

Contribution from the National Water Quality Assessment Program

Relation of shallow water quality in the Central Oklahoma aquifer to geology, soils, and land use

Water-Resources Investigations Report 00-4241



On the Cover: Photograph of the skyline of Oklahoma City; taken by U.S. Geological Survey employee, David Usher.

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

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By Alan H. Rea, Scott C. Christenson, and William J. Andrews

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U.S. Department of the Interior
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FOREWORD

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

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

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

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

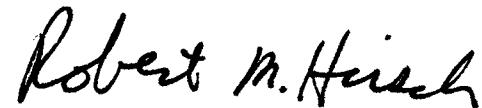
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

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

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

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

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



Robert M. Hirsch
Chief Hydrologist

CONTENTS

Abstract.....	1
Introduction.....	1
Methods of Data Compilation, Association, and Analysis.....	3
Compilation of areally-distributed attributes.....	3
Geologic setting.....	3
Soil properties.....	3
Land use.....	8
Associating point data with areally-distributed attributes	8
Stratification based on geology and land use	8
Buffer-overlay analysis	11
Particle-tracking analysis.....	11
Statistical analysis.....	12
Hypothesis testing.....	12
Sampling biases	13
Relation of Geologic Setting to Ground-Water Quality.....	14
Inorganic constituents	14
Organic compounds	17
Relation of Soil Properties to Ground-Water Quality.....	18
Inorganic constituents	18
Organic compounds	18
Relation of Land Use to Ground-Water Quality.....	18
Inorganic constituents	18
Organic compounds	22
Relation of Population Density to Ground-Water Quality.....	22
Inorganic constituents	22
Organic compounds	22
Relation of Multiple Factors to Detection of Organic Compounds.....	24
Possible Sources of Contaminants	25
Inorganic constituents	25
Organic compounds	27
Conclusions.....	29
References.....	29

ILLUSTRATIONS

Figures 1-7. Maps showing:	
1. Location of the Central Oklahoma study unit and ground-water monitoring networks wells	2
2. Estimated soil runoff curve number in the Central Oklahoma study unit	4
3. Soil profile clay content in the Central Oklahoma study unit	5
4. Soil profile vertical permeability in the Central Oklahoma study unit.....	6
5. Soil profile minimum permeability in the Central Oklahoma study unit	7
6. Land use in the Central Oklahoma study unit.....	9
7. Population density from 1990 Census in the Central Oklahoma study unit.....	10
Figure 8. Schematic diagram of wells with 1/4-mile buffers and particles overlain on land use.....	12
Figures 9.1-9.2. Boxplots of:	
9.1. Physical parameters and inorganic constituents with significantly different concentrations, by geologic unit, Central Oklahoma aquifer.....	16
9.2. Physical parameters and inorganic constituents with significantly different concentrations, by geologic unit, Central Oklahoma aquifer.....	17
Figures 10.1-10.2. Scatter plots of:	

10.1. Inorganic constituent concentrations and soil runoff curve numbers, Central Oklahoma aquifer.....	20
10.2. Inorganic constituent concentrations and soil runoff curve numbers, Central Oklahoma aquifer.....	21
Figure 11. Boxplots of population density by sampling network.....	23
Figure 12 Graph showing observed and predicted cumulative VOC detection probabilities for logistic regression models, including population density and the urban sampling network as explanatory variables.....	26

TABLES

1. Kruskal-Wallis tests of inorganic constituent concentrations between wells completed in different geologic units.....	15
2. Spearman rank-correlation comparisons of inorganic constituent concentrations between groups of wells based on average soil properties within 402 m (a quarter of a mile) of the wells.....	19

CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
Length		
inch (in)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
Area		
square mile (mi^2)	2.590	square kilometer
Flow rate		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second

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

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ABSTRACT

The purpose of this report is to identify, describe, and explain relations between natural and land-use factors and ground-water quality in the Central Oklahoma aquifer NAWQA study unit. Natural factors compared to water quality included the geologic unit in which the sampled wells were completed and the properties of soils in the areas surrounding the wells. Land-use factors included types of land use and population densities surrounding sampled wells. Ground-water quality was characterized by concentrations of inorganic constituents, and by frequencies of detection of volatile organic compounds and pesticides. Water-quality data were from samples collected from wells 91 meters (300 feet) or less in depth as part of Permian and Quaternary geologic unit survey networks and from an urban survey network.

Concentrations of many inorganic constituents were significantly related to geology. In addition, concentrations of many inorganic constituents were greater in water from wells from the Oklahoma City urban sampling network than in water from wells from low-density survey networks designed to evaluate ambient water quality in the Central Oklahoma aquifer study unit. However, sampling bias may have been induced by differences in hydrogeologic factors between sampling networks, limiting the ability to determine land-use effects on concentrations of inorganic constituents.

Frequencies of detection of pesticide and volatile organic compounds (VOC's) in ground-

water samples were related to land use and population density, with these compounds being more frequently detected in densely-populated areas. Geology and soil properties were not significantly correlated to pesticide or VOC occurrence in ground water. Lesser frequencies of detection of pesticides in water from wells in rural areas may be due to low to moderate use of those compounds on agricultural lands in the study unit, with livestock production being the primary agricultural activity. There are many possible sources of pesticides and VOC's in the urban areas of Central Oklahoma. Because only existing water-supply wells were sampled, it is not clear from the data collected whether pesticides and VOC's: (1) occur in low concentrations throughout upper portions of the aquifer in urban areas, or (2) are present in ground water only in the immediate vicinity of the wells due to back-flow of those chemicals into the wells or to inflow around cement seals and through gravel packs surrounding well casings of surface runoff containing those compounds.

INTRODUCTION

The Central Oklahoma aquifer study unit encompasses about 8,000 square kilometers of Central Oklahoma (fig. 1), and is underlain by aquifers composed of sandstone of Permian-age or of unconsolidated sediments of Quaternary age. Those aquifers are used extensively to supply water for municipal, industrial, commercial, and domestic needs. Several water-quality problems exist in these aquifers,

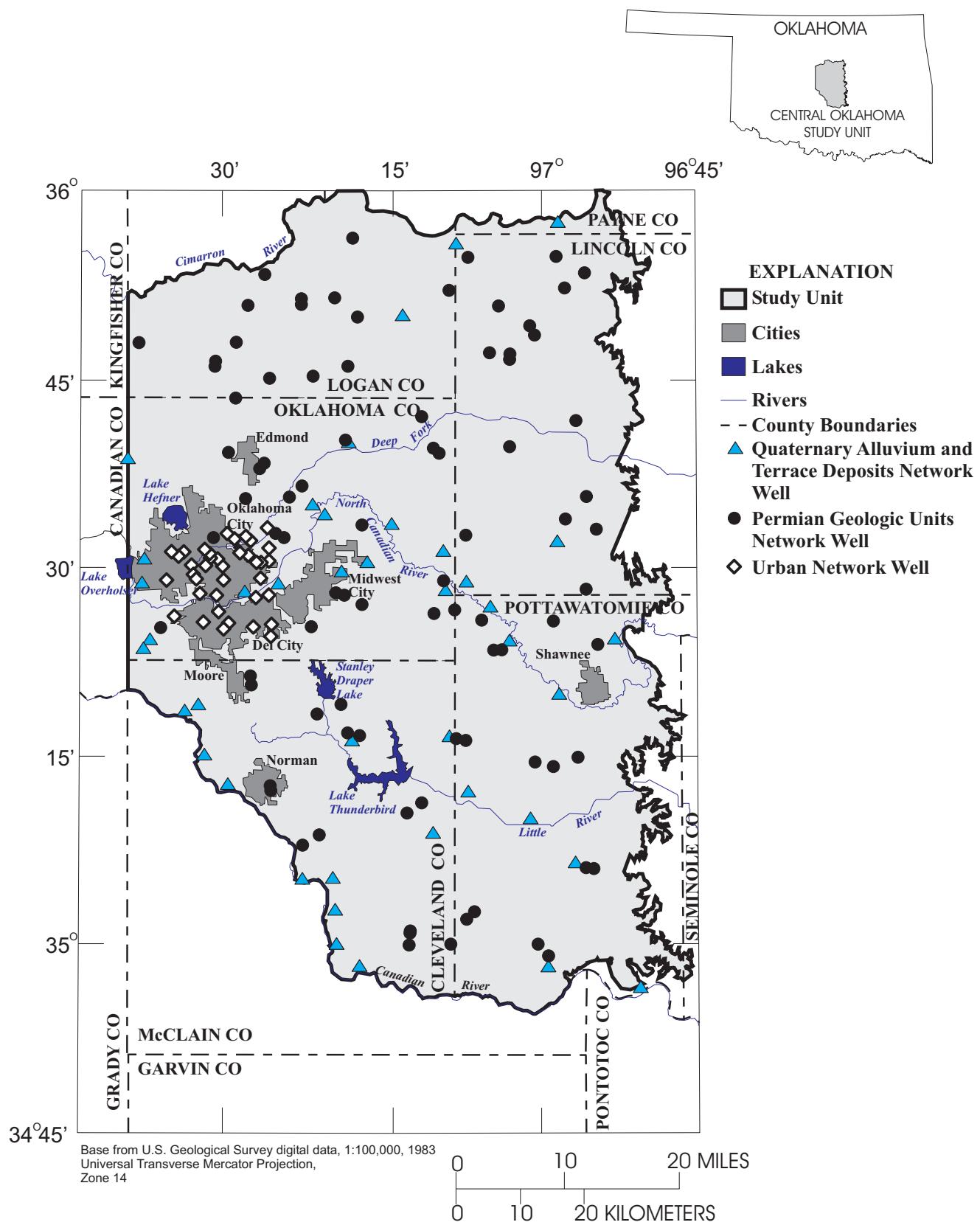


Figure 1. Location of the Central Oklahoma study unit and ground-water monitoring networks wells.

including dissolved concentrations of arsenic, chromium, and selenium in exceedance of drinking-water standards, and the presence of synthetic organic compounds. These aquifers were sampled as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. The primary objective of the Central Oklahoma aquifer NAWQA project was to describe relations between ground-water quality and land use, hydrogeology, and other pertinent factors (Christenson and Parkhurst, 1987).

The purpose of this report is to identify, describe, and explain, to the extent possible, the relations between natural and land-use factors and ground-water quality in the Central Oklahoma aquifer study unit. Relations between those factors and ground-water quality were evaluated using statistical tests. Natural factors compared to ground-water quality include the geologic unit in which the sampled wells were completed, and the properties of soils in the areas surrounding the sampled wells. Land-use factors compared to ground-water quality include land-use types and population densities in the vicinity of sampled wells. Ground-water quality was characterized by concentrations of inorganic constituents, and by the presence or absence of volatile organic compounds and pesticides. Analyses of water samples collected as part of low-density survey and urban-area well networks composed of wells of depths less than 91 meters (300 feet) are described in this report.

METHODS OF DATA COMPILEDATION, ASSOCIATION, AND ANALYSIS

The primary goals of the Central Oklahoma NAWQA project were to identify, describe, and explain relations between natural and land-use factors and ground-water quality in the Central Oklahoma aquifer study unit. Factors potentially affecting water quality were identified, based on knowledge of hydrogeologic processes, results of other investigations, and the feasibility of quantifying the factors. Some factors of possible relevance were not readily quantified and could not be evaluated in a statistical manner. For example, information about the quantities and geographic distributions of application of pesticides and fertilizers used would have been relevant for this report, but such information was not available. All the

factors used in this investigation are spatially distributed, and are shown on maps. Each of those factors is described in the following sections.

Compilation of Areally-Distributed Attributes

Geologic Setting

The primary contributing geologic units for each sampled well were determined by field personnel, based on terrain, depth of well, and knowledge of the extent of the geologic units in the area from well logs and other sources. Bingham and Moore (1975) contains a map of bedrock geology of the study unit. Christenson (1998) contains a map of the surficial outcrops of geologic units in the study unit.

Soil Properties

Soil properties were derived from the six county soil-survey maps (Soil Conservation Service, 1960, 1969, 1970, 1977, 1987a, and 1987b) that encompass the study unit. The soil survey maps were digitized in raster (grid) format, using a grid-cell size of 200 m by 200 m (Soil Conservation Service, written commun., 1991). Soils were not mapped in the central part of the Oklahoma City urban area in the Oklahoma County soil survey (Soil Conservation Service, 1969).

To evaluate the effects of different soil properties on ground-water quality, statistical comparisons were made between water quality and average soil properties in the areas around the wells. The soil survey of Oklahoma County (Soil Conservation Service, 1969) did not delineate soils in the central urbanized area of Oklahoma City (see figs. 2-5), therefore soils information is unavailable for 22 of 41 urban sampling network wells, and 3 of 42 wells in the Quaternary geologic units network. Because of lack of soils data, relations of water-quality data to soils characteristics were only tested for wells from the Permian- and Quaternary geologic unit networks having soils data. Soil properties used for these comparisons were soil-runoff curve number (fig. 2), soil-profile clay content (fig. 3), soil-profile vertical permeability (fig. 4), and soil-profile minimum permeability (fig. 5). For those parameters for which ranges were given in the soil survey, midpoints of the ranges were used.

