

Ground-Water Quality Beneath Irrigated Cropland of the Northern and Southern High Plains Aquifer, Nebraska and Texas, 2003–04

By Jennifer S. Stanton and Lynne Fahlquist

National Water-Quality Assessment Program

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Foreword

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

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

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

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

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

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

Robert M. Hirsch
Associate Director for Water

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Conversion Factors, Abbreviations, and Datum

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
micrometer (μm)	0.00003937	inch (in.)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
acre-foot (acre-ft)	1,233	cubic meter (m^3)
milliliter (mL)	0.338	ounce, fluid (oz)
million gallons per day (Mgal/d)	3,785	cubic meter per day (m^3/d)
gallon (gal)	0.003785	cubic meter (m^3)
Flow rate		
gallon per minute (gal/min)	0.06309	liter per second (L/s)
inch per hour (in/hr)	25.4	millimeter per hour (mm/hr)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Radioactivity		
picocurie per liter (pCi/L)	0.312	tritium unit

Multiply	By	To obtain
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)
Density		
gram per cubic centimeter (g/cm ³)	62.43	pound per cubic foot (lb/ft ³)
Application rate		
pound per acre (lb/acre)	1.121	kilogram per hectare (kg/ha)
Concentration		
microgram per liter (µg/L)	1	part per billion (ppb)
milligram per liter (mg/L)	1	part per million (ppm)
milligram per liter (mg/L)	0.058	grain per gallon (gr/gal)

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

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

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

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

Datum

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

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

Ground-Water Quality Beneath Irrigated Cropland of the Northern and Southern High Plains Aquifer, Nebraska and Texas, 2003–04

By Jennifer S. Stanton and Lynne Fahlquist

Abstract

A study of the quality of ground water beneath irrigated cropland was completed for the northern and southern High Plains aquifer. Ground-water samples were collected from 30 water-table monitoring wells in the northern agricultural land-use (NAL) study area in Nebraska in 2004 and 29 water-table monitoring wells in the southern agricultural land-use (SAL) study area in Texas in 2003. The two study areas represented different agricultural and hydrogeologic settings. The primary crops grown in the NAL study area were corn and soybeans, and the primary crop in the SAL study area was cotton. Overall, pesticide and fertilizer application rates were larger in the NAL study area. Also, precipitation and recharge rates were greater in the NAL study area, and depths to water and evapotranspiration rates were greater in the SAL study area.

Ground-water quality beneath irrigated cropland was different in the two study areas. Nitrate concentrations were larger and pesticide detections were more frequent in the NAL study area. Nitrate concentrations in NAL samples ranged from 1.96 to 106 mg/L (milligrams per liter) as nitrogen, with a median concentration of 10.6 mg/L. Water in 73 percent of NAL samples had at least one pesticide or pesticide degradate detected. Most of the pesticide compounds detected (atrazine, alachlor, metolachlor, simazine, and degradates of those pesticides) are applied to corn and soybean fields. Nitrate concentrations in SAL samples ranged from 0.96 to 21.6 mg/L, with a median of 4.12 mg/L. Water in 24 percent of SAL samples had at least one pesticide or pesticide degradate detected. The pesticide compounds detected were deethylatrazine (a degradate of atrazine and propazine), propazine, fluometuron, and tebuthiuron. Most of the pesticides detected are applied to cotton fields.

Dissolved-solids concentrations were larger in the SAL area and were positively correlated with both nitrate and chloride concentrations, suggesting a combination of human and natural sources. Dissolved-solids concentrations in NAL samples ranged from 272 to 2,160 mg/L, with a median of

442 mg/L, and dissolved solids in SAL samples ranged from 416 to 3,580 mg/L, with a median of 814 mg/L.

Introduction

The High Plains aquifer underlies about 174,400 mi² in the central United States in parts of Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming (fig. 1). Ground water is the primary source for drinking water, irrigation, industry, and water supplies for animal production in the High Plains region. In 1990, the High Plains aquifer supplied drinking water to 2.2 million people or about 82 percent of High Plains residents (Dennehy, 2000). The area's economy has been dominated by agriculture for over a century. About 27 percent of irrigated land in the United States is in the High Plains, and about 30 percent of ground water used for irrigation in the United States is pumped from the High Plains aquifer (Dennehy, 2000).

About 41 percent of the land in the High Plains is cropland and 12 percent is irrigated (U.S. Geological Survey, 1992; Qi and others, 2002). Ground water provides most of the water used for irrigation. The number of irrigated acres has increased substantially since the mid-1900s because of advancements in well drilling and pumping technology and the development of center-pivot irrigation systems. The number of irrigated acres increased from about 2 million acres in 1949 to about 13 million acres in 1992 (Gutentag and others, 1984; Qi and others, 2002). As irrigated agriculture increased, producers were able to grow crops with larger water demands and economic returns; hence, the types of crops grown in the region have changed over time (U.S. Department of Agriculture, variously dated).

Applications of agricultural amendments (such as fertilizers, pesticides, and soil conditioners), changes in soil structure from tillage, increased recharge, and changes to ground-water flow patterns are associated with irrigated cropland. Application of agricultural amendments directly introduces nutrients, pesticides, and dissolved solids to the hydrologic system. Changes in soil structure and application of irrigation water



Figure 1. Location of High Plains aquifer and boundaries of northern and southern High Plains agricultural land-use study areas, Nebraska and Texas.

increase recharge rates, which aid movement of human and natural (such as nitrogen in soil organic matter and dissolved solids) chemical constituents past the root zone to ground water (Scanlon and others, 2005). Indirect effects of agriculture include increased rates of mineral weathering, mineral solubility, and trace element dissolution rates (Böhlke, 2002).

In 1991, the U.S. Geological Survey (USGS) implemented the National Water-Quality Assessment (NAWQA) Program to provide scientifically sound information for managing the Nation's water resources. The goals of the NAWQA Program are to assess the status and long-term trends of the Nation's surface- and ground-water quality and to understand the natural and human factors that affect it (Gilliom and others, 1995). As part of the NAWQA Program, a study of the ground-water quality of the High Plains aquifer was conducted. Because of its large geographic extent and the logistical challenges associated with regional ground-water quality studies, the High Plains aquifer was subdivided into three regions—northern High Plains, central High Plains, and southern High Plains (fig. 1).

To assess the effects of selected irrigated crops and hydrogeologic settings on ground-water quality in the High Plains aquifer, samples of ground water were collected from water-table monitoring wells in three agricultural land-use areas. Monitoring wells were located in an irrigated crop setting in each of the High Plains regions—corn and soybeans (northern High Plains), corn (central High Plains), and cotton (southern High Plains). Results from the study in the central High Plains were reported in Bruce and others (2003) and are not discussed here.

Purpose and Scope

This report describes and compares the quality of ground water at the water table beneath irrigated cropland in the northern High Plains (NHP) and southern High Plains (SHP). The two regions are located in different hydrogeologic and agricultural settings. Thirty water-quality monitoring wells were installed in the NHP agricultural-land use (NAL) study area, and 30 wells were installed in the SHP agricultural land-use (SAL) study area near irrigated fields. The wells were constructed with short well screens (typically 10 ft) near the water table to intercept ground water and, therefore, observe the effects of nearby irrigated cropland on ground-water quality. Ground-water samples were collected once from the 30 wells in the NAL study area in 2004 and once from 29 of the 30 wells in the SAL study area in 2003. One well in the SAL study area went dry after installation and, therefore, was not sampled. Water from all sites was analyzed for physical properties, and concentrations of nitrogen and phosphorus compounds, nitrogen isotopes of nitrate, pesticides and pesticide degradates, dissolved solids, major ions, trace elements, dissolved organic carbon, and tritium. In addition, water samples collected from the NAL study area also were analyzed for oxygen isotopes of nitrate.

Acknowledgments

The authors are grateful to the many landowners who allowed installation of a monitoring well on their property. This study could not have been conducted without their support. The authors also thank the Plains Cotton Growers, Inc.; Texas Cooperative Extension county offices in the southern High Plains study area; Texas A&M Agricultural Research and Extension Center, Lubbock; Texas Tech University, Lubbock; High Plains Underground Water Conservation District No. 1; Llano Estacado Underground Water Conservation District; Sandy Land Underground Water Conservation District; South Plains Underground Water Conservation District; Conservation and Survey Division of the University of Nebraska; and the Upper Big Blue Natural Resources District.

Methods of Investigation

Site Selection and Well Installation

Water-table monitoring wells were located and constructed with the purpose of evaluating the effect of irrigated agriculture on ground-water quality in the NHP and SHP regions. Gutentag and others (1984) describe the boundaries and settings of the NHP and SHP regions; however, the western boundaries of the regions have been revised for the High Plains ground-water-quality studies. Changes to the boundary were made to exclude areas of the unfractured Brule Formation in the NHP region and to account for better geologic information that became available for the SHP region.

The NHP region can be divided into five major hydrogeologic units—the Arikaree and Brule Formations, Ogallala Formation, Eastern Nebraska, Platte River Valley, and Sand Hills. These units represent unique depositional time periods, depositional settings, geologic materials, and hydrologic characteristics. The NAL study area was located within the Eastern Nebraska hydrogeologic unit (fig. 1)—a unit underlying extensive irrigated agriculture. The SAL study area was located within the Ogallala Formation—the major hydrogeologic unit of the High Plains aquifer in the SHP region.

Wells were installed in areas where irrigated agriculture was greater than 30 percent of the local land use. The percentage of irrigated agriculture was determined by overlaying a 1.24- by 1.24-mi grid on maps classified from Landsat Thematic Mapper satellite images that showed irrigated agriculture (nominal 1980 and 1992) (fig. 2) (Thelin and Heimes, 1987; Qi and others, 2002). McMahon (2000) showed that the effect of agriculture on ground-water quality was more likely to be observed in areas with depths to ground water of less than 200 ft; therefore, study areas also were limited to those regions where depth to water was less than 200 ft below land surface. In the most densely irrigated part of the SAL study area, depths to water were generally greater than 200 ft, and the primary crops grown were corn and wheat rather than

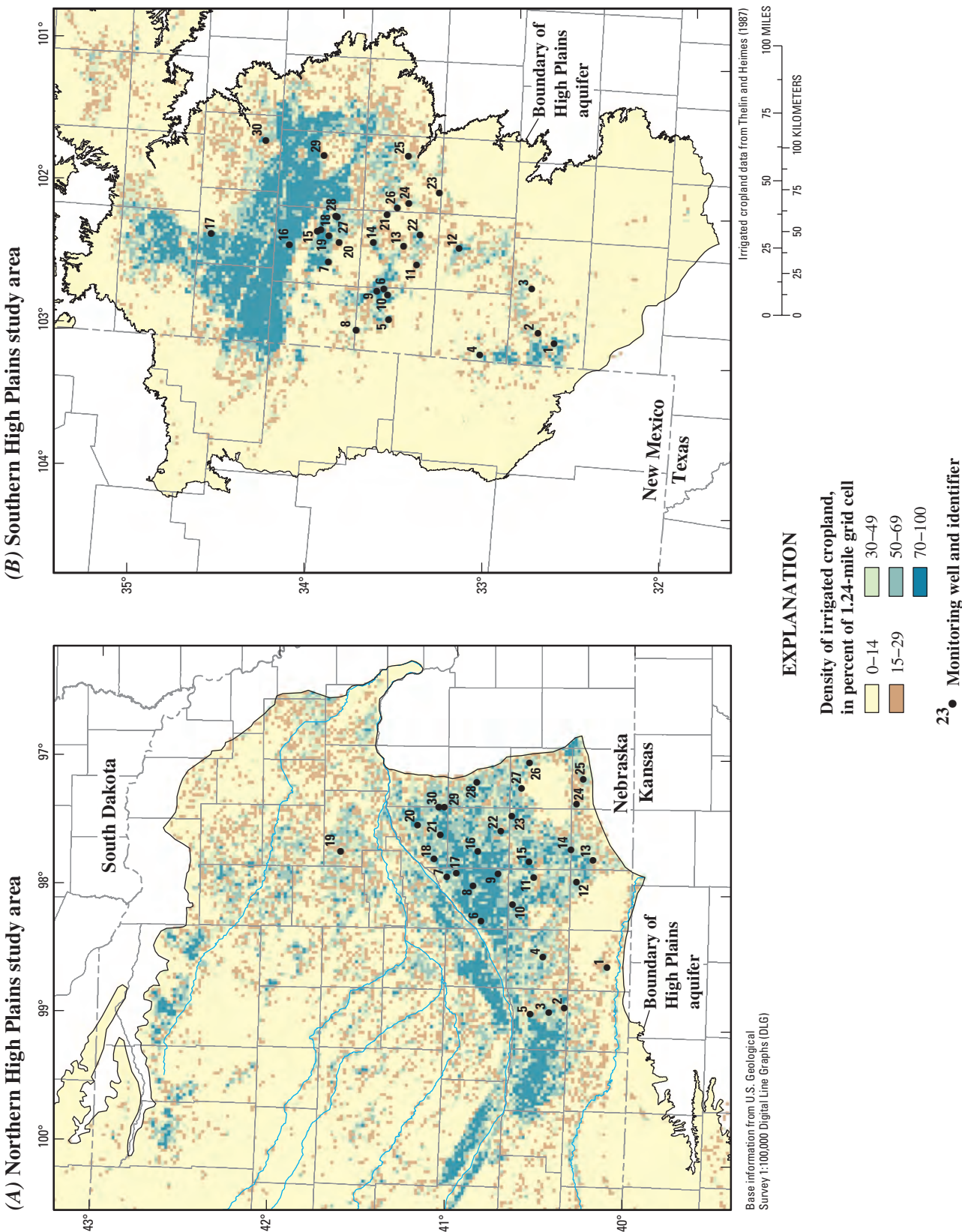


Figure 2. Distribution of irrigated cropland (nominal 1980) and location of wells installed to evaluate ground-water quality in (A) northern and (B) southern High Plains, Nebraska and Texas, 2003–04.

cotton (fig. 3B). As a result, SAL sites were not located in the areas with the most irrigated cropland (fig. 2B). The extent of the NAL study area was modified further to avoid duplication of effort by a similar NAWQA study (U.S. Geological Survey, 2006) in the northern part of the Eastern Nebraska unit.

Potential monitoring well locations were selected using a grid-based, random site-selection computer program (Scott, 1990). Each study area was divided into 30 equal-area cells. The computer program randomly selected one primary and one alternate location from a large population of potential sites within each cell. Areas near each randomly selected location were visited to determine the placement of monitoring wells. Monitoring well sites were selected with the following criteria: (1) within 4 mi of the randomly selected location; (2) next to a field that had been irrigated for approximately 20 years or more; (3) downgradient from the irrigated field on the basis of the direction of regional ground-water flow; (4) crops grown in the upgradient field were primarily corn and soybeans in the NAL area and primarily cotton in the SAL area; (5) located away from surface-water bodies, irrigation wells, or potential sources of contamination such as chemical storage, farm buildings, abandoned wells, and septic fields; (6) not in a water-gathering depression; (7) accessible to a well drilling rig and mobile laboratory; (8) did not receive direct application of irrigation water; and (9) land owner granted permission to drill a well. If no sites within the 4-mi radius were suitable, sites near the alternate randomly selected location were considered.

Well installation methods were used to maximize the likelihood that water-quality samples reflected the effects of irrigated agriculture on ground-water quality, that water-quality samples represented aquifer conditions, and that equipment and construction materials were not a source or sink of sampled analytes. Wells were installed with a hollow-stem auger using no drilling fluids in the NAL study area. In the SAL study area, wells were installed using an air rotary-casing advance technique. The air was filtered to minimize the possibility of introducing contaminants during the drilling process. Well casings were constructed of 2-in. diameter polyvinyl chloride (PVC) in the NAL study area and 2.5-in. PVC in the SAL study area. Typically, wells were constructed with 10-ft screens with a 5-ft blank casing with end cap below the screen. Effects of land-use activities on ground-water chemistry generally are observed at the shallowest part of the aquifer; therefore, the top of the well screen was placed about 5 ft below the estimated water table. The annular space from the bottom of the well to a few feet above the water table was filled with a silica-sand gravel pack. A bentonite well plug at least 2 ft thick was placed in the annular space above the silica sand to provide a seal. The remaining annular space was filled with bentonite/cement grout, and a concrete pad and protective steel cover were placed at the land surface around the well.

Sample Collection and Analysis

Ground-water samples were collected from 30 monitoring wells in the NAL study area, and 29 monitoring wells in the SAL study area (Appendixes 1 and 2). Ground-water samples were collected using procedures described by Koterba and others (1995) and the USGS national field manual (U.S. Geological Survey, variously dated). Water samples were processed onsite in a mobile laboratory using methods designed to minimize changes to the water-sample chemistry. Water was pumped from wells with a stainless-steel submersible pump and delivered to the mobile laboratory through Teflon tubing with stainless-steel connections. Prior to sample collection, stale water was flushed from the well by purging at least three casing volumes from the well. While purging, specific conductance, pH, water temperature, turbidity, and dissolved oxygen were measured until readings were stable (U.S. Geological Survey, variously dated). Once measurements stabilized, water samples were collected in precleaned bottles within an enclosed chamber to prevent sample contamination. To prevent degradation of water samples and to maintain the initial concentration of compounds between the time of sample and laboratory analyses, bottles were preserved according to the requirements of the laboratories. Preservation practices differ among analytes and may include chilling, filtration, and (or) chemical treatment (table 1).

