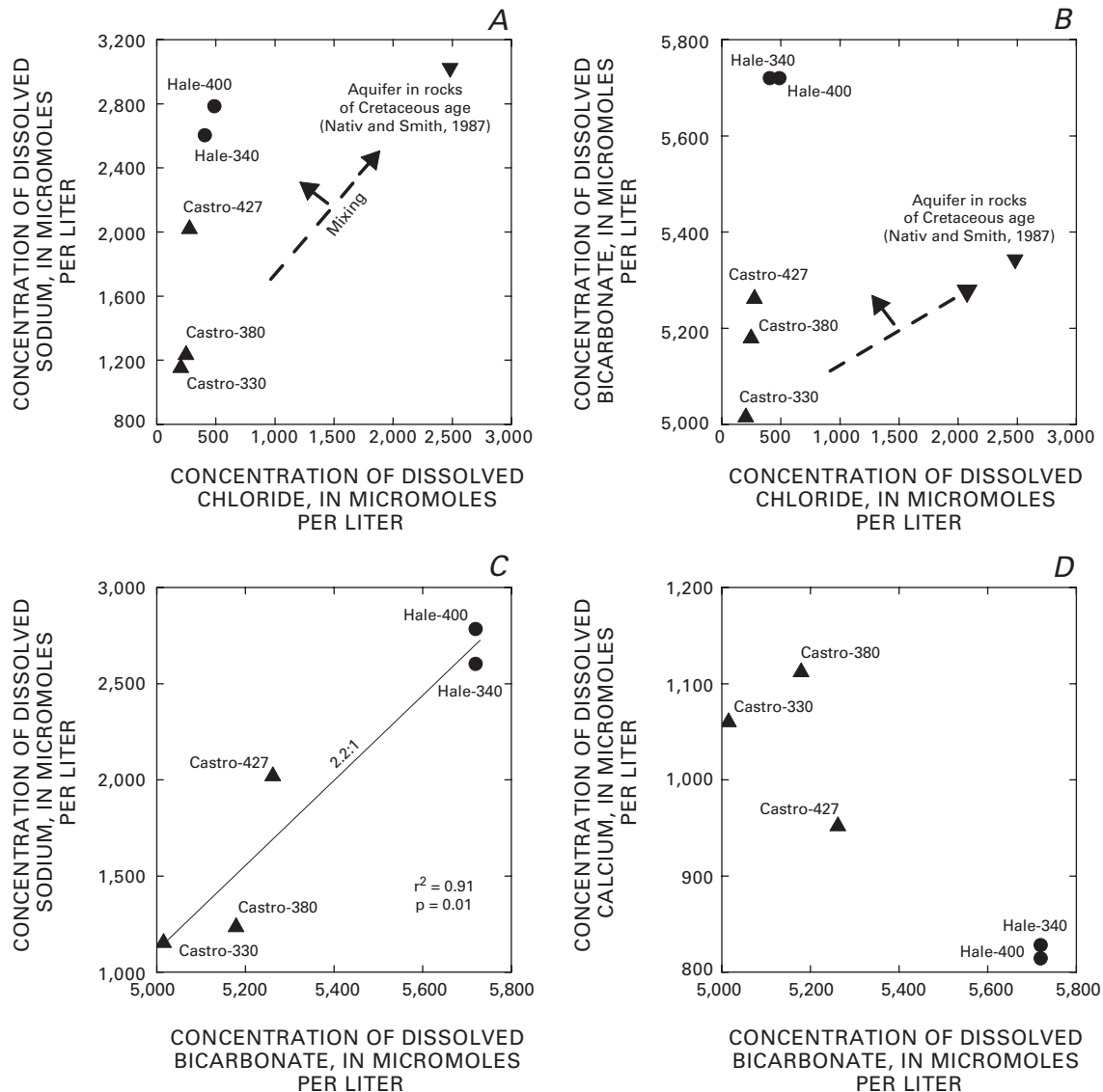


Figure 10. (A) Concentrations of dissolved sodium in relation to dissolved chloride, (B) concentrations of dissolved bicarbonate in relation to dissolved chloride, (C) concentrations of dissolved sodium in relation to dissolved bicarbonate, and (D) concentrations of dissolved calcium in relation to dissolved bicarbonate. Chemical data for the aquifer in rocks of Cretaceous age from Nativ and Smith, 1987. Dashed lines indicate approximate trends.

extensive microbial respiration in the Dockum Group includes measurable sulfide (Appendix 1), large methane concentrations (table 7), and more negative $\delta^{13}\text{C}[\text{DIC}]$ values in the Dockum Group compared to the aquifer (table 5). Microbially mediated manganese, iron, and sulfate reduction are coupled to the oxidation of organic carbon that typically has $\delta^{13}\text{C}$ values ranging from -25 to -20 per mil. Other trace elements in water from the Dockum Group that were present in relatively large concentrations compared to waters from the aquifer include barium, boron, and strontium.

Arsenic adsorbed to surfaces of manganese- and iron-oxide minerals can be released to solution as a result of manganese and iron reduction in anoxic environments. The largest

measured arsenic concentration, $12\ \mu\text{g/L}$ (which exceeds the $10\text{-}\mu\text{g/L}$ drinking-water standard) (U.S. Environmental Protection Agency, 2003b), was in water from Hale-490 (Appendix 1), which also contained the largest concentrations of dissolved manganese and iron. Concentrations of dissolved arsenic in anoxic waters from the aquifer at the Castro County site, however, were not elevated relative to the arsenic concentrations in oxic water from the aquifer (for example, Hale-340).

Nitrate

Nitrogen is naturally present in relatively small concentrations in rocks, soils, organic material, and the water that comes

Table 6. Mineral-saturation indices for water from monitoring wells screened in the southern High Plains aquifer.

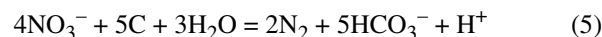
[A positive value indicates the water was supersaturated with respect to the indicated mineral phase and that the potential existed for that mineral to precipitate. A negative value indicates the water was undersaturated with respect to the indicated mineral phase and that the potential existed for that mineral to dissolve. For aluminosilicate minerals, an aluminum concentration of 0.0001 or 0.0005 (in parentheses) milligram per liter was assumed if the measured concentration was below the 0.001 milligram per liter detection level.]

Mineral	Well name and sampling date						
	Castro-241	Castro-330	Castro-380	Castro-427	Hale-255	Hale-340	Hale-400
	04-07-02	04-08-02	04-08-02	04-09-02	04-04-02	04-05-02	04-05-02
Quartz	1.131	0.893	0.847	0.794	0.853	0.933	0.931
SiO ₂ (amorphous)	-0.222	-0.425	-0.476	-0.528	-0.472	-0.384	-0.386
Kaolinite	3.950	0.586 (1.984)	0.573 (1.971)	0.132 (1.530)	1.983	0.352 (1.750)	0.385 (1.783)
Albite	0.075	-2.596 (-1.897)	-2.685 (-1.987)	-2.619 (-1.920)	-0.277	-2.119 (-1.420)	-2.107 (-1.408)
Potassium feldspar	1.603	-0.697 (0.002)	-0.854 (-0.155)	-0.976 (-0.277)	1.339	-0.538 (0.161)	-0.548 (0.151)
Anorthite	-3.268	-6.626 (-5.228)	-6.692 (-5.294)	-6.835 (-5.437)	-3.168	-6.654 (-5.256)	-6.689 (-5.291)
Calcium montmoril- lonite	3.432	-0.786 (0.843)	-0.874 (0.754)	-1.409 (0.220)	1.125	-0.970 (0.658)	-0.946 (0.683)
Illite	2.915	-1.394 (0.214)	-1.507 (0.101)	-1.886 (-0.278)	1.595	-1.420 (0.188)	-1.415 (0.193)
Calcite	0.188	-0.048	-0.018	0.095	0.719	0.045	0.007
Anhydrite	-2.449	-2.782	-2.742	-2.671	-2.145	-2.644	-2.629

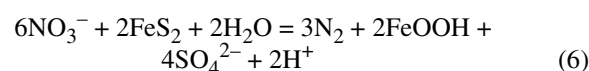
in contact with them (Holloway and Dahlgren, 1999). Nitrogen also is present in relatively large concentrations in animal manure and fertilizers applied to agricultural fields and in treated sewage effluent. Nitrate, the most commonly occurring form of nitrogen in ground water, is of environmental concern because its discharge to surface water can support eutrophication. Nitrate also is a health concern because ingestion of large concentrations of nitrate in drinking water can lead to low oxygen levels in the blood of infants (Fan and Steinberg, 1996). The USEPA has established a primary drinking-water standard for nitrate of 10 mg/L as N (U.S. Environmental Protection Agency, 2003a).

Concentrations of dissolved nitrite plus nitrate in the aquifer ranged from less than 0.05 to 6.1 mg/L as N. Water samples from wells screened near the water table were the only ones with nitrite plus nitrate concentrations larger than 1 mg/L as N (Appendix 1). In all cases, nitrate concentrations were larger than nitrite concentrations. The relatively large nitrate concentrations, pesticide detections, and postbomb tritium concentrations in water from the wells screened near the water table compared to water from deeper parts of the aquifer indicate that recent recharge affected by agricultural activities was present at the top of the aquifer. The consistently small concentrations of nitrate in water farther below the water table might be attributed either to a lack of nitrate in recharge to those wells (tritium data indicate those waters were recharged prior to the start of modern agriculture in the area) or denitrification along flow paths in the aquifer.

Denitrification is a microbially mediated process that reduces nitrate to N₂ gas (eq. 5) in suboxic environments.



In equation 5, reduction of nitrate is coupled to the oxidation of organic carbon, which produces N₂ and bicarbonate. In some environments, denitrification may be coupled to the oxidation of sulfide minerals instead of, or in addition to, organic carbon (Postma and others, 1991; Böhlke and others, 2002), which produces N₂ and dissolved sulfate (eq. 6).



Small amounts of organic carbon and pyrite were detected in the aquifer (tables 3 and 4).

One way to evaluate whether denitrification has occurred in the aquifer is to calculate the amount of N₂ in ground water from denitrification, referred to here as N₂-nonatmospheric (eq. 7).

$$[\text{N}_2\text{-nonatmospheric}] = [\text{N}_2\text{-total}] - [\text{N}_2\text{-air saturation}] - [\text{N}_2\text{-excess air}] \quad (7)$$

In equation 7, N₂-total represents the measured concentration of N₂ dissolved in water (table 7), N₂-air saturation represents the amount of N₂ dissolved in water as a result of air-water equilibration at recharge conditions, and N₂-excess air represents the amount of N₂ in water from dissolution of excess air (air bubbles) in water. The value of N₂-air saturation is dependent on the temperature and elevation of the water table in the recharge area at the time of recharge. Recharge temperatures

Table 7. Dissolved-gas and related data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.