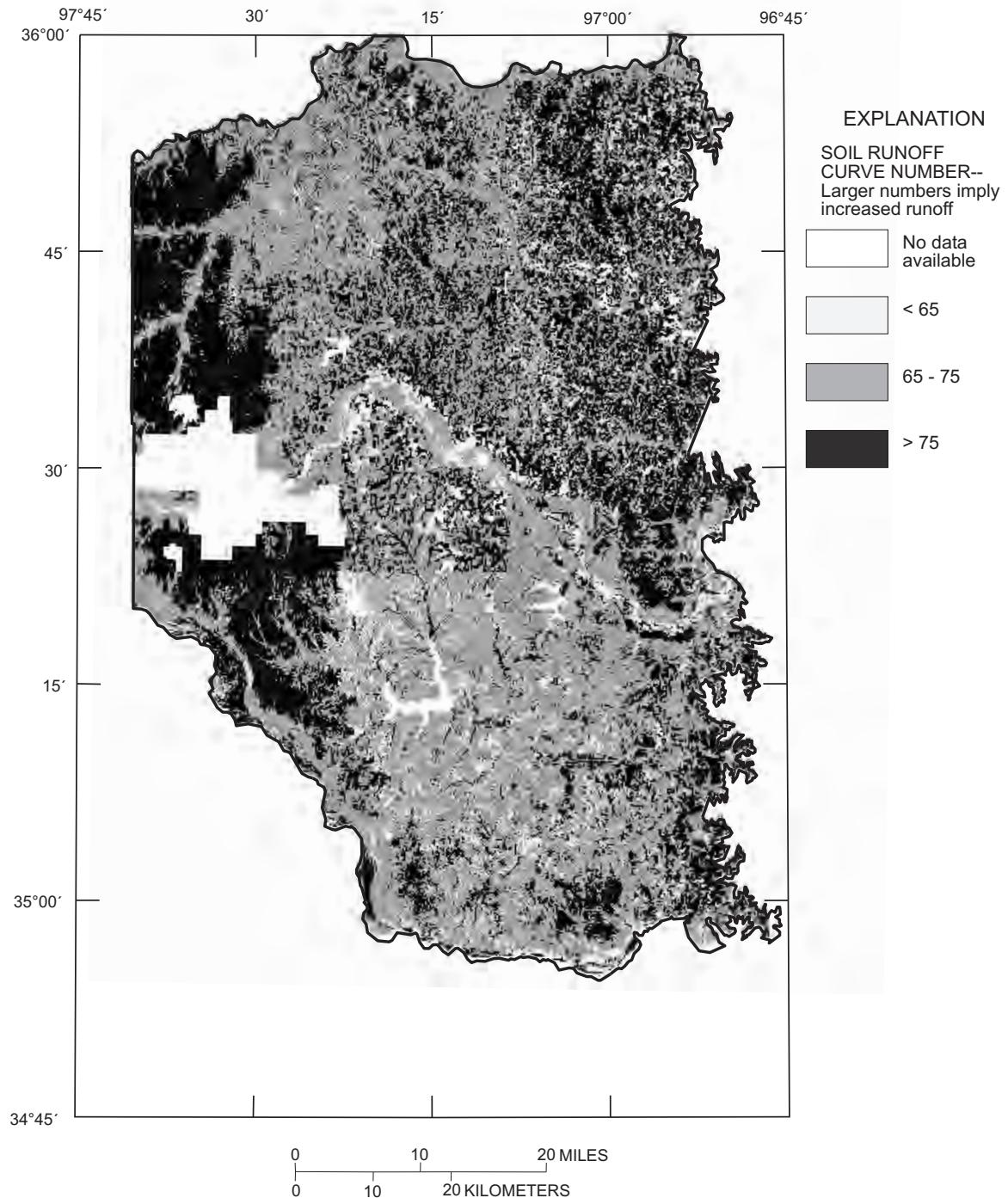


Figure 2. Estimated soil runoff curve number in the Central Oklahoma study unit.

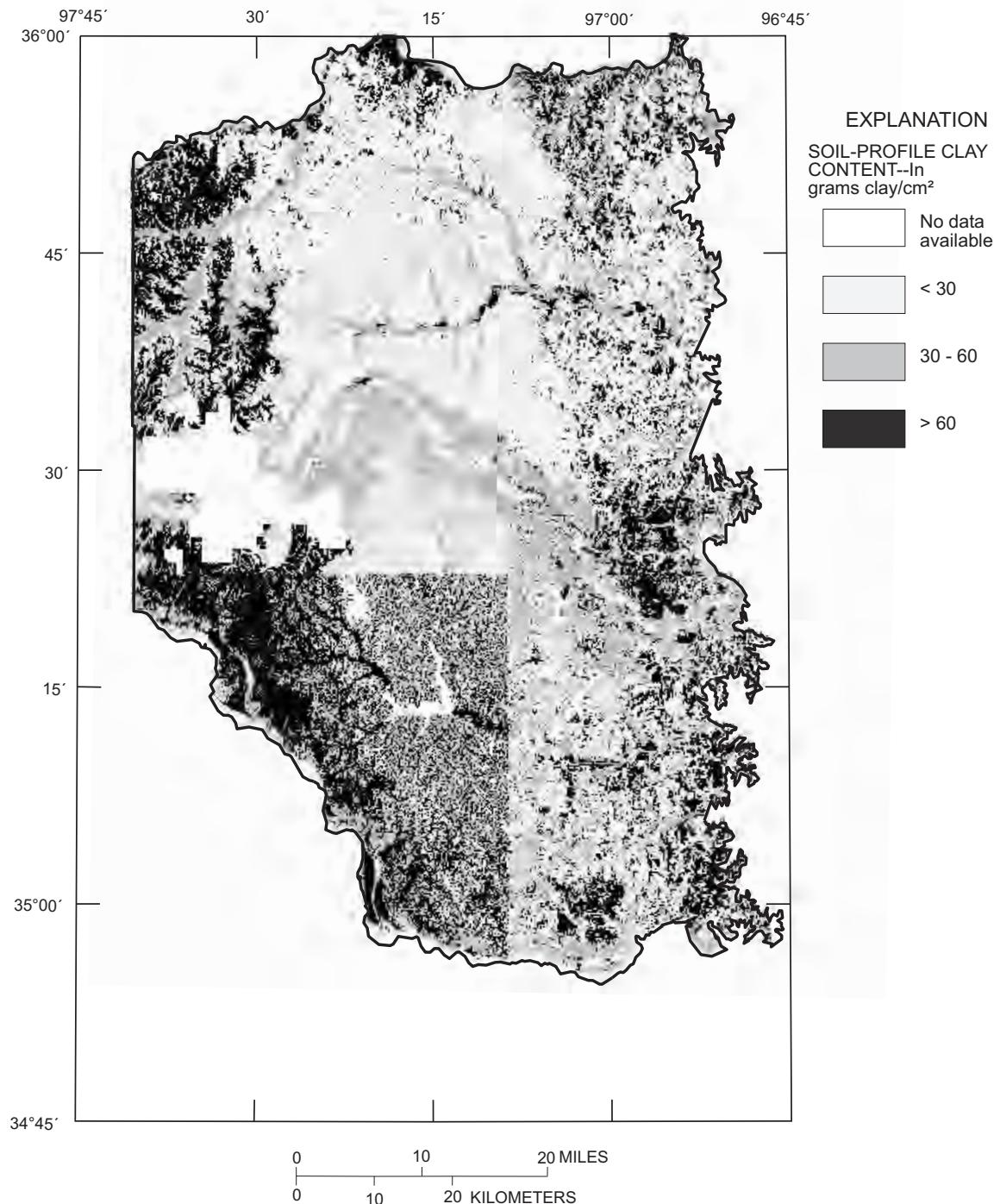


Figure 3. Soil profile clay content in the Central Oklahoma study unit.

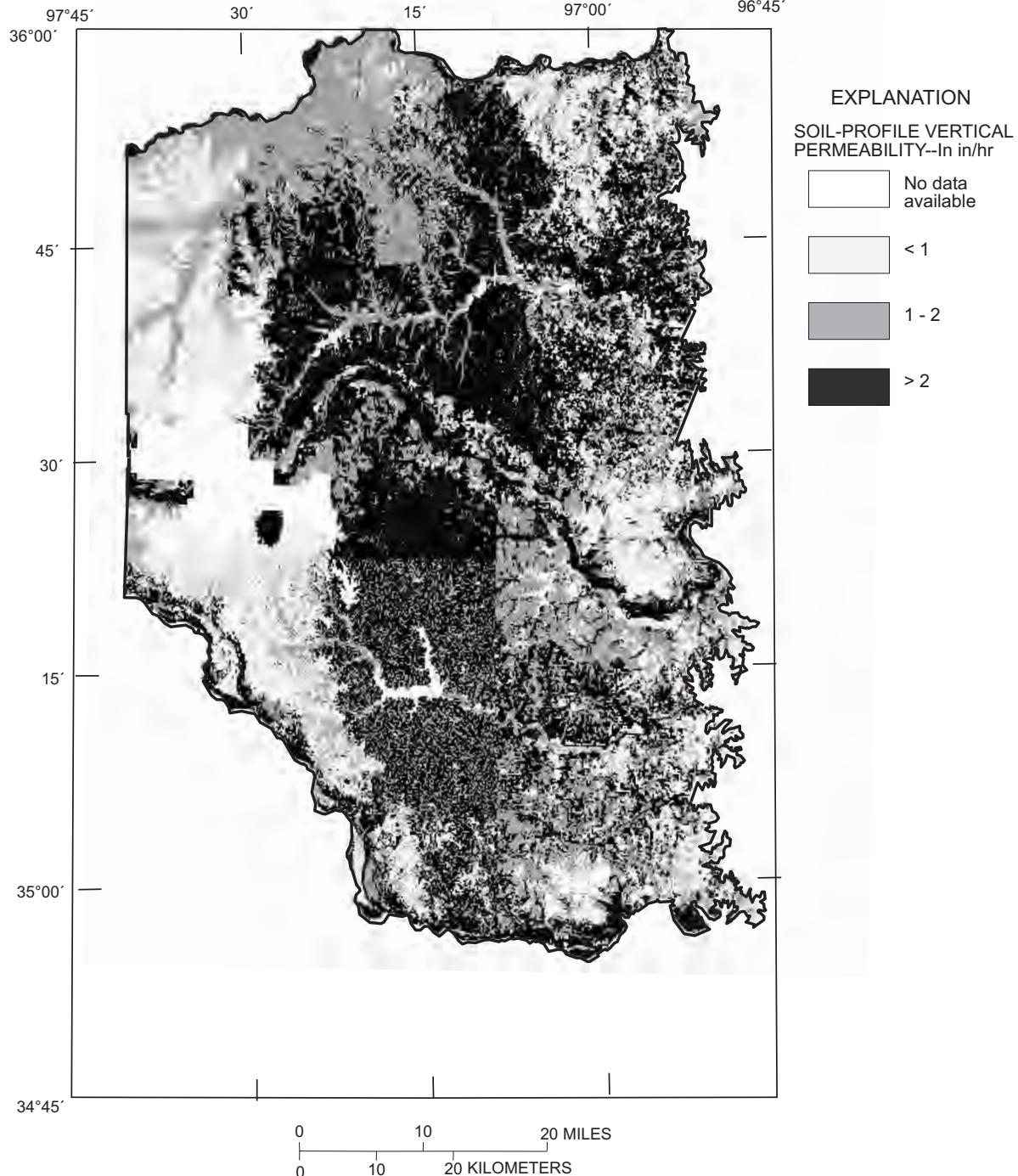


Figure 4. Soil profile vertical permeability in the Central Oklahoma study unit.

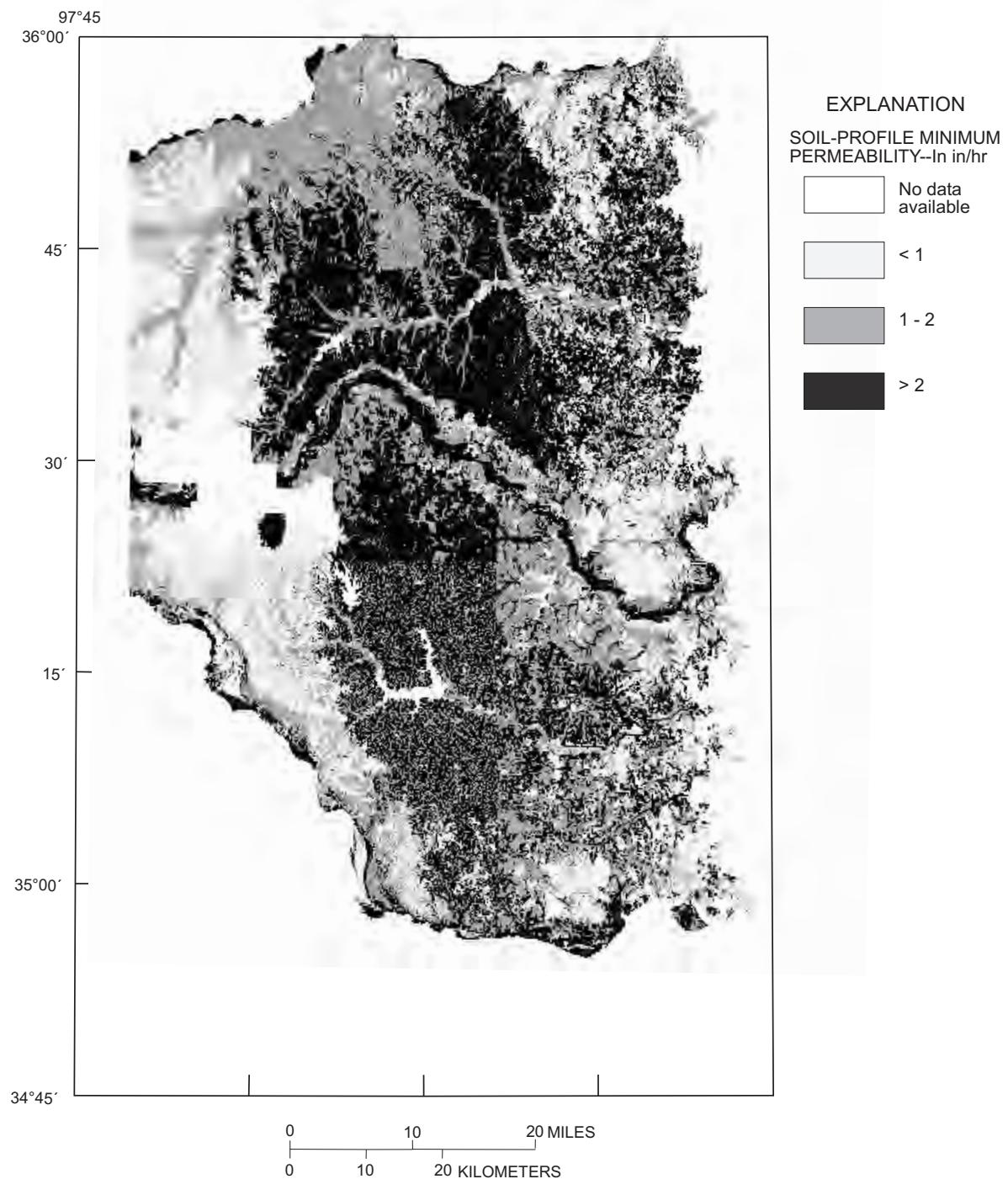


Figure 5. Soil profile minimum permeability in the Central Oklahoma study unit.