Water samples were analyzed to determine physical properties and concentrations of nitrogen and phosphorus compounds, nitrogen isotopes of nitrate, pesticides and pesticide degradates, dissolved solids, major ions, carbonate alkalinity, trace elements, dissolved organic carbon, and tritium. Water samples collected from the NAL study area also were analyzed for oxygen isotopes of nitrate. Forty-seven pesticides and seven pesticide degradates were analyzed for all samples collected from the NAL and SAL study areas (Appendixes 1 and 2). Additional pesticide compounds specific to the crops grown in each area also were analyzed. Pesticide degradates of atrazine, acetochlor, alachlor, dimethanamid, flufenacet, metolachlor, and propachlor were analyzed for NAL samples only. Fluometuron, norflurazon, prometryn, propazine, and their associated degradates were analyzed for SAL samples only. Laboratory analytical methods are briefly summarized for measured water-quality constituents in table 1.

Eleven SAL wells were resampled because dissolved organic carbon concentrations in water samples from those wells were one to two orders of magnitude larger than other samples and were deemed unreliable. Potential dissolved organic carbon contamination sources were not discovered. When those wells were resampled, dissolved organic carbon concentrations were generally within the same order of magnitude as other previously collected samples. Therefore, the dissolved organic carbon concentrations from the second set of samples were considered to be representative of aquifer conditions and were used in interpretations in this report. With the exception of dissolved organic carbon, water-quality data from

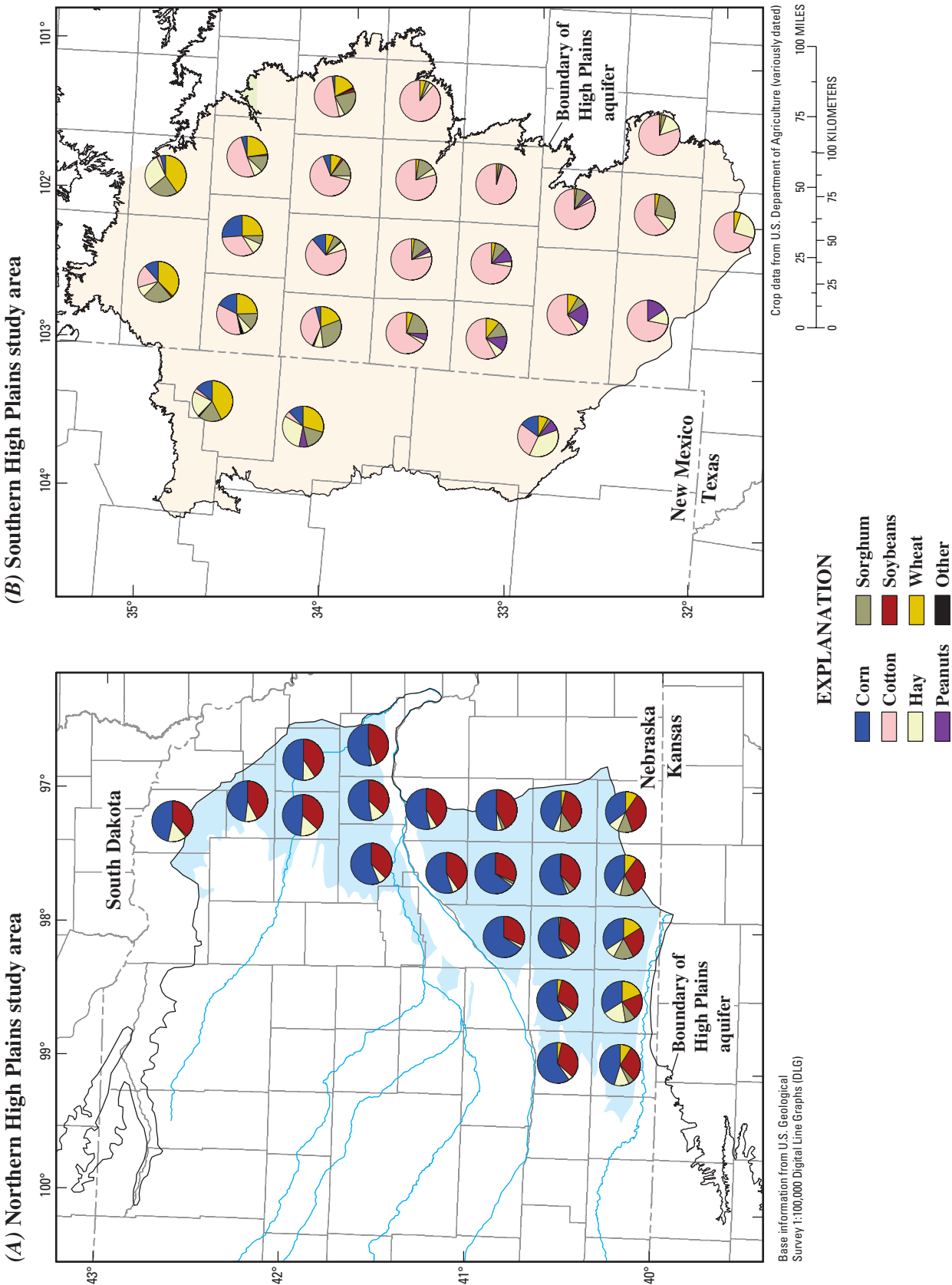


Figure 3. Distribution of major crops grown, by county, in (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2002. (Distributions shown are relative percentages by crop of the total acreage harvested.)

Table 1. Laboratory analysis and onsite treatment and preservation methods for measured water-quality constituents in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; μm , micrometer; $^{\circ}\text{C}$, degrees Celsius; C-18, carbon 18; GC/MS, gas chromatography/mass spectrometry; LC/MS, liquid chromatography/mass spectrometry; <, less than; UV, ultraviolet; mL, milliliter]

Constituent or constituent group	Analyzing laboratory	Analytical method(s)	Reference(s)	Onsite treatment and preservation method(s)
Depth to water, specific conductance, pH, temperature, turbidity, dissolved oxygen	Measured onsite	Various methods	USGS, variously dated	None.
Nitrogen and phosphorus compounds	USGS NWQL, Lakewood, CO	Various methods	Fishman, 1993; Patton and Kryskalla, 2003	Filter through 0.45- μm filter, chill and maintain at 4 $^{\circ}\text{C}$.
Nitrogen and oxygen isotopes of nitrate	USGS Stable Isotope Laboratory, Reston, VA	Continuous flow isotope ratio mass spectrometry	Casciotti and others, 2002	Filter sample through 0.45- μm filter, freeze sample until shipment to laboratory.
Pesticides and pesticide degradates	USGS NWQL, Lakewood, CO	C-18 solid-phase extraction and capillary-column GC/MS	Zaugg and others, 1995; Lindley and others, 1996; Madsen and others, 2003	Filter through 0.7- μm baked glass fiber filter, chill sample and maintain at 4 $^{\circ}\text{C}$.
Selected pesticide degradates	USGS Organic Geochemistry Research Laboratory, Lawrence, KS	Online solid-phase extraction and LC/MS; solid-phase extraction and GC/MS; solid-phase extraction and capillary-column GC/MS with selected-ion monitoring	Zimmerman and Thurman, 1999; Kish and others, 2000; Lee and Strahan, 2003	Filter through 0.7- μm baked glass fiber filter, chill sample and maintain at 4 $^{\circ}\text{C}$.
Dissolved solids and major ions	USGS NWQL, Lakewood, CO	Inductively coupled plasma	Fishman and Friedman, 1989; Fishman, 1993; American Public Health Association, 1998	Anions, filter through 0.45- μm filter; Cations, filter through 0.45- μm filter, acidify sample to pH <2 with nitric acid (HNO_3).
Carbonate alkalinity	Analyzed onsite	Inflection point titration	USGS, variously dated	Filter through 0.45- μm filter.
Trace elements	USGS NWQL, Lakewood, CO	Inductively coupled plasma, atomic absorption spectrometry	Fishman and Friedman, 1989; Faires, 1993; McLain, 1993; Garbarino, 1999	Filter through 0.45- μm filter and acidify sample to < 2 with nitric acid (HNO_3).
Dissolved organic carbon	USGS NWQL, Lakewood, CO	UV-light promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett, 1993	Filter through 0.7- μm baked glass fiber filter, acidify to pH < 2 with 1 mL of 4.5N sulfuric acid (H_2SO_4), chill and maintain at 4 $^{\circ}\text{C}$.
Tritium	USGS Isotope Tracers Laboratory, Menlo Park, CA	Electrolytic enrichment and liquid scintillation	Thatcher and others, 1977	Completely fill bottle to exclude air bubbles. Fill bottle with minimal splashing.

the first set of samples were used in interpretations found in this report.

Data Treatment

In 1998, the USGS National Water Quality Laboratory (NWQL) began implementing a new method for reporting analytical results (Childress and others, 1999). Two concentration levels are used in the new method, the long-term method detection level (LT-MDL) and the laboratory reporting level (LRL) to minimize both false positive and false negative errors. LT-MDLs and LRLs vary among constituents and analytical methods. The LT-MDL is determined from the standard deviation of long-term laboratory spike-sample measurements and is set to the level at which false positive errors are minimized to no more than 1-percent probability. The LRL is set to the level at which false negative errors are minimized to no more than 1-percent probability and is generally equal to twice the LT-MDL. Using this reporting convention, if a reported concentration is greater than both the LRL and the smallest laboratory calibration standard, it is not censored or qualified. If a reported concentration is smaller than the LT-MDL, it is coded as “less than” the LRL, unless information-rich laboratory methods (organic constituent methods that have additional qualitative information provided by the instrumentation) are used. LT-MDLs and LRLs are reevaluated annually by the NWQL on the basis of laboratory spike-sample measurements and may change with time.

Concentrations are qualified as estimated in several situations. If a reported concentration is smaller than either the LRL or the smallest laboratory calibration standard but greater than the LT-MDL, the value is qualified as estimated using an “E” remark code. An “E” remark code also is used if the reported concentration is larger than the largest laboratory calibration standard. Pesticide and volatile organic compounds were analyzed and reported using information-rich laboratory methods. These methods report concentrations smaller than the LT-MDL if an analyte is positively identified and all other laboratory quality-control criteria are satisfied. The reported concentrations smaller than the LT-MDL are qualified with an “E” remark code. Finally, if a compound does not meet method-specific performance criteria, it is qualified with an “E” remark code.

Water-quality data characteristically include “outliers” (observations much larger or smaller than most of the data), censored data, and positive skewness (most data occur at small values but a few extreme large values are present). For these reasons, nonparametric statistical methods were used in this report. The nonparametric Wilcoxon, or Mann-Whitney, rank sum test (two-sided) was used to compare observations between groups of data (Wilcoxon, 1945). In this report, a p-value of 0.05 or less indicated sufficient evidence that there was a significant difference between two groups of data. If more than 50 percent of the values were censored, no statistical comparison was attempted. The nonparametric

Spearman’s rho was used to test the correlation between variables in a data set (Bhattacharyya and Johnson, 1977). In this report, a p-value of 0.05 or less indicated sufficient evidence that two variables were correlated. Fisher’s Exact test (Agresti, 1990) was used to detect group differences in categorical data. A p-value of 0.05 or less indicated that there was a significant difference between the two groups of data.

To apply statistical tests, it was sometimes necessary to substitute censored (“less than”) values with a numeric value. Substitutions were applied using methods described by Helsel (2005) and were dependent upon the laboratory reporting methods of each constituent. Censored data were set to a value smaller than the smallest LT-MDL to effectively be treated as a tied rank that was smaller than any estimated or uncensored value. Estimated values were treated as quantitative results.

Quality Control

Additional samples were collected to assess the reliability of sample processing and analytical methods. These quality-control samples included field-blank, replicate, and environmental-matrix spike samples.

Field-Blank Samples

Field-blank samples were collected to determine the occurrence and magnitude of sample contamination during sample collection, equipment cleaning, transport, and analysis. When blank samples were collected, sample bottles were filled with water that was specially prepared at the NWQL instead of water from the sampled well. Prior to use, the prepared water was analyzed and certified to be free of the environmental sample analytes. Field-blank samples were otherwise collected using the same procedures and equipment as environmental samples. Blank samples were collected and analyzed for nitrogen and phosphorus compounds, pesticide compounds, major ions, trace elements, and dissolved organic carbon. It is not possible to prepare meaningful tritium or isotope blank samples; therefore, tritium and isotope blank samples were not collected.

Results of blank sample analyses are summarized in table 2. Concentrations of analytes detected in blank samples were compared with concentrations of analytes in environmental samples to determine the potential for environmental sample contamination. If the magnitude of the blank sample concentrations approached the environmental sample concentrations, environmental sample concentrations may have been affected by sampling contamination. Concentrations of aluminum, copper, manganese, nickel, and dissolved organic carbon in at least one field-blank sample were larger than the smallest concentration found in environmental samples. Therefore, at small concentrations, it was not possible to determine if environmental concentrations of these constituents were representative of aquifer conditions or the result of

Table 2. Constituents detected in field-blank samples collected for northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[<, less than; E, estimated; --, only one detection in field-blank samples, median not calculated]

Constituent	Number of detections ¹ / number of field-blank samples	Median concentration of detected analytes in field-blank samples	Maximum concentration in field-blank samples	Range of concentra- tions in environmental samples
Nitrogen and phosphorus compounds (concentrations in milligrams per liter)				
Nitrate	1/6	--	0.08	0.65 – 106
Pesticide compounds				
None detected				
Major ions (concentrations in milligrams per liter)				
Calcium	4/4	0.06	.10	29.9 – 473
Magnesium	1/4	--	.009	6.83 – 198
Sodium	3/4	.14	.17	9.18 – 735
Silica	3/4	.16	.84	20.9 – 81.7
Trace elements (concentrations in micrograms per liter)				
Aluminum	1/6	--	10	<2 – E2
Boron	2/6	17	19	23 – 943
Copper	4/6	.65	1.3	0.4 – 5.2
Lithium	1/6	--	.7	8.1 – 278
Manganese	3/6	.3	.5	<0.2 – 621
Nickel	6/6	.06	.75	0.7 – 52.1
Strontium	2/6	.6	.64	237 – 7,250
Vanadium	3/6	.4	.6	2.4 – 118
Dissolved organic carbon (concentrations in milligrams per liter)				
Dissolved organic carbon	1/6	--	.5	E0.3 – 16.2

¹Equal to or greater than the highest laboratory reporting level (LRL).

sampling contamination. Because relatively few analytes were detected in field-blank samples, equipment decontamination and sample handling procedures adequately prevented positive bias of reported concentrations.

Replicate Samples

Replicate samples are two environmental samples collected sequentially to represent a duplication of the same sample water. They are collected to determine variability of the data as a result of sampling and analytical procedures. The relative percentage difference (RPD) between concentrations of paired replicate samples was calculated using the formula:

$$RPD = \frac{|Sample\ 1 - Sample\ 2|}{\left(\frac{Sample\ 1 + Sample\ 2}{2}\right)} \times 100. \quad (1)$$

When there is no variability between the paired analytes, the RPD is zero. The RPD was not calculated if one or

both of the paired replicate concentrations were less than the largest laboratory reporting level (LRL) or identified as an estimated value by the laboratory. The median RPDs of the constituent groups ranged from 0.3 to 5.1 percent (table 3). With the exception of trace elements and dissolved organic carbon, about 90 percent of the RPDs were less than 5 percent. The larger RPDs for trace elements might be explained by many constituents with small concentrations near the LRL. With small concentrations and less precision, small differences can yield large calculated variability. For example, an environmental sample concentration of 0.01 mg/L and a replicate sample concentration of 0.02 mg/L yield an RPD of 50 percent. The individual constituents having the largest average RPDs were chromium (16.0 percent), silver (15.4 percent), lithium (13.2 percent), fluoride (11.1 percent), and iron (10.2 percent). In general, small RPDs for constituents indicated that the amount of variability between paired environmental and replicate samples was within acceptable limits.

Table 3. Summary of relative percentage differences for replicate samples collected for northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[--, percentile not calculated]

Compound class	Num- ber of samples	Number of repli- cate pairs used in cal- culation ¹	Mini- mum	Percentile					Maxi- mum
				10	25	50	75	90	
Environmental sample replication (relative percentage differences)									
Nitrogen and phosphorus compounds (5 constituents)	4	9	0	--	--	0.3	--	--	10.6
Nitrogen and oxygen isotopes of nitrate (2 constituents)	2	3	0	--	--	2.3	--	--	3.4
Pesticides and pesticide degradates (81 compounds)	4	2	0	--	--	5.1	--	--	10.2
Dissolved solids	4	4	.35	--	--	.83	--	--	1.86
Major ions (10 constituents)	4	39	0	0	0.5	1.2	2.3	4.4	40.0
Trace elements (23 constituents)	6	91	0	0	.5	1.9	5.5	15.4	42.9
Dissolved organic carbon	6	6	0	--	--	3.2	--	--	23.2
Tritium	2	2	2.7	--	--	4.4	--	--	6.1

¹Percentage difference was not calculated if the laboratory results of either the environmental or replicate sample were qualified with “E” or “<”. Only the 50th percentile was reported if there were fewer than 10 percentage-difference values calculated in a compound class.

