GROUND-WATER QUALITY OF THE CENTRAL OKLAHOMA (GARBER-WELLINGTON) AQUIFER CONFERENCE: PROCEEDINGS, FEBRUARY 20, 1992

Edited by Scott Christenson and Lyn Carpenter

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Dallas L. Peck, Director

For additional information
write to:
District Chief
U.S. Geological Survey
Building 7, Broadway Executive Park
202 NW 66th Street
Oklahoma City, Oklahoma 73116

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply unit	By	To obtain
foot	0.3048	meter
gallon	0.003785	cubic meter
gallons per minute	0.0000631	cubic meters per second
inch	2.540	centimeter
mile	1.609	kilometer
square mile	2.590	square kilometer

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

$$°F = (1.8 \times °C) + 32$$

Sea level: In this report “sea level” refers to the National Geodetic Vertical Datum (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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INTRODUCTION

Beginning in 1986, the Congress annually has appropriated funds for the U.S. Geological Survey to conduct a National Water-Quality Assessment (NAWQA) Program. The long-term goals of the Program are to:

(1) Provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources,

(2) Define long-term trends (or lack of trends) in water quality, and

(3) Identify, describe, and explain, as possible, the major factors that affect the observed water-quality conditions and trends.

This information, which will be obtained on a continuing basis, will be made available to water managers, policy makers, and the public to provide an improved scientific basis for evaluating the effectiveness of water-quality management programs and for predicting the likely effects of contemplated changes in land- and water-management practices.

Initially, seven project areas were selected as pilot studies to test and refine the assessment concept. The Central Oklahoma aquifer (fig. 1) was selected for study in the pilot NAWQA Program because it is a major source for water supplies in central Oklahoma and because it has several known or suspected water-quality problems. These problems include arsenic, chromium, and selenium concentrations in excess of public drinking-water standards; large gross alpha particle activity; contamination by synthetic organic compounds; and contamination by oil-field brines and drilling fluids. The aquifer also was chosen because it underlies large urban areas, and the effects of an urban environment on regional ground-water quality have not been studied extensively.

The objectives of the Central Oklahoma aquifer project are to: (1) Investigate regional ground-water quality throughout the aquifer, emphasizing the occurrence and distribution of potentially toxic substances in ground water, including trace elements, organic compounds, and radioactive constituents; (2) describe the relation of ground-water quality to hydrogeologic and other pertinent factors; and (3) provide a general description of the location, nature, and causes of selected water-quality problems within the study unit.

In 1986 the Central Oklahoma aquifer pilot project began an intensive water-quality investigation. This intensive investigation continued until 1992, when the project entered a low-activity phase. During this low-activity phase, project activity decreased to trend monitoring, but the project is scheduled to enter another intensive-investigation phase in 1997.

The Central Oklahoma aquifer pilot project used a Liaison Committee to ensure that the scientific information produced by the program was relevant to local and regional interests. Specific activities included: (1) Exchanging information about local and regional water-quality and water-data management issues; (2) identifying water-quality constituents and