Soil-runoff curve numbers (fig. 2) were estimated for each soil component based on estimated typical cover types and hydrologic conditions, and average runoff conditions, as interpreted from the Engineering Field Manual (Soil Conservation Service, 1989, tables 2-3). In general, the soil runoff curve number ranges from 40 to 100, with greater curve numbers indicating more runoff and consequently less infiltration.

The soil-profile clay content (fig. 3) was calculated by multiplying the thickness of each soil layer by the percentage of clay for that layer, multiplying the result by the bulk density of that layer, and summing the result for each layer in the soil profile. The end result is the number of grams of clay in the soil profile per square centimeter of land-surface area. The soil-profile vertical permeability (fig. 4) was calculated using the following relationship (adapted from Jorgensen, 1980):

$$P'_{profile} = \frac{B}{\frac{b_1}{P'_1} + \frac{b_2}{P'_2} + \dots + \frac{b_n}{P'_n}}$$

in which $P'_{profile}$ is the soil-profile vertical permeability, B is the thickness of the entire soil profile, and P'_1, \dots, P'_n and b_1, \dots, b_n are the vertical permeabilities and thicknesses of soil horizons $1 \dots n$, respectively. The soil-profile minimum permeability (fig. 5) is the permeability of the soil horizon with the lowest permeability.

Many soil-mapping units were identified as soil complexes, which are made up of two or more soils grouped together because of the scale of mapping. Soil properties were averaged using the areal percentages of each soil component within complexes as a weighting factor, to arrive at an area-weighted average property for each soil-mapping unit. Some soils had no properties listed in the soil-property data base. Areal percentages of those soils were not included in soil-complex averages.

Land Use

An important characteristic of the Central Oklahoma aquifer is that much of the aquifer is overlain by a large urban area composed of Oklahoma City and surrounding communities (fig. 6). Because chemical usage and discharges within the urban area may be

important influences on the ground-water quality in the study unit, an urban survey well network was established to evaluate the effects of urban land uses on ground-water quality.

The Geographic Information Retrieval and Analysis System (GIRAS) Land-use and Land-cover Map (Fegeas and others, 1983) was used to characterize land use for this report. That map was compiled and digitized from 1975 and 1981 high-altitude aerial photography at a base scale of 1:250,000. For this report, GIRAS land-use categories were classified into three categories: urban, agricultural, and other (fig. 6).

Population density was calculated using data from the 1990 Census of Population and Housing. Population data at the block-group level were extracted from census data files (Bureau of the Census, 1990a), and combined with block-group boundaries from the Topologically Integrated Geographically Referenced (TIGER/Line) (Bureau of the Census, 1990b) digital data files. Population densities were calculated by dividing block-group population by the area of each block group (fig. 7).

Associating Point Data with Areally-Distributed Attributes

Several methods were used for associating wells with areally-distributed attributes, depending upon the types of attributes. Because there was no clear best association method, results of several methods are presented. If several of the methods indicated significant relations between an attribute and ground-water quality, then confidence in the validity of those relations is greater. Similarly, if relations of the different association methods do not agree, the association may be an artifact of the methods used, rather than being representative of relations in the hydrologic system. For statistical analyses, wells were classified based upon sampling networks, buffer-overlay analysis, and particle-tracking analysis.

Stratification based on Geology and Land Use

As discussed in Christenson and others (1998), sampling networks were stratified based on geology and land use. The urban network was designed to evaluate ground-water quality in the Oklahoma City urban area. The two low-density survey networks were designed to evaluate water quality in the two principal

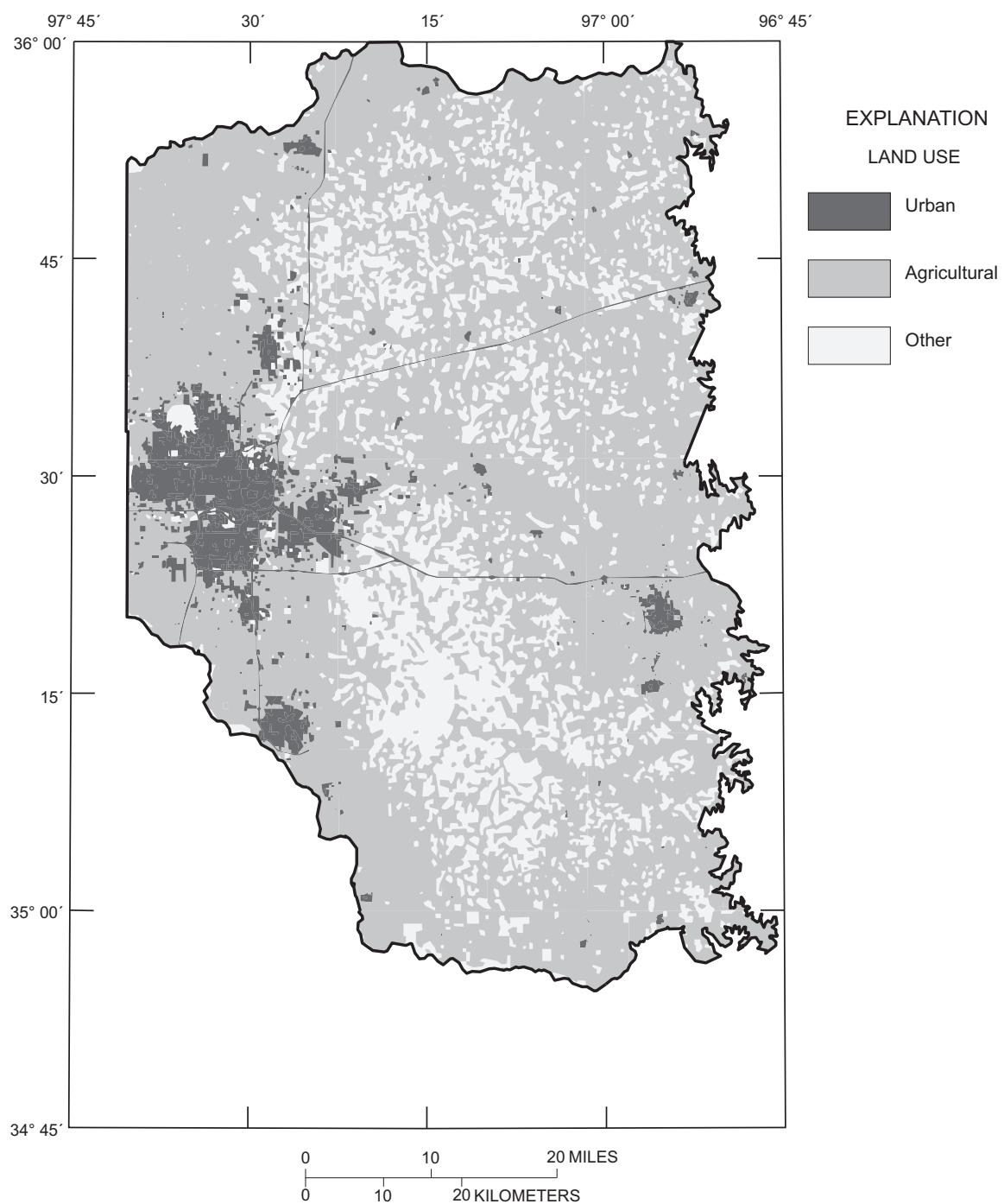


Figure 6. Land use in the Central Oklahoma study unit.

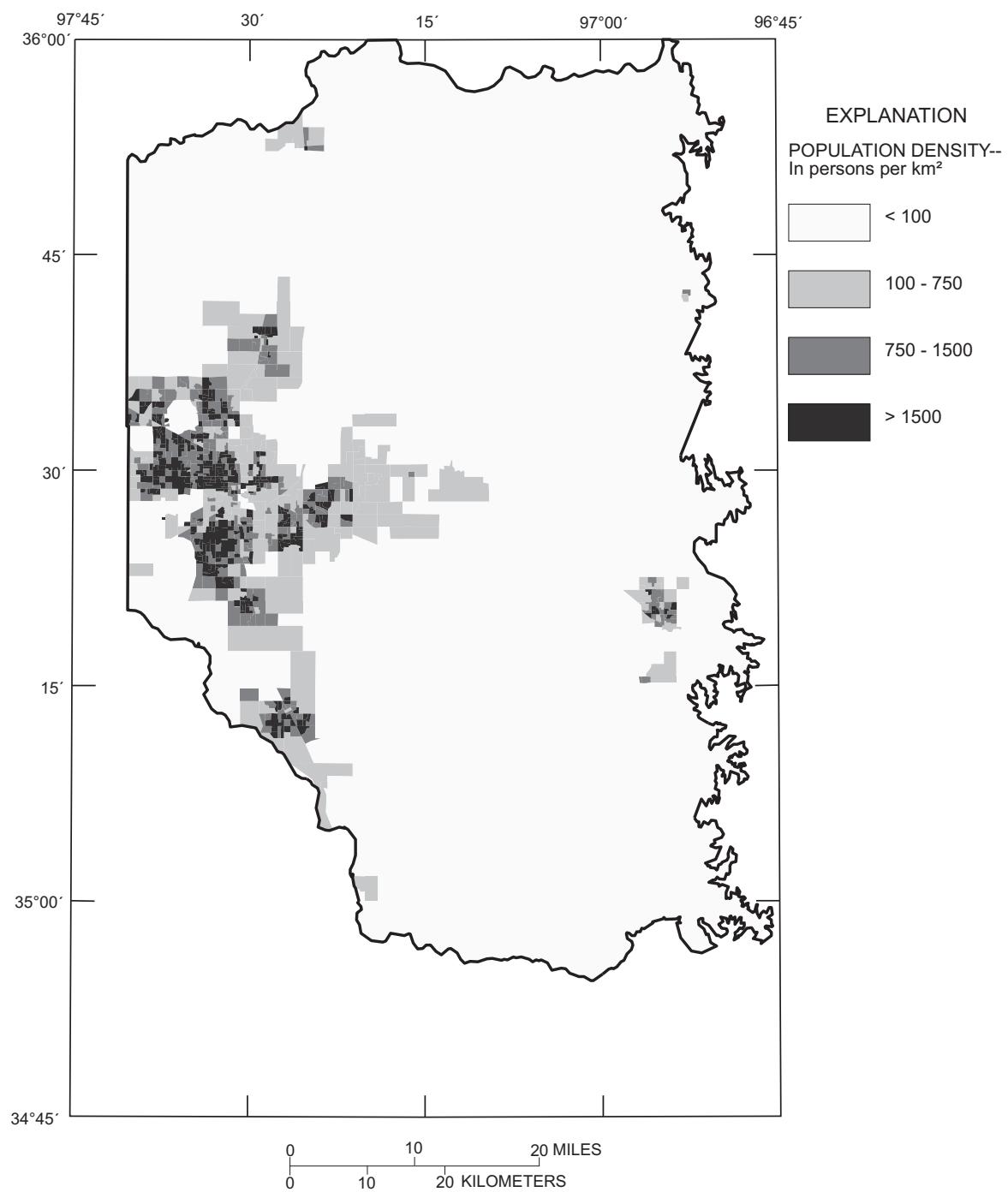


Figure 7. Population density from 1990 Census in the Central Oklahoma study unit.

hydrogeologic units of the Central Oklahoma aquifer study unit--alluvial/terrace deposits of Quaternary age (Quaternary geologic units network), and sedimentary bedrock of Permian age (Permian geologic units network). Therefore, one method of characterizing the effects of land use on ground-water quality in the Oklahoma City area is to compare ground-water quality from the urban sampling network with those of the low-density survey-sampling networks.

Buffer-Overlay Analysis

The simplest method of associating wells with spatial factors is a point-in-polygon overlay. Using this method, the land use assigned to a well would be that of the polygon within which the well lies on the land-use map. However, errors in well locations or in boundaries on the land-use map may result in misclassification of land use for a well. Misclassification also can occur due to generalization inherent in any map, commonly a function of map scale. For example, in the GIRAS land-use map, polygons of some land-use categories having areas smaller than 4 hectares or widths less than 200 meters were not digitized. The minimum delineation area for other land-use categories was 16 hectares, with a minimum width of 400 meters (Fegeas and others, 1983). This generalization eliminated polygons too small to distinguish easily at the base map scale of 1:250,000, so any well located in a land-use area smaller than the minimum delineation area could be misclassified when overlaid on the GIRAS land-use map.