Environmental-Matrix Spike Samples

Environmental-matrix spikes typically are utilized to quantify the gain or loss of organic-compound analytes due to water-matrix properties, sample holding time, or onsite and laboratory procedures. A spike recovery of 100 percent suggests no matrix interference or degradation and good analytical recovery. Environmental-matrix pesticide spike samples were prepared by injecting known amounts of 52 pesticide compounds into replicate samples while onsite. The average percentage recovery of individual pesticide compounds was calculated from the four matrix spike samples and is reported in Appendix 3. Forty-one of the 52 pesticide compounds analyzed were within an acceptable range of 60 to 120 percent recovery (Furlong and others, 2001). Of the 11 pesticide compounds analyzed that did not fall into the range of acceptable recovery, three (deethylatrazine, carbaryl, and carbofuran) always were reported as estimated values by NWQL because of known problems with gas chromatography or extraction or because they did not otherwise meet method performance criteria (Zaugg and others, 1995).

Hydrogeologic Setting

Northern High Plains

The NAL study area was limited to the Eastern Nebraska hydrogeologic unit in the NHP region. For this report, the Eastern Nebraska unit refers to the Pleistocene and Pliocene deposits in the eastern part of the NHP where the underlying Ogallala Formation is thin or absent. According to previous studies (Johnson and Keech, 1959; Richmond and others, 1994; Gosselin and others, 1996; Verstraeten and others, 1998), the Eastern Nebraska unit consists primarily of sand and gravel but also includes wind-deposited silt and clay (loess), paleosols, and unsorted and unstratified glacial till. The earlier Pliocene sediments consist of granite, anorthosite, and quartz sediment eroded from the Laramie Range and Medicine Bow Mountains in Wyoming to the west. Later, glacial processes transported Pleistocene sand and gravel, composed primarily of quartz, from the north. The hydrologic conditions in the NAL study area can be unconfined, perched, semiconfined, or confined. The thickness of the Eastern Nebraska unit is variable and ranges from 0 to more than 300 ft. Either the Ogallala Formation or bedrock of Cretaceous age underlies this unit. It is hydraulically connected to the Ogallala Formation where it is present (Johnson and Keech, 1959; Richmond and others, 1994; Gosselin and others, 1996; Verstraeten and others, 1998).

Depths to ground water in the Eastern Nebraska unit range from less than 5 to over 300 ft below land surface (Sharon Qi, U.S. Geological Survey, written commun., 2005). Hydraulic conductivity in this area generally varies from less than 25 to 200 ft/d and averages about 70 ft/d (Gutentag and others, 1984; Sharon Qi, U.S. Geological Survey, written commun., 2006). Well yields in this area range from just a few gallons per minute (gal/min) in small-capacity domestic and stock wells to more than 2,000 gal/min in irrigation and public supply wells (Nebraska Department of Natural Resources, 2003).

Thick layers of glacial till and (or) loess and soils of low permeability between the land surface and the water table limit the amount of precipitation that enters ground water as recharge. For these reasons, most precipitation is lost to surface runoff or evapotranspiration. Ground-water recharge in the NAL study area is estimated to be about 20 percent of mean annual precipitation (Dugan and Zelt, 2000). Average percentage of sand, silt, and clay, bulk density, organic matter content, and vertical and horizontal permeability for soils within a 1,640-ft radius around each of the 30 wells was calculated from the 1994 State soil geographic (STATSGO) database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997). STATSGO soil mapping unit identifiers were averaged on a coarse (1-km, 0.6214-mi) resolution grid prior to calculating average properties within 1,640-ft of each monitoring well. The median of the 30 average values calculated for each soil characteristic is presented in table 4.

The land surface in the NAL study area is characterized by flat plains or gently rolling loess hills that have been dissected by stream channels. Streams are relatively abundant compared with other areas of the High Plains. Many small reservoirs that catch precipitation runoff are located in the area and typically are used to water livestock.

The climate is subhumid, and the area receives mean annual precipitation of between about 25 in/yr in the west to

about 27 in/yr in the east (Johnson and Keech, 1959). Most precipitation falls from thunderstorms during the summer growing season (May through September). Mean annual pan evaporation rates range from about 65 to 75 in/yr (Gutentag and others, 1984). Natural ground-water recharge rates (not including recharge from irrigation) have been estimated to be between 4 and 6 in/yr (Dugan and Zelt, 2000).

Southern High Plains

The SAL study area was limited to the areal extent of the Ogallala Formation of Tertiary age within the SHP region. Previous studies provided hydrogeologic characteristics of the study area (Seni, 1980; Gutentag and others, 1984; Fahlquist, 2003). The Ogallala Formation is made of stream-deposited gravel, sand, silt, and clay originating from the Rocky Mountains to the west (Seni, 1980). Sediments were deposited in a complex, braided-stream alluvial-fan environment. Paleovalleys incised into the underlying bedrock generally contain coarser sand and gravel. The Ogallala Formation is primarily unconfined but may be locally confined or semiconfined where extensive clay layers are present. Layers of caliche are common. The saturated thickness of the Ogallala Formation varies from less than 20 to more than 500 ft. In the study area, this unit overlies bedrock of Cretaceous or Triassic age and may be hydraulically connected to these bedrock units in some areas. The Blackwater Draw Formation overlies and is considerably less extensive than the Ogallala Formation but, where saturated, is considered to be part of the High Plains aquifer. It consists of aeolian, fluvial, and lacustrine sediment and lies between the Ogallala Formation and the land surface in some areas. For this report, the Blackwater Draw Formation is part of the study area.

Depth to ground water ranges from less than 100 ft in the south to more than 400 ft in parts of the north (Fahlquist, 2003). Hydraulic conductivity in the SAL study area typi-

Table 4. Median values of average soil properties within 1,640 feet of monitoring wells in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas.

[Source: 1994 STATSGO database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997). NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use; <, less than]

Variable	NAL study area	SAL study area	p-value (Wilcoxon rank-sum) ¹
Average sand content of soils, in percent	3.9	44.8	<0.001
Average silt content of soils, in percent	62.4	28.9	<.001
Average clay content of soils, in percent	33.9	26.3	.066
Average bulk density of soils, in grams per cubic centimeter	1.33	1.52	<.001
Average organic matter content, in percent by weight	.54	.17	<.001
Average vertical permeability of soils, in inches per hour	.57	1.36	<.001
Average horizontal permeability of soils, in inches per hour	.83	1.56	<.001

¹p-values indicate the statistical probability that there was a real difference between two groups of data. Variables were considered to be significantly different between the two study areas if p was less than or equal to 0.05.

cally varies from 1 to 100 ft/d, with a geometric mean of about 7 ft/d (Blandford and others, 2003). Paleovalleys filled with coarse gravel and sand typically have greater hydraulic conductivity than the finer sediments located in the interchannel regions. Well yields range from a few gallons per minute to about 1,000 gal/min (Texas Water Development Board, 2002).

The land surface is a gently sloping plateau that grades from the highest altitude of about 5,600 ft in the northwest to about 2,700 ft in the southeast (Fahlquist, 2003). Playas (closed-basin depressions) cover about 2 percent of the land surface and capture rainfall and irrigation runoff. Only a few streams exist in the area, and most are ephemeral. Some streams are captured by reservoirs to supply water to municipalities. The median values for average percentage of sand, silt, and clay, bulk density, organic matter content, and vertical and horizontal permeability of soils within a 1,640-ft radius of the 29 sampled monitoring wells are found in table 4.

The SAL study area is semiarid to subhumid, receiving a mean annual precipitation between 13 in/yr in the southwest to about 20 in/yr in the northeast (Bomar, 1983). Evaporation rates are some of the highest in the Nation. Mean annual pan evaporation rates range from about 95 to more than 105 in/yr (Gutentag and others, 1984). Natural ground-water recharge rates have been estimated to be from no recharge to about 1 in/yr (Dugan and Zelt, 2000; Scanlon and others, 2005).

Land-Use Setting

To examine the effect of irrigated agriculture on ground-water quality at the water table, the NAL and SAL study areas were located in regions where irrigated agriculture was currently greater than 30 percent of the local land use. In addition to irrigation water, fertilizers and pesticides are commonly applied in these areas to produce consistent crop yields. There are no easily obtainable historical data to evaluate the changes in nutrient, pesticide, and irrigation-water applications. However, it is generally thought that because of more efficient farming practices, application rates are less today than 30 or 40 years ago. For example, application of irrigation water has moved from primarily flood and furrow methods to more efficient center-pivot systems. Also, many crop producers now are testing soils for nitrogen levels to adjust fertilizer application rates and prevent overapplication of nutrients to cropland. Although the estimated application rates presented in the following sections do not necessarily represent conditions during the time that water composing the ground-water samples was recharged, they do provide a general idea of the types and relative amounts of nutrients, pesticides, and irrigation water that are applied.

Northern High Plains

In 1992, an estimated 83 percent (4.9 million acres) of the land in the NAL study area was used for cropland and

12 percent was rangeland. The remaining 5 percent was classified as forest, wetlands, open water, or urban (fig. 4A) (U.S. Geological Survey, 1992). Land-use classes were estimated from Landsat Thematic Mapper satellite images as part of the National Landcover Dataset (NLCD). The most common crops grown in the study area in 2002 were corn and soybeans. Secondary crops included hay, sorghum, and wheat (fig. 3A) (U.S. Department of Agriculture, variously dated). About 34 percent of the study area was irrigated in 1980 (Thelin and Heimes, 1987).

Nitrogen fertilizers commonly are applied to cropland in the NAL study area. The amount of nitrogen applied to cropland from manure (Barb Ruddy and David Lorenz, U.S. Geological Survey, written commun., 1997) in 1997 and commercial fertilizer (David Lorenz, U.S. Geological Survey, written commun., 1998) in 1998 in the NAL study area was about 558 million lb. The total nitrogen divided by the total number of cropland acres yields an average nitrogen application rate of about 114 lb/acre of cropland. Fertilizer application rates were based on state-level fertilizer sales obtained from the Statistical Reporting Service (SRS) of the U.S. Department of Agriculture (Alexander and Smith, 1990). Estimates of county fertilizer use were calculated by multiplying the total state fertilizer sales by the portion of the state's fertilized acreage that was in each county. Manure application rates were calculated from county-level livestock populations obtained from the Census of Agriculture (U.S. Department of Agriculture, 1999). Nitrogen content of manure was estimated using methods described by Goolsby and others (1999). Loss of nitrogen through volatilization was not accounted for when estimating animal manure nitrogen.

The estimated nitrogen application rate within 1,640 ft of sampled wells in the NAL ranged from 52 to 136 lb/acre, with a median of 104 lb/acre. Nitrogen applications within 1,640 ft of each monitoring well were calculated using average estimated county-level manure data from 1992 to 1997 and commercial fertilizer application data from 1992 to 2001 coupled with the 1992 NLCD data enhanced with Geographic Information Retrieval and Analysis System (GIRAS) data (Kerie Hitt, U.S. Geological Survey, written commun., July 2005). For each well, the estimated county-level nitrogen application was multiplied by the fraction of the county's cropland that was in the 1,640-ft buffer of the well.

Pesticides (insecticides, herbicides, and fungicides) commonly are applied to cropland to control weeds and insects. When pesticides move past the soil profile to a ground-water resource that is used for drinking water, they can cause potential health concerns (U.S. Environmental Protection Agency, 2004). An average of 1.62 lb/acre of pesticides was applied to cropland in the NAL study area in 1997 (table 5) (Naomi Nakagaki, U.S. Geological Survey, written commun., July 2005). Atrazine and metolachlor were the pesticides most commonly applied to crops. The types and amounts of pesticides applied to each area are related to the types of crops grown.

Most water used in the northern High Plains is for cropland irrigation. In 2000, an estimated 1,940 Mgal/d was

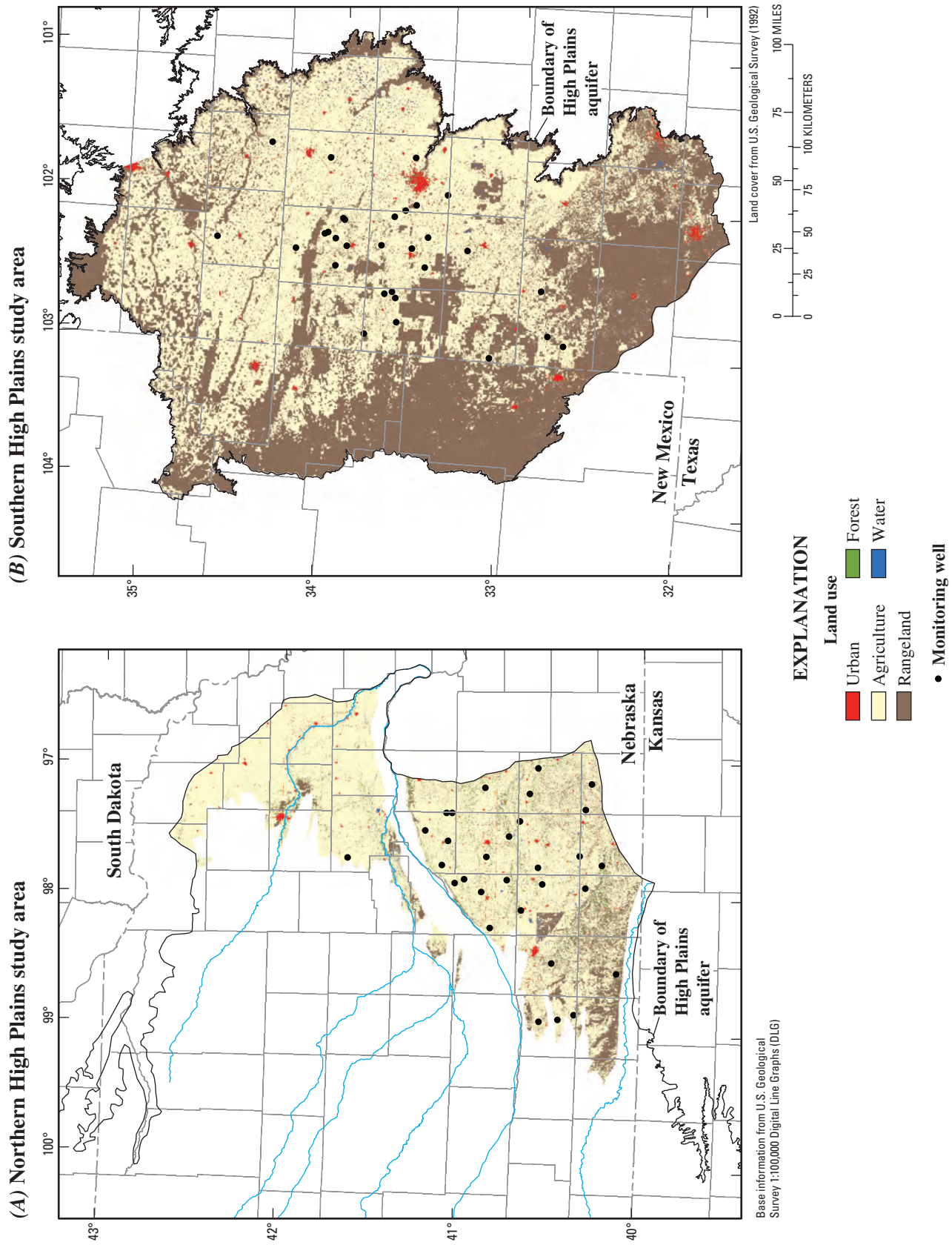


Figure 4. Distribution of primary land-use types in (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 1992.

Table 5. Ten most frequently applied pesticides in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 1997.

[Pesticide application rates on crops were estimated from the National Center of Food and Agricultural Policy (NCFAP) (1997) and county-level information of harvested crops in the 1997 Census of Agriculture (U.S. Department of Agriculture, 1999); lb/acre, pound per acre; a.i., active ingredient]

NAL study area		SAL study area	
Pesticide name	Average amount applied to cropland (lb/acre of a.i.)	Pesticide name	Average amount applied to cropland (lb/acre of a.i.)
Atrazine	0.46	Trifluralin	0.17
Metolachlor	.44	Malathion	.09
Acetochlor	.18	2,4-D ¹	.09
Glyphosate ¹	.18	Atrazine	.08
Alachlor	.08	Pendimethalin	.07
Cyanazine	.06	Sodium-chlorate ¹	.06
Pendimethalin	.06	Metolachlor	.05
2,4-D ¹	.06	Ethephon ¹	.05
Terbufos	.05	Glyphosate ¹	.04
Carbofuran	.05	Tribufos ¹	.03
TOTAL	1.62	TOTAL	.73

¹Not analyzed in water samples collected as part of this study.

used for that purpose in the NAL study area (U.S. Geological Survey, 2004). Ground-water withdrawals for irrigation varied by county and ranged from 15 to 315 Mgal/d (fig. 5A). Irrigation water is applied mainly during the summer months (June through August) when crop water demands are largest. Other water uses include publicly supplied drinking water (41 Mgal/d), livestock (16 Mgal/d), industrial (13 Mgal/d), and rural household drinking water (8 Mgal/d).

Southern High Plains

According to the NLCD, cropland covered about 53 percent (9.8 million acres) of the SAL study area in 1992. Forty-six percent of the study area was designated as rangeland, and the remaining 1 percent was classified as forest, wetlands, open water, or urban (fig. 4B) (U.S. Geological Survey, 1992). In 2002, cotton was the primary crop grown in the area. Secondary crops were wheat and sorghum (fig. 3B) (U.S. Department of Agriculture, variously dated). About 11 percent of the study area was irrigated in 1992 (Qi and others, 2002).