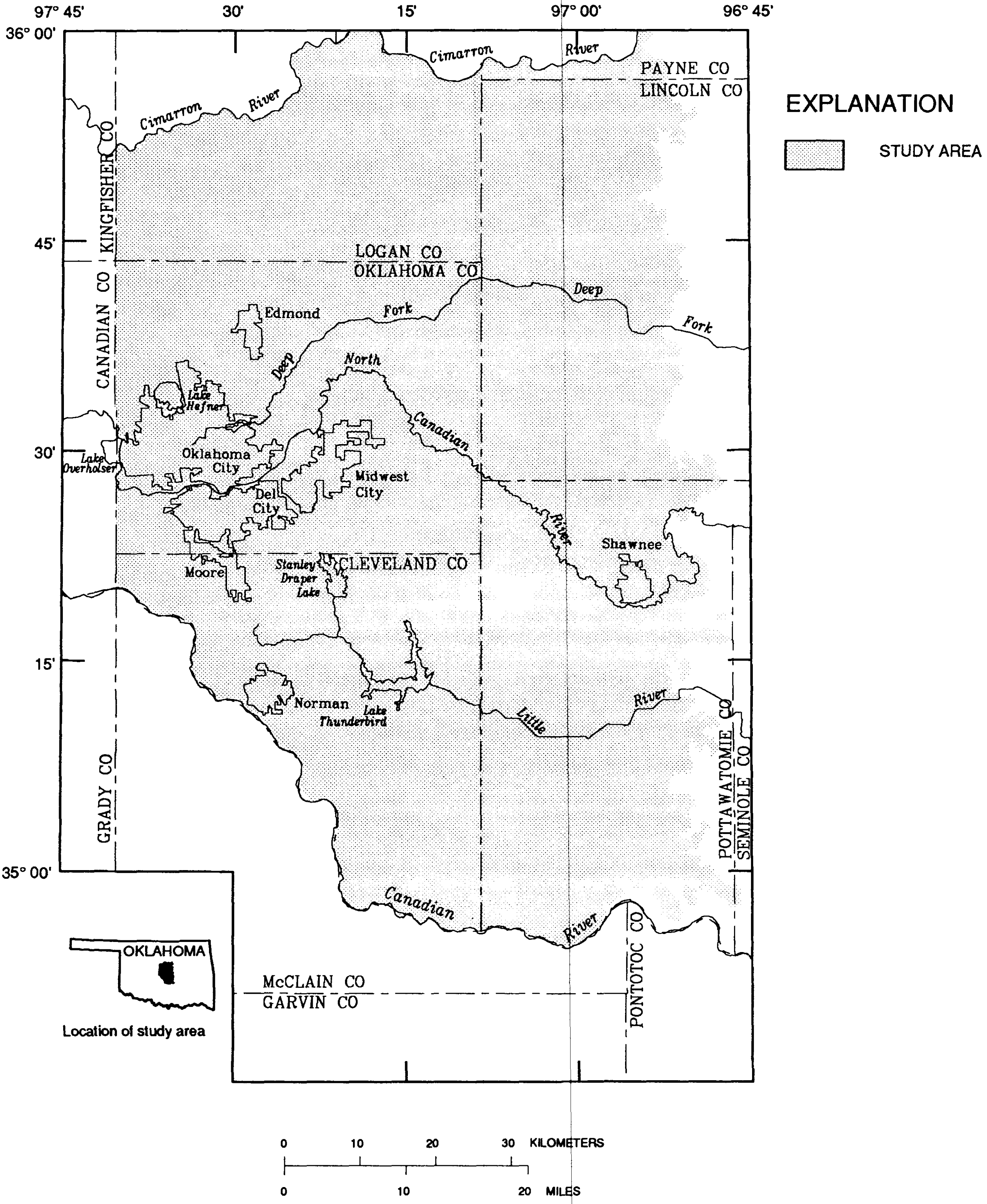

Figure 1: –Location of the Central Oklahoma (Garber-Wellington) aquifer

studying locations of local and regional interest; (3) discussing adjustments in NAWQA or other U.S. Geological Survey sampling-program objectives; and (4) reviewing and commenting on draft planning documents and reports from the study. Organizations represented in the Central Oklahoma aquifer Liaison Committee included: The Association of Central Oklahoma Governments, the Directorate of Environmental Management from Tinker Air Force Base, the Environmental and Ground Water Institute at the University of Oklahoma, Oklahoma Corporation Commission, Oklahoma Department of Agriculture, Oklahoma Department of Pollution Control, Oklahoma Geological Survey, Oklahoma State Department of Health, Oklahoma Water Resources Board, U.S. Army Corps of Engineers, U.S. Bureau of Reclamation, U.S. Environmental Protection Agency, and the University Center for Water Research at Oklahoma State University.