A common approach for reduction of misclassification errors is to draw a circular buffer around the well location and overlay the buffer on the maps of the factors of interest. In addition to reducing misclassification errors, the buffer area also serves as a simplified representation of the recharge area for a well. By use of a Geographic Information System (GIS), buffers with a radius of 402 meters (0.25 mile) were generated around each well. The area of each land-use category within each buffer was calculated, and the predominant (largest area) land-use category within each buffer was determined. This summarization can reduce the effects of misclassification errors. As an example, figure 8 shows four wells in the urban network with buffers overlaid on the GIRAS land-use map. All of those buffer areas contain primarily urban land uses.

A buffer overlay method was used to determine soil properties in the vicinity of the sampled wells.

Digital soil maps used in the analyses represent the soil mapping units on a grid of 200-meter by 200-meter cells. A buffer was defined as a nine-cell array centered around each sampled well, approximately an area of a 402-meter buffer. The soil properties for the nine cells were used to assign a soil property for the well, using an area-weighted average technique. If soil properties were missing for a cell in the vicinity of a sampled well, that cell was not used in the area-weighted average.

In addition to land use, buffer-overlay analysis was used with the population-density map by applying an area-weighted averaging technique. Adaptations of these methods were also used with the maps of soil properties, mentioned earlier in this report. To the extent that such buffers do not correspond to the recharge areas for wells, misclassification can also be introduced by this method.

Particle-Tracking Analysis

A ground-water flow model of the study unit (Christenson, Parkhurst, and Breit, 1998) was developed to estimate recharge areas for each sampled well, using the finite-difference method (McDonald and Harbaugh, 1988). The Central Oklahoma aquifer study unit was discretized into three-dimensional cells 2 kilometers on each side and 30 meters (100 feet) thick. Hypothetical particles of water were placed in each simulated well between the base of the well and the water table, as interpolated from the water-table map in Christenson, Morton, and Mesander (1992). A particle-tracking program (Pollock, 1989) was used in conjunction with the ground-water-flow model to trace the particles of water backward from each well to their recharge locations.

Particles shown on figure 8 represent recharge locations for ground water flowing to each well. Particles are aligned along ground-water flow lines because the finite-difference model is based on the assumption of steady-state conditions, with no pumping of the individual wells. Under these assumptions, the model simulates regional ground-water flow, rather than flow conditions near a pumped well. Modifying the model to simulate conditions around each well was beyond the scope of this report. In a manner similar to the buffer-overlay analysis, the use of a large number of particles leads to a summarization process, which reduces misclassification errors. Land use in the recharge area for each well was determined by the

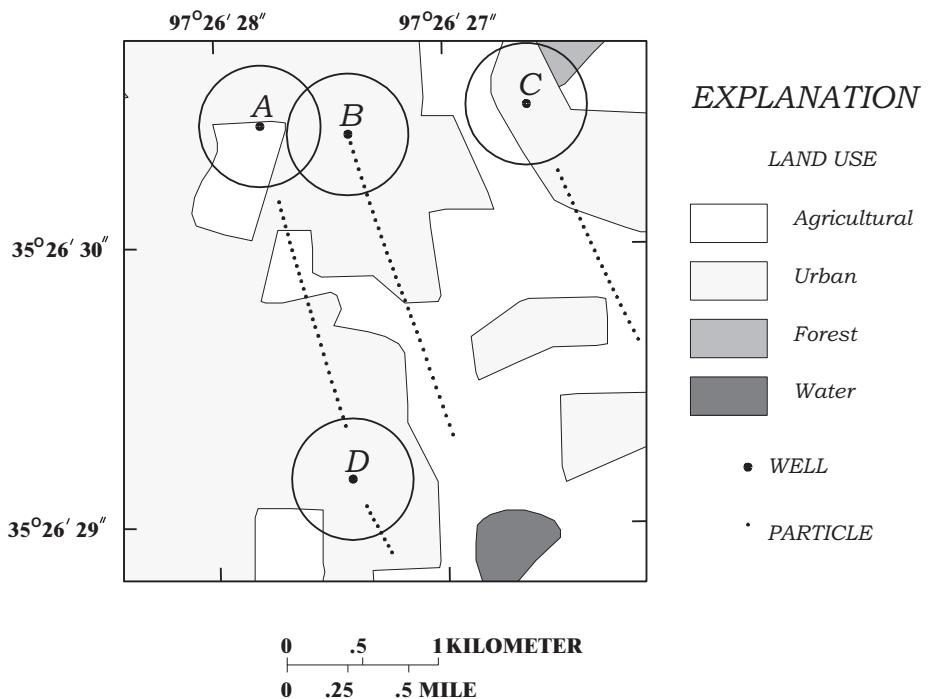


Figure 8. Schematic diagram of wells with 1/4-mile buffers and particles overlaid on land use.

category associated with the largest number of particles. The population density associated with each well was the average of the population densities for all particle recharge locations related to each well. Because of computer programming complications, particle-tracking analysis was not used for associating wells with soil properties. The ground-water-flow model was calibrated to match flow conditions in the Permian geologic units, but calculated ground-water flow velocities did not correlate well with isotopic ground-water recharge age estimates for wells completed in the Quaternary units.

Statistical Analysis

Hypothesis Testing

A variety of statistical tests were used to evaluate the significance of relations between ground-water quality and potentially related factors. Statistical tests were chosen based on the type of data--continuous or categorical. Concentrations of inorganic constituents are continuous variables. Because most of the concentrations of detected organic constituents were near laboratory reporting levels, organic constituent detection was treated as a categorical variable (detected or not detected). The associated sampling network, geologic units, and land-use factors were also categorical variables. Estimated soil runoff curve numbers, soil-profile clay contents, soil-profile vertical permeabilities, soil-profile minimum permeabilities, and population densities were continuous variables.

Relations between two categorical variables were tested using contingency-table analyses with chi-square test statistics (P-STAT, Inc., 1989). The null hypothesis for each test was that the variables were independent. The alternate hypothesis was that the variables were dependent (Helsel and Hirsch, 1992).

The Mann-Whitney test (P-STAT, Inc., 1989) was used to compare concentrations of inorganic constituents grouped by two categorical variables. A generalization of the Mann-Whitney test, the Kruskal-Wallis one-way analysis of variance (P-STAT, Inc.,

1989) was used to compare concentrations of inorganic constituents grouped by more than two categories. For both tests, the null hypothesis was that the constituent concentrations were the same between the groups. The alternate hypothesis was that the concentrations were different between groups.

If significant differences between groups were indicated by the Kruskal-Wallis tests, Tukey's Studentized Range test (Tukey, 1977) was applied to rank-transformed data to determine which group mean ranks differed. The mean ranked values are estimates of the median of distributions (Helsel and Hirsch, 1992). Tukey's Studentized Range test was used to indicate which groups had significantly different median concentrations.

The Spearman rank correlation test (P-STAT, Inc., 1989) is a non-parametric test of correlation between two continuous variables. The null hypothesis was that the variables were independent. The alternate hypothesis was that a monotonic (increasing or decreasing, but not necessarily linear) relation between the variables existed.

Logistic regression (SAS Institute, Inc., 1990) was used to test the relation between a categorical response variable and one or more continuous or categorical independent variables. Logistic regression does not require an assumption of multivariate normality or equal variances of the independent variables (Helsel and Hirsch, 1992).

For all statistical tests, the null hypothesis was rejected if the achieved level of significance (*p*-value) was less than 0.05.

Sampling Biases

Although efforts were made to obtain a random, unbiased sampling of wells in each sampling network, some biases exist. One probable source of bias is that the sampling was limited to existing water-supply wells with installed pumps. If a known water-quality problem existed in an area, wells probably would not be in use in that area, meaning that the extent of contamination may have been underestimated. Only being able to sample wells for which owners have given permission also may have biased the sampling network.

The manner in which the sampled wells were constructed may have biased the water-quality data. Domestic supply wells completed in consolidated

Permian geologic units in the study unit generally are constructed in the following manner: (1) drilled by rotary methods, (2) cased to the full depth of the well, screened or perforated at depths corresponding to the most permeable strata, (3) gravel-packed from the bottom of the well to 3 meters (10 feet) below land surface, and (4) sealed with cement to the land surface. This method of construction may effectively increase lengths of well screens and sampled intervals to the saturated thickness penetrated by each well. This type of construction also may increase the likelihood that water from a well can be contaminated from substances introduced at or near the land surface. Even if most of the water produced by a well is coming from deep strata, a contaminant introduced at or near the land surface could migrate down the gravel pack, affecting the quality of produced water. This bias could be particularly noticeable for organic constituents, as very small quantities of an organic compound would produce the relatively low concentrations of organic compounds that typically were detected.

Oklahoma City is located along the gradational contact between the Hennessey Group and the Garber Sandstone. Beneath much of the Oklahoma City urban area, a thin layer of the Hennessey Group overlies and confines the Garber Sandstone. Many wells are drilled through the Hennessey Group and completed in the confined Garber Sandstone. Outside of the urban area, few wells were sampled where the Hennessey Group overlies the Garber Sandstone, so the urban sampling network could be biased by that difference in geologic setting.

Christenson, Parkhurst, and Breit (1998) reported that water samples from the Hennessey Group and from the shallow (less than 93-meters deep) confined zones of the Garber Sandstone and Wellington Formation generally had greater concentrations of sodium, calcium, magnesium, and chloride than water samples from unconfined areas of the Garber Sandstone and Wellington Formation. Water samples from the Hennessey Group also had greater sulfate concentrations than shallow water samples from the Garber Sandstone and Wellington Formation.

Few of the wells sampled in the Permian geologic units network were in a geologic setting similar to that of the urban sampling network. Travel times from recharge areas to wells, calculated by the particle-tracking model, were greater for urban-network wells than for wells in the Permian geologic units network (Mann-Whitney test *p*-value of 0.0056).

Differences in water quality between the urban network and Permian geologic units network may be due, in part, to differences in geologic settings.

RELATION OF GEOLOGIC SETTING TO GROUND-WATER QUALITY

The primary contributing geologic unit in which a well is completed may affect the quality of water in the well substantially due to variations in physical and chemical properties of the minerals, stratigraphy, and topography, which influence flow rates, ground-water residence times, and chemical reactions. These geologic properties may also affect concentrations of organic compounds, due to differences in permeability, naturally-occurring organic compounds, oxidation states, and pH.

To analyze the effects of geology on ground-water quality, statistical comparisons were made of water-quality data grouped by primary contributing geologic units from the Permian and Quaternary geologic units networks. Because most wells in the urban network were completed in the same geologic unit (Garber Sandstone) and were in a limited geographical area, data from the urban-network wells were not used to evaluate the effects of geology on ground-water quality.

Inorganic Constituents

For statistical analysis, water-quality data were divided into three geologic-unit groups: (1) the Chase, Council Grove, and Admire Groups, undivided (Christenson, 1998); (2) the Garber Sandstone and Wellington Formation, which are geologically similar; and (3) alluvial and terrace deposits of Quaternary age.

Geology had significant effects on concentrations of inorganic constituents in ground water in the Central Oklahoma aquifer study unit. Kruskal-Wallis test p-values listed in table 1 indicate significant differences between the distributions of many inorganic constituent concentrations in water from wells completed in the three geologic-unit groups.

Generalizations about the concentrations of inorganic constituents in the geologic-unit groups may be made from the groups with the greatest mean ranks

listed in table 1. The geologic-unit group with the greatest mean rank is indicated in table 1 only for those constituents that were significantly different between geologic units. Figure 9 shows boxplots of the distributions of the constituents that had significant differences between geologic units. Boxplots with the same letter code represent groups with mean-rank (median) constituent concentrations that are not significantly different, according to Tukey's Studentized Range test on rank-transformed data. For cadmium, Tukey's Studentized Range test did not indicate significant differences in mean ranks, whereas the Kruskal-Wallis test indicated significant differences in the distributions of cadmium concentrations between the geologic-unit groups.

Water samples from Quaternary-age geologic unit wells had similar values of pH and alkalinity and similar concentrations of gross alpha radiation, nitrite plus nitrate, cadmium, sodium, bicarbonate, and carbonate as water samples from the Garber Sandstone and Wellington Formation (fig. 9). Water from Quaternary geologic units had significantly lesser concentrations of dissolved oxygen and significantly greater concentrations of radon, uranium, iron, manganese, and potassium than water from the Garber Sandstone and Wellington Formation (fig. 9). Water from Quaternary geologic units had similar values of alkalinity and similar concentrations of dissolved oxygen, radon, uranium, nitrite plus nitrate, cadmium, iron, manganese, sodium, potassium, and bicarbonate as water samples from the Chase, Council Grove, and Admire Groups (fig. 9). Water from Quaternary geologic units had significantly lesser values of pH, and significantly less gross alpha radiation than water samples from the Chase, Council Grove, and Admire Groups (fig. 9).

Water samples from wells completed in the Garber Sandstone and Wellington Formation had similar concentrations of radon, uranium, cadmium, iron, manganese, and potassium as water samples from the Chase, Council Grove, and Admire Groups (fig. 9). Water from the Garber Sandstone and Wellington Formation had significantly lesser values of pH and alkalinity, and lesser concentrations of gross alpha radiation, sodium, and bicarbonate than water from the Chase, Council Grove, and Admire Groups (fig. 9). Water from the Garber Sandstone and Wellington Formation had significantly greater concentrations of dissolved oxygen, nitrite plus nitrate, and carbonate than water from the Chase, Council Grove, and Admire Groups (fig. 9).