Fertilizers and pesticides are commonly applied to cropland in this area. Nitrogen application rates were calculated using the same method as in the NAL study area. Over the entire SAL study area, the total amount of nitrogen applied to cropland from manure (Barb Ruddy and David Lorenz, U.S. Geological Survey, written commun., 1997) in 1997 and commercial fertilizer (David Lorenz, U.S. Geological Survey, written commun., 1998) in 1998 was about 712 million lb. Dividing the total nitrogen application by the total number of cropland acres within the extent of the hydrogeologic unit

yields an average application rate of 73 lb/acre of cropland. The nitrogen application rate within 1,640 ft of the monitoring wells in the SAL study area ranged from 32 to 189 lb/acre, with a median of 58 lb/acre. Application rates of the 10 pesticides most often applied in 1997 are shown in table 5. An average of about 0.73 lb/acre of pesticides was applied to cropland. The pesticides most commonly applied were trifluralin, malathion, and 2,4-D.

Similar to the northern High Plains, water use in the southern High Plains is dominated by cropland irrigation. In 2000, an estimated 3,680 Mgal/d was used for that purpose (U.S. Geological Survey, 2004). Ground-water withdrawals for irrigation varied by county in the SAL study area and ranged from less than 2 to about 420 Mgal/d (fig. 5B). Irrigation water is applied mainly during the summer months (May through September) when crop water demands are largest. Other water uses in the study area include publicly supplied drinking water (59 Mgal/d), livestock (50 Mgal/d), mining (27 Mgal/d), and industrial (16 Mgal/d).

Ground-Water Quality Beneath Irrigated Cropland

Nitrate

Nitrogen in the form of nitrate is of interest in ground water because it is mobile, persistent, and exceeds the upper concentration limit for public drinking water more often than any other agricultural chemical. Sources of nitrogen

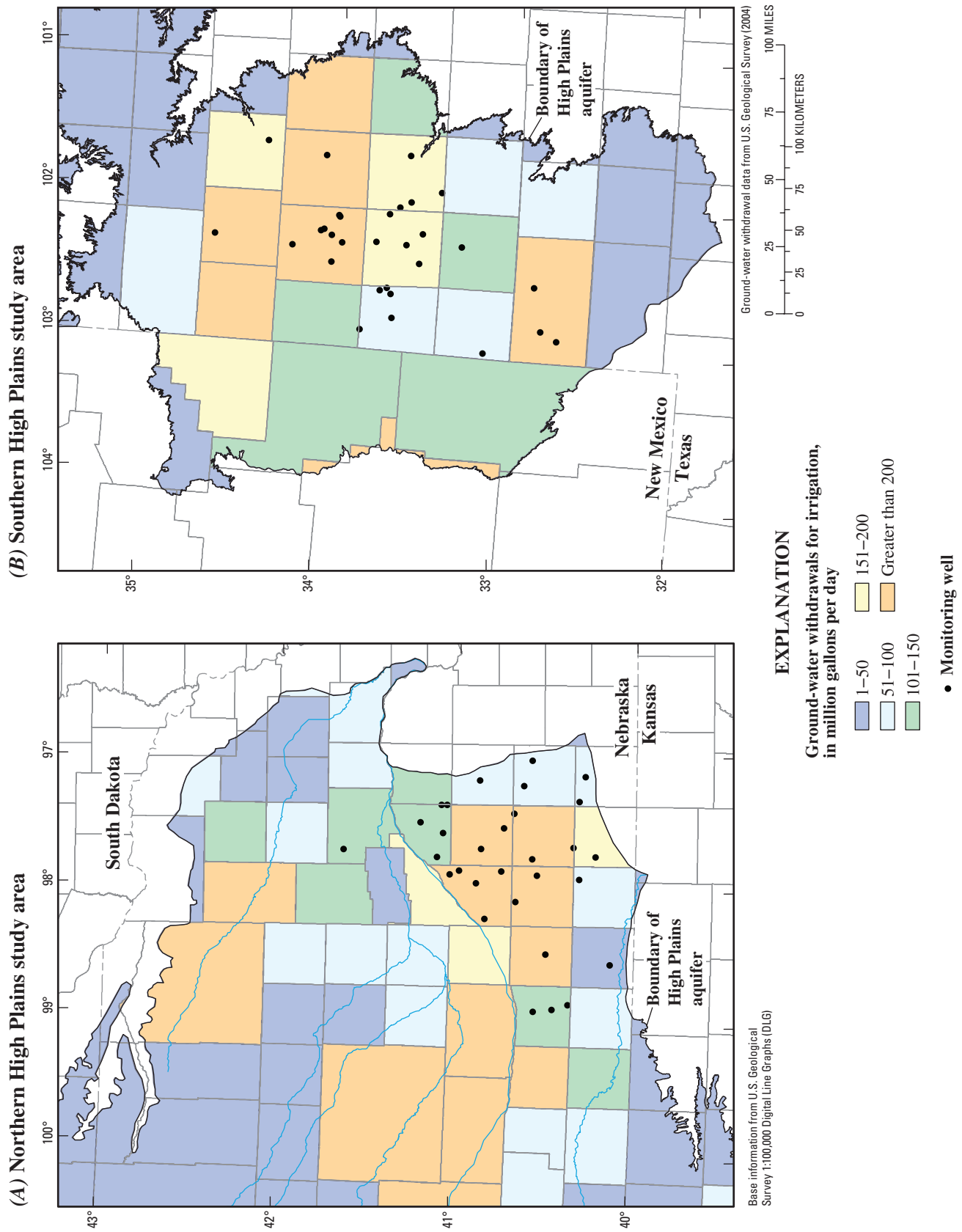


Figure 5. Ground-water withdrawals for irrigation, by county, in (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2000.

include manure, commercial fertilizers, septic system effluent, atmospheric deposition, some minerals, and natural grassland soils. Converting natural grasslands to cultivated cropland can release naturally occurring soil nitrogen from the soil horizon (Scanlon and others, 2005). McMahon and others (2006) estimated that in some parts of the High Plains as much as 57 percent of nitrate in the unsaturated zone under cropland was from natural soil nitrogen. Although nitrate is found naturally in ground water, elevated concentrations generally are caused by human-related sources (Spalding and Kitchen, 1988; Bruce and others, 2003; McMahon and Böhlke, 2006). The maximum background concentration of nitrate representing naturally occurring sources in ground water has been estimated to be about 2 to 4 mg/L (Madison and Brunett, 1985; Gosselin, 1991; Mueller and Helsel, 1996; McMahon, 2001; Becker and others, 2002).

Water samples were analyzed for nitrite (reported as nitrogen), nitrite plus nitrate (as nitrogen), ammonium (as nitrogen), ammonium plus organic nitrogen (as nitrogen), and orthophosphate (as phosphorus) (Appendixes 1 and 2, table 6). Nitrate is the dominant form of nitrogen in oxygenated water, whereas nitrite, ammonium, and organic nitrogen are more stable when oxygen concentrations are small. Dissolved oxygen concentrations indicated that almost all ground-water samples collected in the NAL and SAL study areas were oxygenated

(greater than 1.0 mg/L dissolved oxygen). Nitrite concentrations ranged from less than 0.008 to 0.116 mg/L, composing a maximum of 2.2 percent of the nitrite plus nitrate concentration where nitrite was detected. Therefore, nitrate plus nitrite concentrations will be referred to as nitrate concentrations in this report.

Northern High Plains

Nitrate concentrations of samples collected in the NAL study area ranged from 1.96 to 106 mg/L, with a median of 10.6 mg/L (table 6, Appendix 1). Nitrate concentrations in 27 samples (90 percent) were greater than 4.00 mg/L, suggesting that human activities have affected nitrate concentrations in ground water at the water table over a large portion of the NAL study area. Although the sampled wells are not used as a source of drinking water, concentrations were compared with U.S. Environmental Protection Agency (USEPA) drinking-water standards (U.S. Environmental Protection Agency, 2004) to relate the quality of ground-water samples at the water table to nationally recognized public water-supply criteria. Concentrations in 16 samples (53 percent) were larger than 10.0 mg/L, the USEPA Maximum Contaminant Level for nitrate in drinking water (fig. 6A).

Table 6. Summary statistics for nitrogen and phosphorus compounds and nitrogen and oxygen isotopes of nitrate in ground-water samples collected from northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[Constituents are dissolved; NAL, northern High Plains agricultural land-use study area; SAL, southern High Plains agricultural land-use study area; USEPA, U.S. Environmental Protection Agency; mg/L, milligrams per liter; <, less than; MCL, Maximum Contaminant Level; --, no data; E, estimated; LTHA, Lifetime Health Advisory, the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure; NA, not analyzed]

Constituent or property	Concentrations						USEPA drinking-water standard/ type of standard ¹	p-value (Wilcoxon rank-sum) ²
	NAL samples			SAL samples				
	Minimum	Median	Maximum	Minimum	Median	Maximum		
Nitrite as N, in mg/L	<0.008	<0.008	<0.008	<0.008	<0.008	0.116	1 / MCL	--
Nitrite plus nitrate as N, in mg/L	1.96	10.6	106	.65	4.12	21.6	10 / MCL	<0.001
Ammonia as N, in mg/L	<.04	<.04	.05	<.04	<.04	E.04	30 / LTHA	--
Ammonia plus organic nitrogen as N, in mg/L	NA	NA	NA	<.1	<.1	.21	--	--
Orthophosphate as P, in mg/L	.078	.27	.513	<.007	E.01	.03	--	<.001
Nitrogen isotope ratio ($\delta^{15}\text{N}$) of nitrate, in per mil	2.23	6.31	11.59	4.3	6.1	10.3	--	.964
Oxygen isotope ratio ($\delta^{18}\text{O}$) of nitrate, in per mil	-2.40	3.08	5.66	NA	NA	NA	--	--

¹Source: U.S. Environmental Protection Agency, 2004.

²p-values indicate the statistical probability that there was a real difference between two groups of data. Variables were considered to be significantly different between the two study areas if p was 0.05 or less. p-values were not calculated when more than 50 percent of the concentrations were less than the largest laboratory reporting level.

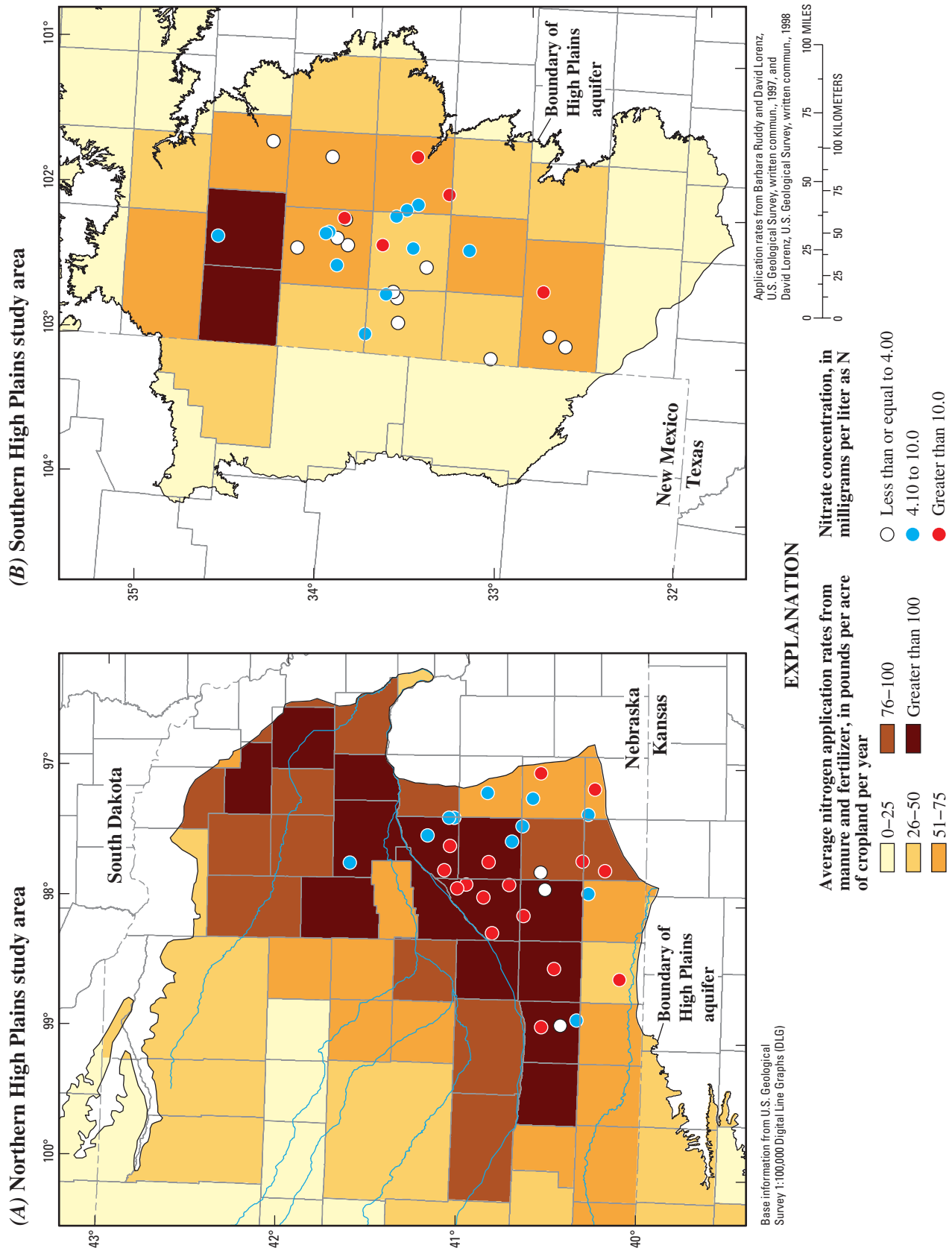


Figure 6. Distribution of average nitrogen application rates from manure and commercial fertilizer, by county, and nitrate concentrations in ground-water samples collected from (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

Nitrogen isotope ratio ($\delta^{15}\text{N}$) of nitrate was analyzed to indicate the possible sources of nitrate in ground water. $\delta^{15}\text{N}$ values represent the ratio of stable-isotopic abundances of $^{15}\text{N}/^{14}\text{N}$ of nitrate in a sample to those of atmospheric nitrogen. The units of $\delta^{15}\text{N}$ are per mil (parts per thousand) and are computed using the formula (Kendall and McDonnell, 1998):

$$\delta^{15}\text{N} = \left(\frac{R(\text{sample})}{R(\text{standard})} - 1 \right) \times 1,000 \quad , \quad (2)$$

where $R(\text{sample})$ is the ratio of the heavier stable isotope (^{15}N) to the lighter stable isotope (^{14}N) of nitrate in the ground-water sample, and $R(\text{standard})$ is the ratio of ^{15}N to ^{14}N in atmospheric nitrogen.

Some possible sources of nitrate in ground water include fertilizer, natural soil nitrogen, and animal manure (including human waste). In general, fertilizer has $\delta^{15}\text{N}$ values in the range of 0 to +6 per mil, natural soil nitrogen has $\delta^{15}\text{N}$ values in the range of +4 to +8 per mil, and $\delta^{15}\text{N}$ values larger than +10 per mil generally indicate an animal manure source (Heaton, 1986; Clark and Fritz, 1997; Mengis and others, 2001; Böhlke, 2002). The use of nitrogen isotopes to identify sources of nitrate in ground water may be complicated by several factors. For example, the ranges of $\delta^{15}\text{N}$ values of natural soil nitrogen and fertilizer partially overlap, making it difficult to distinguish between these two sources of nitrate in some cases. Ground water containing a mixture of nitrate from fertilizer and manure sources could produce nitrate $\delta^{15}\text{N}$ values that are similar to values for natural soil nitrogen, possibly resulting in an incorrect interpretation of the isotope data. Additionally, microbial processes such as denitrification in the soil and aquifer, and volatilization of anhydrous ammonia can alter the original $\delta^{15}\text{N}$ of the nitrogen source (Mengis and others, 2001). Despite these potential complications, nitrogen isotope data can provide useful source information for ground-water nitrate in many circumstances.

Concentrations and $\delta^{15}\text{N}$ values of nitrate in NAL samples ranged from 1.96 to 106 mg/L and +2.23 to +11.59 per mil, respectively (fig. 7). For comparison, the median concentration and $\delta^{15}\text{N}$ values of nitrate in old ground water in western Nebraska were 2.17 mg/L as N and +3.5 per mil, respectively (fig. 7) (McMahon and Böhlke, 2006). Nitrate in the old ground water was derived from natural soil nitrogen. Only two NAL samples appear to have $\delta^{15}\text{N}$ values that can be clearly associated with a particular nitrate source. Nitrate in the sample with the smallest $\delta^{15}\text{N}$ value (+2.23 per mil) appears to have been derived from fertilizer, and nitrate in the sample with the largest $\delta^{15}\text{N}$ value (+11.59 per mil) appears to have been derived from animal waste. The remaining samples could contain a mixture of nitrate from fertilizer, soil nitrogen, and (or) animal waste sources, on the basis of the isotope data. One sample was not evaluated because the dissolved oxygen concentration was less than 2.0 mg/L and the $\delta^{15}\text{N}$ value may have been affected by denitrification. All the other samples

had dissolved oxygen concentrations larger than 2.0 mg/L. The nitrate concentration data could help to differentiate between nitrate derived from fertilizer and soil nitrogen if the median concentration in old ground water in western Nebraska is representative of nitrate derived from soil nitrogen in the NAL study area. All but one of the NAL samples contained nitrate concentrations larger than 2.17 mg/L, the median concentration in old ground water, indicating that soil nitrogen was not a major source of nitrate in the NAL ground water. If this interpretation is correct, then fertilizer and manure could be the primary sources of nitrate in those samples with mixed sources.