The Liaison Committee met once or twice per year during the intensive-activity phase of the project between 1986 and 1992. These meetings generally consisted of members of the Oklahoma NAWQA staff presenting or discussing project plans and findings with the members of the Liaison Committee. As the project neared completion in 1991, the Oklahoma NAWQA staff decided to organize a conference on the ground-water quality of the Central Oklahoma aquifer for the final Liaison Committee meeting. Rather than limit presentations to only those by the Oklahoma NAWQA staff, papers were solicited from the water-resources community in Oklahoma, thus providing a forum for presentations from many sources. The abstracts compiled in this report are of papers presented at the conference. Abstracts written by authors employed by the U.S. Geological Survey have been approved for publication by the Director of the U.S. Geological Survey.

GROUND-WATER QUALITY OF THE CENTRAL OKLAHOMA (GARBER-WELLINGTON) AQUIFER
February 20, 1992

Agenda

8:30 Introductory Remarks: *Kathy Peter, U.S. Geological Survey*

8:45 The National Water-Quality Assessment Program: *Patrick Leahy, U.S. Geological Survey*

9:00 Geohydrology and Ground-Water Flow Simulation of the Central Oklahoma Aquifer: *Scott Christenson, U.S. Geological Survey*

9:30 The Geochemical Evolution of Ground Waters in the Central Oklahoma Aquifer: *David Parkhurst, U.S. Geological Survey*

10:00 Break

10:30 Geochemical Studies of Solid-Phase Materials in the Central Oklahoma Aquifer: Relation to Water Quality: *Elwin Mosier and Jamie Schlottmann, U.S. Geological Survey*

11:00 Mineralogy and Petrography of Permian Rocks in the Central Oklahoma Aquifer: Implications for Ground-Water Quality: *George Breit, U.S. Geological Survey*

11:30 Improving Water Quality and Quantity in Perforated Water Wells: *Larry Simpson, Garber-Wellington Association*

12:00 Lunch

1:00 Spatial Distribution of Chlorides in Drinking Water Wells in the Central Oklahoma Aquifer: *Baxter Vieux, Robert Knox, and Nalneesh Gaur, University of Oklahoma*

1:30 Contaminant Migration in the Central Oklahoma (Garber-Wellington) Aquifer: Laboratory Studies: *David Sabatini, B. Shiau, T. Sorens, and C. Palmer, University of Oklahoma*

2:00 High Performance Capillary Electrophoresis Methods for the Separation of Pesticides: *Ziad El Rassi and Jianyi Cai, Oklahoma State University*

2:30 Ground Water Quality Beneath Agricultural Lands in Central Oklahoma: *S.J. Smith, J.W. Naney, and A.N. Sharpley, U.S. Agricultural Research Service*

3:00 Break

3:30 Factors Related to Ground-Water Quality in the Oklahoma City Urban Area: *Alan Rea and Scott Christenson, U.S. Geological Survey*

4:00 Managing the Central Oklahoma Aquifer: *Noel Osborn, Oklahoma Water Resources Board*

4:30 Health Aspects of the Central Oklahoma Aquifer: *Judith Duncan, Oklahoma State Department of Health*

5:00 Concluding Remarks: *Scott Christenson, U.S. Geological Survey*

GEOHYDROLOGY AND GROUND-WATER FLOW SIMULATION OF THE CENTRAL OKLAHOMA AQUIFER

By Scott Christenson
U.S. Geological Survey
Oklahoma City, Okla.

ABSTRACT

The Central Oklahoma aquifer underlies 3,000 square miles of central Oklahoma and consists of Permian-age red beds including, in descending stratigraphic order, the Garber Sandstone, Wellington Formation, and Chase, Council Grove, and Admire Groups. These Permian-age geologic units are overlain by Quaternary-age alluvium and terrace deposits, which occur along streams. The aquifer is a major source of water for municipal, industrial, commercial, and domestic use. Ground-water withdrawals, except for domestic use, were estimated to have peaked in 1985 at 13,900 million gallons but declined to 7,860 million gallons by 1989. Domestic withdrawals were estimated to be 1,685 million gallons in 1980.