[Multiple entries indicate replicate samples or measurements. Reported 1-sigma uncertainties are based on the reproducibility of the measured gas concentrations and isotope values; μM , micromoles per liter; \pm , plus or minus 1 standard deviation; $\text{cm}^3 \text{STP/L}$, cubic centimeters per liter at standard temperature and pressure; $\delta^{15}\text{N}[\text{NO}_3]$, nitrogen isotope composition of nitrate; $\delta^{15}\text{N}[\text{N}_2\text{-nonatmospheric}]$, nitrogen isotope composition of nonatmospheric nitrogen gas; --, no data; <, less than]

Parameter	Well name and sampling date							
	Castro-241	Castro-330	Castro-380	Castro-427	Hale-255	Hale-340	Hale-400	Hale-490
	04-07-02	04-08-02	04-08-02	04-09-02	04-04-02	04-05-02	04-05-02	04-06-02
Estimated elevation of water table in recharge area, in feet	3,490	3,570	3,620	3,655	2,995	3,150	3,400	3,480
Dissolved oxygen, in μM	139	5	1	11	177	111	121	< 1
	139	6	2	12	181	112	120	< 1
		5		15				< 1
		7		11				< 1
Dissolved methane, in μM	9.74	0.4	8.7	0.3	< 0.1	< 0.1	< 0.1	649
	10.6	0.4	8.5	0.3	< 0.1	< 0.1	< 0.1	646
		0.4		0.3				653
		0.4		0.3				661
Dissolved nitrogen (N_2 -total), in μM	547	612	617	600	659	611	604	719
	547	616	606	590	661	614	609	716
		618		590				734
		613		592				710
$\delta^{15}\text{N}[\text{N}_2\text{-total}]$, in per mil	0.68	1.51	1.61	1.60	0.55	0.96	0.93	1.02
	0.80	1.54	1.75	1.72	0.50		0.89	1.05
		1.53		1.75				1.40
				1.75				1.58
Dissolved argon (Ar -total), in μM	13.80	14.39	14.22	13.86	15.00	14.94	14.73	14.77
	13.81	14.49	14.04	13.74	15.05	14.97	14.85	14.78
		14.54		13.68				15.00
		14.40		13.73				14.62
Dissolved neon, in μM ($\times 10^{-3}$)	7.79 \pm 0.05	8.22 \pm 0.03	--	8.20 \pm 0.03	8.81 \pm 0.05	9.10 \pm 0.06	9.07 \pm 0.05	--
				8.19 \pm 0.05				
				8.21 \pm 0.03				
				8.07 \pm 0.03				
Recharge temperature, in degrees Celsius	14.4 \pm 0.1	12.7 \pm 0.2	14.0 \pm 1.0 ^a	15.2 \pm 0.3	12.6 \pm 0.1 (16.0 \pm 1.0) ^b	13.1 \pm 0.1	13.3 \pm 0.3	14.0 \pm 1.0 ^a
Excess air, in $\text{cm}^3 \text{STP/L}$	0.23 \pm 0.06	0.64 \pm 0.04	0.88 \pm 0.6	0.81 \pm 0.09	1.2 \pm 0.1 (3.6 \pm 0.6) ^c	1.6 \pm 0.1	1.7 \pm 0.1	2.3 \pm 0.7
Dissolved nitrogen from air saturation (N_2 -air saturation), in μM	519 \pm 1	536 \pm 3	521 \pm 9	508 \pm 3	549 \pm 1 (512 \pm 8) ^c	539 \pm 1	532 \pm 3	523 \pm 9

Table 7. Dissolved-gas and related data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.—Continued

[Multiple entries indicate replicate samples or measurements. Reported 1-sigma uncertainties are based on the reproducibility of the measured gas concentrations and isotope values; μM , micromoles per liter; \pm , plus or minus 1 standard deviation; $\text{cm}^3 \text{STP/L}$, cubic centimeters per liter at standard temperature and pressure; $\delta^{15}\text{N}[\text{NO}_3]$, nitrogen isotope composition of nitrate; $\delta^{15}\text{N}[\text{N}_2\text{-nonatmospheric}]$, nitrogen isotope composition of nonatmospheric nitrogen gas; --, no data; <, less than]

Parameter	Well name and sampling date							
	Castro-241	Castro-330	Castro-380	Castro-427	Hale-255	Hale-340	Hale-400	Hale-490
	04-07-02	04-08-02	04-08-02	04-09-02	04-04-02	04-05-02	04-05-02	04-06-02
Dissolved nitrogen from excess air ($\text{N}_2\text{-excess air}$), in μM	8.1 \pm 2.2	22 \pm 1	32 \pm 21	28 \pm 3	40 \pm 2 (125 \pm 17) ^c	56 \pm 3	59 \pm 2	80 \pm 24
Dissolved nitrogen from nonatmospheric sources ($\text{N}_2\text{-nonatmospheric}$), in μM	20 \pm 1	57 \pm 3	60 \pm 12	56 \pm 5	71 \pm 2 (23 \pm 16) ^c	17 \pm 2	16 \pm 3	116 \pm 13
$\delta^{15}\text{N}[\text{N}_2\text{-nonatmospheric}]$, in per mil	-- ^d	9.6 \pm 0.4	11.1 \pm 2.0	11.6 \pm 1.1	-- ^d	-- ^d	-- ^d	4.6 \pm 1.6
Nitrate, measured, in μM	143	< 3.6	10	39	436	26	27	< 3.6
$\delta^{15}\text{N}[\text{NO}_3]$, measured, in per mil	12.98	--	--	14.02 14.30	11.26	--	--	--
Nitrate, initial, in μM	143 ^d	114 \pm 6	130 \pm 24	151 \pm 8	436 ^d	26 ^d	27 ^d	232 \pm 26
$\delta^{15}\text{N}[\text{NO}_3]$, initial, in per mil	12.98 ^d	9.6 \pm 0.4	11.1 \pm 2.0 ^e	12.3 \pm 0.7	11.26 ^d	--	--	4.6 \pm 1.6
(Nitrate, measured)/ (nitrate, initial)	1.0	<0.03	0.08 \pm 0.01	0.26 \pm 0.01	1.0	1.0	1.0	<.03

^aRecharge temperature estimated from nitrogen and argon data.

^bRecharge temperature equal to mean annual air temperature plus 1 degree Celsius (see "Nitrate" section).

^cCalculation assumes recharge temperature equal to mean annual air temperature plus 1 degree Celsius.

^dAssumes sample has no nonatmospheric nitrogen gas.

^eMinimum value.

were calculated using measured concentrations of dissolved Ne and Ar (Stute and Schlosser, 1993) and assuming complete dissolution of excess air during recharge. The elevation of the water table in the recharge area of a well depends on several factors, including depth of the well screen below the water table, location of the well in the regional flow system, and recharge rate (Cook and Böhlke, 2000). In general, the elevation of the water table in the recharge area of a well increases relative to the local water-table elevation as the depth of the well screen below the water table increases. Coupled ground-water flow and particle-tracking simulations were used to estimate the elevation of the water table in the recharge area of wells in the central High Plains aquifer that were constructed the same way as those used in this study (McMahon and others, in press). Results of those simulations also were used to estimate the elevation of the water table in the recharge area of the southern High Plains wells by taking the difference between recharge elevation and local water-table elevation from central High Plains wells and adding the difference to local water-table elevations of southern High Plains wells with similar screen depths below the water table. The estimated water-table elevations in the recharge area are listed in table 7. Uncertainty in the amount of nonatmospheric N₂ resulting from these estimates is discussed later in this section.

The value of N₂-excess air was calculated using equation 8:

$$[\text{N}_2\text{-excess air}] = [\text{N}_2/\text{Ar}]\text{-air} \times \{[\text{Ar-total}] - [\text{Ar-air saturation}]\} \quad (8)$$

where [N₂/Ar]-air is the ratio of N₂ and Ar mole fractions in air (83.6), Ar-total represents the measured concentration of Ar dissolved in water (table 7), and Ar-air saturation represents the amount of Ar dissolved in water as a result of air-water equilibrium, as determined from the Ne and Ar data. Equation 8 assumes that the gas composition of the dissolved air bubbles was identical to that of air.

Excluding Hale-255, recharge temperatures calculated using the Ne and Ar data ranged from 12.7±0.2 to 15.2±0.3°C (table 7). A recharge temperature of 14.0±1.0°C was estimated from N₂ and Ar data for two wells that did not have Ne analyses. As will be discussed, the recharge temperature calculated for Hale-255 using the Ne and Ar data is believed to have been affected by fractionation of the excess air, so a recharge temperature of 16.0±1.0°C was assigned to that well. This temperature is equal to the mean annual (1890 to 2000; CO₂ Science Magazine, 2003) air temperature at Plainview, Tex., plus 1°C. Stute and others (1995) proposed that noble-gas recharge temperatures are approximately equal to the mean annual air temperature at the time of recharge plus 0° to 2°C. The amount of nonatmospheric N₂ in each sample (table 7) can be calculated once recharge temperature is determined.

Concentrations of N₂-nonatmospheric in the water samples ranged from 16±3 to 116±13 μM (table 7). In a plot of δ¹⁵N[N₂] as a function of Ar/N₂ mole ratios, three groups of samples were identified with distinct O₂ concentrations and

sample depths (fig. 11). Two groups of samples contained more than 60 μM O₂ and less than 25 μM N₂-nonatmospheric and one sample group contained less than 60 μM O₂ and 56 to 116 μM N₂-nonatmospheric (table 7 and fig. 11). The shallow samples containing more than 60 μM O₂ are from the water-table wells and have values near those expected for air-saturated water or along a mixing line between air and air-saturated water, indicating that they contained little or no N₂-nonatmospheric. In contrast, the samples containing less than 60 μM O₂ have values farthest from those expected for air-saturated water, indicating the presence of substantial N₂-nonatmospheric in those samples. The deep samples containing more than 60 μM O₂ plotted between the other two sample groups and might represent a mixture or transition between the water types represented by those groups. In general, the pattern illustrated in figure 11 is consistent with denitrification in deeper parts of the aquifer where sufficient amounts of O₂ had been consumed prior to denitrification.

A small degree of uncertainty in the amount of N₂-nonatmospheric in the samples resulted from uncertainty in the elevation of the water table in the recharge area of the wells. The maximum possible elevation of the water table in the recharge areas, represented by the water-table elevation at the upgradient edge of the aquifer, was about 1,000 ft higher than the water table at either site. If this 1,000-ft elevation difference was used to calculate the amount of N₂-nonatmospheric in the water sample from Castro-427, which contained a relatively large amount of N₂-nonatmospheric, instead of the 165-ft difference that was actually used, the amount of N₂-nonatmospheric in the sample would decrease by about 5 percent. For the sample from Hale-400, which contained a relatively small amount of N₂-nonatmospheric, the amount would decrease by about 12 percent.

The small apparent concentrations of N₂-nonatmospheric in the shallow oxic samples might indicate there were small biases in the gas ratios caused by either recharge processes (for example, fractionation of excess air) or analytical inconsistencies (Ne and Ar samples were collected and analyzed using different procedures). At Hale-255, the low noble-gas recharge temperature and large amount of N₂-nonatmospheric calculated on the basis of that recharge temperature (table 7) might be accounted for by diffusive loss of the light noble gas Ne from solution or by preferential dissolution of the heavy noble gas Ar. Water from Hale-255 might have been susceptible to fractionation of excess air because of the large (20 ft) water-level fluctuations and seasonally dry conditions in that well (fig. 7B), which would reduce the confinement of excess air below the water table. More rigorous adjustments of recharge temperatures and nonatmospheric N₂ might be possible with additional noble-gas analyses (for example, Aeschbach-Hertig and others, 2000).

The calculations of N₂-nonatmospheric indicate that small nitrate concentrations in suboxic waters were the result of denitrification. The fraction of nitrate remaining in the suboxic water samples at the time of collection was less than 3 to 26 percent of the nitrate concentration in water at the time of recharge (table 7). In other words, denitrification removed 74 to more

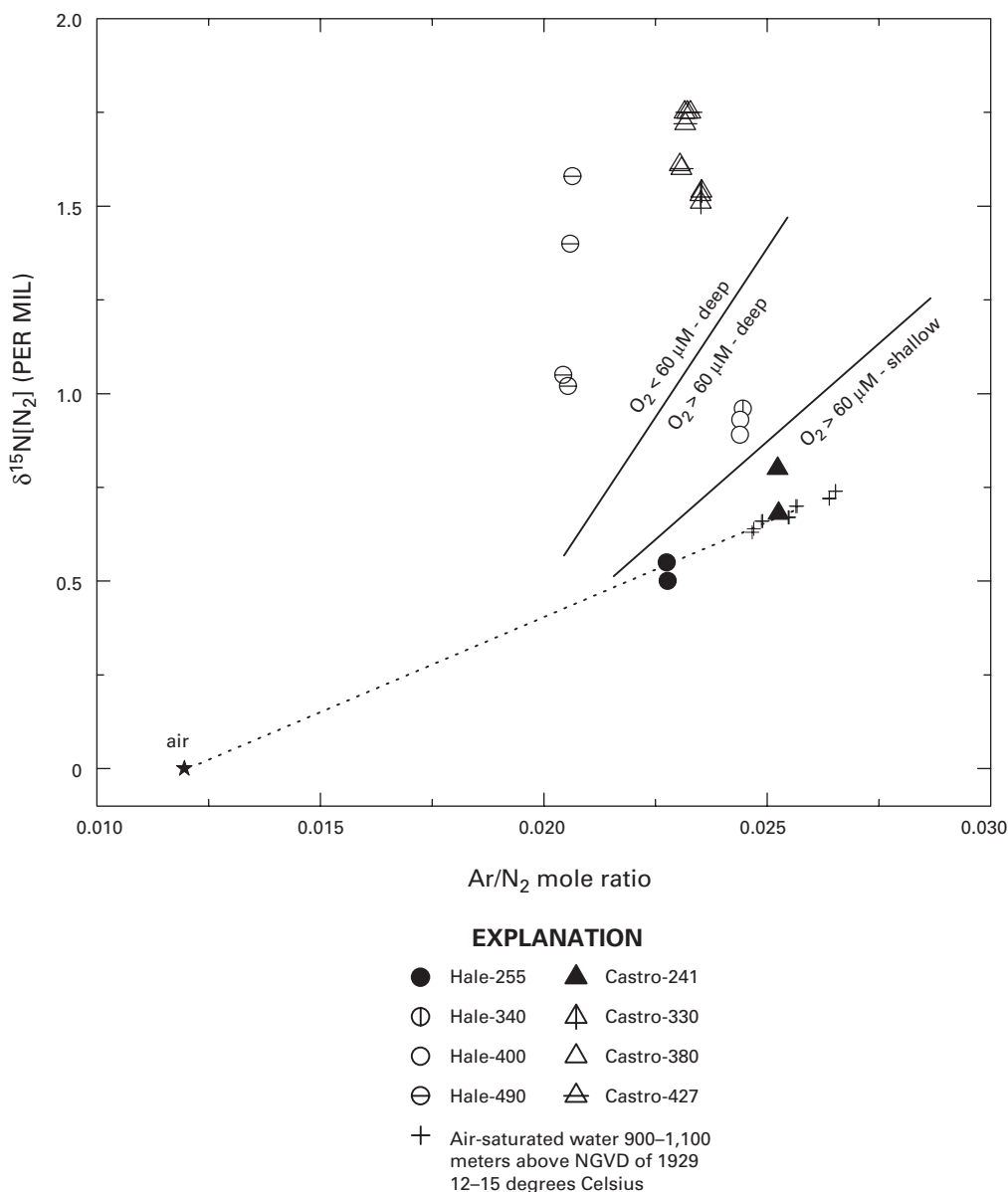


Figure 11. Nitrogen isotope composition of nitrogen gas as a function of argon/nitrogen gas ratios.