Hydrogeologic variables were examined to determine their relation to nitrate concentrations in the NAL study area. Water levels were measured at each well immediately before sample collection. Measurements ranged from 35.10 to 164.41 ft, with a median of 84.58 ft below land surface. The relation between nitrate concentrations and depth to water was evaluated using the Spearman's rho correlation test. Nitrate was not statistically correlated with depth to water in the NAL samples ($\rho = -0.278$, $p = 0.134$). However, the three largest nitrate concentrations were found in samples from monitoring wells that had depths to water of less than 75 ft below land surface.

The relation between tritium and nitrate concentrations was examined to evaluate the effect of residence time on nitrate concentrations. Tritium occurs naturally but also was released to the atmosphere in large quantities during above-ground nuclear weapons testing in the 1950s and 1960s. As of 2000, recharge water that had been exposed to the atmosphere since the 1950s would be expected to have more than 1.5 pCi/L tritium (Thatcher, 1962; Clark and Fritz, 1997). Thus, tritium concentrations greater than or equal to 1.5 pCi/L indicate that at least a portion of the sample water entered the aquifer within the last 50 years. Widespread irrigation and application of agricultural chemicals generally have been used in the High Plains for about 50 years. Therefore, tritium concentrations can indicate whether water entered the aquifer recently enough to be affected by agricultural chemicals.

In NAL samples, tritium concentrations indicated that at least a portion of the water from 27 of the 30 samples was recharged in the last 50 years. Tritium concentrations ranged from values that were less than the LRL (1 pCi/L) to 34 pCi/L, with a median of 14 pCi/L. Nitrate concentrations were larger ($p = 0.020$) in samples with a residence time of less than 50 years; the median nitrate concentration in samples with a residence time of less than 50 years was 12.4 mg/L, and the median nitrate concentration in samples with a residence time of more than 50 years was 4.32 mg/L. Nitrate concentrations also were positively correlated with tritium concentrations ($\rho = 0.517$, $p = 0.006$) in the NAL study area. Because tritium concentrations in precipitation have been decreasing since the 1960s, this result may indicate that nitrate concentrations in recharge water also may have been larger previously but that more recent recharge water contained smaller quantities of nitrate. Another possible explanation is that ground-

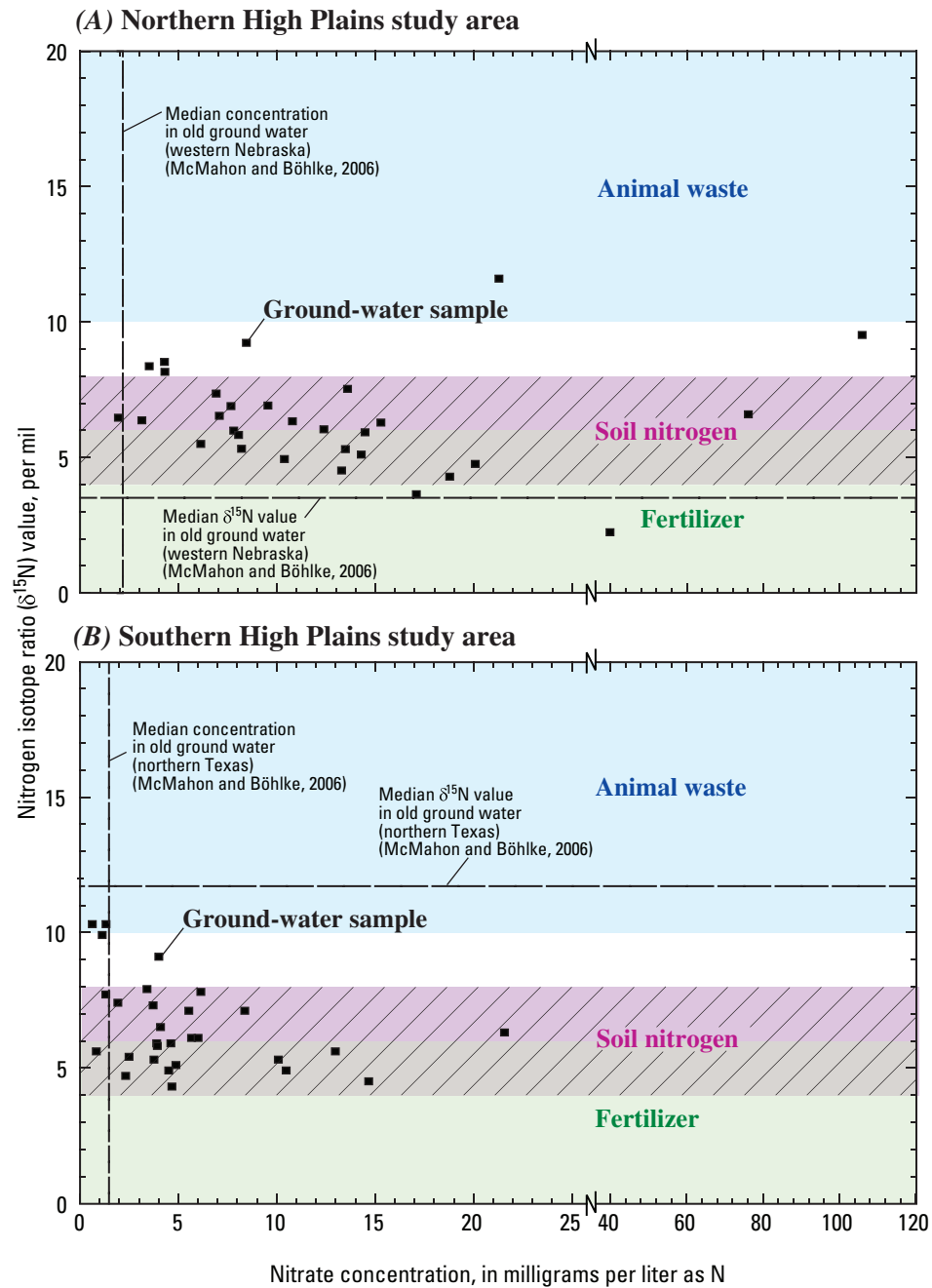


Figure 7. Nitrogen isotope ratio ($\delta^{15}\text{N}$) values of nitrate in nitrogen sources and in ground-water samples collected from (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

water samples containing smaller tritium concentrations are receiving a smaller portion of recently recharged water and a larger portion of older water that is not affected by agricultural activities at the land surface.

The percentage of coarse-grained materials in each well borehole and average values for percentage of sand, silt, and clay, bulk density, organic matter content, and vertical and horizontal permeability for soils within a 1,640-ft radius around each well were compiled to determine their effect on nitrate concentrations. Borehole descriptions were obtained from the well driller's logs, and soil characteristics were determined from the 1994 STATSGO database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997). The relations between nitrate concentrations and borehole and soil characteristics were determined statistically with the Spearman's rho correlation test (table 7). Nitrate concentrations were not significantly correlated to the examined borehole and soil characteristics (Spearman's rho p-values were greater than 0.05). The lack of correlation between nitrate and soil characteristics may be related to the coarse spatial resolution (1-km, 0.6214-mi) or the effect of vertically averaged soil properties of the soils dataset.

Domestic wells draw water from a range of depths across the aquifer, and a set of samples from randomly selected domestic wells provides a good indication of the variability of water quality with depth and an evaluation of the overall water-quality conditions within the aquifer. Alternatively, samples collected from water-table wells usually have the highest concentrations of human-related contaminants and other chemical constituents that originate from above the aquifer. Nitrate concentrations in NAL samples were compared with nitrate concentrations in rural domestic wells to determine whether concentrations were different at the water table

than throughout the aquifer. The median nitrate concentration in 30 randomly distributed domestic wells throughout the Eastern Nebraska hydrogeologic subunit was 1.92 mg/L (Stanton, in press), and the median concentration in the 30 water-table wells was 10.6 mg/L ($p < 0.001$). Domestic well samples were collected at depths ranging from 19.60 to 179.10 ft below the water table, and all NAL samples were collected at depths of about 5 ft below the water table. The larger nitrate concentrations in samples collected from water-table wells located near irrigated cropland provide evidence that nitrogen applied to irrigated agricultural land is reaching ground water but may not be reaching rural domestic wells in the area.

Southern High Plains

Nitrate concentrations in the SAL samples ranged from 0.65 to 21.6 mg/L, with a median concentration of 4.12 mg/L (table 6, Appendix 2). Nitrate concentrations in 16 samples (55 percent) were larger than 4.00 mg/L, and concentrations in five samples (17 percent) were larger than the USEPA Maximum Contaminant Level of 10.0 mg/L (fig. 6). $\delta^{15}\text{N}$ values of nitrate ranged from about +4.3 to +10.3 per mil in SAL samples (fig. 7, table 6, appendix 2). None of the SAL samples had a $\delta^{15}\text{N}$ value that could indicate conclusively a specific source of nitrogen. Two samples were not assessed because dissolved oxygen concentrations were less than 2.0 mg/L. The median nitrate concentration in old ground water representing nitrate from natural soil nitrogen in northern Texas was 1.48 mg/L (fig. 7) (McMahon and Böhlke, 2006). Nitrate concentrations in 24 (83 percent) SAL samples were larger than the median concentration in old ground water,

Table 7. Relations between nitrate concentrations in ground-water samples and borehole and soil characteristics in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use]

Variable	NAL study area		SAL study area	
	Spearman's rho	p-value ³	Spearman's rho	p-value ³
Percentage of coarse-grained sediments in well borehole ¹	0.198	0.288	0.239	0.206
Average sand content of soils, in percent ²	.075	.687	-.129	.493
Average silt content of soils, in percent ²	-.027	.883	.123	.517
Average clay content of soils, in percent ²	-.185	.317	.131	.489
Average bulk density of soils, in grams per cubic centimeter ²	.170	.361	-.050	.790
Average organic matter content of soils, in percent by weight ²	-.229	.216	.713	.360
Average vertical permeability of soils, in inches per hour ²	.011	.956	-.128	.498
Average horizontal permeability of soils, in inches per hour ²	.117	.530	-.131	.488

¹Source: well driller's logs.

²Source: 1994 STATSGO database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997).

³p-values indicate the statistical probability confidence that there was a real correlation between two variables. Variables were considered to be significantly correlated with nitrate if p was 0.05 or less.

suggesting that nitrate in SAL samples primarily is the result of human activities.

Hydrogeologic variables were examined to determine their relation to nitrate concentrations in the SAL study area. Depth to ground water in the SAL study area ranged from 78.85 to 195.24 ft, with a median of 153.16 ft below land surface (Appendix 2). Nitrate concentrations in the SAL samples were inversely correlated ($\rho = -0.417$, $p = 0.027$) with depth to water, indicating that nitrate concentrations at the water table decreased as the thickness of the unsaturated zone increased. In SAL samples, tritium concentrations indicated that at least a portion of the water from 17 of the 29 (59 percent) samples had been recharged in the last 50 years (young water). Tritium concentrations ranged from less than the LRL (1 pCi/L) to 41 pCi/L, with a median of 3 pCi/L (Appendix 2). Nitrate concentrations were larger ($p = 0.009$) in samples with a residence time of less than 50 years; the median nitrate concentration in samples containing young water was 4.70 mg/L, and the median nitrate concentration in samples with old water was 2.24 mg/L. Nitrate concentrations also were positively correlated with tritium concentrations ($\rho = 0.479$, $p = 0.011$) in the SAL study area. The relations between nitrate and borehole and soil characteristics were evaluated statistically with the Spearman's rho correlation test (table 7). Nitrate concentrations in the SAL study area were not significantly correlated to the borehole and soil characteristics (all p -values greater than 0.05).

Nitrate concentrations in SAL wells were compared with nitrate concentrations in rural domestic wells. Sample collection depths at domestic wells ranged from about 5 to 200 ft below the water table, and all SAL wells were sampled at depths of around 5 ft below the water table. The median nitrate concentration in 48 randomly distributed domestic wells throughout the Ogallala Formation in the SHP was 2.98 mg/L (Fahlquist, 2003), and the median concentration in the 29 SAL wells was 4.12 mg/L. Although the median concentration in SAL wells was slightly larger, the difference in nitrate concentrations between domestic and SAL monitoring wells was not statistically significant ($p = 0.202$).

Pesticides

Northern High Plains

Figure 8 shows pesticide concentrations both greater than and less than the largest laboratory reporting level (LRL). Pesticide concentrations not qualified with a "less than" remark code are presented. However, for this report, a pesticide concentration was only identified as a detection if the value was equal to or greater than the largest LRL for that compound. Twenty-two NAL samples (73 percent) had at least one pesticide compound detected at a concentration equal to or greater than the largest LRL (fig. 9). Pesticides detected were: atrazine (20 samples), alachlor (one sample), metolachlor (one sample), and simazine (one sample). These

pesticides are herbicides that control broadleaf and grassy weeds. Atrazine is used primarily on corn and sorghum fields. Alachlor is used on corn, soybeans, and peanuts. Metolachlor is used for corn, soybeans, peanuts, sorghum, cotton, and other crops. Simazine typically is applied to field, fruit, vegetable, and ornamental crops (Cornell University Cooperative Extension, 2005). Pesticide degradates detected were deethylatrazine (17 samples), alachlor ethanesulfonic acid (ESA) (16 samples), metolachlor ESA (10 samples), alachlor ethanesulfonic acid second amide (ESA SA) (seven samples), metolachlor oxanilic acid (OA) (five samples), alachlor OA (one sample), and acetochlor/metolachlor ESA SA (one sample). The pesticide degradates of alachlor and metolachlor were detected more frequently than their associated parent pesticide compounds. Pesticide concentrations were small and did not exceed public drinking-water standards where established. The largest pesticide compound concentration was 3.09 $\mu\text{g/L}$ (alachlor ESA).

The LRL can affect the detection frequency of pesticide compounds; analytes with smaller LRLs are likely to have greater detection frequencies. To remove the effect of variable LRLs, detection frequencies of pesticide compounds were compared using a common assessment level of 0.05 $\mu\text{g/L}$. When examining pesticide detections at concentrations equal to or greater than 0.05 $\mu\text{g/L}$, pesticide degradate compounds were more frequently detected than parent compounds. Parent compounds detected were atrazine (10 samples) and metolachlor (one sample). Pesticide degradate compounds detected were alachlor ESA (12 samples), deethylatrazine (11 samples), metolachlor ESA (eight samples), alachlor ESA SA (four samples), metolachlor OA (two samples), acetochlor/metolachlor ESA SA (one sample), and alachlor OA (one sample) (fig. 8).

Figure 10 compares the frequencies of pesticides detected in ground water at concentrations equal to or greater than 0.05 $\mu\text{g/L}$ in samples collected from the NAL study area and in 345 samples collected from 14 NAWQA agricultural study areas (fig. 11) across the Nation where corn and soybeans were the primary crops (Appendix 4). The pesticide compounds shown are those that were analyzed in all NAWQA corn and soybean study areas. Except for deethylatrazine, only pesticide parent compounds are compared. Atrazine and deethylatrazine were detected more than twice as frequently in NAL samples than in other NAWQA study area samples; whereas metolachlor was detected more frequently in samples from other NAWQA study areas. Acetochlor, alachlor, carbofuran, metribuzin, prometon, propyzamide, and simazine were detected in samples collected from other NAWQA study areas but not in samples collected from the NAL study area.