The Garber Sandstone and the Wellington Formation consist of lenticular beds of fine-grained, cross-bedded sandstone interbedded with siltstone and mudstone. The sand grains are predominantly quartz, and the sandstone is friable. These units are believed to have been deposited in a fluvial-deltaic sedimentary environment, and the lithologic variability can be very large, even over distances as short as a few feet. In the central part of the aquifer, the lithology of the Garber Sandstone is predominantly sandstone. However, away from the central part of the aquifer, the Garber Sandstone grades into alternating layers of sandstone, siltstone, and mudstone, and is difficult to distinguish from the underlying Wellington Formation. In a few wells completed in the Garber Sandstone and Wellington Formation in the central part of the aquifer, more than 70 percent of the total thickness penetrated is sandstone. Percent sandstone decreases in all directions from the central part of the aquifer; about 40 percent of the total thickness is sandstone near the aquifer's boundaries. Median percent sandstone in the Garber Sandstone and Wellington Formation is about 60 percent.

The Garber Sandstone and Wellington Formation are at the surface in the central part of the aquifer, but have been removed by erosion in the east. Where a complete section is present, the combined thickness of these geologic units ranges from 1,165 to 1,600 feet, with a median thickness of 1,510 feet, as estimated from 257 selected wells distributed throughout the aquifer. A few wells completed in the Garber Sandstone and Wellington Formation yield as much as 600 gallons per minute, but because the sandstone is fine-grained, yields generally range from 200 to 400 gallons per minute in wells designed for maximum yield.

Stratigraphically below the Wellington Formation are the Permian-age Chase, Council Grove, and Admire Groups. Where a complete section is present, the combined thickness of these groups ranges from 570 to 940 feet, with a median thickness of 745 feet, as estimated from 321 selected wells distributed throughout the aquifer. In surface exposures in the eastern part of the aquifer, these groups appear to have similar lithologies. They consist of beds of fine-grained, cross-bedded sandstone, shale, and thin limestone. Median percent sandstone is 26 percent. In the central part of the aquifer, wells are completed in the Wellington Formation and in one or more of the underlying Chase, Council Grove, and Admire Groups. East of the outcrop of the Wellington Formation, wells that are completed only in the Chase, Council Grove, and Admire Groups generally yield 10 to 100 gallons per minute; a few wells yield as much as 120 gallons per minute.

The structural geology of the Central Oklahoma aquifer is very simple, with no major faults mapped at the surface. The regional dip is to the west at about 50 feet per mile. The Permian-age geologic units are confined in the western third of the aquifer by the overlying Hennessey Group. Freshwater in the aquifer is underlain everywhere by brines. Maximum thickness of the freshwater zone is about 900 feet, near the center of the aquifer.

Median values of aquifer properties were estimated as follows: recharge, 1.6 inches per year; porosity 0.22; storage coefficient, 0.0002; transmissivity, 350 feet squared per day; and the horizontal hydraulic conductivity of sandstone strata, 4.5 feet per day. The ratio of horizontal to vertical hydraulic conductivity was estimated to be between 100:1 and 10,000:1.

A digital ground-water flow model was used to simulate the Central Oklahoma aquifer flow system. The model simulates flow in three dimensions and uses a block-centered, finite-difference approach. The Central Oklahoma aquifer flow model contained 40 columns, 60 rows, and, because vertical flow is significant, 12 layers. In the x- and y-dimensions, cells are 6,562 feet (2,000 meters) on a side, and cell spacing is constant throughout the simulated area. The model layers do not correspond to individual, dipping geologic units, as in many flow models. Instead, the layers are horizontal, and each cell is assigned to represent the geologic unit that is the thickest in that cell. All layers are 100 feet thick.

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

The ground-water flow and particle-tracking models simulated hydraulic heads, sulfate concentration, and ages of ground water (based on carbon-14 and tritium concentrations). Simulated heads could always be brought into reasonable agreement with measured heads by adjusting recharge and the ratio of horizontal to vertical hydraulic conductivity. Two slightly different sets of simulated aquifer properties were needed to reconcile the ground-water flow and particle-tracking models with measured sulfate concentrations and ground-water ages. A ratio of horizontal to vertical hydraulic conductivity of 10,000:1 was necessary to produce a good match between ages computed using the particle-tracking model and carbon-14 ages, as well as sulfate concentrations, but a ratio of 100:1 was necessary to produce the best agreement between ages computed using the particle-tracking model and tritium ages. The reason for this discrepancy has not been resolved.