than 97 percent of the nitrate originally present in recharge. The amount of nitrate in the water samples at the time of recharge was calculated, or reconstructed, by summing the amount of nitrate in the sample at the time of collection and the amount of nitrogen in N_2 -nonatmospheric. For water samples not affected by modern agricultural activity (the three deepest wells at each site), nitrate concentrations at the time of recharge ranged from 26 to 232 μM (0.4 to 3.2 mg/L as N) (table 7), with an average of 113 μM (1.6 mg/L as N). This average nitrate concentration is considered the average background nitrate concentration at these sites and is about 40 percent smaller than the average background nitrate concentration of 193 μM (2.7 mg/L) determined from samples collected along a transect in the central High Plains aquifer (McMahon and others, in press).

The reconstructed nitrogen isotope composition ($\delta^{15}N[NO_3]$) of background nitrate in the aquifer ranged from 9.6 to 12.3 per mil and was enriched in ^{15}N by 1.4 to 6.0 per mil relative to background nitrate along the central High Plains transect (McMahon and others, in press). The smaller average concentration and larger $\delta^{15}N$ values for background nitrate in the southern High Plains aquifer relative to the central High Plains aquifer are consistent with increased nitrogen loss during recharge in the southern High Plains either by volatilization of ammonia or by denitrification (Böhlke, 2002); however, more work is required to fully evaluate these possibilities. The isotope composition of background nitrate in the southern High Plains aquifer was similar to the isotope composition of nitrate in water from the water-table wells that may have been affected

by agriculture (table 7). This similarity indicates that nitrate in both groups of wells was derived from sources having similar isotope compositions or that the nitrogen from different sources was subjected to fractionation processes during recharge that resulted in similar isotope compositions. The reconstructed isotope composition of nitrate in water from the Dockum Group (Hale-490) was depleted in ^{15}N by at least 5 per mil relative to the aquifer samples; however, it is known that exceptionally large CH_4 concentrations (like those measured in water from Hale-490) cause problems with the $\delta^{15}\text{N}[\text{N}_2]$ analysis, so the reconstructed initial isotope composition of nitrate in that sample is questionable.

Pesticides

The two water-table wells (Castro-241 and Hale-255) were the only wells to produce water that contained detectable concentrations of pesticides or pesticide degradation products (Appendix 1). Atrazine and cyanazine, triazine herbicides largely used to control annual grass and broadleaf weeds in corn, were detected in water from Castro-241 at concentrations of 1.04 $\mu\text{g}/\text{L}$ and 0.0526 $\mu\text{g}/\text{L}$. Both of these concentrations are less than the drinking-water standards or health advisory levels established for these chemicals (U.S. Environmental Protection Agency, 2003a,b). Deethylatrazine, a degradation product of atrazine, was detected in water from Castro-241 and Hale-255 at estimated concentrations less than 0.2 $\mu\text{g}/\text{L}$.

Tritium data indicate that the lack of pesticide detections in water from the three deepest wells at each site probably is due to that water having been recharged prior to the widespread use of pesticides in the study area. Even though irrigation pumping has resulted in water-level declines and downward hydraulic gradients in some areas (fig. 7), those disturbances did not result in the detection of pesticides deeper in the aquifer.

VERTICAL GRADIENTS IN GROUND-WATER AGE

As discussed in the "Tritium" section, water from the water-table wells was recharged after the early 1950s, whereas water from the three deeper wells at each site was recharged before the early 1950s. These data indicate vertical gradients in ground-water age were present at the Castro and Hale County sites. The magnitude of the gradient, however, cannot be determined using tritium data alone. Measurements of $^{14}\text{C}[\text{DIC}]$ have been used by several researchers to estimate ground-water ages greater than about 1,000 years (Plummer and others, 1990, 2001; Aravena and others, 1995). Applying $^{14}\text{C}[\text{DIC}]$ measurements to ground-water age-dating problems requires that those measurements be adjusted for the addition or removal of dissolved inorganic carbon along flow paths leading to the sampled wells. Construction of mass-balance models to account for changes in concentrations of dissolved constituents between

initial and final waters along flow paths is one approach for making those adjustments (Plummer and others, 1994).

Mass-Balance Models

Mass-balance models require chemical and isotope data for an initial (upgradient) and a final (downgradient) water. The initial and final waters are from wells assumed to be located on the same flow path, and it is further assumed that the chemistry of the initial water has not changed over time. In other words, the chemistry of the initial water should be representative of the chemistry of the final water at the time it was recharged. For radiocarbon dating purposes, the samples should be free of post-bomb ^{14}C . For the High Plains aquifer, water containing less than 0.5 TU tritium is assumed to be free of postbomb ^{14}C . McMahon and others (in press) constructed mass-balance models for the central High Plains aquifer by using samples from the most upgradient water-table wells in a regional transect as initial waters because simulations of ground-water movement indicated those areas were the most likely upgradient sources of water to downgradient wells and because they contained less than 0.5 TU tritium.

The selection of appropriate initial waters for mass-balance modeling of the southern High Plains transect is complicated by the fact that the chemistry of water from the water-table wells was affected by recent land-use activities, so it is not representative of past chemistry. Samples from water-table wells also contained more than 0.5 TU tritium. Examination of regional water-table maps confirms that the Castro and Hale County sites were approximately located on the same flow path, but detailed simulations of ground-water movement were not done to verify this. As a result, there is uncertainty associated with the chemistry of initial waters in the mass-balance models described in this report. However, as will be discussed in the "Radiocarbon Ages" section, radiocarbon ages were relatively insensitive to the uncertainty in carbon mass transfers identified by the mass-balance models.

Two different chemical analyses were used to define the chemistry of initial waters: an average water composition for High Plains recharge (table 8) and the chemical analysis from Castro-330 (Appendix 1). High Plains recharge represents the average composition of water from eight wells with screens placed near the water table in the southern High Plains aquifer near Amarillo, Tex. (Fryar and others, 2001). Water from all eight wells had tritium concentrations less than 0.5 TU. The sample from Castro-330 also was chosen as an initial water because that well was the shallowest upgradient well sampled in this study that was not affected by recent land-use activities. The computer code PHREEQC (Parkhurst and Appelo, 1999) was used to determine mass-balance models because it allows the user to assign uncertainties to the chemical and isotope data for initial and final waters. Initially, an uncertainty of 5 percent was assigned to the chemical analysis for each initial and final water composition because that was about the maximum charge-balance error measured in any of the chemical analyses.

Table 8. Additional water-quality data used in mass-balance models.

[The chemical analysis for High Plains recharge is the average of the following eight analyses reported by Fryar and others (2001): T. Bradshaw, D. Gabel, C. Kirkland, S. McGregor, OM-46, OM-47, OM-48, and OM-105. Wells had screens placed near the water table in the southern High Plains aquifer and tritium concentrations less than 0.5 tritium unit; mg/L, milligrams per liter; N, nitrogen; $\delta^{13}\text{C}[\text{DIC}]$, stable carbon isotope composition of dissolved inorganic carbon; $^{14}\text{C}[\text{DIC}]$, radiocarbon content of dissolved inorganic carbon; $\delta^{34}\text{S}[\text{SO}_4]$, stable sulfur isotope composition of dissolved sulfate; pmc, percent modern carbon; TU, tritium units; --, no data]

Parameter	High Plains recharge (Fryar and others, 2001)	Aquifer in rocks of Cretaceous age (Nativ and Smith, 1987)
pH, standard units	7.69	8.0
Calcium, dissolved (mg/L)	37.0	64.8
Magnesium, dissolved (mg/L)	27.0	48.3
Potassium, dissolved (mg/L)	6.5	13.6
Sodium, dissolved (mg/L)	21.1	69.5
Bicarbonate, dissolved (mg/L)	264.	326
Chloride, dissolved (mg/L)	8.5	88.0
Sulfate, dissolved (mg/L)	20.9	81.0
Nitrate, dissolved (mg/L as N)	1.2	3.4
Silica, dissolved (mg/L)	41.5	--
Tritium (TU)	.2	5.9
$\delta^{13}\text{C}[\text{DIC}]$ (per mil)	-7.3	-7.5
$^{14}\text{C}[\text{DIC}]$ (pmc)	40.4	--
$\delta^{34}\text{S}[\text{SO}_4]$ (per mil)	--	5.0

Uncertainties assigned to the isotope data are listed in table 9. Uncertainty in the chemical data for each initial water was increased in increments of 2.5 percent if plausible mass-balance models could not be obtained with smaller uncertainties. The maximum uncertainty used in any model was 12.5 percent for the model in which Hale-400 was the final water. PHREEQC will determine the number of possible mass-balance models that satisfy mole and isotope balance requirements, given specified uncertainties. Models are plausible if they are in agreement with calculated mineral saturation indices (table 6), aquifer mineralogy, and constraints imposed by isotope data.

Eleven constraints were used in models identified by PHREEQC that satisfied the mole and isotope balance requirements: aluminum, calcium, carbon, chloride, iron, magnesium, nitrogen, potassium, silica, sodium, and sulfur; however, not all constraints were used in each model. The following phases were included in the various models: albite, anorthite, calcite, Ca-montmorillonite, Ca/Na₂ exchange, CO₂, goethite, illite, kaolinite, K-feldspar, Mg/Na₂ exchange, N₂, pyrite, SiO₂, and SOC. Phases were selected on the basis of mineralogic analyses from this study (table 3) and the work of Fryar and others (2001). Not all phases were used in each model. The mass-balance models were further constrained by isotope data subject to uncertainties listed in table 9. The $\delta^{13}\text{C}$ values assigned to CO₂ and calcite are based on measured values for these phases in the southern High Plains (Thorstenson and others, 1983; Karlsson

and others, 1995). The $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ values assigned to SOC (-25±5 per mil) and pyrite (-20±5 per mil) are reasonable approximations for organic matter and pyrite in terrestrial sediments (Deines, 1980; Krouse and Mayer, 2000).

Table 9. Uncertainties assigned to measured isotope variables and isotope values assigned to unmeasured variables in PHREEQC simulations.