The relation between pesticides and water depth was investigated by comparing measured water levels at sites with no pesticides detected and sites with at least one pesticide compound detected using the Wilcoxon rank-sum statistical test. Samples collected in areas with shallower depths to water were more likely to have detectable pesticides ($p = 0.018$). Water samples containing at least one detectable pesticide (22 samples) had a median depth to water of 82.82 ft, whereas

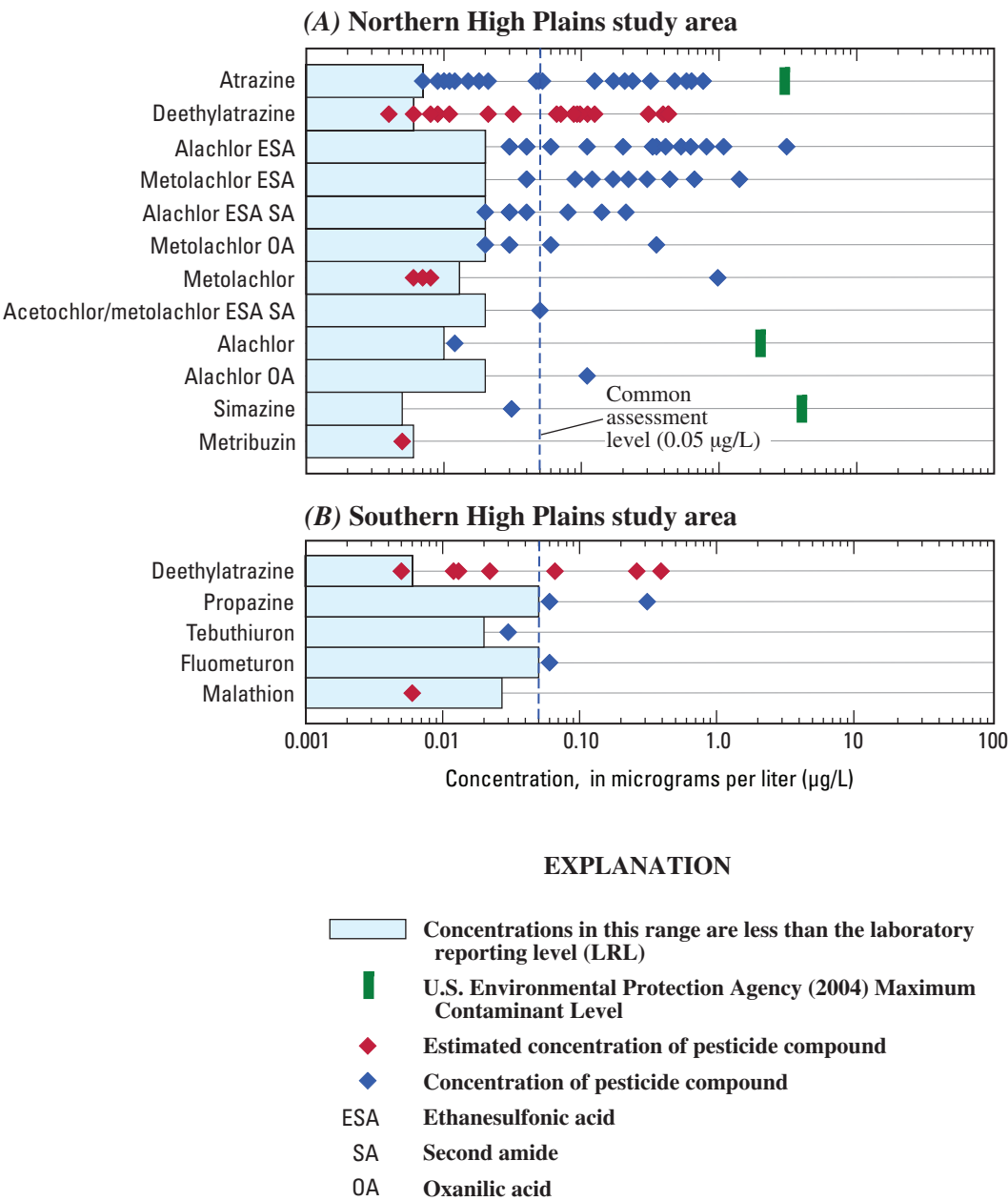


Figure 8. Concentrations of pesticide compounds in ground-water samples collected from (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04. Pesticides are listed in order of decreasing detection frequency.

samples with no detected pesticides (8 samples) had a median depth to water of 110.36 ft. The number of pesticide detections increased as the depth to water decreased ($\rho = -0.467$, $p = 0.012$).

The effect of ground-water residence time on pesticide detections was evaluated using tritium concentrations. In NAL samples, at least one pesticide was detected in 22 of the 27 water samples with residence times of 50 years or less (young water) and in none of the three water samples with residence times of more than 50 years (old water). The Fisher’s Exact test for independence between categorical vari-

ables indicated that samples with young water were statistically more likely to have a pesticide compound detection than samples with old water ($p = 0.014$). In addition, water samples containing at least one detectable pesticide compound had a median tritium concentration of 15 pCi/L, whereas samples with no detected pesticide compounds had a median tritium concentration of 8 pCi/L ($p = 0.019$). The number of pesticide compound detections also increased as tritium concentrations increased ($\rho = 0.508$, $p = 0.006$).

The relations between pesticides and borehole and soil characteristics were investigated by comparing aver-

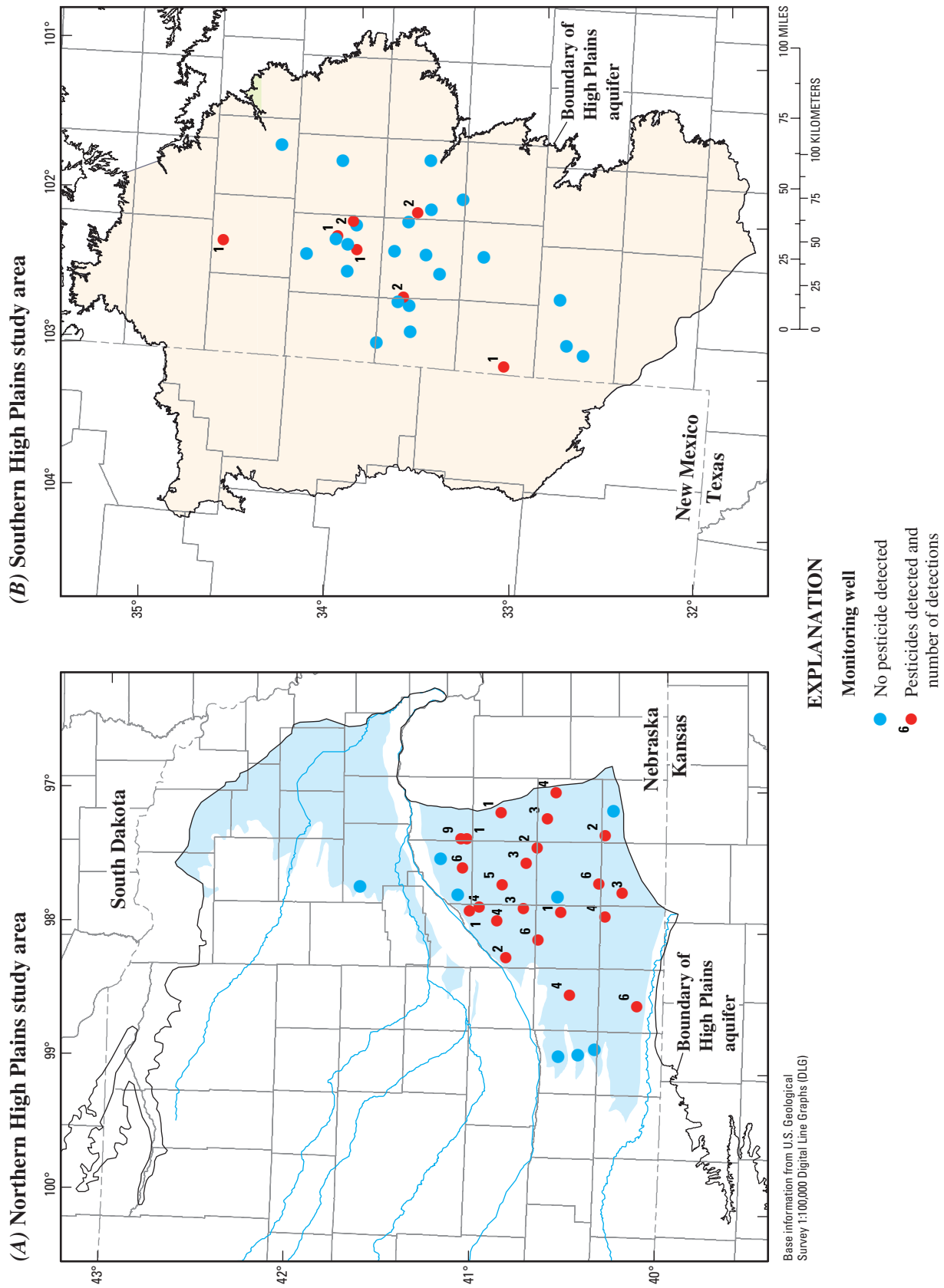


Figure 9. Number of pesticide compounds detected at concentrations equal to or greater than laboratory reporting level in ground-water samples collected from (A) northern and (B) southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

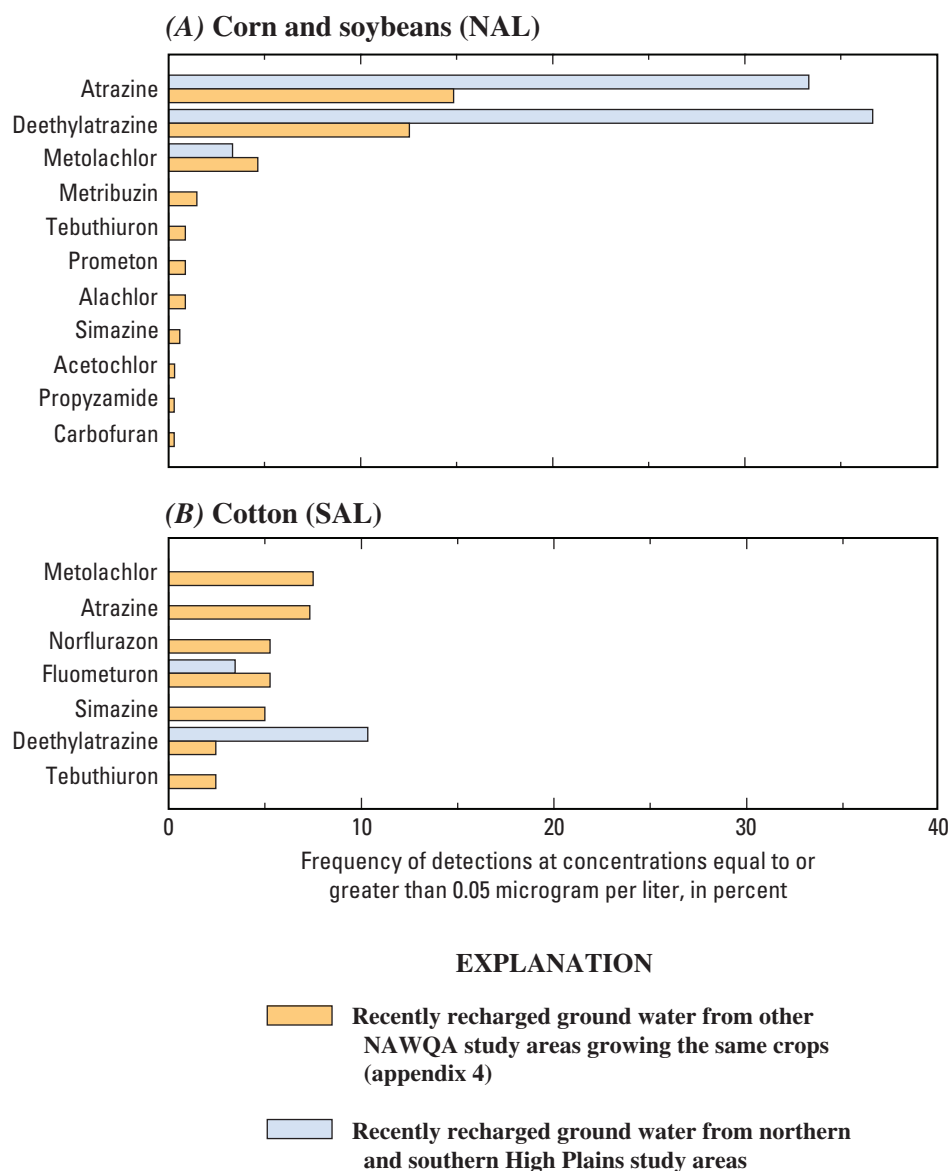


Figure 10. Frequency of pesticide detections at concentrations equal to or greater than 0.05 microgram per liter in ground-water samples collected from northern High Plains agricultural land-use study area, where primarily corn and soybeans are grown, and from southern High Plains agricultural land-use study area, where primarily cotton is grown, relative to samples collected from other National Water-Quality Assessment study areas where the same crops are grown. Pesticides are listed in order of decreasing detection frequency.

age soil properties near NAL wells with no pesticide compound detections and NAL wells with at least one detectable pesticide compound using the Wilcoxon rank-sum statistical test (table 8). The difference between the two groups was considered to be significant if the test statistic p-value was 0.05 or less. Samples that had at least one detectable pesticide were located in areas with soils having a smaller percentage of silt content ($p=0.017$) and smaller horizontal permeability rates ($p=0.022$). These results are counterintuitive and may be related to the coarse spatial resolution of the soils dataset or the effect of vertically averaged soil properties from the STATSGO database.

The number of pesticide compound detections in the water-table monitoring wells was compared with detections in domestic wells. Similar to the difference in nitrate concentrations, pesticides were detected more often in NAL wells than in domestic wells ($p=0.002$) — 30 percent of samples collected from domestic wells (Stanton, in press) and 73 percent

of samples collected from NAL wells had at least one detectable pesticide compound.

Southern High Plains

Seven SAL samples (24 percent) contained at least one pesticide compound detected at or above the LRL (figs. 8 and 9). Pesticides detected were propazine (two samples), fluometuron (one sample), and tebuthiuron (one sample). Propazine is an herbicide that controls broadleaf and grassy weeds and is used on sorghum fields. Fluometuron is used to control weeds in cotton fields. Tebuthiuron is a broad-spectrum herbicide that is used to control weeds in noncropland areas such as rangelands, rights-of-way, and industrial sites (Cornell University Cooperative Extension, 2005). The pesticide degradate deethylatrazine was detected in six samples. Deethylatrazine usually is formed from degradation of atrazine, a pesticide that generally is not used on cotton but may have been used on

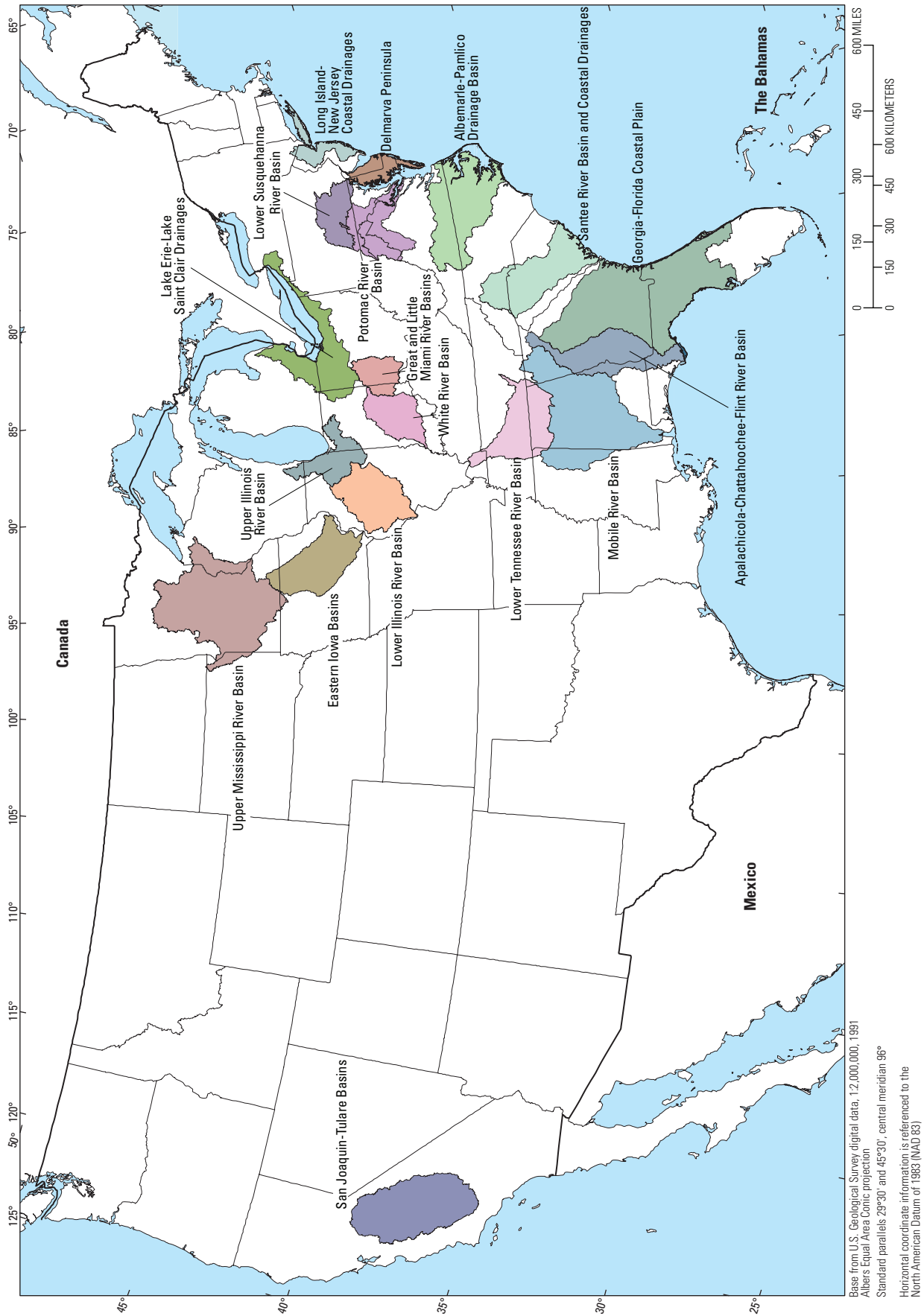


Figure 11. Location of National Water-Quality Assessment (NAWQA) agricultural study areas across the United States.

Table 8. Pesticide compound detections in ground-water samples related to borehole and soil characteristics in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use]

Variable	NAL study area			SAL study area		
	Median value near wells with no pesticides detected	Median value near wells with one or more pesticides detected	p-value (Wilcoxon rank-sum) ¹	Median value near wells with no pesticides detected	Median value near wells with one or more pesticides detected	p-value (Wilcoxon rank-sum) ¹
Percentage of coarse-grained sediments in well borehole ²	4.5	12.0	0.424	4.2	5.8	0.733
Average sand content of soils, in percent ³	4.4	3.2	.136	44.8	44.8	.610
Average silt content of soils, in percent ³	70.5	62.4	.017	28.9	28.9	.684
Average clay content of soils, in percent ³	24.8	34.8	.084	26.3	26.3	.573
Average bulk density of soils, in grams per cubic centimeter ³	1.38	1.33	.587	1.52	1.52	.851
Average organic matter content of soils, in percent by weight ³	.56	.53	.869	.18	.16	1.000
Average vertical permeability of soils, in inches per hour ³	1.20	.77	.210	1.36	1.36	.809
Average horizontal permeability of soils, in inches per hour ³	1.13	.47	.022	1.56	1.56	.573

¹p-values indicate the statistical probability that there was a real difference between two groups of data. Variables were considered to be significantly different between the two groups if p was less than or equal to 0.05.