The ground-water flow and particle-tracking models show that the regional ground-water flow system in the Central Oklahoma aquifer is very complex. In most of the eastern, unconfined part of the aquifer, ground water is recharged by infiltration from the land surface and then flows to nearby streams. In the western, confined part of the aquifer, ground water is recharged at a potentiometric high just east of the confining unit, flows westward under the confining unit, and then flows northward to discharge to streams far removed from the recharge area. The flowlines under the confining unit are long and travel times are large, on the order of tens of thousands of years.

THE GEOCHEMICAL EVOLUTION OF GROUND WATERS IN THE CENTRAL OKLAHOMA AQUIFER

By D.L. Parkhurst
U.S. Geological Survey
Denver, Colo.

ABSTRACT

The Central Oklahoma aquifer is a freshwater flow system that circulates in parts of the Garber Sandstone, Wellington Formation, and Chase, Council Grove, and Admire Groups. Most of the aquifer is unconfined, but the westernmost part is confined by the Hennessey Group. Water in the Central-Oklahoma aquifer and its confining layers varies widely in composition. Generally, calcium-magnesium bicarbonate water is found in the unconfined part of the Garber Sandstone and Wellington Formation; sodium bicarbonate water is found in the confined part of the Garber Sandstone and Wellington Formation and in the Chase, Council Grove, and Admire Groups; sulfate-rich water is found in and, in places, below the Hennessey Group; and sodium chloride water is found below fresh water throughout the study unit. Analysis of the chemical and petrographic data and geochemical modeling have identified the predominant geochemical reactions that control the ground-water compositions to be (1) uptake of carbon dioxide, (2) dissolution of dolomite and to a lesser extent calcite, (3) cation exchange of calcium and magnesium onto clay minerals with the release of sodium, (4) dissolution of gypsum, and (5) dispersion of fresh water with pre-existing brines. These reactions take place to different extents in different parts of the flow system, subject to the availability of the reactant phases.

In the unsaturated zone, recharge water takes up carbon dioxide that is generated by the respiration of plants. Partial pressures of carbon dioxide tend to be in the range of 0.1 to 0.01 atmospheres in recently recharged water, and carbon-13 isotope ratios are in the range of -10 to -20 permil (relative to Peedee Belemnite). The partial pressures and the isotope ratios indicate an unsaturated-zone source and not an atmospheric source of carbon dioxide. The unsaturated zone appears to be the only source of carbon dioxide in the aquifer system; no evidence is available to indicate production of carbon dioxide from organic matter within the saturated zone or upward migration of carbon dioxide from depth.

As a result of the uptake of carbon dioxide by water percolating through the unsaturated zone, dolomite and calcite dissolve, either within the unsaturated or within the saturated zone. Three lines of evidence suggest that dolomite is the primary carbonate reactant: (1) The abundance of dolomite (1 to 7 weight percent) is much greater than that of calcite (generally less than 1 percent or undetectable); (2) calcium and magnesium are present in equimolar concentrations in ground water; and (3) exchangeable calcium and magnesium in clays are present in approximately equimolar concentrations. The combination of uptake of carbon dioxide by recharge water and dissolution of dolomite produces waters in which calcium and magnesium are the predominant cations, and bicarbonate is the predominant anion.

In many parts of the shallow, unconfined aquifer, water is undersaturated with dolomite and calcite. In these locations, lack of carbonate minerals seems to limit the amount of carbonate dissolution. The pH in these parts of the aquifer ranges from about 6.0 to 7.25. In all other parts of the aquifer, water is saturated with dolomite and calcite, which indicates dolomite is dissolving in sufficient quantities to produce dolomite equilibrium. Dolomite equilibrium produces water compositions very close to calcite equilibrium; therefore, it is

not certain whether calcite dissolves, precipitates, or is not present to react. Ground water that has reacted to equilibrium with dolomite has a pH of about 7.5, in the absence of cation-exchange reactions. This ground-water composition is present almost exclusively in the unconfined part of the aquifer.