[$\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon; SO₄, dissolved sulfate; SOC, sedimentary organic carbon; CO₂, carbon dioxide; --, not applicable]

Isotope variable	Uncertainty assigned to measured variable (±), in per mil	Value assigned to unmeasured variable, in per mil
$\delta^{13}\text{C}[\text{DIC}]$ - initial water	2.0	--
$\delta^{34}\text{S}[\text{SO}_4]$ - initial water	2.0	--
$\delta^{13}\text{C}[\text{DIC}]$ - final water	.2	--
$\delta^{34}\text{S}[\text{SO}_4]$ - final water	.2	--
$\delta^{13}\text{C}[\text{SOC}]$	--	-25±5
$\delta^{13}\text{C}[\text{CO}_2]$	--	-20±5
$\delta^{13}\text{C}[\text{calcite}]$	--	-7±2
$\delta^{34}\text{S}[\text{pyrite}]$	--	-20±5

As previously discussed, some of the increases in concentrations of dissolved constituents along flow paths to the Hale County wells may have resulted from mixing with water entering the southern High Plains aquifer from the underlying aquifer in rocks of Cretaceous age. Nativ and Smith (1987) reported the chemistry of water from two wells screened in rocks of Cretaceous age in Hale County (fig. 3), and those data were used to assign a chemical composition to that aquifer (table 8) for the purpose of calculating mixing in the mass-balance models. Chloride was used to determine the amount of conservative mixing.

Several models were identified for most pairs of initial and final waters that satisfied mole- and isotope-balance requirements and were consistent with calculated mineral-saturation indices, given the stated uncertainties (Appendix 2). Most models required small amounts of silicate-mineral and calcite dissolution; SiO₂, goethite, and clay-mineral precipitation; SOC and pyrite oxidation; denitrification; and cation exchange. Models in which the Hale County wells were the final waters also required mixing of the initial water (83 to 92 percent) with water from the aquifer in rocks of Cretaceous age (8 to 17 percent).

Small increases in concentrations of dissolved sulfate with depth at the Castro County site were accompanied by decreases in the $\delta^{34}\text{S}[\text{SO}_4]$ values (fig. 9B). In the mass-balance models, those changes were accounted for by oxidizing small amounts of pyrite, with subsequent goethite precipitation. Increases in concentrations of dissolved sulfate along the regional hydraulic gradient from the Castro to Hale County wells were accompanied by increases in $\delta^{34}\text{S}[\text{SO}_4]$ values, which cannot be explained by pyrite oxidation. Water from the aquifer in rocks of Cretaceous age contained elevated sulfate concentrations and $\delta^{34}\text{S}[\text{SO}_4]$ values larger than those measured in water from the Hale County wells (fig. 9B). Thus, the increase in sulfate concentrations in going from the initial waters to the final Hale County waters was accounted for by mixing 8 to 17 percent water from the aquifer in rocks of Cretaceous age with the initial waters (Appendix 2).

In the mass-balance models, DIC additions were accounted for by oxidation of SOC and dissolution of calcite. Oxidation of SOC was coupled to O₂ reduction and denitrification. The amount of denitrification was assumed to equal the amount of nonatmospheric N₂-N present in the final waters, as previously discussed. Chemical data in Appendix 1 indicate that other redox processes like manganese, iron, and sulfate reduction were not important along the flow paths in the aquifer. Of the two electron donors, SOC and pyrite, SOC had larger mass transfers (was more important in terms of supporting O₂ reduction and denitrification) in models of water from the Castro County wells (Appendix 2). SOC and pyrite had more similar (and relatively small) mass transfers in models of water from the Hale County wells in which denitrification did not occur.

Carbon dioxide gas was included as a phase in the models to evaluate whether SOC oxidation and calcite dissolution can fully account for increases in DIC concentrations along flow

paths. Carbon dioxide mass transfers will equal zero if SOC oxidation and calcite dissolution account for increases in DIC concentrations. There are no known sources of CO₂ gas (other than SOC oxidation) in the aquifer, and the ground-water system below the water table is considered closed to exchange with soil-zone CO₂; therefore, nonzero CO₂ mass transfers probably represent uncertainties in (a) selecting the appropriate initial water, (b) alkalinity titrations, and (c) the charge balance of major-ion analyses. Plummer and Sprinkle (2001) presented mass-balance models that required small CO₂ mass transfers along flow paths in confined parts of the Upper Floridan aquifer, which was considered closed to soil-zone CO₂. They suggested that small CO₂ additions in the models could indicate evolution from recharge waters that had slightly larger DIC concentrations than were used in the models. In this study, the median CO₂ mass transfer was 0.1905 mmol/kg, which is a relatively small amount and represents about 4 percent of the bicarbonate present in the initial waters. This relation means that radiocarbon ages will be relatively insensitive to adjustments made on the basis of CO₂ mass transfers.

Radiocarbon Ages

Adjusted radiocarbon ages of ground water were calculated using the PHREEQC phase mass transfers as input to NETPATH (Plummer and others, 1994) and the radioactive decay equation:

$$\Delta t = \frac{5,570}{\ln 2} \ln \left(\frac{A_{nd}}{A} \right) \quad (9)$$

where Δt (in radiocarbon years) is the time since ground water was isolated from the atmosphere; 5,730 is the half-life of ¹⁴C (in years); A_{nd} (in percent modern carbon, pmc) is the ¹⁴C[DIC] value of the final water adjusted for carbon mass transfers in the absence of radioactive decay; and A (pmc) is the measured ¹⁴C[DIC] value of the final water. The value of A_{nd} is dependent on the value of A_0 (¹⁴C[DIC] value of recharge) and carbon mass transfers calculated in the mass-balance models. Sedimentary organic carbon and calcite in the mass-balance models were assigned ¹⁴C values of 0. Carbon dioxide was assigned values of 40 or 65 pmc (refer to discussion below).

In this study, A_0 was measured directly in the water-table wells Castro-241 and Hale-255 (about 67 to 51 pmc, table 5) and also computed as the average of eight measured values reported by Fryar and others (2001) (about 40 pmc, table 8), as previously discussed. Measurements of A_0 must avoid water containing a component of ¹⁴C derived from atmospheric nuclear weapons testing, and water from the eight wells sampled by Fryar did not contain a component of postbomb ¹⁴C, as indicated by the absence of postbomb tritium in those waters. Water from Castro-241 and Hale-255 did contain postbomb tritium, but their ¹⁴C[DIC] values were similar to the values in water from water-table wells in the central High Plains (65 to 73 pmc; McMahon and others, in press) that did not contain postbomb tritium. Also, Thorstenson and others (1983) reported

¹⁴C[CO₂] values in the deep unsaturated zone of the Texas High Plains of about 55 to 60 pmc, even though diffusion models indicated that CO₂ containing postbomb ¹⁴C should have been present. The similarity between ¹⁴C[DIC] values in southern and central High Plains recharge and deep unsaturated-zone CO₂ may indicate that they are buffered by abundant calcite (presumably depleted in ¹⁴C) in the deep unsaturated zone.

Unadjusted radiocarbon ages of ground water calculated using the approximate range in A₀ values from Fryar and others (2001) and samples from Castro-241 and Hale-255 are reported in table 10. For comparison, values of A₀ equal to 100 pmc also were used to calculate maximum possible radiocarbon ages. Unadjusted ages assume that radioactive decay was the only process that reduced the radiocarbon content of DIC along flow paths. The radiocarbon ages presented here do not account for the possibility that ¹⁴C[DIC] of recharge varied over time due to variations in the Earth’s geomagnetic field strength and solar fluctuations (Mazaud and others, 1991; Bard and others, 1993), nor were the ages corrected for the effects of matrix diffusion (Bethke and Johnson, 2002). McMahon and others (in press) concluded that matrix diffusion could reduce radiocarbon ages of water in the central High Plains aquifer by about 20 percent. The maximum possible age of ground water at the Castro and Hale County sites ranged from 8,800 to 12,900 ¹⁴C years before present (BP), corresponding to the condition A₀=A_{nd}=100 pmc (table 10). Unadjusted radiocarbon ages ranged from 1,200 to 5,400 ¹⁴C years BP and from 5,200 to 9,400 ¹⁴C years BP for A₀=A_{nd}=40 and 65 pmc (table 10).

Radiocarbon ages adjusted for carbon mass transfers ranged from less than 1,000 to 9,000 ¹⁴C years BP (table 11). Adjusted radiocarbon ages were much more sensitive to the A₀ value than to carbon mass transfers or the composition of the initial water. For example, the difference between unadjusted

radiocarbon ages (table 10) and median adjusted radiocarbon ages (table 11) and ranged from 100 to 1,100 years, with a median difference of 600 years. The largest difference in median adjusted age between models with the same final water and A₀ value also was 600 years. In contrast, the minimum difference in median adjusted age between models with the same final water and A₀ equal to 40 or 65 pmc was 3,400 years. The combined 1-sigma uncertainty in radiocarbon ages resulting from variability in recharge chemistry and A₀ was ±2,000 years. Although relatively large uncertainties in the radiocarbon ages result from the selected range in A₀ values, it appears that deep water in the aquifer at these sites was considerably older (at least 1,000 years) than water near the water table.

Ground-water ages are plotted as a function of depth below the water table in figure 12. The largest age gradients occurred between the water table and next deepest well (fig. 12), indicating a relatively rapid transition from recent recharge near the water table to much older water deeper in the aquifer. Age gradient is defined as (change in age)/(change in well depth). The age gradients in the upper part of the southern High Plains aquifer are similar to the gradients observed in the upper part of the central High Plains aquifer (fig. 12). Age gradients between deeper wells at the Castro and Hale County sites were small and, considering the large uncertainty in estimated radiocarbon ages at each depth, may be close to zero (fig. 12). A negative age gradient at depth was observed in one area of the central High Plains aquifer and is attributed to pumping of nearby irrigation wells screened in the lower one-half of the aquifer that caused vertical mixing of water in the aquifer. Areas of the central High Plains aquifer unaffected by local irrigation pumping had positive vertical age gradients throughout the saturated thickness (fig. 12). The Castro and Hale County sites are located in areas of extensive irrigation (fig. 5); therefore, mixing in the

Table 10. Unadjusted radiocarbon ages of water from selected wells.

[Unadjusted ages assume that the radiocarbon content of dissolved inorganic carbon in recharge was 40, 65, or 100 percent modern carbon and that radioactive decay was the only process that reduced the radiocarbon content of dissolved inorganic carbon along flow paths; pmc, percent modern carbon; ¹⁴C[DIC], radiocarbon content of dissolved inorganic carbon; A₀, ¹⁴C[DIC] of initial water; ¹⁴C years BP, radiocarbon years before present]

Final water	¹⁴ C[DIC], final water, measured (pmc)	Unadjusted radiocarbon age of final water (¹⁴ C years BP)		
		A ₀ =40 pmc	A ₀ =65 pmc	A ₀ =100 pmc
Castro-330	22.2	4,900	8,900	12,400
Castro-380	22.0	4,900	9,000	12,500
Castro-427	20.9	5,400	9,400	12,900
Hale-340	34.6	1,200	5,200	8,800
Hale-400	31.4	2,000	6,000	9,600

Table 11. Adjusted radiocarbon ages of water from selected wells.

[The radiocarbon content of dissolved inorganic carbon in initial water was adjusted for addition or removal of carbon along flow paths according to the phase mass transfers calculated with PHREEQC (Parkhurst and Appelo, 1999; Appendix 2). Adjusted radiocarbon ages were calculated assuming two different radiocarbon contents of dissolved inorganic carbon in initial water ($A_0 = 40$ and $A_0 = 65$ percent modern carbon). In PHREEQC, uncertainties were assigned to the chemical compositions of initial and final waters, as indicated in parentheses; pmc, percent modern carbon; $^{14}\text{C}[\text{DIC}]$, radiocarbon content of dissolved inorganic carbon; A_0 , $^{14}\text{C}[\text{DIC}]$ of initial water; ^{14}C years BP, radiocarbon years before present]

Initial water 1 (uncertainty)	Initial water 2 (uncertainty)	Final water (uncertainty)	Adjusted radiocarbon age, final water ($A_0=40$ pmc)			Adjusted radiocarbon age, final water ($A_0=65$ pmc)		
			Age (^{14}C years BP)			Age (^{14}C years BP)		
			Minimum	Median	Maximum	Minimum	Median	Maximum
High Plains recharge Fryar and others (2001) (5 percent)	not applicable	Castro-330 (5 percent)	4,100	4,100	4,100	8,100	8,100	8,100
Castro-330 (5 percent)	not applicable	Castro-330 (5 percent)	4,400	4,500	4,700	8,400	8,600	8,700
High Plains recharge Fryar and others (2001) (5 percent)	not applicable	Castro-380 (5 percent)	3,700	3,900	4,100	7,800	7,900	8,100
Castro-330 (5 percent)	not applicable	Castro-380 (5 percent)	4,200	4,500	4,700	8,200	8,500	8,800
High Plains recharge Fryar and others (2001) (10 percent)	not applicable	Castro-427 (5 percent)	4,300	4,900	4,900	8,300	8,900	8,900
Castro-330 (10 percent)	not applicable	Castro-427 (5 percent)	4,300	4,600	5,000	8,300	8,600	9,000
High Plains recharge Fryar and others (2001) (10 percent)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (10 percent)	Hale-340 (5 percent)	< 1,000	< 1,000	1,200	4,400	4,400	5,200
Castro-330 (10 percent)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (10 percent)	Hale-340 (5 percent)	< 1,000	< 1,000	1,200	4,500	4,800	5,200
High Plains recharge Fryar and others (2001) (12.5 percent)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (12.5 percent)	Hale-400 (5 percent)	1,200	1,400	1,500	5,200	5,400	5,600
Castro-330 (12.5 percent)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (12.5 percent)	Hale-400 (5 percent)	1,200	1,900	2,000	5,200	5,900	6,000