²Source: well driller's logs.

³Source: 1994 STATSGO database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997).

corn and sorghum grown in the SHP prior to conversion to cotton or may have been used for Conservation Reserve Program (CRP) land or roadside areas (U.S. Environmental Protection Agency, 2001). Deethylatrazine also can be a degradate of propazine (Barbash and Resek, 1996). Pesticide concentrations were considerably less than respective concentration limits for public drinking-water supplies. The largest pesticide concentration detected in ground-water samples collected from the SAL study area was 0.392 µg/L (estimated) of deethylatrazine.

Three pesticide compounds were detected at concentrations equal to or greater than the 0.05-µg/L common assessment level in SAL samples — deethylatrazine (three samples), propazine (two samples), and fluometuron (one sample) (fig. 8). These results were compared with the detection frequencies in 41 ground-water samples collected from three NAWQA agricultural study areas where cotton was a primary crop (fig. 10, Appendix 4). The pesticide compounds shown are those that were analyzed in all NAWQA cotton study areas. Except for deethylatrazine, only pesticide parent compounds were compared. Propazine concentrations were not analyzed in samples collected from other NAWQA cotton study areas, and therefore, the detection frequencies could not

be compared. Deethylatrazine was detected about twice as frequently at concentrations equal to or larger than 0.05 µg/L in SAL samples as in samples collected from other NAWQA study areas. Fluometuron was detected less frequently in SAL samples (3 percent) than in other NAWQA samples (5 percent). Atrazine, metolachlor, norflurazon, simazine, and tebuthiuron were detected at concentrations equal to or greater than 0.05 µg/L in other NAWQA cotton study samples but not in SAL samples. One reason that most pesticide compounds were detected less frequently in the SAL samples than in samples collected from other cotton studies might be the large evaporation rates in the SHP. All but one of the other cotton studies were completed in the southeast part of the country where recharge is greater and downward movement of chemicals may be more likely.

In the SAL study area, depth to water did not have a significant effect on pesticide compound detections. Water samples containing at least one detectable pesticide compound (7 samples) had a median depth to water of 153.36 ft, and samples with no detected pesticide compounds (22 samples) had a median depth to water of 149.45 ft (p=0.862). The number of pesticide compound detections was not correlated with depth to water in the SAL area (rho=−0.003, p=0.987).

At least one pesticide compound was detected in 29 percent of SAL samples that also contained water recharged less than 50 years ago (samples with tritium concentrations equal to or greater than 1.5 pCi/L) and in 17 percent of samples with water recharged more than 50 years ago (samples with a tritium concentration less than 1.5 pCi/L). Although a larger percentage of samples with young water had at least one detectable pesticide, it was not a statistically significant difference ($p=0.369$). However, tritium concentrations were significantly different ($p=0.019$) between samples with and without pesticide detections; SAL water samples containing at least one detectable pesticide compound had a median tritium concentration of 15 pCi/L, and samples with no detected pesticide compounds had a median tritium concentration of 3 pCi/L. It should be expected that any sample with a detectable pesticide compound should have a residence time of less than 50 years because pesticide applications, at least as a large-scale agricultural practice, have only been in use for about 50 years. This inconsistency might be explained by the difference in the way that pesticide compounds and tritium may be affected by mixing of water having a residence time of less than 50 years and water having a residence time of more than 50 years in the aquifer. Pesticide compounds can be detected at small concentrations. Therefore, even when a water sample contains a small amount of young water, the presence of pesticide compounds may still be detectable. Conversely, if mixing of young and old water is occurring and only a small portion of the sampled water in a well has a residence time of less than 50 years, the tritium concentration may be diluted such that the concentration is less than 1.5 pCi/L, and the sample may be classified as having old water.

The relations between pesticides and borehole and soil characteristics were examined by comparing the soil characteristics near SAL wells with no pesticide compound detections and SAL wells with at least one detectable pesticide compound (table 8). The difference between the two groups of samples was considered to be significant if the test statistic p -value was 0.05 or less. Borehole and soil characteristics did not differ significantly between the two groups of samples.

The number of pesticide compound detections in the SAL wells was compared with detections in domestic wells. Pesticides were detected more often in SAL wells, but the difference in frequencies was not statistically significant ($p=0.554$)—24 percent of samples collected from SAL wells and 17 percent of samples collected from domestic wells (Fahlquist, 2003) had at least one detectable pesticide compound.

Dissolved Solids

The concentration of dissolved solids is an indicator of ground-water quality. High concentrations of dissolved solids can limit the use of ground water for drinking water, application to crops, and industrial purposes. Major ions account for the bulk of dissolved solids in a water sample. The major

cations in ground water typically are calcium, magnesium, sodium, and potassium. The major anions in ground water typically are carbonate alkalinity [reported as calcium carbonate (CaCO_3) equivalent], sulfate, chloride, and fluoride. When nitrate is present in substantial quantities, it also can be a major anion. Trace elements (mostly metals) make up a component of dissolved solids but at concentrations so small that they are relatively negligible when compared to concentrations of major ions. Measurements of water properties and concentrations of major ions and selected trace elements are presented in Appendixes 1 and 2 and summarized in table 9.

Ground water contains dissolved solids derived mostly from dissolution of soil or rock minerals that come in contact with water. Fertilizers also contain minerals and trace elements that, when applied at the land surface, can move downward to the aquifer. In addition to the direct application of dissolved solids that are contained in commercial fertilizers, fertilizers can have an indirect effect on concentrations of dissolved solids. The biochemical process of converting manure and commercial fertilizer to nitrate lowers the pH of pore water, thereby increasing the dissolution and mobility of ions and metals that are present in soils and geologic materials (Böhlke, 2002). Consequently, concentrations of major ions and trace elements sometimes are positively correlated with nitrate concentrations.

Northern High Plains

Dissolved-solids concentrations in ground water collected from the NAL study area ranged from 272 to 2,160 mg/L, with a median of 442 mg/L. The relative proportions of the major cations and anions are shown in figure 12. A cation or anion is referred to as dominant if it accounts for more than 60 percent of the total cations or anions. The dominant cation was most commonly calcium, and the dominant anion was most commonly carbonate alkalinity, principally in the form of bicarbonate (HCO_3^-). Some samples had no dominant cation or anion but had nearly equal mixtures of more than one cation or anion. One sample (NAL-205, Appendix 1) was dominated by chloride; this sample had the largest dissolved-solids concentration of all NAL samples. Nitrate was sufficiently large in one sample (NAL-113, Appendix 1) to be the dominant anion.

Dissolved-solids, major ion, and trace element concentrations were compared with USEPA drinking-water standards (U.S. Environmental Protection Agency, 2004) to relate the quality of water-table samples to nationally recognized public water-supply criteria. However, because the wells sampled as part of this study were screened near the water table and located adjacent to irrigated cropland, water-quality results do not represent the water quality that might be found in water collected from wells that are used for drinking-water purposes. Eight NAL samples had dissolved-solids concentrations greater than the USEPA Secondary Drinking-Water Regulation (SDWR) of 500 mg/L (U.S. Environmental Protection Agency, 2004). One sample (NAL-205) exceeded the USEPA SDWRs

Table 9. Summary statistics for physical properties, major ions, selected trace elements, and dissolved organic carbon in ground-water samples collected from northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[Constituents are dissolved. NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use; USEPA, U.S. Environmental Protection Agency; <, less than; $\mu\text{S}/\text{cm}$, microsiemen per centimeter; $^{\circ}\text{C}$, degrees Celsius; SDWR, Secondary Drinking-Water Regulation; NTU, nephelometric turbidity unit; >, greater than; TT, Treatment Technique; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; MCL, Maximum Contaminant Level; LTHA, Lifetime Health Advisory, the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure]

Constituent or property	NAL samples			SAL samples			USEPA drinking water standard/ type of standard ¹	p-value (Wilcoxon rank-sum) ²
	Minimum	Median	Maximum	Minimum	Median	Maximum		
Physical properties								
Water level, in feet below land surface	35.10	84.58	164.41	78.85	153.16	195.24	--	<0.001
Specific conductance, in μS/cm at 25 °C	421	709	3,320	676	1,260	4,630	--	<.001
pH, in standard units	6.0	7.1	7.3	7.0	7.2	7.4	6.5-8.5/SDWR	.001
Temperature, in °C	13.0	14.5	21.1	17.5	19.0	21.2	--	<.001
Turbidity, in NTU	.1	.6	>1,000	.2	.9	5.9	5/TT	.220
Oxygen, in mg/L	1.3	6.5	8.0	.8	6.5	8.8	--	.671
Dissolved solids (concentrations in milligrams per liter)								
Dissolved solids	272	442	2,160	416	814	3,580	500/SDWR	<.001
Major ions (concentrations in milligrams per liter)								
Carbonate alkalinity, as CaCO ₃	46	232	418	155	234	355	--	.612
Calcium	48.4	89.4	473	29.9	79.4	195	--	.255
Magnesium	6.83	14.8	70.1	24.6	65.9	198	--	<.001
Sodium	9.18	31.45	114	29.0	59.4	735	--	<.001
Potassium	3.79	6.91	26.3	2.16	9.08	27.5	--	.048
Sulfate	14.0	32.5	255	17.4	160	1,300	250/SDWR	<.001
Bromide	.04	.11	2.13	.11	.95	4.86	--	<.001
Chloride	3.08	13.3	502	11.2	165	701	250/SDWR	<.001
Fluoride	<.2	.3	.5	.98	2.80	5.55	4/MCL	<.001
Silica	20.9	35.5	53.7	28.4	51.1	81.7	--	<.001
Selected trace elements (concentrations in micrograms per liter)								
Arsenic	1.3	4.2	9.3	1.7	7.5	25.9	10/MCL	<.001
Barium	43	230	741	14	56	196	2,000/MCL	<.001
Boron	23	35	68	108	226	943	600/LTHA	<.001
Cobalt	.125	.311	1.68	.102	.310	1.20	--	.964
Copper	.4	.9	5.2	.6	1.4	4.9	1,300/TT	.010
Iron	<10	<10	1,020	<10	<10	55	300/SDWR	--
Lithium	8.1	16.7	47.5	43.6	119	278	--	<.001
Manganese	<.2	.7	331	<.2	6	621	300/LTHA	<.001
Molybdenum	.2	1.8	22.7	.9	5.3	52.9	40/LTHA	<.001

Table 9. Summary statistics for physical properties, major ions, selected trace elements, and dissolved organic carbon in ground-water samples collected from northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.—Continued

[Constituents are dissolved. NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use; USEPA, U.S. Environmental Protection Agency; <, less than; $\mu\text{S}/\text{cm}$, microsiemen per centimeter; $^{\circ}\text{C}$, degrees Celsius; SDWR, Secondary Drinking-Water Regulation; NTU, nephelometric turbidity unit; >, greater than; TT, Treatment Technique; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; MCL, Maximum Contaminant Level; LTHA, Lifetime Health Advisory, the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure]

Constituent or property	NAL samples			SAL samples			USEPA drinking water standard/ type of standard ¹	p-value (Wilcoxon rank-sum) ²
	Minimum	Median	Maximum	Minimum	Median	Maximum		
Selected trace elements (concentrations in micrograms per liter)—Continued								
Selenium	1.4	9.4	90.2	1.1	14.4	93.5	50/MCL	0.211
Strontium	237	409	1,820	1,050	2,500	7,250	4,000/LTHA	<.001
Uranium	.04	3.90	83.0	1.95	9.25	30.8	30/MCL	.001
Dissolved organic carbon (concentrations in milligrams per liter)								
Dissolved organic carbon	E.3	1.3	16.2	.8	2.2	10.8	--	<.001

¹Source: U.S. Environmental Protection Agency, 2004.

²p-values indicate the statistical probability that there was a real difference between two groups of data. Variables were considered to be significantly different between the two study areas if p was less than or equal to 0.05. p-values were not calculated when more than 50 percent of the concentrations were less than the largest laboratory reporting level.

for both sulfate (250 mg/L) and chloride (250 mg/L) concentrations. Trace elements exceeding drinking-water standards were uranium (two samples), iron (one sample), manganese (one sample), and selenium (one sample).

The relations between dissolved-solids concentrations and depth to water and residence time were tested. Dissolved solids were inversely correlated with water depth in samples from the NAL study area ($\rho = -0.447$, $p = 0.016$), indicating that dissolved-solids concentrations were larger in areas where the water table was closer to the land surface. Dissolved-solids concentrations also were related to tritium concentrations ($p = 0.032$); the median dissolved-solids concentration in samples with water recharged in the last 50 years was 452 mg/L , and the median dissolved-solids concentration in samples with water recharged more than 50 years ago was 298 mg/L .

The relations between dissolved-solids concentrations and borehole and soil characteristics were examined with the same method as nitrate concentrations. Dissolved solids in ground water were not significantly correlated to the examined borehole or soil characteristics (table 10).

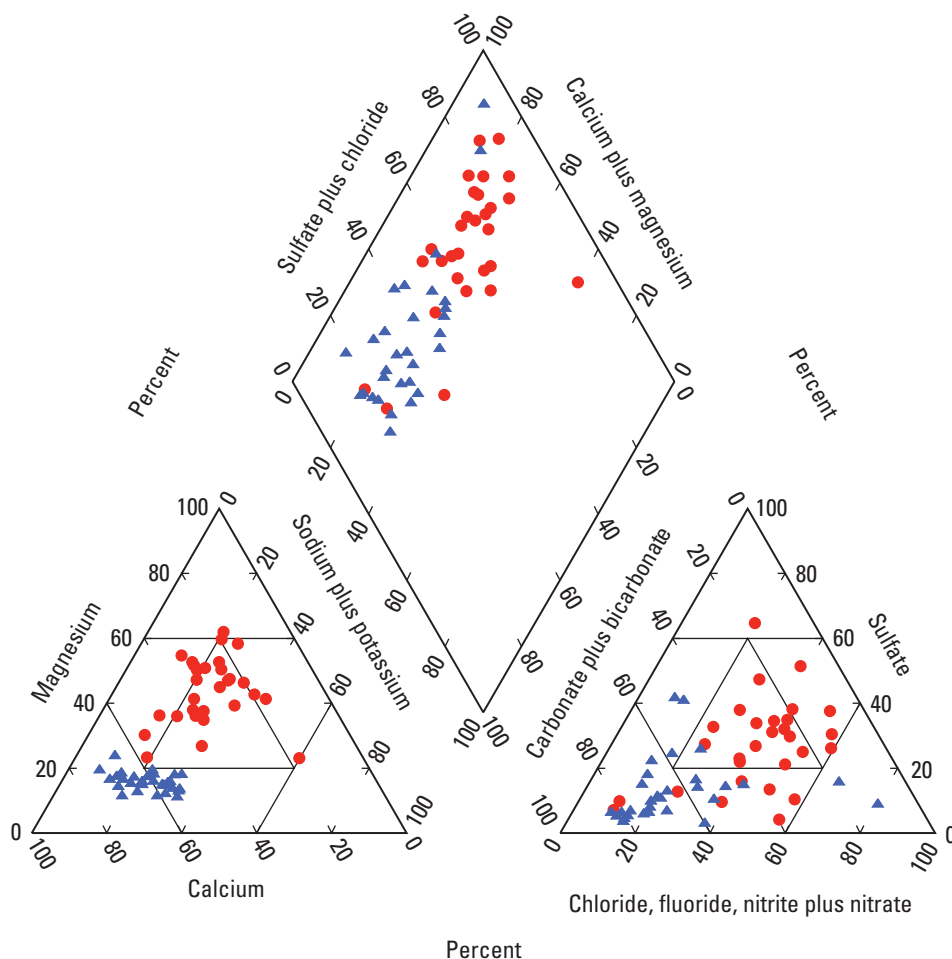
Application of nitrogen fertilizers may have affected dissolved-solids concentrations. As mentioned previously, the process of converting nitrogen fertilizer to nitrate produces acidity that can dissolve minerals in the soil and increase the concentration of dissolved solids that eventually recharges ground water (Böhlke, 2002). The relation between nitrate and major ion and trace element concentrations in ground water was examined statistically with the Spearman's rho correlation test. If the test statistic p-value was less than or equal

to 0.05, nitrate was considered to be positively correlated with the ion or metal. Nitrate was not correlated with pH but was positively correlated with dissolved solids, carbonate alkalinity, calcium, magnesium, sodium, potassium, bromide, barium, cobalt, copper, lithium, and strontium (table 11). Several factors may explain the lack of correlation between nitrate and pH. Acidity is consumed by the biogeochemical reactions in the soil and subsoil (prior to recharge) that cause dissolved ion and metal concentrations to increase. In addition, the buffering capacity of ground water and aquifer sediments also could have raised the pH of acidic recharge water.

Southern High Plains

In the SAL study area, dissolved-solids concentrations ranged from 416 to 3,580 mg/L , with a median of 814 mg/L (table 9). Most samples had no dominant cation or anion (fig. 12). The dominant cation was sodium in one sample; this sample had the largest dissolved-solids concentration of all SAL samples. In three samples, the dominant anion was carbonate alkalinity, principally in the form of bicarbonate (HCO_3^-); in one sample, the dominant anion was sulfate. In general, as dissolved-solids concentrations increased, the anion balance shifted from carbonate alkalinity to chloride to sulfate.