Apart from the uptake of carbon dioxide and the dissolution of dolomite, the most important reaction in the freshwater flow system is cation exchange on clays. Where calcium-magnesium bicarbonate water exists in the unconfined part of the aquifer, sodium concentrations in the water are small. Here, clays contain a small fraction of exchangeable sodium, frequently less than 1 percent of the exchangeable cations. By contrast, in the confined part of the aquifer and in the clay-rich parts of the unconfined aquifer, sodium concentrations in the water are large and calcium and magnesium concentrations are small. In these parts of the aquifer, the clays contain a large fraction of exchangeable sodium, up to 50 percent of the exchangeable cations. The transition in water compositions from small to large sodium concentrations is explained by an exchange of calcium and magnesium onto the clays with the release of sodium to the water. The cation-exchange reaction causes a small amount of dolomite to dissolve to maintain dolomite equilibrium. However, the primary effect of the dissolution is to raise the pH to the range 8.5 to 9.1 with only a small increase in the bicarbonate concentration.

Large sulfate concentrations in ground water in the study unit are caused by dissolution of gypsum. Large sulfate concentrations are found most commonly in the Hennessey Group. Large sulfate concentrations in the confined part of the Garber Sandstone appear to be caused by downward leakage from the Hennessey Group. Gypsum has been identified in cores from the Hennessey Group. Sulfur-34 ratios of ground-water samples with large sulfate concentrations generally are consistent with the sulfur-34 ratios of Permian-age gypsum (7.0 to 12.0 permil relative to Canyon Diablo Troilite). The other most likely source of sulfur, pyrite, can not account for the observed concentrations of sulfate because (1) the amount of oxidants initially in the ground water are insufficient to account for the amount of sulfate that is produced; (2) pyrite is a very rare constituent in core samples; and (3) the sulfur-34 ratios in sulfate in ground water are heavier than most pyrite sources.

One other reaction that is important to the major element chemistry of the Central Oklahoma aquifer is the mixing of fresh water with sodium chloride brines. Brines underlie the fresh water throughout the study unit and it is reasonable to assume that brines are present in fluid inclusions in rocks within the freshwater flow system. Bromide to chloride ratios in the brines indicate that the brines are derived from seawater. Similar bromide to chloride ratios indicate that the brines may be the source of chloride in fresh water. Large concentrations of chloride in ground water are most common in the deep parts of the aquifer and especially in the northwest part of the deep, confined aquifer.

Reaction-transport modeling using the the program PHREEQM provides a plausible synthesis of the available brine and freshwater data. The program is capable of modeling the simultaneous processes of advection, dispersion, and chemical reactions. The modeling scenario assumed the aquifer initially was filled with a brine composition typical of the most concentrated brine analyses. Fresh water was assumed to enter the aquifer and gradually displace the brines by advection and dispersion. Dolomite and calcite were assumed to be present within the aquifer at concentrations sufficient to maintain equilibrium throughout the modeled time period. The clays in the aquifer initially were in exchange equilibrium with the sodium, calcium, and magnesium concentrations in the brines. The modeled evolution of ground-water composition and exchangeable cations on clays is consistent with most of the available data. At a fixed point within the aquifer, the ground-water composition evolves with time from a sodium chloride brine, to a sodium bicarbonate water, and finally to a calcium magnesium bicarbonate water as fresh water displaces brines. At the same time, the clay composition evolves from a sodium-rich clay to a sodium-poor clay. Another modeling scenario that includes gypsum equilibrium can explain large sulfate concentrations, but only a few of the ground-water analyses have large sulfate concentrations and require this scenario.

GEOCHEMICAL STUDIES OF SOLID-PHASE MATERIALS IN THE CENTRAL OKLAHOMA AQUIFER: RELATION TO WATER QUALITY

By E.L. Mosier and J.L. Schlottmann
U.S. Geological Survey
Denver, Colo.