Table 1. Kruskal-Wallis tests of inorganic constituent concentrations between wells completed in different geologic units

[Well group I, 102 low-density survey sampling network wells less than 91 m (300 ft) deep; Highest Mean Rank: C, Chase, Council Grove, and Admire Groups, undivided; G, Garber Sandstone and Wellington Formation, undivided; A, Alluvial and Terrace deposits; Highest Mean Rank values given only when *p*-value is significant; *p*-values less than 0.05 are underlined]

Constituent	Geologic-Unit Groups Well Group I	
	Highest Mean Rank	Kruskal-Wallis <i>p</i> -value
pH	C	<u>.0058</u>
Oxygen, dissolved	G	<u>.0000</u>
Alkalinity	C	<u>.0064</u>
Calcium		.1965
Magnesium		.8384
Sodium	C	<u>.0018</u>
Potassium	A	<u>.0071</u>
Bicarbonate	C	<u>.0088</u>
Carbonate	C	<u>.0225</u>
Sulfate		.1737
Chloride		.3218
Fluoride		.5413
Nitrite plus nitrate	G	<u>.0335</u>
Arsenic		.5477
Barium		.2197
Cadmium	A	<u>.0478</u>
Chromium		.9071
Copper		.1238
Iron	A	<u>.0001</u>
Lead		.0749
Manganese	A	<u>.0001</u>
Mercury		.8172
Selenium		.1300
Silver		.2246
Gross alpha	C	<u>.0034</u>
Radon	A	<u>.0000</u>
Uranium	C	<u>.0024</u>

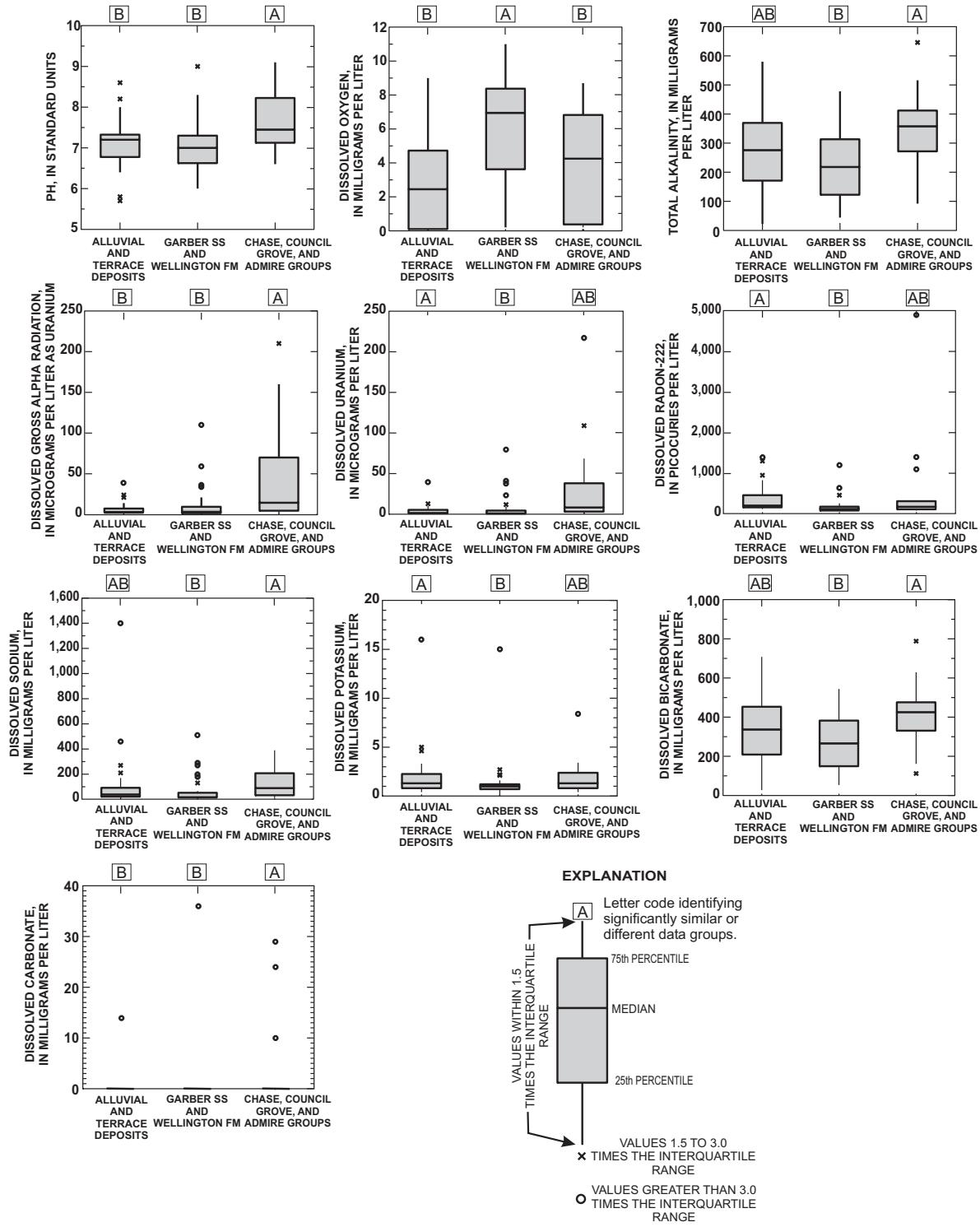


Figure 9.1. Boxplots of physical parameters and inorganic constituents with significantly different concentrations, by geologic unit, Central Oklahoma aquifer.

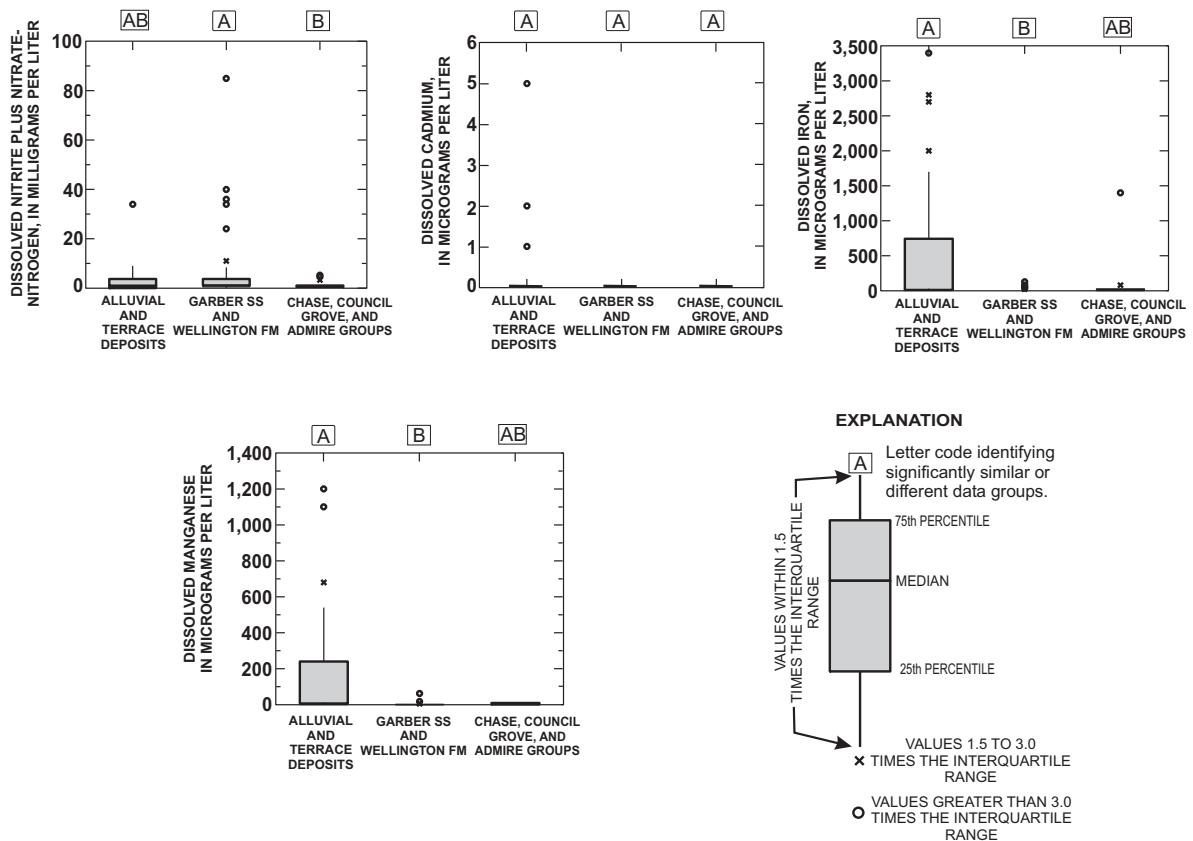


Figure 9.2. Boxplots of physical parameters and inorganic constituents with significantly different concentrations, by geologic unit, Central Oklahoma aquifer.

Organic Compounds

Relations between the geologic-unit groups and detection of organic constituents were tested using contingency-table analysis with a chi-square test statistic (P-STAT, Inc., 1989) for data from 102 wells in the Permian and Quaternary geologic unit networks. Frequencies of detection of pesticides and volatile organic compounds (VOC's) were included for each analysis because most of the organic compounds were reported in only a few water samples. If the groups are too small, the expected value for some cells of a contingency table may be too small, and the assumptions of the contingency-table analysis would not be valid. The null hypothesis was that the frequencies of detection of organic compounds were the same for each geologic unit, whereas the alternate hypothesis was that the frequency of detection of organic

compounds was different between geologic-unit groups.

For pesticides, the calculated p-value was 0.695, and for VOC's the p-value was 0.971—both much greater than 0.05. Thus, the frequencies of detection of these compounds were similar for these geologic-unit groups. The lack of significant differences in frequencies of detection of these compounds between geologic units was unexpected, because the Permian geologic units have substantially different hydrologic characteristics from the Quaternary geologic units. Well construction may have played a significant role in this similarity, by possibly facilitating seepage of these compounds in the vicinity of well gravel packs, as previously described in the Sampling Biases section of this report.

RELATION OF SOIL PROPERTIES TO GROUND-WATER QUALITY

Soil permeability affects infiltration and runoff rates of precipitation, influencing the quantity and spatial distribution of water recharging aquifers in the study unit. Because much of the chemical reactivity in soils is associated with clay-sized particles (Brady, 1974), clay content of soils in recharge areas may affect ground-water quality.

Inorganic Constituents

The *p*-values from statistical tests of relations between inorganic constituent concentrations and soil properties are listed in table 2. A total of 99 wells from the low-density networks were used in the analyses.

Spearman's rank correlation tests indicated significant positive monotonic correlation between estimated soil runoff curve number and values of pH and alkalinity, and concentrations of sodium, bicarbonate, carbonate, sulfate, chloride, fluoride, gross alpha radiation, and uranium; and significant negative monotonic correlation with barium and cadmium concentrations (table 2). There was a marginally significant, positive, monotonic correlation (*p*-value 0.0534) between estimated soil runoff curve number and radon concentrations. Scatter plots of the constituent concentrations that had significant correlations with estimated soil runoff curve number are shown in figure 10. Although the correlations are statistically significant, plots of the data indicate that several of the correlations (sulfate, sodium, chloride, cadmium, gross alpha radiation, barium, and uranium) are unlikely to be meaningful.

Spearman's rank correlation tests indicated significant negative monotonic correlation between soil-profile clay content and dissolved oxygen. Greater clay concentrations in soils may impede infiltration of oxygen into aquifers. Spearman's rank correlation tests indicated significant positive monotonic correlation between soil-profile clay content and radon concentration. As increased clay content impedes downward movement of oxygen into aquifers, it may impede upward seepage of radon gas into the atmosphere. A marginally significant, positive, monotonic correlation (*p*-value 0.0538) was observed between soil-profile clay content and selenium concentration.

Spearman's rank correlation tests indicated significant, negative, monotonic correlations between both soil-profile vertical permeability and soil-profile minimum permeability and pH, sodium, selenium, gross alpha radiation, radon, and uranium concentrations. Spearman's rank correlation tests indicated statistically significant, positive, monotonic correlations between both soil-profile vertical permeability and soil-profile minimum permeability and barium concentrations.

Organic Compounds

The estimated soil runoff curve number, soil-profile clay content, soil-profile vertical permeability, and soil-profile minimum permeability, all continuous variables, were evaluated as explanatory variables in logistic regression analyses of frequencies of detection of pesticides and VOC's. None of the resulting logistic regression model coefficients were significant, meaning that there were no significant relations between these soil properties and the frequencies of detection of pesticides or VOC's in ground water.

RELATION OF LAND USE TO GROUND-WATER QUALITY

Land use was classified into three categories: urban, agricultural, and other. Because land use affects the kinds and quantities of anthropogenic compounds used, spilled or discharged, land use can have a significant influence on ground-water quality.

Inorganic Constituents

No statistical comparisons of inorganic-constituent concentrations by land-use groups are presented because geology was a significant factor affecting inorganic-constituent concentrations. Because different geologic settings were represented by the urban and low-density survey networks, the effects of land use on water-quality would be biased by differences imparted by geologic settings. Only four wells from the two low-density networks were classified as having urban land use based on the GIRAS maps--an inadequate sample size for statistical tests.