The USEPA concentration standards for publicly supplied drinking-water quality were exceeded for several constituents in the SAL study area (table 9). Twenty-five samples exceeded the USEPA SDWR of 500 mg/L for dissolved-solids



EXPLANATION

- ▲ Sample from northern High Plains agricultural land-use study area
- Sample from southern High Plains agricultural land-use study area

Figure 12. Relative proportions, in percentage equivalents, of major ions in ground-water samples collected from northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

concentrations, nine samples exceeded the SDWR of 250 mg/L for sulfate concentrations, and five samples exceeded the SDWR of 250 mg/L for chloride concentrations. The SDWRs for each of these constituents are nonenforceable guidelines. Trace elements that exceeded their respective USEPA public drinking-water standard were: arsenic (11 samples), strontium (six samples), boron (three samples), manganese (three samples), molybdenum (one sample), selenium (one sample), and uranium (one sample).

Likely sources of dissolved solids in the SAL study area include fertilizers, natural minerals, and underlying bedrock units. As mentioned previously, fertilizers containing dissolved solids are commonly at the land surface in the SAL study area and can potentially move past the root zone into ground water. Dissolved solids that are concentrated in the subsoil by evaporative processes potentially are another substantial source of larger dissolved-solids concentrations in ground water in the SAL study area. Evidence of this is suggested by the positive correlation between concentrations of

dissolved solids and chloride in the SAL samples ($\rho=0.800$, $p<0.001$). Chloride is considered to be a conservative constituent that will accumulate in soils where evapotranspiration rates are large and recharge rates are small (Allison and others, 1985; Scanlon and Goldsmith, 1997; Scanlon and others, 2005). The presence of large chloride concentrations in SAL ground-water samples indicates that prior to widespread irrigation, recharge rates were much smaller in the SAL study area and caused dissolved solids to concentrate in the unsaturated zone. Because the wells sampled as part of this study were located adjacent to irrigated cropland, irrigation water may have transported dissolved solids from the unsaturated zone to ground water. However, potassium chloride (KCl) also is known to have been applied as a nutrient source in parts of the SAL study area and may be a source of chloride in ground water (McMahon and others, 2006). Another source of dissolved solids in ground water of the SAL study area may be the underlying mineralized bedrock. In an area where irrigation wells pumped water from the lower part of

Table 10. Dissolved-solids concentrations in ground-water samples related to borehole and soil characteristics in northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use]

Variable	NAL study area		SAL study area	
	Spearman's rho	p-value ¹	Spearman's rho	p-value ¹
Percentage of coarse-grained sediments in well borehole ²	–0.109	0.558	0.023	0.905
Average sand content of soils, in percent ³	.125	.502	.333	.078
Average silt content of soils, in percent ³	.188	.313	–.331	.080
Average clay content of soils, in percent ³	–.268	.148	–.332	.079
Average bulk density of soils, in grams per cubic centimeter ³	.278	.134	.500	.008
Average organic matter content of soils, in percent by weight ³	–.354	.056	–.279	.140
Average vertical permeability of soils, in inches per hour ³	.331	.075	.269	.155
Average horizontal permeability of soils, in inches per hour ³	.194	.297	.332	.080

¹p-values indicate the statistical probability that there was a correlation between two variables. Variables were considered to be significantly correlated with dissolved solids if p was less than or equal to 0.05.

²Source: well driller's logs.

³Source: 1994 STATSGO database (U.S. Department of Agriculture, 1994; Schwarz and Alexander, 1995; Wolock, 1997).

Table 11. Major ions and trace elements related to nitrate concentrations in ground-water samples collected from northern and southern High Plains agricultural land-use study areas, Nebraska and Texas, 2003–04.

[NAL, northern High Plains agricultural land use; SAL, southern High Plains agricultural land use; <, less than]

NAL study area			SAL study area		
Constituent ¹	Spearman's rho	p-value	Constituent ¹	Spearman's rho	p-value
Dissolved solids	0.781	<0.001	Dissolved solids	0.485	0.010
Carbonate alkalinity	.469	.012	Magnesium	.526	.005
Calcium	.711	<.001	Sodium	.412	.029
Magnesium	.732	<.001	Boron	.408	.031
Sodium	.457	.014	Lithium	.502	.008
Potassium	.551	.003	Selenium	.485	.010
Bromide	.525	.005	Strontium	.629	.001
Barium	.641	.001			
Cobalt	.535	.004			
Copper	.584	.002			
Lithium	.450	.016			
Strontium	.683	<.001			

¹ Constituents listed are those positively correlated with nitrate as indicated by the Spearman's rho test statistic (p-value less than or equal to 0.05).

the High Plains aquifer, McMahon and others (2004) observed an upward hydraulic gradient between the bedrock and the aquifer during the irrigation season.

Irrigation practices may be mobilizing sources of dissolved solids in the unsaturated zone. The introduction of widespread irrigation has increased the downward movement of water, providing a mechanism for transporting dissolved solids to ground water. McMahon and others (2006) reported that ground-water flux rates in the SHP were much larger under irrigated cropland (between about 0.66 and 1.3 in/yr) than rangeland (about 0.008 in/yr).

The relations between dissolved-solids concentrations and depth to water and residence time were inspected. Dissolved solids were inversely correlated with water-table depth in samples collected from the SAL study area ($\rho = -0.495$, $p = 0.009$), indicating that dissolved-solids concentrations are larger in areas where the water table is closer to the land surface. Unlike the NAL samples, dissolved-solids concentrations in SAL samples were not related to residence time as determined from tritium concentrations; concentrations were not significantly different between old and young water ($p = 0.166$) and not correlated with tritium concentrations ($\rho = 0.098$, $p = 0.605$). This result may indicate that recent agricultural activities may not be the source of elevated dissolved-solids concentrations presently observed at the water table.

The relations between dissolved-solids concentrations and borehole and soil characteristics also were examined. Dissolved-solids concentrations in SAL samples were significantly correlated only with bulk density ($\rho = 0.500$, $p = 0.008$) (table 10). However, dissolved solids were positively (but not significantly) correlated with horizontal permeability and percentage of sand, and negatively correlated with percentage of silt and clay at slightly larger p -values ($p = 0.080$, 0.078 , 0.080 , and 0.079 , respectively).

The relation between nitrate and major ion and trace element concentrations was examined with the Spearman's ρ correlation test. Nitrate concentrations were positively correlated with dissolved solids, magnesium, sodium, boron, lithium, selenium, and strontium concentrations (table 11), indicating that major ion and trace element concentrations may be affected by the indirect effects of fertilizer applications at the land surface.

Eleven (38 percent) SAL samples exceeded the enforceable drinking-water standard for arsenic ($10 \mu\text{g/L}$); more often than for any other constituent analyzed in ground-water samples collected from the SAL study area. Arsenic concentrations ranged from 1.7 to $25.9 \mu\text{g/L}$, with a median of $7.5 \mu\text{g/L}$. Sources of arsenic can be natural or introduced by humans. Arsenic is naturally present in some geologic formations such as marine shales, volcanic rocks, and metamorphic rocks formed from sedimentary deposits. Human sources of arsenic include organic and inorganic pesticide compounds. Pesticides containing arsenic have been used historically on cotton in the SHP (Hudak, 2000) and may be a potential source to ground water. Arsenic concentrations were not

significantly different between the SAL water-table wells and domestic wells (Fahlquist, 2003) ($p = 0.287$), indicating that arsenic concentrations are similar at all depths in the aquifer. This result may provide some evidence that the primary source of arsenic is natural geologic deposits and not a source at the land surface.

Comparison of Ground-Water Quality in Two Study Areas

Land use and hydrogeologic variables in the NAL and SAL study areas were compared to evaluate their potential effect on nitrate, pesticides, and dissolved-solids concentrations in ground water. Many factors in the NAL study area are more favorable for movement of chemicals applied at the land surface into ground water than in the SAL study area. Depths to water are less, precipitation is greater, evapotranspiration rates are smaller, and recharge rates are greater in the NAL study area than in the SAL study area. About twice the amount of pesticides was applied to cropland in the NAL study area than in the SAL study area, and nitrogen application rates near monitoring wells also were estimated to be greater in the NAL study area.

The effect of irrigated agriculture on ground water at the water table was more apparent in samples collected from the NAL study area. Samples collected in the NAL study area had larger nitrate concentrations and more detectable pesticide compounds than samples collected in the SAL study area. The median nitrate concentration of NAL samples (10.6 mg/L) was significantly larger ($p < 0.001$) than the median concentration in SAL samples (4.12 mg/L). Twenty-two NAL samples (73 percent) and seven SAL samples (24 percent) had at least one pesticide compound detected at concentrations greater than the largest LRL.

The primary crops grown near wells in the NAL area are corn and soybeans, whereas the primary crop in the SAL area is cotton. The types of pesticides detected in the two areas were related to the types of crops grown. Atrazine, alachlor, metolachlor, simazine, and degradates of those compounds were detected most frequently in ground-water samples collected from the NAL study area. Except for simazine, these pesticides commonly are applied to corn or soybean fields and are on the list of most applied pesticides in the NAL area (table 5). In the SAL study area, deethylatrazine (a degradate of atrazine and propazine) was detected most often in ground-water samples. Although atrazine is not applied to cotton fields, it may have been applied in or near those same fields, for example when sorghum was the dominant cash crop. Propazine may have been applied to cotton fields and was the second most frequently detected pesticide compound in ground-water samples.

Although elevated nitrate concentrations and pesticide compound detections in ground water likely resulted from agricultural activities, dissolved solids were probably from a

combination of natural and human sources. SAL samples had larger dissolved-solids, major ion, and trace element concentrations than NAL samples. Dissolved-solids concentrations in SAL samples were correlated with chloride concentrations ($\rho=0.800$, $p<0.001$), indicating that evaporative processes potentially are a significant source of dissolved solids. There was, however, a relation between nitrate and dissolved solids, indicating a human source of both. Dissolved solids probably were not significantly affected by evaporative processes in the NAL study area. With the exception of one sample (NAL-205, 502 mg/L, Appendix 1), chloride concentrations were small (less than 60 mg/L) in the NAL samples and were not significantly correlated with concentrations of dissolved solids ($\rho=0.315$, $p=0.090$).

Summary

To observe the effect of irrigated agriculture on ground-water quality at the water table, monitoring wells screened at the top of the High Plains aquifer were installed adjacent to irrigated cropland areas of the northern and southern High Plains (NHP and SHP, respectively) regions of Nebraska and Texas. Water samples were collected from monitoring wells in 2003 and 2004; 30 samples were collected from the northern High Plains agricultural land-use (NAL) study area, and 29 samples were collected from the southern High Plains agricultural land-use (SAL) study area.

The NAL study area is located within the Eastern Nebraska hydrogeologic unit of the NHP region. This unit is located in an area affected by past glacial activity. The unit consists primarily of sand and gravel that is overlain by a mantle of low permeability glacial till and (or) loess. Mean annual pan evaporation rates range from 65 to 75 in/yr, and estimated recharge rates range from 4 to 6 in/yr. About 83 percent of the land in the NAL study area was used for cropland in 1992, and about 34 percent of the land in the study area was irrigated in 1980. In 2000, an estimated 1,940 Mgal/d of water was used for irrigation. The most common crops grown in the area in 2002 were corn and soybeans. In 1997–98, the average amount of nitrogen fertilizer applied in the study area was 114 lb/acre, and the median amount of nitrogen applied within 1,640 ft of the sampled monitoring wells was estimated to be 104 lb/acre. In 1997, an average of about 1.62 lb/acre of pesticides was applied to cropland in the NAL study area. The pesticides applied most (in pounds of active ingredient) were atrazine and metolachlor.

The SAL study area is located within the Ogallala Formation hydrogeologic unit of the SHP region. The Ogallala Formation consists of gravel, sand, silt, and clay sediment that were deposited in a complex stratigraphy. Mean annual pan evaporation rates range from about 95 to more than 105 in/yr, and estimated recharge rates range from no recharge to about 1 in/yr. About 53 percent of the area was used for growing crops in 1992. Approximately 11 percent of land in the

study area was irrigated. In 2002, cotton was the primary crop grown. In 1997–98, the average amount of nitrogen fertilizer applied over the study area was 73 lb/acre, and the median estimated rate of nitrogen application within 1,640 ft of the sampled wells was 58 lb/acre. In 1997, an average of 0.73 lb/acre of pesticides was applied to cropland. The three pesticides applied most (in pounds of active ingredient) were trifluralin, malathion, and 2,4-D.

Nitrate concentrations in NAL ground-water samples ranged from 1.96 to 106 mg/L, with a median of 10.6 mg/L. Ninety percent of the samples had a concentration greater than 4.00 mg/L, indicating that elevated nitrate concentrations were likely a result of human activities. More than one-half (53 percent) of the samples had nitrate concentrations larger than the USEPA drinking-water Maximum Contaminant Level (MCL) of 10 mg/L. Nitrate concentrations decreased with depth below land surface, were larger in samples containing water recharged in the last 50 years, and were larger than nitrate concentrations observed in domestic wells.

Nitrate concentrations in the SAL samples ranged from 0.65 to 21.6 mg/L, with a median concentration of 4.12 mg/L. Nitrate concentrations in 55 percent of samples were larger than 4.00 mg/L, and concentrations in five (17 percent) samples were larger than the drinking-water MCL. Nitrate concentrations decreased with depth below land surface and were larger in samples containing water recharged within the last 50 years. Nitrate concentrations in SAL wells were not significantly larger than in domestic wells.

Seventy-three percent (22 samples) of NAL samples contained at least one detectable pesticide or pesticide degradate. The compounds detected were primarily atrazine, alachlor, metolachlor, simazine, and their degradates. Concentrations of detected pesticides ranged up to 3.09 $\mu\text{g/L}$. When detection frequencies of pesticide compounds were compared at a common assessment level of 0.05 $\mu\text{g/L}$, pesticide degradates were detected more frequently than parent compounds. Pesticide concentrations did not exceed their respective USEPA drinking-water standards. Atrazine and deethylatrazine were detected more than twice as frequently in NAL samples than in other NAWQA study area samples where corn and soybeans were the primary crops grown, whereas metolachlor was detected more frequently in samples collected from other NAWQA study areas. Acetochlor, alachlor, carbofuran, metribuzin, prometon, propyzamide, simazine, and tebuthiuron were detected in samples collected from other NAWQA study areas but not in samples collected from the NAL study area. Samples collected in areas with smaller depths to water were more likely to have detectable pesticides. Pesticides also were more likely to be detected in samples containing water that had been recharged in the last 50 years. NAL monitoring wells more frequently had at least one detectable pesticide than domestic wells.

Twenty-four percent (six samples) of SAL samples contained at least one detectable pesticide or pesticide degradate. The compounds detected were primarily deethylatrazine (a degradate of atrazine and propazine), propazine, fluometuron,

and tebuthiuron. The maximum concentration of any pesticide was an estimated 0.392 µg/L. When detection frequencies of pesticide compounds were compared at a common assessment level of 0.05 µg/L, deethylatrazine was detected most often (10 percent of samples). Except for deethylatrazine, pesticide compounds were detected less frequently in the SAL study area than in other NAWQA study areas where cotton was a primary crop. Pesticide concentrations did not exceed their respective USEPA drinking-water standards. Depth to water and residence time were not significantly related to pesticide detections. There also was no significant difference in the frequency of pesticide detections in SAL monitoring wells and domestic wells.

Dissolved-solids concentrations in ground-water samples collected from the NAL study area ranged from 272 to 2,160 mg/L, with a median of 442 mg/L. The relative proportions of the major ions composing the dissolved solids indicated that most ground water was a calcium bicarbonate type. Water generally was acceptable for drinking-water purposes with respect to dissolved solids, major ions, and trace elements. Dissolved-solids concentrations decreased with depth below land surface and were larger in samples with a residence time of 50 years or less.

Dissolved-solids concentrations in ground-water samples collected from the SAL study area ranged from 416 to 3,580 mg/L, with a median of 814 mg/L. The relative proportions of the major ions composing the dissolved solids indicated that ground water generally was nearly equally codominated by mixtures of more than one cation or anion. Eighty-six percent of samples exceeded the USEPA nonenforceable SDWR for dissolved solids (500 mg/L). Sulfate and chloride concentrations in some samples exceeded their respective SDWR (250 mg/L) as well. Dissolved-solids concentrations decreased with depth below land surface but were not significantly larger in samples with a residence time of 50 years or less.

Land use and hydrogeologic variables in the NAL and SAL study areas were compared to evaluate their potential effect on nitrate, pesticide, and dissolved-solids concentrations in ground water. Many factors in the NAL study area are more favorable than in the SAL study area for movement of chemicals applied at the land surface into ground water. Depths to water are less, precipitation is greater, evapotranspiration rates are smaller, and recharge rates are greater in the NAL study area than in the SAL study area. More than twice the amount of pesticides was applied to cropland in the NAL study area than in the SAL study area. Manure and commercial fertilizer application rates near monitoring wells were greater in the NAL study area. The occurrence of nitrate and pesticide compounds indicates more extensive human effects on ground water at the water table in the NAL study area than in the SAL study area. Samples collected from the SAL study area had larger dissolved-solids concentrations. Larger dissolved-solids concentrations in the SAL study area may be related to evapotranspiration and recharge rates.

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Appendixes