ABSTRACT

The site(s) and mechanism(s) for the mobilization of potentially toxic naturally occurring trace elements (arsenic, chromium, selenium, and uranium) into the ground water are among key questions concerning the water quality of the Central Oklahoma aquifer. To address these questions, we analyzed surficial and subsurface solid-phase materials collected from the Central Oklahoma aquifer to determine the abundance of their chemical constituents. The surficial material sampled included B-horizon soils and outcrop rocks from throughout the Central Oklahoma aquifer study area. Subsurface rock samples were collected from eight drill cores obtained from test holes placed at locations in the aquifer with known water-quality problems. Water samples were also collected from several water-bearing intervals within each of the test holes. The solid-phase samples were analyzed for their chemical constituents by an induction-coupled plasma-atomic emission technique for 40 elements, by hydride generation-atomic absorption spectroscopy for arsenic and selenium, and by delayed neutron activation analysis for uranium and thorium. Chemical and mineralogical studies of subsurface samples collected from the cores identified residence sites of the potentially toxic elements and variations in the composition of the rocks that relate to water-quality problems. The subsurface rocks have median concentrations of 6.2 ppm (parts per million) arsenic, 55 ppm chromium, 0.1 ppm selenium, and 2.59 ppm uranium. Abundances as great as 62 ppm arsenic, 170 ppm chromium, 110 ppm selenium, and 123 ppm uranium were detected; however, all elements are not necessarily enriched in any one sample. The enriched samples were mostly isolated limonitic sandstone lenses and small "grayish-green reduction spots."

The mobility of the elements in both typical and enriched subsurface rocks was assessed using a $NaHCO_3$ partial extraction technique and a 5-step sequential partial dissolution procedure. The $NaHCO_3$ extraction technique was used to mimic waters in the aquifer and was effective in extracting small amounts of arsenic, selenium, and uranium. Sequential extractions provide information about the mode of occurrence, availability, mobilization, and transport of trace elements. The sequential extraction procedure includes steps for dissolving elements contained in soluble (KCl), ligand-exchangeable (KH_2PO_4), acid-soluble (HCl), oxidizable (HCl-$KClO_3$), and residual (HF-HNO_3-$HClO_4$) phases on or in solid materials. Appreciable amounts of arsenic, selenium, and uranium were extracted from some samples by the soluble and ligand-exchangeable extractions, indicating that significant portions of these elements reside in phases that are readily available. Chromium was not detected in the soluble or ligand-exchangeable extraction steps, possibly because of a higher analytical detection level for chromium than for the other elements.

Results from the analyses of the surficial materials collected from the area of the Central Oklahoma aquifer show normal abundances for both major and trace elements when compared to elemental concentration ranges for soils from Western United States and worldwide sedimentary rocks. Although neither major nor trace elements were abnormally enriched in the surficial materials from the Central Oklahoma aquifer, areal distribution plots of anomalous concentrations within the sample data sets indicate areas of local enrichment.

Our interpretations suggest that as recharge water moves through the aquifer, its chemical composition changes, mainly owing to ion exchange with clay minerals and to dissolution of carbonate cements. Coupled with these changes, elements such as arsenic, chromium, selenium, and uranium disseminated in the rocks are oxidized to more soluble forms. The high pH of some aquifer waters (pH=9) along with the presence of dissolved oxygen augment desorption and oxidation of the elements; in turn, this process facilitates mobilization of the elements in the ground water.

MINERALOGY AND PETROGRAPHY OF PERMIAN ROCKS IN THE CENTRAL OKLAHOMA AQUIFER: IMPLICATIONS FOR GROUND-WATER QUALITY

By G.N. Breit
U.S. Geological Survey
Denver, Colo.