Table 2. Spearman rank-correlation comparisons of inorganic constituent concentrations between groups of wells based on average soil properties within 402 m (a quarter of a mile) of the wells

[Well Group II, 99 low-density survey sampling network wells with soils data available that are less than 91 m (300 ft) deep; Sign of rho given only for tests with significant p -values; p -values less than 0.05 are underlined; (), Sign of rho given even though p -value is not significant]

Constituent	Soil Runoff Curve Number		Soil-Profile Clay Content		Soil-Profile Vertical Permeability Well Group II		Soil-Profile Minimum Permeability Well Group II	
	Well Group II	Sign of rho <i>p</i> -value	Well Group II	Sign of rho <i>p</i> -value	Well Group II	Sign of rho <i>p</i> -value	Well Group II	Sign of rho <i>p</i> -value
pH	+	.0088		.2078	–	.0336	–	.0420
Oxygen, dissolved		.9742	–	.0312		.8594		.8640
Alkalinity	+	.0006		.4526		.2350		.3998
Calcium		.1990		.2600		.7784		.9632
Magnesium		.1234		.9060		.9378		.6152
Sodium	+	.0004		.2402	–	.0142	–	.0304
Potassium		.6412		.8888		.7392		.6952
Bicarbonate	+	.0008		.4670		.2284		.3938
Carbonate	+	.0182		.6908		.4348		.5320
Sulfate	+	.0002		.7534		.1848		.4446
Chloride	+	.0118		.5038		.0940		.2642
Fluoride	+	.0032		.6968		.0826		.1612
Nitrite plus nitrate		.6224		.9016		.1426		.1082
Arsenic		.0908		.8376		.3080		.5408
Barium	–	.0006		.8646	+	.0010	+	.0026
Cadmium	–	.0202		.4292		.1632		.4144
Chromium		.7200		.8570		.3650		.2948
Copper		.2660		.8818		.5200		.4592
Iron		.5544		.3384		.8296		.5380
Lead		.1474		.9738		.1456		.1828
Manganese		.1316		.9378		.9574		.7684
Mercury		.7658		.7918		.6646		.7944
Selenium		.2262	(+)	.0538	–	.0044	–	.0088
Silver		.0996		.1684		.1636		.2922
Gross alpha	+	.0094		.2236	–	.0020	–	.0068
Radon	(+)	.0534	+	.0084	–	.0106	–	.0030
Uranium	+	.0002		.0796	–	.0002	–	.0008

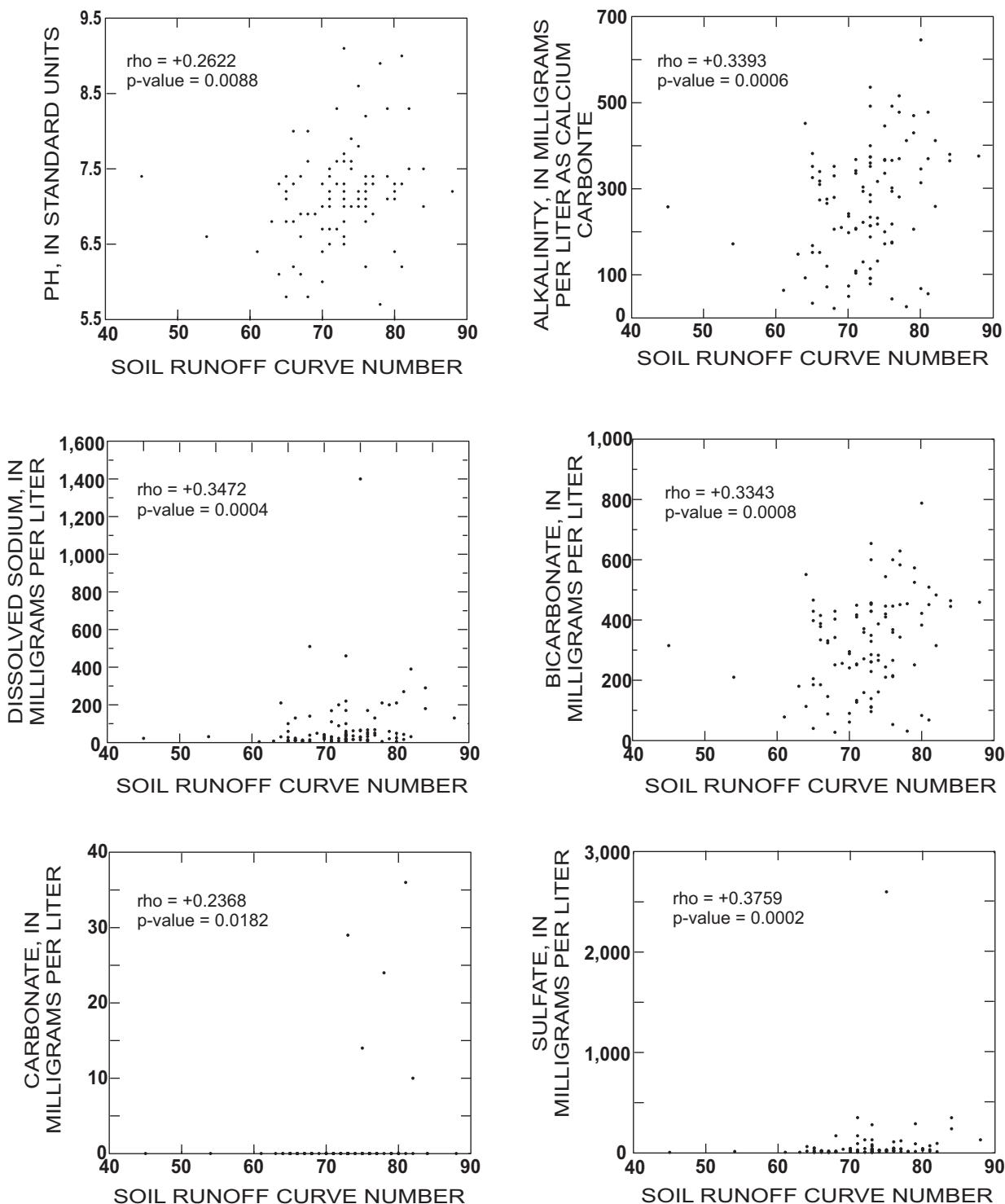


Figure 10.1. Scatter plots of inorganic constituent concentrations and soil runoff curve numbers, Central Oklahoma aquifer.

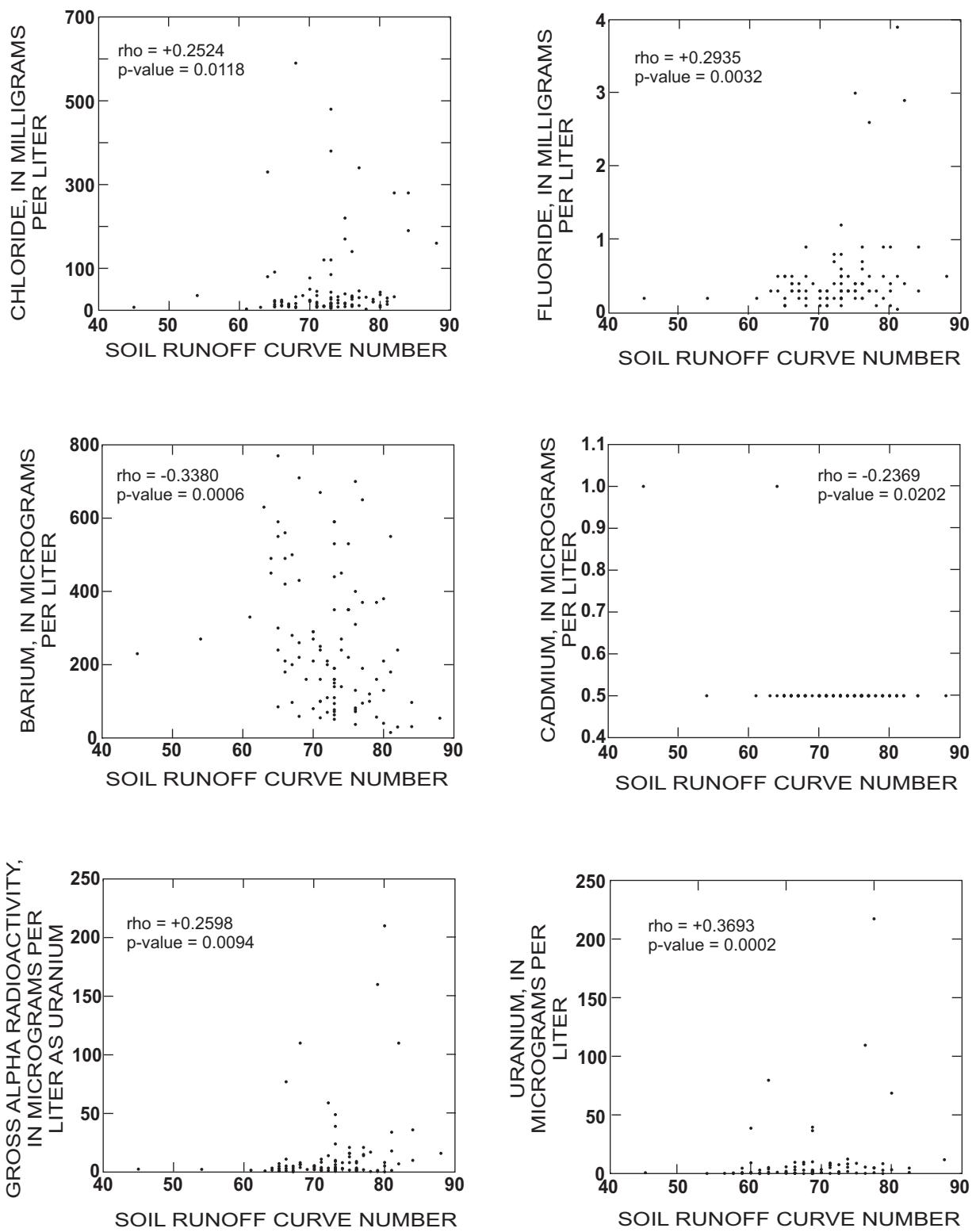


Figure 10.2. Scatter plots of inorganic constituent concentrations and soil runoff curve numbers, Central Oklahoma aquifer.

Organic Compounds

Because geology was not significantly related to the detection of organic compounds, differences in geologic settings of the sampling networks do not preclude use of data from the urban network wells in evaluations of correlations between land use and detection of organic compounds. Frequencies of detection of organic compounds in water samples from the sampling networks were compared using contingency tables with a chi-square test statistic. The null hypothesis was that the frequencies of detection of organic compounds were the same in water samples from the urban network and the low-density networks. The alternative hypothesis was that the frequencies of detection of organic compounds were different in those networks. A sample size of data from 143 wells was used for buffer-overlay analysis, and a sample size of data from 86 wells was used for particle-tracking analysis. Particle-tracking analysis was not used for wells completed in Quaternary geologic units.

Contingency-table analysis comparing frequencies of detection of pesticides between groups of wells based on the predominant GIRAS land-use category within 402-meter buffers had a p-value of 0.107, and for particle-tracking analyses had a p-value of 0.458, so the null hypothesis is accepted, meaning that land use was not significantly correlated to detection of pesticides in ground water in the study unit.

Contingency-table analysis of land use and frequency of detection of VOC's, based on buffer-overlay analysis had a p-value of <0.001, whereas the test based on particle-tracking analysis had a p-value of 0.002; indicating rejection of the null hypothesis, meaning that urban land use had a significant, positive correlation to frequencies of detection of VOC's in ground-water in the study unit.

RELATION OF POPULATION DENSITY TO GROUND-WATER QUALITY

The population density associated with wells was categorized using buffer-overlay and particle-tracking analyses with a map derived from the 1990 Census and TIGER/Line files (U.S. Department of Commerce, 1990a and 1990b). Population density is related to land use, but is measured differently. Popu-

lation density is a continuous numerical variable and thus provides more detailed information about the intensity of land use for residential purposes than the categorical variable land use.

Inorganic Constituents

Because the geologic unit in which the sampled wells were completed was an important factor influencing inorganic constituent concentrations, and geologic settings varied between the urban and low-density networks, data from the urban network wells were not used in comparisons of inorganic concentrations by population density. By excluding data from the urban network, however, the range of population densities around the remaining wells is much reduced, and greater population densities are precluded. Figure 11 shows boxplots of average population density within 402-meter buffers of wells in the three networks. Because any comparisons not including the urban network wells would not adequately represent the range of population densities in the study unit, no comparisons are presented of inorganic concentrations and population density.

Organic Compounds

Logistic regression was used to test the relation between population density and frequencies of detection of organic compounds. Wells from the urban and low-density networks were used, resulting in a sample size of 143 wells for the buffer-overlay analysis, and a sample size of 86 for the particle-tracking analysis. Population density was a significant (p-value = 0.0036) predictor of pesticide occurrence probability. The resulting logistic regression model is:

$$P_{pest} = \frac{e^{(-2.0108 + 0.00101D_{buff})}}{1 + e^{(-2.0108 + 0.00101D_{buff})}}$$

where P_{pest} is the probability of a pesticide being reported in a water sample, e is 2.703, and D_{buff} is the area-weighted population density in a 402-meter buffer around the well, expressed in persons per square kilometer. The positive value of the coefficient for D_{buff} indicates that, the probability of detection of a pesticide increases with increasing population density.