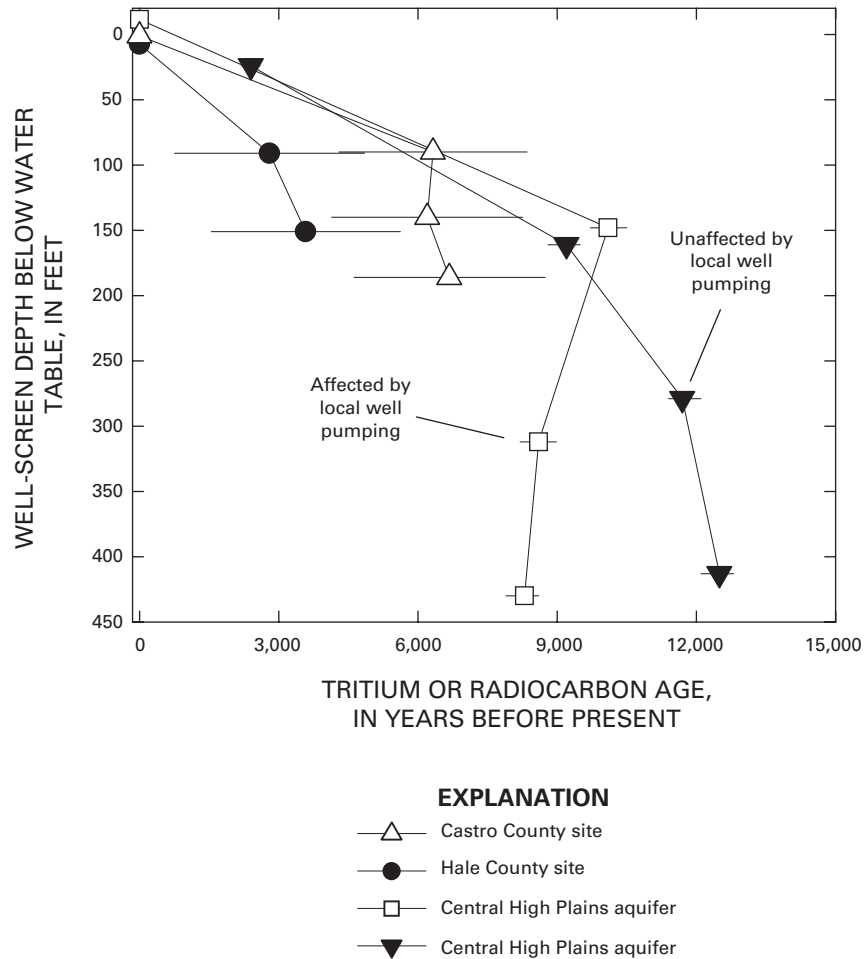


Figure 12. Median ground-water age as a function of well-screen depth below the water table. Horizontal bars represent the 1-sigma uncertainty in estimated ages. Data for the central High Plains aquifer are from McMahon and others (in press).

deep aquifer by irrigation-well pumping is the most likely explanation for negligible age gradients in the deep aquifer at these sites. Because of possible mixing effects, radiocarbon ages reported here should be considered apparent ages.

Dutton (1995) concluded that water in the High Plains aquifer generally was less than 1,000 years old and locally younger than 50 years. Inspection of the data in figure 12 supports the idea that recent recharge occurs locally in the aquifer (primarily near the water table). Data in figure 12, however, indicate that water in some parts of the southern High Plains aquifer is considerably older than 1,000 years, and water in the central High Plains aquifer could represent recharge from the early Holocene or late Pleistocene. Recharge rates in parts of the aquifer studied here probably were sufficiently fast to remove any remnants of recharge from the last glacial maximum (about 18,000 years BP), whereas recharge from the last glacial maximum was still present in formations directly beneath the southern and central High Plains aquifers (Dutton, 1995; McMahon and others, in press).

In areas of the central High Plains aquifer that were unaffected by local pumping, systematic decreases in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and recharge temperatures of water were observed with depth below the water table (McMahon and others, in press). The decreases were attributed to colder climatic conditions during the early Holocene (represented by water at the aquifer base) compared to modern recharge at the water table. Systematic decreases in recharge temperature with depth were not observed in the southern High Plains aquifer (table 7), probably because of vertical mixing caused by local pumping. The average recharge temperature of the five deep samples ($13.7 \pm 1.0^\circ\text{C}$) plotted in figure 12, however, was colder than the average recharge temperature of the two water-table samples ($15.2 \pm 1.1^\circ\text{C}$). About 30 percent of the 1.5°C temperature difference can be accounted for by the 240-ft difference in average water-table elevation between the two sample groups (table 7), assuming a $-0.18^\circ\text{C}/100$ ft air temperature-elevation gradient (McMahon and others, in press). The small remaining temperature difference (about 1.1°C) might be the result of climate change during the Holocene. Castro and Goblet (2003) reported

32 Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002

a larger, 3.4°C, increase in recharge temperatures in the Carrizo aquifer in southwest Texas starting about 900 years ago. McMahon and others (in press) also reported a larger, 2.4°C, increase in recharge temperatures beginning after about 9,000 ¹⁴C years BP in the central High Plains aquifer. Apparently, any climatically driven shift in recharge temperatures in the southern High Plains aquifer that may have been recorded by noble gases has been at least partially erased by vertical mixing.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for the water samples generally plot along the local meteoric water line and show no evidence of

evaporation (fig. 13). Samples from the aquifer group by age, with the youngest samples from the water table having the least negative values, the oldest samples (Castro County) having the most negative values, and the intermediate-aged samples (Hale County) having isotope values between the other two groups. Small isotope values for water in the southern High Plains aquifer have been attributed to colder recharge temperatures in the past (Dutton, 1995); therefore, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data also appear to preserve a climate record that indicates warming occurred during the Holocene. Other environmental factors,

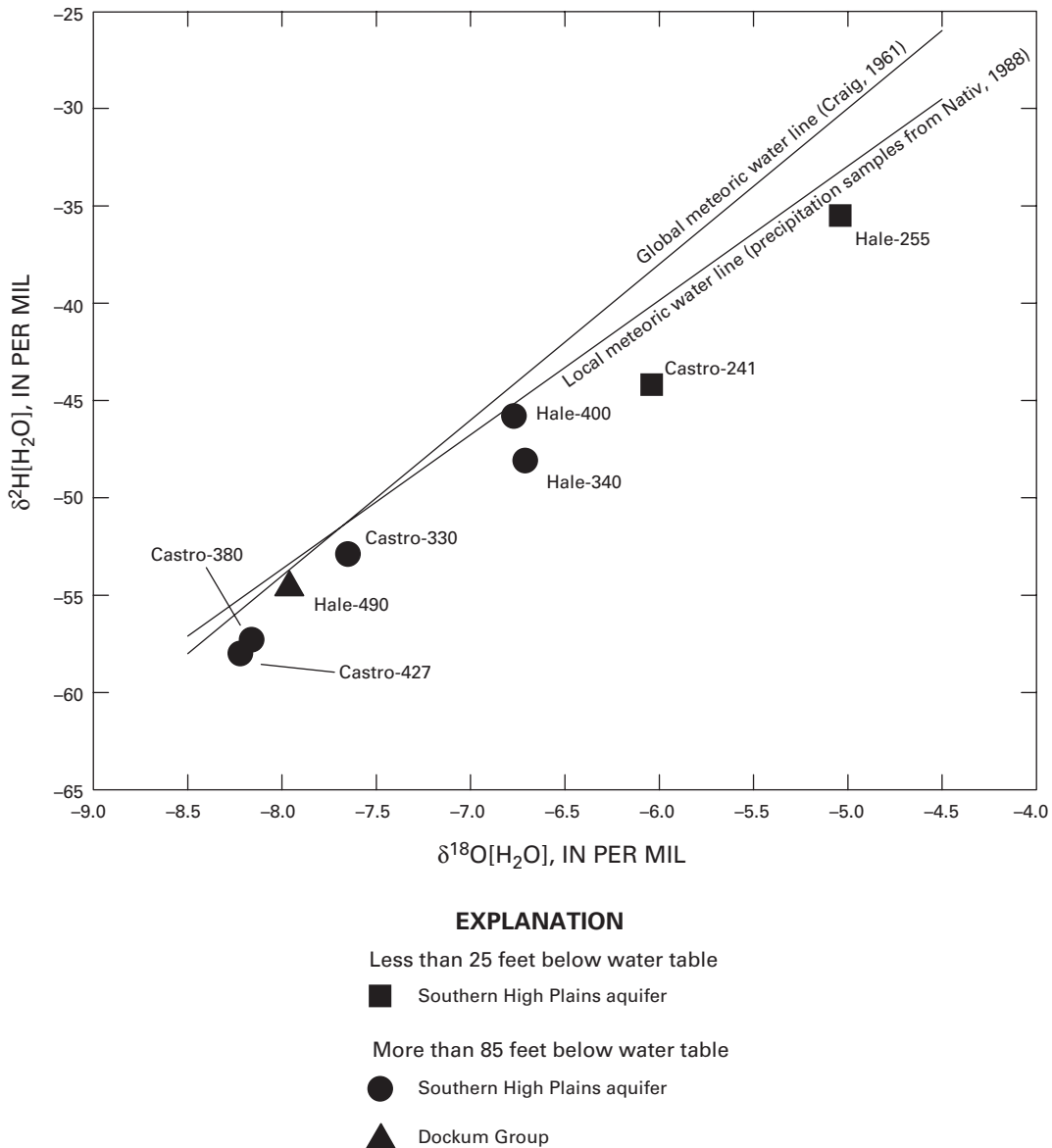


Figure 13. Stable isotope values for water from monitoring wells screened in the southern High Plains aquifer and Dockum Group. Local Meteoric Water Line based on the isotopic composition of precipitation samples collected in the southern High Plains (Nativ, 1988).

however, such as elevation differences in the recharge areas and temporal variability in air-mass sources for precipitation also could affect the isotope data. Water samples from parts of the aquifer unaffected by local well pumping are needed to construct a more reliable record of paleorecharge conditions in the southern High Plains aquifer.

Apparent rates of O₂ reduction and denitrification were estimated on the basis of decreases in O₂ concentrations and increases in concentrations of nonatmospheric N₂ and ground-water ages along flow paths from the water table to the deep wells. All five of the radiocarbon-dated samples had some O₂ uptake assuming that they were recharged with at least 4.1 mg/L (128 μM) O₂, which was the average concentration in water from Castro-241 and Hale-255. Only the radiocarbon-dated Castro County samples contained nonatmospheric N₂. For O₂, calculations assume reduction began at the water table and was constant along flow paths to the wells. For nitrate, calculations assume denitrification began at a distance downgradient from the water table that would result from a traveltime equal to half the adjusted radiocarbon age of water from Castro-330 (2,050 to 4,350 ¹⁴C years, table 11). Results of the rate calculations are listed in table 12. Median O₂ reduction rates ranged from 6×10⁻⁵ to 6×10⁻⁴ mg/L/yr and were fastest at the Castro County sites where measured O₂ concentrations were

smallest. Median denitrification rates ranged from 3×10⁻⁴ to 4×10⁻⁴ mg/L/yr as N and also were fastest at the Castro County sites. The denitrification rates estimated here are about 4 to 5 times faster than estimated rates in the central High Plains aquifer (McMahon and others, in press) but are several orders of magnitude slower than rates in several shallow aquifers containing recent recharge (Korom, 1992; Böhlke and others, 2002).