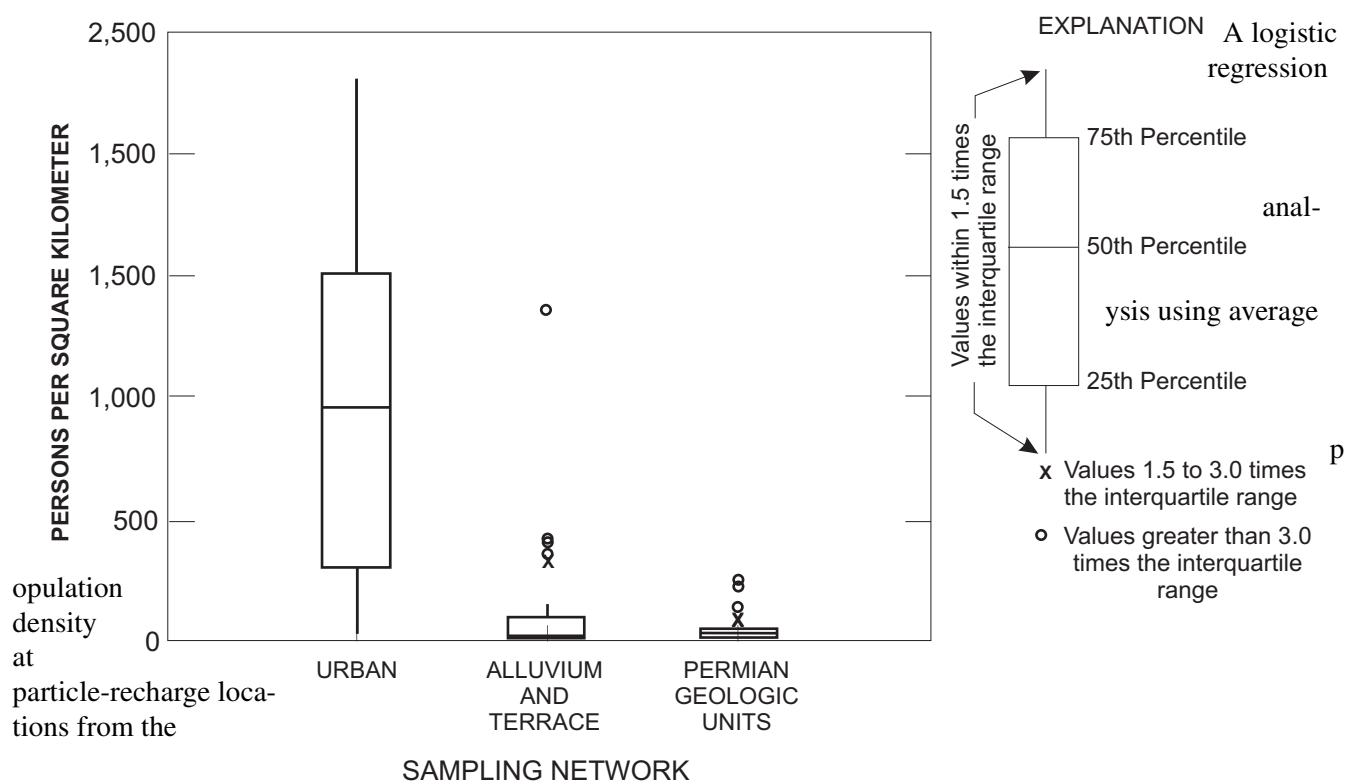


Figure 11. Boxplots of population density by sampling network

particle-tracking analyses did not have a significant *p*-value for the population-density regression coefficient. The lack of significance may have been the result of reduction of the sample size from 143 to 86, because it was not possible to use the particle-tracking model for the wells completed in Quaternary geologic units. If contaminant sources were in the immediate vicinity of the sample, then detection of contaminants would not be substantially affected by ground-water flow directions and upgradient population densities.

Logistic regression of population densities and frequencies of detection of VOC's resulted in the following logistic regression model:

$$P_{voc} = \frac{e^{(-1.7806 + 0.00183D_{buff})}}{1 + e^{(-1.7806 + 0.00183D_{buff})}}$$

where P_{voc} is the probability of a VOC being detected in a well. The population-density variable was a significant (*p*-value of 0.0001) predictor of VOC detection probability. The positive value of the coefficient for D_{buff} indicates that the probability of detection of a VOC increases with increasing population density.

Logistic regression of population densities and frequencies of detection of VOC's using average population density at particle-recharge locations resulted in the following logistic regression model:

$$P_{voc} = \frac{e^{(-1.6928 + 0.00131D_{part})}}{1 + e^{(-1.6928 + 0.00131D_{part})}}$$

where P_{voc} is the probability of a VOC being detected in a well, and D_{part} is the average population density, in persons per square kilometer, at particle-recharge

locations. The population-density variable was significant (*p*-value of 0.0072). The positive value of the coefficient for D_{part} indicates that the probability of detection of a VOC increases with increasing population density. For VOC's, a comparison of *p*-values and plots of predicted and observed cumulative detection probabilities versus Blom ranks (SAS Institute, 1990) indicated that the logistic regression model based on the buffer-overlay analysis fit the data better than the logistic regression model based on the particle-tracking analysis. Reduction of the sample size for the model using the particle-tracking analysis or very localized sources of contaminants may have caused the poorer fit of the particle-tracking model.

RELATION OF MULTIPLE FACTORS TO DETECTION OF ORGANIC COMPOUNDS

All of the comparisons discussed so far in this report have compared water quality with single factors. Multivariate statistical methods are useful for comparisons involving more than one factor, allowing interpretation of the interaction and relative importance of factors. Because of the bias problems previously discussed, no multivariate statistical comparisons were made for inorganic constituents. Multivariate tests are better suited for interpretation affecting frequencies of detection of organic constituents.

The logistic regression model is appropriate for comparing the occurrence of organic constituents, a categorical variable, with a combination of continuous and categorical factors (Helsel and Hirsch, 1992). Categorical variables such as land use and geologic setting were recoded into a series of binary variables, one for each category. For example, land use was regrouped to three categories: urban, agricultural, and other. The urban variable was coded "1" if land use was urban, and "0" if land use was agricultural or other. These binary variables may be used in logistic regression models, provided that at least one binary variable from each original categorical variable is not included in the model, to prevent problems caused by closure (Barringer and others, 1990).

Numerous logistic regression models were tested, using many combinations of explanatory vari-

ables. The models were evaluated based on the *p*-values of model coefficients, Akaike's Information Criterion (Helsel and Hirsch, 1992), and subjective evaluations of model fit using plots of predicted and observed organic constituent detection probabilities. The stepwise logistic regression procedure (SAS Institute, 1990) was used to evaluate the relations between pesticide occurrence and geologic unit, soil runoff curve number, soil-profile clay content, soil-profile vertical permeability, soil-profile minimum permeability, urban sampling network, buffer-overlay land use, and population density based both on buffer-overlay analysis and on particle-tracking analysis. None of the resulting logistic regression model coefficients were statistically significant, including the coefficient for population density, which had a significant coefficient when used in a single-variable logistic regression. The sample size used in the multiple logistic regression model was smaller than the sample size used in the single-variable logistic regression model because soil properties were not available for wells in the central part of the urban area, and because the particle-tracking analysis could not be used for all wells. The wells in the central part of the urban area also were the wells with the greatest surrounding population densities. The lack of statistical significance may have been a result of the reduction in sample size from 143 to 115 wells.

If the soil properties and the population-density variable based on the particle-tracking analyses were eliminated from the logistic regression analysis for pesticide occurrence, the stepwise procedure resulted in a model that used population density based on buffer-overlay analysis only, and thus was exactly the same model as was used in the single-variable logistic regression of buffer-overlay population density versus occurrence of pesticides. Using the stepwise procedure, none of the land-use, geologic-unit, or urban-sampling network variables could be used to significantly increase the degree to which the logistic regression model fit the data.

A stepwise logistic regression model was used to evaluate relations between VOC detection and geologic unit, soil runoff curve number, soil-profile clay content, soil-profile vertical permeability, soil-profile minimum permeability, urban sampling network, buffer-overlay land use, and population density based both on buffer-overlay analysis and on particle-tracking analysis. As with pesticides, none of the resulting logistic regression model coefficients

were statistically significant if the soil properties were included in the analysis. If the soil properties were excluded, and the particle-tracking population density variable was included, the stepwise procedure resulted in the same model as resulted from the single-variable logistic regression of particle-tracking population density versus VOC frequency of detection.

When soil properties and the particle-tracking population density variables were left out of the analysis, the stepwise procedure resulted in a logistic regression model that produced significant relations for both buffer-overlay population density (p-value was 0.0328) and the binary variable for the urban sampling network (p-value was 0.0272). The following equation is the logistic regression model which produced significant relations for VOC frequencies of detection:

$$P_{voc} = \frac{e^{(-1.997 + 0.00107D_{buff} + 1.2993U)}}{1 + e^{(-1.997 + 0.00107D_{buff} + 1.2993U)}}$$

where P_{voc} is the probability of a VOC being detected in the well, D_{buff} is the area-weighted population density in a 402-meter buffer around the well, and U is a “1” if the well is in the urban network, and a “0” otherwise. The positive values of the coefficients for D_{buff} and U indicate that, according to the model, the probability of detection of a VOC increases with increasing population density and the presence of the well in the urban sampling network. This model fits the data the best of all the multivariate logistic regression models tested. Figure 12 shows predicted and observed VOC detection probabilities for this model.

POSSIBLE SOURCES OF CONTAMINANTS

The term contaminant is used in this report as any substance in ground water that was introduced as a result of human activity. The following two sections identify some of the possible sources of contaminants, and how those sources may be related to the natural and anthropogenic factors. Available data were not adequate to test some hypotheses, and in some cases, relations were not significant.

Inorganic Constituents

Christenson and Rea (1993) reported that median concentrations of alkalinity, calcium, magnesium, sodium, potassium, bicarbonate, chloride, iron, gross-alpha radioactivity, and uranium were greater in water from urban wells than in water from other wells sampled for the Central Oklahoma NAWQA Project. However, because of the previously discussed possible bias in the urban sampling network, no clear relation has been established between land-use, population density, and the concentrations of inorganic constituents. The following factors are presented as possible sources of inorganic contaminants. Available data are not sufficient to determine whether greater concentrations of inorganic constituents in water from urban wells are due to land use or to natural hydrogeologic factors.

Paved surfaces in urban areas increase runoff and decrease the amount of recharge to the aquifer. Decreasing recharge from precipitation, which is low in dissolved constituents, may lead to greater concentrations of dissolved constituents in ground water. In contrast, lawn watering, a common practice in residential areas in the Oklahoma City urban area, and irrigation of agricultural land from surface-water sources could increase recharge to the aquifer, facilitating transport, but also dilution of constituents leaching from the land surface to the water table.

Treated water from municipal treatment plants seeping to the aquifer from lawn watering or from leaking water lines in the urban areas is a possible source of ground-water contamination. Municipal supplies for Oklahoma City and Norman are primarily from surface-water reservoirs, whereas most of the smaller municipal supplies in the study unit rely on ground water. Concentrations of sodium, potassium, chloride, and sulfate from two of Oklahoma City's three surface-water reservoirs (Betty Fox, City of Oklahoma City, written commun., 1991) tend to be greater than background concentrations in the aquifer.

Leakage from sewer lines and effluent from septic tanks may contaminate ground water in the area. Oklahoma City does not measure concentrations of major cations and anions in water entering its sewage treatment plants, but chemists at the City's waste-water treatment plants believe the major-ion concentrations would resemble treated public-supply water because municipal water is the major component of residential

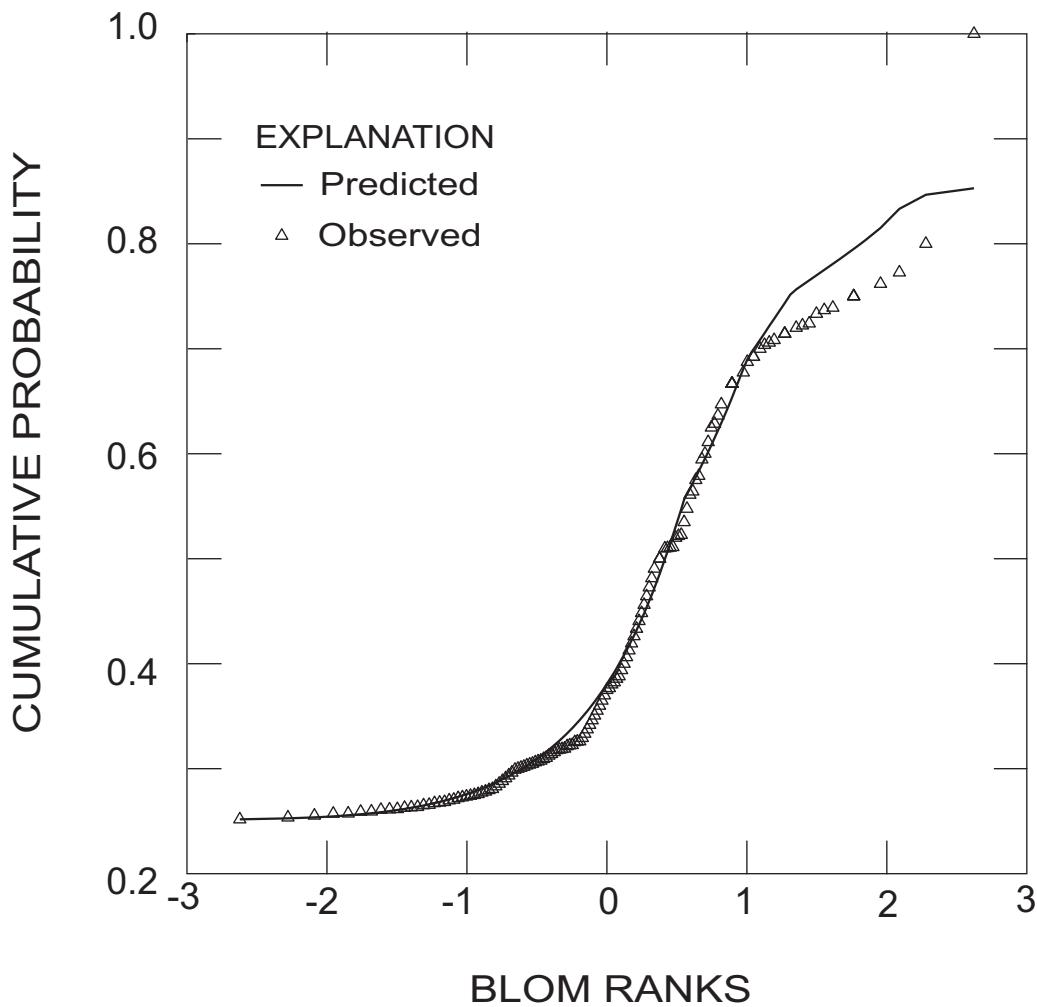


Figure 12. Observed and predicted cumulative VOC detection probabilities for logistic regression models, including population density and the urban sampling network as explanatory variables.

sewage (Willard Keith, City of Oklahoma City, oral commun., 1991).