Large vertical age gradients in areas of the High Plains aquifer unaffected by local pumping indicate that several thousand years might be required for agricultural nitrate at the water table to move deeper in the aquifer, which might be sufficient time for denitrification (even at very slow rates) to reduce nitrate to background concentrations. The small age gradients at depth at the Castro and Hale County sites, however, indicate that those long traveltimes can be greatly reduced by local pumping of large-capacity wells. Bruce and Oelsner (2001) proposed that pumping rate and duration were the primary reasons why water from municipal water-supply wells in the central High Plains aquifer contained younger water and more pesticide detections than water from domestic wells. Considering the slow denitrification rates estimated for the aquifer, this process may not attenuate nitrate movement that is accelerated by processes like pumping.

Table 12. Estimated rates of dissolved-oxygen reduction and denitrification.

[The change in dissolved-oxygen concentration was calculated as the difference between the dissolved-oxygen concentration in recharge (assumed to be 4.1 milligrams per liter) and the concentration measured in water from the well. A dissolved-oxygen concentration of 0.25 milligram per liter was assumed for samples that had less than 0.5 milligram per liter of dissolved oxygen. A radiocarbon age of 500 years was assumed for samples with ages less than 1,000 years; ΔO₂, change in dissolved-oxygen concentration; mg/L, milligrams per liter; N, nitrogen; mg/L/yr, milligrams per liter per year; BP, before present; --, not applicable]

	Well name				
	Castro-330	Castro-380	Castro-427	Hale-340	Hale-400
ΔO ₂ , in mg/L	3.85	3.85	3.85	0.4	0.2
Nonatmospheric N ₂ , in mg/L as N	1.60	1.68	1.57	0	0
Minimum radiocarbon age, in ¹⁴ C years BP	4,100	3,700	4,300	< 1,000	1,200
Median radiocarbon age, in ¹⁴ C years BP	6,300	6,200	6,700	2,500	3,600
Maximum radiocarbon age, in ¹⁴ C years BP	8,700	8,800	9,000	5,200	6,000
Median and range in O ₂ reduction rates, in mg/L/yr	6×10 ⁻⁴	6×10 ⁻⁴	6×10 ⁻⁴	2×10 ⁻⁴	6×10 ⁻⁵
Median and range in denitrification rates, in mg/L/yr as N	4×10 ⁻⁴ to 9×10 ⁻⁴	4×10 ⁻⁴ to 1×10 ⁻³	4×10 ⁻⁴ to 9×10 ⁻⁴	8×10 ⁻⁵ to 8×10 ⁻⁴	3×10 ⁻⁵ to 2×10 ⁻⁴
	4×10 ⁻⁴	4×10 ⁻⁴	3×10 ⁻⁴	0	0
	2×10 ⁻⁴ to 8×10 ⁻⁴	2×10 ⁻⁴ to 1×10 ⁻³	2×10 ⁻⁴ to 7×10 ⁻⁴	0	0

SUMMARY AND CONCLUSIONS

In 1991, the USGS 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 water quality. The High Plains Regional Ground-Water study, which began in June 1998, is one of more than 50 major river basins and aquifers being studied by the NAWQA Program. The High Plains aquifer is a nationally important water resource that underlies about 174,000 mi² in parts of eight States. Due to the large areal extent of the High Plains aquifer, three geographic regions have been delineated for logistical purposes: northern High Plains, central High Plains, and southern High Plains. The southern High Plains aquifer is the focus of this investigation.

Chemical data and tritium and radiocarbon ages show that water in the southern High Plains aquifer was chemically and temporally stratified in the study area, with a layer of recently (less than 50 years) recharged water near the water table containing major ions, pesticides, and nitrate above background concentrations overlying a thicker layer of much older (by at least 1,000 years) and more dilute water. Elevated chemical concentrations near the water table were attributed to agricultural activity on the overlying land surface. Below the zone of agricultural influence, changes in chemical concentrations with depth and along flow paths were attributed to small amounts of silicate-mineral and calcite dissolution; SiO₂, goethite, and clay-mineral precipitation; organic-carbon and pyrite oxidation; denitrification; cation exchange; and mixing with water from the underlying aquifer in rocks of Cretaceous age. Dissolved-gas and nitrogen-isotope data from the deep wells at the Castro County site indicate that denitrification removed 74 to more than 97 percent of the nitrate originally present in recharge.

Carbon mass transfers along flow paths in the aquifer were estimated using the geochemical model PHREEQC. Radiocarbon ages in the deep aquifer, adjusted for carbon mass transfers, ranged from less than 1,000 to 9,000 ¹⁴C years before present. Radiocarbon ages were much more sensitive to uncertainties in the ¹⁴C content of recharge than uncertainties in carbon mass transfers, leading to 1-sigma uncertainties in adjusted ages of about ±2,000 years. The largest age gradients occurred between the water table and next deepest wells. Within the deep aquifer, vertical age gradients were relatively small. The small age gradients at depth indicate water in the aquifer was vertically mixed, most likely by local irrigation-well pumping. The small age gradients at depth also indicate that pumping has the potential to accelerate the movement of contaminants like nitrate and pesticides at the water table deeper in the aquifer. Estimated denitrification rates in the aquifer were slow, averaging about 3.5×10⁻⁴ mg/L/yr as N. Considering these slow denitrification rates, this process may not attenuate nitrate that is transported deeper into the aquifer by processes like pumping.

REFERENCES CITED

- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., and Kipfer, R., 2000, Paleotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air: *Nature*, v. 405, p. 1040–1044.
- Aravena, R., Wassenaar, L.I., and Plummer, L.N., 1995, Estimating ¹⁴C ground-water ages in a methanogenic aquifer: *Water Resources Research*, v. 31, p. 2307–2317.
- Bard, E., Arnold, M., Fairbanks, R.G., and Hamelin, B., 1993, ²³⁰Th-²³⁴U and ¹⁴C ages obtained by mass spectrometry on corals: *Radiocarbon*, v. 35, p. 191–199.
- Bethke, C.M., and Johnson, T.M., 2002, Ground-water age: *Ground Water*, v. 40, p. 337–339.
- Böhlke, J.K., 2002, Groundwater recharge and agricultural contamination: *Hydrogeology Journal*, v. 10, p. 153–179.
- Böhlke, J.K., and Coplen, T.B., 1995, Interlaboratory comparison of reference materials for nitrogen-isotope-ratio measurements, *in* Reference and intercomparison materials for stable isotopes of light elements: International Atomic Energy Agency, IAEA-TECDOC-825, p. 51–66.
- Böhlke, J.K., and Denver, J.M., 1995, Combined use of ground-water dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland: *Water Resources Research*, v. 31, p. 2319–2339.
- Böhlke, J.K., Wanty, R., Tuttle, M., Delin, G., and Landon, M., 2002, Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota: *Water Resources Research*, v. 38, p. 10.1–10.26.
- Bruce, B.W., and Oelsner, G.P., 2001, Contrasting water quality from paired domestic/public supply wells, central High Plains: *Journal of the American Water Resources Association*, v. 37, p. 1389–1403.
- Busenberg, Eurybiades, Weeks, E.P., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating ground water by use of chlorofluorocarbons (CCl₃F and CCl₂F₂) and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho, USA: U.S. Geological Survey Water-Resources Investigations Report 93–4054, 47 p.
- CO₂ Science Magazine, 2003: <http://co2science.org/ushcn/tx/tx.htm> (accessed on 04/28/2003).
- Carmody, R.W., Plummer, L.N., Busenberg, E., and Coplen, T.B., 1997, Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition: U.S. Geological Survey Open-File Report 97–234, 91 p.
- Castro, M.C., and Goblet, P., 2003, Noble gas thermometry and hydrologic ages—Evidence for late Holocene warming in southwest Texas: *Geophysical Research Letters*, v. 30, 2251, doi:10.1029/2003GL018875.

- Cook P.G., and Böhlke, J.K., 2000, Determining timescales for groundwater flow and solute transport, *in* Cook, P.G., and Herczeg, A.L., eds., *Environmental tracers in subsurface hydrology*: Boston, Kluwer Academic Publishers, p. 1–30.
- Coplen, T.B., 1988, Normalization of oxygen and hydrogen isotope data: *Chemical Geology*, v. 72, p. 293–297.
- Coplen, T.B., Wildman, J.D., and Chen, J., 1991, Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis: *Analytical Chemistry*, v. 63, p. 910–912.
- Coplen, T.B., and Krouse, H.R., 1998, Sulfur isotope data consistency improved: *Nature*, v. 392, p. 32.
- Craig, H., 1961, Isotopic variations in meteoric waters: *Science*, v. 133, p. 1702–1703.
- Deines, Peter, 1980, The isotopic composition of reduced organic carbon, *in* Fritz, Peter, and Fontes, J.C., eds., *Handbook of environmental isotope geochemistry*, v. 1, *The terrestrial environment*: Amsterdam, Elsevier, p. 407–433.
- Dutton, A.R., 1995, Ground-water isotopic evidence for paleorecharge in U.S. High Plains aquifers: *Quaternary Research*, v. 43, p. 221–231.
- Epstein, Samuel, and Mayeda, T., 1953, Variation of O-18 content of water from natural sources: *Geochimica et Cosmochimica Acta*, v. 4, p. 213–224.
- Fan, A.M., and Steinberg, V.E., 1996, Health implications of nitrate and nitrite in drinking water—An update on methemoglobinemia occurrence and reproductive and developmental toxicity: *Regulatory Toxicology and Pharmacology*, v. 23, p. 35–43.
- Feagas, R.G., Claire, R.W., Guptill, S.C., Anderson, K.E., and Hallam, C.A., 1983, Land use and land cover digital data: U.S. Geological Survey Circular 895–E, 21 p.
- Feder, G.L., and Krothe, N.C., 1981, Results of a reconnaissance water-quality sampling program of the Ogallala aquifer in Colorado, Kansas, Nebraska, Oklahoma, South Dakota, and Texas: U.S. Geological Survey Water-Resources Investigations Report 81–65, 7 p.
- Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.
- Fryar, A.E., Macko, S.A., Mullican, W.F., Romanak, K.D., and Bennett, P.C., 2000, Nitrate reduction during ground-water recharge, Southern High Plains, Texas: *Journal of Contaminant Hydrology*, v. 40, p. 335–363.
- Fryar, A.E., Mullican, W.F., and Macko, S.A., 2001, Ground-water recharge and chemical evolution in the southern High Plains of Texas, USA: *Hydrogeology Journal*, v. 9, p. 522–542.
- Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.
- Gustavson, T.C., Baumgardner, R.W., Caran, S.C., Holliday, V.T., Mehnert, H.H., O’Neill, J.M., and Reeves, C.C., 1991, Quaternary geology of the southern Great Plains and an adjacent segment of the Rolling Plains, *in* Morrison, R.B., ed., *Quaternary nonglacial geology—Conterminous U.S.*: Geological Society of America, *The Geology of North America*, v. K–2, p. 477–501.
- Gutentag, E.D., Heimes, F.J., Krothe, N.C., Luckey, R.R., and Weeks, J.B., 1984, *Geohydrology of the High Plains aquifer in parts of Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming*: U.S. Geological Survey Professional Paper 1400–B, 63 p.
- Hach Company, 1992, *Water analysis handbook*: Hach Chemical Co., Loveland, Colo., 835 p.
- Haukos, D.A., and Smith, L.M., 1994, The importance of playa wetlands to biodiversity of the southern High Plains: *Land-scape and Urban Planning*, v. 28, p. 83–98.
- Holloway, J.M., and Dahlgren, R.A., 1999, Geologic nitrogen in terrestrial biogeochemical cycling: *Geology*, v. 27, p. 567–570.
- Hopkins, Janie, 1993, *Water-quality evaluation of the Ogallala aquifer, Texas*: Austin, Texas Water Development Board Report 342, 41 p.
- Hübner, H., 1986, Isotope effects of nitrogen in the soil and biosphere, *in* Fritz, P., and Fontes, J.C., eds., *Handbook of environmental isotope geochemistry*: Amsterdam, Elsevier, v. 2, p. 361–425.
- Hudak, P.F., 2000, Regional trends in nitrate content of Texas ground water: *Journal of Hydrology*, v. 228, p. 37–47.
- Karlsson, H.R., Lehman, T., Alomar, L., O’Reilly, J., Soliz, B., and Browning, J., 1995, Stable isotope studies of the southern High Plains caliche: *Geological Society of America Abstracts with Programs*, v. 27, p. A–422.
- Keys, W.S., 1990, Borehole geophysics applied to ground-water investigations: U.S. Geological Survey *Techniques of Water-Resources Investigations*, book 2, chap. E2, 150 p.
- Klots, C.E., and Benson, B.B., 1963, Isotope effect in the solution of oxygen and nitrogen in distilled water: *Journal of Chemical Physics*, v. 38, p. 890–892.
- Korom, S.F., 1992, Natural denitrification in the saturated zone—A review: *Water Resources Research*, v. 28, p. 1657–1668.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, *Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data*: U.S. Geological Survey Open-File Report 95–399, 113 p.
- Krouse, H.R., and Mayer, B., 2000, Sulfur and oxygen isotopes in sulfate, *in* Cook, P.G., and Herczeg, A.L., eds., *Environmental tracers in subsurface hydrology*: Boston, Kluwer Academic Publishers, p. 195–231.

- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95–398, 69 p.
- Luckey, R.R., Gutentag, E.D., Heimes, F.J., and Weeks, J.B., 1986, Digital simulation of ground-water flow in the High Plains aquifer in parts of Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming: U.S. Geological Survey Professional Paper 1400–D, 57 p.
- Ludin, Andrea, Weppernig, R., Bönisch, G., and Schlosser, P., 1998, Mass spectrometric measurement of helium isotopes and tritium: Lamont-Doherty Technical Report 98–06, [http://www.ldeo.columbia.edu/~etg/ms_ms/Ludin_et_al_MS_Paper.html].
- Mazaud, Alain, Laj, C., Bard, E., Arnold, M., and Tric, E., 1991, Geomagnetic field control of ^{14}C production over the last 80 ky—Implications for the radiocarbon time scale: *Geophysical Research Letters*, v. 18, p. 1885–1888.
- McGowen, J.H., Granata, G.E., and Seni, S.J., 1977, Depositional systems, uranium occurrence and postulated ground water history of the Triassic Dockum Group, Texas Panhandle and eastern New Mexico: Texas Bureau of Economic Geology, prepared for the U.S. Geological Survey, 104 p.
- McGuire, V.L., and Sharpe, J.B., 1997, Water-level changes in the High Plains aquifer—Predevelopment to 1995: U.S. Geological Survey Water-Resources Investigations Report 97–4081, 2 maps.
- McMahon, P.B., Chapelle, F.H., and Jagucki, M.L., 1992, Atrazine mineralization potential of alluvial aquifer sediments under aerobic conditions: *Environmental Science and Technology*, v. 26, p. 1556–1559.
- McMahon, P.B., 2001, Vertical gradients in water chemistry in the central High Plains aquifer, southwestern, Kansas and Oklahoma Panhandle, 1999: U.S. Geological Survey Water-Resources Investigations Report 01–4028, 47 p.
- McMahon, P.B., Böhlke, J.K., Christenson, S.C., in press, Geochemistry, radiocarbon ages, and paleorecharge conditions along a transect in the central High Plains aquifer, southwestern Kansas USA: *Applied Geochemistry*.
- Mehta, Sunil, Fryar, A.E., and Banner, J.L., 2000, Controls on the regional-scale salinization of the Ogallala aquifer, southern High Plains, Texas, USA: *Applied Geochemistry*, v. 15, p. 849–864.
- Nativ, Ronit, 1988, Hydrogeology and hydrochemistry of the Ogallala aquifer, southern High Plains, Texas Panhandle and eastern New Mexico: Texas Bureau of Economic Geology Report of Investigations No. 177, 64 p.
- Nativ, Ronit, and Smith, D.A., 1987, Hydrogeology and geochemistry of the Ogallala aquifer, southern High Plains: *Journal of Hydrology*, v. 91, p. 217–253.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (ver. 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99–4259, p. 312.
- Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B., 1990, Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: *Water Resources Research*, v. 26, p. 1981–2014.
- Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH, version 2.0: U.S. Geological Survey Water Resources-Investigations Report 94–4169, 130 p.
- Plummer, L.N. and Sprinkle, C.L., 2001, Radiocarbon dating of dissolved inorganic carbon in ground water from confined parts of the Upper Floridan aquifer, Florida, USA: *Hydrogeology Journal*, v. 9, p. 127–150.
- Postma, Dieke, Boesen, C., Kristiansen, H., and Larsen, F., 1991, Nitrate reduction in an unconfined sandy aquifer—Water chemistry, reduction processes, and geochemical modeling: *Water Resources Research*, v. 27, p. 2027–2045.
- Qi, S.L., Konduris, A., Litke, D.W., and Dupree, Jean, 2002, Classification of irrigated land using satellite imagery, the High Plains aquifer, nominal date 1992: U.S. Geological Survey Water-Resources Investigations Report, 02–4236, 35 p.
- Scanlon, B.R., and Goldsmith, R.S., 1997, Field study of spatial variability in unsaturated flow beneath and adjacent to playas: *Water Resources Research*, v. 33, p. 2239–2252.
- Seni, S.J., 1980, Sand-body geometry and depositional systems, Ogallala Formation, Texas: Austin, Texas Bureau of Economic Geology Report of Investigations no. 105, 36 p.
- Solley, W.B., Pierce, R.R., and Perlman, H.A., 1993, Estimated use of water in the United States in 1990: U.S. Geological Survey Circular 1081, available on the World Wide Web at <http://water.usgs.gov/watuse/wucircular2.html> (accessed 01/15/2003).
- Stute, Martin, and Schlosser, P., 1993, Principles and applications of the noble gas paleothermometer, in Swart, P.K., Lohmann, K.C., McKenzie, J., and Savin, S., eds., *Climate change in continental isotope records: Geophysical Monograph* 78, p. 89–100.
- Stute, Martin, Clark, J.F., Schlosser, P., Broeker, W.S., and Bonani, G., 1995, A 30,000 year continental paleotemperature record derived from noble gases dissolved in ground water from the San Juan Basin, New Mexico: *Quaternary Research*, v. 43, p. 209–220.
- Thatcher, L.L., 1962, The distribution of tritium fallout in precipitation over North America: *Bulletin of the International Association of Scientific Hydrology*, v. 7, p. 48–58.
- Thatcher, L.L., Janzer, V.J., and Edwards, K.W., 1977, Methods for determination of radioactive substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, chap. A–5, 95 p.

- Thorstenson, D.C., Weeks, E.P., Haas, H., and Fisher, D.W., 1983, Distribution of gaseous $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and $^{14}\text{CO}_2$ in the sub-soil unsaturated zone of the western US Great Plains: *Radiocarbon*, v. 25, p. 315–346.
- U.S. Department of Agriculture, 1999, 1997 Census of agriculture: National Agricultural Statistics Service, CD-ROM Sets 1A, 1B, 1C.
- U.S. Environmental Protection Agency, 2003a, Current drinking water standards: <http://www.epa.gov/safewater/mcl.html#mcls> (accessed on 04/28/2003).
- U.S. Environmental Protection Agency, 2003b, Maximum contaminant levels and health advisory levels: <http://www.epa.gov/safewater/uic/classv/pdfs/appd.pdf> (accessed on 04/28/2003).
- U.S. Geological Survey, 1998, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, Section A, book 9, chap. 6, <http://water.usgs.gov/owq/Fieldprocedures.html> (accessed on 04/07/2004).
- U.S. Geological Survey, EROS Data Center, 1999, National Elevation Dataset: <http://gisdata.usgs.net/ned/default.asp> (accessed on 04/07/2004).
- Wood, W.W., and Sanford, W.E., 1995, Chemical and isotopic methods for quantifying ground-water recharge in a regional, semiarid environment: *Ground Water*, v. 33, p. 458–468.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 60 p.

Appendixes

Appendix 1
Water-Quality Data from Monitoring Wells Screened
in the Southern High Plains Aquifer and Dockum
Group

Appendix 1. Water-quality data from monitoring wells screened in the southern High Plains aquifer and Dockum Group.

[mg/L, milligrams per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25°C; °C, degrees Celsius; CaCO_3 , calcium carbonate; <, less than; N, nitrogen; P, phosphorus; NTU, nephelometric turbidity units; $\mu\text{g}/\text{L}$, micrograms per liter; --, no data; E, estimated]

Parameter	Well name and sampling date							
	Castro-241	Castro-330	Castro-380	Castro-427	Hale-255	Hale-340	Hale-400	Hale-490
	04-07-02	04-08-02	04-08-02	04-09-02	04-04-02	04-05-02	04-05-02	04-06-02
Turbidity (NTU)	98.	7.	0.6	0.7	0.2	0.4	8.	27.
Oxygen, dissolved (mg/L)	2.6	< 0.5	< 0.5	< 0.5	5.6	3.7	3.9	< 0.5
pH, field (standard units)	7.69	7.41	7.41	7.60	8.60	7.57	7.54	7.05
Specific conductance ($\mu\text{S}/\text{cm}$)	713.	518.	537.	564.	891.	616.	631.	12,130.
Water temperature (°C)	12.6	17.7	17.0	16.9	16.5	17.8	17.8	17.8
Sulfide, field, total (mg/L)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2
Calcium, dissolved (mg/L)	40.1	42.5	44.6	37.8	31.2	33.2	32.6	474.
Magnesium, dissolved (mg/L)	32.4	27.0	28.8	22.6	32.4	27.0	26.8	306.
Potassium, dissolved (mg/L)	6.9	7.8	6.9	7.2	14.	8.5	8.6	25.
Sodium, dissolved (mg/L)	64.4	26.5	28.4	45.4	94.5	59.8	64.0	1,888.
Bicarbonate, dissolved (mg/L)	379.	306.	316.	321.	210.	349.	349.	223.
Bromide, dissolved (mg/L)	.4208	0.1007	0.1118	0.0897	0.6804	0.1281	0.1343	1.849
Chloride, dissolved (mg/L)	17.3	7.26	8.84	9.79	95.8	14.5	17.4	4,155.
Fluoride, dissolved (mg/L)	3.7	1.9	1.5	1.4	2.1	3.0	3.4	0.40
Silica, dissolved (mg/L as SiO_2)	54.9	38.1	33.4	29.6	34.8	42.0	41.8	16.4
Sulfate, dissolved (mg/L)	44.5	17.7	18.9	25.5	127.	32.3	34.1	446.
Solids, residue at 180°C, dissolved (mg/L)	444.	312.	331.	349.	550.	398.	396.	7,687.
Nitrogen, ammonia, dissolved (mg/L as N)	0.08	.41	< 0.04	< 0.04	0.49	< 0.04	< 0.04	0.64
Nitrogen, ammonia + organic, dissolved (mg/L as N)	0.2	.4	< 0.1	< 0.1	0.7	< 0.1	< 0.1	0.4
Nitrogen, nitrite + nitrate, dissolved (mg/L as N)	2.0	< 0.05	0.14	0.55	6.1	0.36	0.38	< 0.05

Appendix 2
Calculated Phase Mass Transfers and
Isotope Balances for Selected Pairs of
Initial and Final Waters

Appendix 2. Calculated phase mass transfers and isotope balances for selected pairs of initial and final waters.