Road salt is another possible source of sodium and chloride in ground water underlying the urban area. Oklahoma City uses a mixture of salt and sand on roads for several days during a typical winter. In recent years, the road salt has been purchased from a mine in Hutchinson, Kansas. The chemical composition of the salt is 95 to 97 percent sodium chloride, 2 to 4 percent calcium sulfate, 1 to 2 percent water insolubles, and less than 1 percent magnesium chloride, iron oxide, calcium chloride, magnesium sulfate, and moisture (Max Liby, Hutchinson Salt Company, written commun., 1991).

Fertilizer is a possible source of inorganic constituents in ground water beneath the urban or agricultural areas. Lawns and gardens in the Oklahoma City area typically are fertilized with chemical fertilizers, which commonly contain calcium, magnesium, sodium, potassium, and chloride (Brady, 1974). Phosphate in some fertilizers contains substantial quantities of uranium (Spalding and Sackett, 1972), which might increase uranium and gross-alpha particle activity in ground water beneath areas where fertilizers are applied. Information on fertilizer application is incomplete. Fertilizer sales data are available by county (Oklahoma Department of Agriculture, 1990), but those data may include fertilizer purchased in one

county and used in another county. Fertilizer sales data also may not account for sales of fertilizer through department stores and garden stores to urban and suburban homeowners.

Petroleum production activities comprise an additional source of possible contaminants of ground water in the study area which are not necessarily related to the three main categories of land use previously described in this report. Brines from oil and gas wells may contaminate ground water in the area. Oil and gas have been produced from approximately 13,000 wells in the study unit since the beginning of the 20th century. The Oklahoma City oil field, located in the southeastern part of the urban area, is one of the 10 largest oil fields in the conterminous United States (Landes, 1970). Most oil wells produce brines as well as hydrocarbons. At present (2001), these brines are reinjected into deep strata, generally through old production wells that have been converted into injection wells. In the past, these brines have been spread on the land surface or dumped in holding pits, potentially contaminating ground water. Many wells in the Oklahoma City urban area were drilled before stricter regulations regarding casing requirements and brine disposal were enacted. Median concentrations of major ions in brines produced from some oil and gas wells in Oklahoma County (Parkhurst and Christenson, 1987) are: pH, 6.3; alkalinity, 46.4 mg/L as CaCO_3 ; calcium, 13,000 mg/L; magnesium, 2,510 mg/L; sodium, 75,500 mg/L; chloride, 146,000 mg/L; sulfate, 232 mg/L; and dissolved solids 237,000 mg/L. Snavely (1989) reported that brines produced during hydrocarbon production are enriched in radium isotopes. Radium-228 concentrations in 113 wells in Oklahoma, Texas, and along the Gulf Coast ranged from 19 to 1,507 pCi/L, and radium-226 concentrations ranged from 0.1 to 1,620 pCi/L. Radium-226 is an alpha-particle emitter and is part of the uranium-238 decay series, of which radon-222 is a by-product. Disposal of brines from deeper units, therefore, may increase concentrations of major ions and radionuclides in shallow ground water in the area.

Organic Compounds

Local use of organic compounds may increase their frequencies of detection in ground water. Field observations indicated that the organic compounds detected in ground water commonly had been used or

applied to the land immediately surrounding wells, or were being stored in well houses. During the first year of sampling (1988), all wells producing water with detectable concentrations of pesticides or VOC's were revisited by field personnel to identify possible sources of those compounds. At about half of these wells, a likely source of the detected organic compounds was identified in the immediate vicinity of the wells. In many cases, the well owners had used the compound near the well or was storing substances containing these compounds near the wellhead. As discussed in the Sampling Biases section, the manner in which most of the sampled wells were constructed may have provided conduits for organic constituents to seep to the water table. Because domestic supply wells in the study unit generally are gravel packed for the entire depth of the well except for a 3-meter (10-foot) cement seal at the top, small quantities of water containing man-made organic compounds may enter the well through the gravel pack. Some of the wells in which organic compounds were detected were hand-dug wells with plywood or concrete covers and unmortared stone linings. In general, organic compounds were detected only at very low concentrations (less than 1 $\mu\text{g}/\text{L}$), when they were detected. At least some of the occurrences of organic compounds in ground water may be due to localized use or to spills, rather than indicating widespread, low concentrations of these compounds in the aquifers. Because only existing wells were sampled, the data are not sufficient to determine whether the organic compounds are widespread or very localized in ground water. Deeper well seals or more careful management of pesticides and VOC's in the immediate vicinity of wells might decrease the frequency of detection of these compounds in water from domestic wells in the study unit.

As there are no natural sources of the pesticide compounds analyzed, detection of these compounds in ground water is due to human use of those compounds at the land surface. Detection of pesticides in general, and of chlordane, dieldrin, and prometon in particular, were most frequent in water from wells in the urban sampling network. All of the detected pesticides have been used in the study unit. Other studies in Nevada (Lawrence and Whitney, 1990), Minnesota (Andrews and others, 1998); New York, Connecticut and Massachusetts (Hanchar and Grady, 1994); and Long Island (Eckhardt, Siwiec, and Cawller, 1989) have reported detecting some of the same pesticides in ground water

in urban areas. Although much attention has been directed to the agricultural use of pesticides, many pesticides are used in urban areas on residential lawns and gardens, along roads and utility corridors, as termaticides around buildings, and in houses and other buildings. Pesticide use may be greater in urban areas because the cost of pesticides is a less important economic factor for a home owner than a farmer. No data are available concerning the amount of pesticides used in central Oklahoma, but it is possible that more pesticides have been applied per acre in the urban area than in outlying agricultural areas, particularly termaticides such as chlordane. The fact that the frequency of pesticide detection in ground water in central Oklahoma was greater in the urban area than in the surrounding rural areas also may be related to the relatively low use of agricultural chemicals in the area. Battaglin and Goolsby (1995) published maps showing the use of agricultural chemicals, harvested cropland, and amounts of selected crops and animals grown by county for the conterminous United States. The maps indicate that, relative to the rest of the country, use of agricultural chemicals in central Oklahoma is low to moderate. Cattle, sorghum and wheat account for much of the agricultural activity in the area.

The organochlorine insecticides reported in water samples collected as part of this investigation have been used widely in central Oklahoma, although their use was declining as of 1995. Chlordane and dieldrin have been used to control termites, and DDE is a breakdown product of DDT, which was used extensively as an insecticide before 1973 (Sine, 1988).

Phenoxy-acid herbicides are widely used for weed control. Of the triazine herbicides, atrazine is an agricultural herbicide used to control annual grasses in corn and sorghum (Winkelmann and Klaine, 1991). Atrazine use in the study unit in 1992 ranged from 1-5.6 pounds per square mile, in the lower range of use nationwide (U.S. Geological Survey, 1999a). During the period of sampling and before, atrazine was applied in amounts exceeding 66 pounds per square mile to the west in the Texas Panhandle, and to the north in Kansas. Investigations in 1995 in Minnesota (Don Goolsby, U.S. Geological Survey, written commun., 1996) indicated concentrations of atrazine approaching the drinking-water standard of 3 µg/L can occur in rainfall in urban areas, from volatilization and particulates entrained in the atmosphere. Prometon is a nonselective, long-lasting, pre- and post-emergent

herbicide used to control perennial broadleaf weeds and grasses on right-of-ways (Sine, 1993). Prometon is relatively slow to degrade in soils, with an estimated half-life of 200-500 days (Rao and Alley, 1993; Weber, 1994). Prometon has a relatively low sorption coefficient to organic carbon in soils, making it more likely to leach to ground water than many other pesticide compounds (Weber, 1994).

Volatile organic compounds detected in water samples from these aquifers also are unlikely to be natural. Most of the VOC's reported in water samples are in use or have been used as solvents, propellants, fumigants, or in manufacturing processes. Styrene is a compound used in the manufacturing of many different types of plastics (Verschueren, 1983). Trihalomethanes, such as bromoform, chlorodibromomethane, dichlorobromomethane, and, in particular, chloroform, were the VOC's most commonly detected in water from urban wells. One common source of trihalomethanes is the chlorination of drinking water for city water supplies, which may be a component of recharge water in urban areas. Trihalomethanes form when chlorine or bromine react with dissolved organic carbon (Thurman, 1985). Water in the Oklahoma City distribution system has had total concentrations of trihalomethanes as great as 262 micrograms per liter ($\mu\text{g}/\text{L}$) (Judith Duncan, Oklahoma State Department of Health, written commun., 1990). The drinking water standard for the total concentration of trihalomethanes is 100 $\mu\text{g}/\text{L}$. Trihalomethanes also are associated with manufacturing, particularly the manufacturing of chlorofluorocarbon refrigerants and fire extinguishers (Verschueren, 1983). The chlorofluorocarbon refrigerants dichlorodifluoromethane and trichlorofluoromethane are used or occur in air conditioners, refrigerators, sewage, and the atmosphere.

Gasoline from leaking underground storage tanks was expected to be a common contaminant of ground water in the urban area. The composition of gasoline varies among refiners, and has changed over time. Some of the VOC's detected in water samples collected in the urban area are present in some gasoline formulations, including 1,2-dibromoethane; 1,1-dichloroethane; 1,2-dichloroethane; and toluene, but these compounds have many other uses as solvents, fumigants, and manufacturing agents (Lucius and others, 1989). Toluene is a major component in gasoline, accounting for as much as 30 percent by weight of gasoline (Kreamer and Stetzenbach, 1990), but is

also a common constituent in paint, asphalt, and adhesives (Verschueren, 1983). Benzene, ethylbenzene, and xylene also are major components of gasoline, but those compounds were not detected in any samples. Thus, it is not possible to determine if the fuel-component VOC's detected in ground-water samples in the urban area were related to gasoline.

CONCLUSIONS

Numerous statistical tests were used to identify, describe, and explain relations between selected natural and land-use factors and shallow water quality in the Central Oklahoma aquifer NAWQA study unit well networks: urban, Permian geologic units, and Quaternary geologic units.

Concentrations of many inorganic constituents were significantly related to geologic settings. However, no significant relations were determined between geologic settings and the detection of organic constituents (pesticides and VOC's), which was unexpected because the Permian geologic units are lithologically and hydrologically quite different from the Quaternary geologic units.

Estimated soil runoff curve number, soil-profile clay content, soil-profile vertical permeability, and soil-profile minimum permeability were compared to ground-water quality. Of the four soil properties, the estimated soil runoff curve number was most closely related to the concentrations of inorganic constituents. None of the four soil properties had statistically significant relations to the detection of organic constituents. Lack of significant relations between soil properties and detection of organic constituents was unexpected, because large differences in the mobility of organic constituents should occur between soils having different properties, such as clay content or permeability.

Sampling networks were designed to evaluate the effects of land use on the ground-water quality in the Oklahoma City urban area. However, differences in geologic units sampled by the three well networks induced sampling bias for inorganic constituents in the urban sampling network. This sampling bias does not apply to the organic compounds. Land use from the GIRAS land-use map was significantly related to VOC detection, but not to pesticide detection. Buffer-overlay analyses and particle-tracking analyses

produced similar results in comparing land use with ground-water quality.

Logistic regression models indicated the probability of detecting pesticides or VOC's in a well significantly increased with increasing population density in the area near the well. Multivariate, stepwise logistic regression procedures indicated that the probability of pesticide occurrence could best be modeled using population density as the only explanatory variable. Similar analyses for VOC's indicated that the probability of VOC occurrence could best be modeled using population density and the urban network as explanatory variables.

The lack of significant relations between geologic settings and soil properties to frequencies of detection of pesticides or VOC's may have been due to use or storage of compounds near wellheads, either through back-flows into the wells or by seepage of these compounds with recharging water around the top shallow cement seals and through the underlying gravel packs surrounding well casings. Because water samples were only collected from existing water-supply wells, it is not clear whether pesticides and VOC's occur in low concentrations in ground water throughout the urban area, or whether pesticides and VOC's preferentially seep to ground water only in the immediate vicinity of wells.

Detection of pesticides in ground water has been considered to be most likely in agricultural areas, but in Central Oklahoma, detection of those compounds is related with greater population densities of urban areas. Greater frequencies of detection of pesticides in water from urban wells may be due to low to moderate use of agricultural chemicals on agricultural areas in the study unit, with most agricultural activity centered around livestock production.

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