[All phase mass-transfer calculations were performed with PHREEQC (Parkhurst and Appelo, 1999). The minimum and maximum phase mass transfers are based on all plausible models; however, not all phases were required in each model. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, negative numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution; mmol/kg water, millimoles per kilogram of water; $\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon, SO_4 , dissolved sulfate; SOC, sedimentary organic carbon, CO_2 , carbon dioxide; --, phase not included in any models]

Initial water 1 (uncertainty)	High Plains recharge Fryar and others (2001) (5 percent)		Castro-330 (5 percent)	
Initial water 2 (uncertainty)	not applicable		not applicable	
Final water (uncertainty)	Castro-330 (5 percent)		Castro-330 (5 percent)	
Phase mass transfer (mmol/kg water)	Minimum	Maximum	Minimum	Maximum
SiO ₂	-0.1010	-0.0883	-0.5582	0.0921
Kaolinite	-.0110	-.0110	-.4853	-.0032
Albite	--	--	.0089	.1602
K-feldspar	.0137	.0220	.0076	.0090
Anorthite	.0088	.0088	.0103	.0801
Ca-montmorillonite	-.0135	-.0095	-.0038	-.4166
Illite	--	--	--	--
SOC	.3426	.3426	.3420	.3535
CO ₂	.0833	.0836	--	--
Calcite	.1966	.2042	.0183	.0608
Goethite	--	--	-.0002	-.0002
Pyrite	--	--	.0002	.0002
Ca/Na ₂ exchange	-.0885	-.0885	-.0278	-.0522
Mg/Na ₂ exchange	--	--	.0089	.0278
Fraction of initial well 1 in mixture	1.0	1.0	1.0	1.0
Fraction of initial well 2 in mixture	0.0	0.0	0.0	0.0
$\delta^{13}\text{C}$ [SOC] (per mil)	-20.0	-20.0	-20.0	-20.0
$\delta^{13}\text{C}$ [CO ₂] (per mil)	-15.0	-15.0	--	--
$\delta^{13}\text{C}$ [calcite] (per mil)	-6.0	-5.0	-6.0	-6.0
$\delta^{34}\text{S}$ [pyrite] (per mil)	--	--	-25.0	-25.0
$\delta^{13}\text{C}$ [DIC final well, computed] (per mil)	-6.5	-6.5	-6.3	-6.3
$\delta^{13}\text{C}$ [DIC final well, measured] (per mil)	-6.3	-6.3	-6.3	-6.3
$\delta^{34}\text{S}$ [SO ₄ final well, computed] (per mil)	1.9	1.9	1.9	1.9
$\delta^{34}\text{S}$ [SO ₄ final well, measured] (per mil)	1.9	1.9	1.9	1.9

Appendix 2. Calculated phase mass transfers and isotope balances for selected pairs of initial and final waters.
—Continued

[All phase mass-transfer calculations were performed with PHREEQC (Parkhurst and Appelo, 1999). The minimum and maximum phase mass transfers are based on all plausible models; however, not all phases were required in each model. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, negative numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution; mmol/kg water, millimoles per kilogram of water; $\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon, SO_4 , dissolved sulfate; SOC, sedimentary organic carbon, CO_2 , carbon dioxide; --, phase not included in any models]

Initial water 1 (uncertainty)	High Plains recharge Fryar and others (2001) (5 percent)		Castro-330 (5 percent)	
Initial water 2 (uncertainty)	not applicable		not applicable	
Final water (uncertainty)	Castro-380 (5 percent)		Castro-380 (5 percent)	
Phase mass transfer (mmol/kg water)	Minimum	Maximum	Minimum	Maximum
SiO ₂	-0.1477	-0.1348	-0.9395	0.0642
Kaolinite	-.0003	-.0003	-.7490	-.0075
Albite	--	--	.0060	.2472
K-feldspar	.0006	.0090	--	--
Anorthite	--	--	.0086	.1236
Ca-montmorillonite	-.0006	-.0003	-.1061	.6429
Illite	--	--	--	--
SOC	.3003	.3132	.3374	.3548
CO ₂	.2027	.2227	--	--
Calcite	.3304	.3381	.0359	.1698
Goethite	--	--	-.0063	-.0001
Pyrite	--	--	.0001	.0063
Ca/Na ₂ exchange	-.1986	-.1507	-.1171	-.0030
Mg/Na ₂ exchange	.0708	.0708	-.0390	.0757
Fraction of initial well 1 in mixture	1.0	1.0	1.0	1.0
Fraction of initial well 2 in mixture	0.0	0.0	0.0	0.0
$\delta^{13}\text{C}$ [SOC] (per mil)	-20.0	-20.0	-20.0	-20.0
$\delta^{13}\text{C}$ [CO ₂] (per mil)	-15.0	-15.0	--	--
$\delta^{13}\text{C}$ [calcite] (per mil)	-6.0	-6.0	-6.0	-6.0
$\delta^{34}\text{S}$ [pyrite] (per mil)	--	--	-21.8	-21.8
$\delta^{13}\text{C}$ [DIC final well, computed] (per mil)	-6.6	-6.6	-6.2	-6.2
$\delta^{13}\text{C}$ [DIC final well, measured] (per mil)	-6.4	-6.4	-6.4	-6.4
$\delta^{34}\text{S}$ [SO ₄ final well, computed] (per mil)	--	--	0.4	0.5
$\delta^{34}\text{S}$ [SO ₄ final well, measured] (per mil)	.4	.4	.4	.4

Appendix 2. Calculated phase mass transfers and isotope balances for selected pairs of initial and final waters.
—Continued

[All phase mass-transfer calculations were performed with PHREEQC (Parkhurst and Appelo, 1999). The minimum and maximum phase mass transfers are based on all plausible models; however, not all phases were required in each model. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, negative numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution; mmol/kg water, millimoles per kilogram of water; $\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon, SO_4 , dissolved sulfate; SOC, sedimentary organic carbon, CO_2 , carbon dioxide; --, phase not included in any models]

Initial water 1 (uncertainty)	High Plains recharge Fryar and others (2001) (10 percent)		Castro-330 (10 percent)	
Initial water 2 (uncertainty)	not applicable		not applicable	
Final water (uncertainty)	Castro-427 (5 percent)		Castro-427 (5 percent)	
Phase mass transfer (mmol/kg water)	Minimum	Maximum	Minimum	Maximum
SiO ₂	-3.841	-0.1981	-1.673	-0.1412
Kaolinite	-2.032	-.1254	-1.332	-.1886
Albite	.2507	.9583	.3772	.6324
K-feldspar	.1425	1.375	--	--
Anorthite	.1254	.3353	.1338	.1886
Ca-montmorillonite	-.1254	2.693	-.2611	1.143
Illite	-2.263	-.2089	--	--
SOC	.2315	.3164	.2580	.2580
CO ₂	.1548	.1877	.0226	.1933
Calcite	.2334	.4170	.0643	.2600
Goethite	-.0254	-.0130	-.0248	-.0248
Pyrite	.0130	.0254	.0248	.0248
Ca/Na ₂ exchange	-.5286	-.1202	-.3700	.0362
Mg/Na ₂ exchange	-.3381	.2382	-.2226	-.0242
Fraction of initial well 1 in mixture	1.0	1.0	1.0	1.0
Fraction of initial well 2 in mixture	0.0	0.0	0.0	0.0
$\delta^{13}\text{C}$ [SOC] (per mil)	-20.0	-20.0	-20.0	-20.0
$\delta^{13}\text{C}$ [CO ₂] (per mil)	-15.0	-15.0	-15.0	-15.0
$\delta^{13}\text{C}$ [calcite] (per mil)	-6.0	-6.0	-6.0	-6.0
$\delta^{34}\text{S}$ [pyrite] (per mil)	-16.4	-15.0	-15.0	-15.0
$\delta^{13}\text{C}$ [DIC final well, computed] (per mil)	-6.5	-6.3	-6.3	-6.3
$\delta^{13}\text{C}$ [DIC final well, measured] (per mil)	-6.3	-6.3	-6.3	-6.3
$\delta^{34}\text{S}$ [SO ₄ final well, computed] (per mil)	-.04	.4	.08	.08
$\delta^{34}\text{S}$ [SO ₄ final well, measured] (per mil)	.2	.2	.2	.2

Appendix 2. Calculated phase mass transfers and isotope balances for selected pairs of initial and final waters.
—Continued

[All phase mass-transfer calculations were performed with PHREEQC (Parkhurst and Appelo, 1999). The minimum and maximum phase mass transfers are based on all plausible models; however, not all phases were required in each model. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, negative numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution; mmol/kg water, millimoles per kilogram of water; $\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon, SO_4 , dissolved sulfate; SOC, sedimentary organic carbon, CO_2 , carbon dioxide; --, phase not included in any models]

Initial water 1 (uncertainty)	High Plains recharge Fryar and others (2001) (10 percent)		Castro-330 (10 percent)	
Initial water 2 (uncertainty)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (10 percent)		Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (10 percent)	
Final water (uncertainty)	Hale-340 (5 percent)		Hale-340 (5 percent)	
Phase mass transfer (mmol/kg water)	Minimum	Maximum	Minimum	Maximum
SiO_2	-2.025	0.0177	-5.000	0.2333
Kaolinite	-4036	-0154	-9052	-0006
Albite	.0124	.9361	.0296	1.226
K-feldspar	.0109	.4350	.0017	2.035
Anorthite	.0344	.4399	.0910	.2317
Ca-montmorillonite	-4111	.1504	-4909	1.947
Illite	-6714	.0586	-3.390	-0007
SOC	.0421	.0570	.0337	.0337
CO_2	.6231	.7293	.0092	.8719
Calcite	.5244	.6178	.2076	.3893
Goethite	-0145	-0109	-0191	-0166
Pyrite	.0109	.0145	.0166	.0191
Ca/ Na_2 exchange	-7658	-1902	-7772	-0737
Mg/ Na_2 exchange	-2196	-0516	-1820	.6702
Fraction of initial well 1 in mixture	.90	.92	.88	.88
Fraction of initial well 2 in mixture	.08	.10	.12	.12
$\delta^{13}\text{C}$ [SOC] (per mil)	-20.0	-20.0	-20.0	-20.0
$\delta^{13}\text{C}$ [CO_2] (per mil)	-15.0	-15.0	-15.0	-15.0
$\delta^{13}\text{C}$ [calcite] (per mil)	-6.0	-5.0	-7.7	-5
$\delta^{34}\text{S}$ [pyrite] (per mil)	-15.0	-15.0	-15.0	-15.0
$\delta^{13}\text{C}$ [DIC final well, computed] (per mil)	-6.7	-6.5	-6.7	-6.5
$\delta^{13}\text{C}$ [DIC final well, measured] (per mil)	-6.5	-6.5	-6.5	-6.5
$\delta^{34}\text{S}$ [SO_4 final well, computed] (per mil)	2.8	2.8	2.6	2.8
$\delta^{34}\text{S}$ [SO_4 final well, measured] (per mil)	2.8	2.8	2.8	2.8

Appendix 2. Calculated phase mass transfers and isotope balances for selected pairs of initial and final waters.
—Continued

[All phase mass-transfer calculations were performed with PHREEQC (Parkhurst and Appelo, 1999). The minimum and maximum phase mass transfers are based on all plausible models; however, not all phases were required in each model. Positive numbers for mineral mass transfer indicate dissolution; negative numbers indicate precipitation. For exchange reactions, negative numbers indicate a decrease in calcium and (or) magnesium and an increase in sodium in solution; mmol/kg water, millimoles per kilogram of water; $\delta^{13}\text{C}$, stable carbon isotope composition; $\delta^{34}\text{S}$, stable sulfur isotope composition; DIC, dissolved inorganic carbon, SO_4 , dissolved sulfate; SOC, sedimentary organic carbon, CO_2 , carbon dioxide; --, phase not included in any models]

Initial water 1 (uncertainty)	High Plains recharge Fryar and others (2001) (12.5 percent)		Castro-330 (12.5 percent)	
Initial water 2 (uncertainty)	Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (12.5 percent)		Aquifer in rocks of Cretaceous age Nativ and Smith (1987) (12.5 percent)	
Final water (uncertainty)	Hale-400 (5 percent)		Hale-400 (5 percent)	
Phase mass transfer (mmol/kg water)	Minimum	Maximum	Minimum	Maximum
SiO ₂	-1.323	0.0143	-2.801	0.3641
Kaolinite	-.0550	-.0021	-2.147	-.0021
Albite	.0043	.0101	.0042	1.399
K-feldspar	.0087	.8194	.0042	.4921
Anorthite	--	--	.0003	.3641
Ca-montmorillonite	-.0486	.9707	-.5625	2.134
Illite	-1.340	.0492	-.8221	-.0018
SOC	.0330	.1196	.0482	.0587
CO ₂	.4543	.6571	.0039	1.067
Calcite	.4082	.5729	.1488	.4004
Goethite	-.0182	-.0100	-.0180	-.0093
Pyrite	.0100	.0182	.0093	.0180
Ca/Na ₂ exchange	-.8031	-.6092	-.6988	-.0707
Mg/Na ₂ exchange	-.1861	-.0848	-.2322	.2495
Fraction of initial well 1 in mixture	.84	.87	.83	.85
Fraction of initial well 2 in mixture	.13	.16	.15	.17
$\delta^{13}\text{C}$ [SOC] (per mil)	-20	-20	-20	-20
$\delta^{13}\text{C}$ [CO ₂] (per mil)	-15	-15	-15	-15
$\delta^{13}\text{C}$ [calcite] (per mil)	-5	-5	-5	-5
$\delta^{34}\text{S}$ [pyrite] (per mil)	-15	-15	-15	-15
$\delta^{13}\text{C}$ [DIC final well, computed] (per mil)	-6.4	-6.4	-6.2	-6.2
$\delta^{13}\text{C}$ [DIC final well, measured] (per mil)	-6.2	-6.2	-6.2	-6.2
$\delta^{34}\text{S}$ [SO ₄ final well, computed] (per mil)	2.8	3.0	2.8	3.0
$\delta^{34}\text{S}$ [SO ₄ final well, measured] (per mil)	3.0	3.0	3.0	3.0