ABSTRACT

Water within the Central Oklahoma aquifer contains variable concentrations of major ions and potentially toxic elements such as arsenic, chromium, selenium, and uranium. These compositional variations are partly the result of reactions between water and the solid constituents of the aquifer. To understand these reactions, a detailed mineralogic and petrographic study of Permian rocks within the aquifer is underway as part of the U.S. Geological Surveys's NAWAQ Program. Variations in the abundance and composition of solids detected by this study are consistent with changes in ground-water composition and suggest that dissolution, precipitation, oxidation, and ion exchange are active processes in the aquifer.

Cores from eight test holes were sampled to reflect the abundances of rock types intersected by each hole. Limonitic sandstones and zones of gray-green reduced rocks were also sampled because they tend to have unusually high concentrations of arsenic, chromium, selenium, or uranium. Bulk mineralogy of the aquifer was determined by analyzing 196 samples using whole-rock X-ray diffraction. A petrographic study of sandstones, conglomerates, and siltstones was conducted using optical microscopy and a scanning electron microscope to establish the origin and alteration of solid constituents. In addition, the <2 μm fraction from 70 samples was analyzed to determine the mineralogy of clay-sized phases.

Detrital components of Permian rocks in the aquifer include quartz, illitic clays, feldspars, dolomite, biotite, muscovite, chlorite, chert, rock fragments, and heavy minerals. Quartz and illitic clays, which average 56 and 31 weight percent respectively, are the most abundant constituents. The clay-sized fraction typically contains illite, illite-smectite, kaolinite, chlorite, and chlorite-smectite; a few samples contain abundant vermiculite and smectite. Recognized authigenic minerals include barite, calcite, dolomite, geothite, hematite, kaolinite, manganese oxides, and quartz as overgrowths. Small black "spots" and adjacent rocks within reduced zones contain several rare phases include häggite ($V_2O_3(OH)_3$), tyuyamunite ($Ca(UO_2)_2(VO_4)_2 \bullet H_2O$), clausthalite ($PbSe$), native selenium, volborthite ($Cu_3(VO_4)_2 \bullet 3H_2O$), and a U-Ti phase.

Samples from each of the test holes are mineralogically similar; small variations in mineral abundances can be explained by the relative amount of mudstone and sandstone in the cored intervals. Samples from one test hole (NOTS4), in an area having relatively good water quality, lack dolomite, chlorite, and plagioclase relative to the other test holes. The absence of these minerals suggests that larger volumes of recharge water passed through rocks near NOTS4 and removed the minerals by dissolution.

Petrographic observations suggest that dissolution, precipitation, and oxidation have altered solid constituents of the aquifer and that these processes, as well as ion exchange, affect the composition of modern ground water. Feldspars, carbonates, rock fragments, chert, and some chlorite have dissolved, which could account for the large porosity (average of 22 volume percent) in most sandstones. As these minerals dissolve, elements such as

silicon, aluminum, iron, and manganese are redistributed and precipitate as quartz overgrowths, kaolinite, and iron and manganese oxides. Minerals that contain metals in a low oxidation state such as biotite, pyrite, häggite, dolomite, and clausthalite are typically associated with secondary oxidized phases such as goethite, hematite, tyuyamunite, volborthite, manganese oxides, and native selenium. A more subtle change in solid constituents in the aquifer is through ion exchange between dissolved ions and elements bound to clay and iron oxide minerals. The abundance of exchangeable calcium and magnesium relative to exchangeable sodium in clay minerals varies in the aquifer and is reflected in the abundance of major ions in the ground water. Iron oxides contain local concentrations of arsenic, some of which is bound in exchangeable sites. Changes in water chemistry may cause arsenic and other metal anions to desorb resulting in locally large abundances of metals in the ground water. Changes in solid constituents in the aquifer and processes responsible for these changes are being applied by other scientists in the NAWQA Project to understand the chemical composition of the ground water.

IMPROVING WATER QUALITY AND QUANTITY IN PERFORATED WATER WELLS

By L.C. Simpson
Garber-Wellington Association
Oklahoma City, Okla.

ABSTRACT

The Garber-Wellington Aquifer of central Oklahoma is utilized by thousands of water wells. Most of the municipal and some of the deep industrial wells were completed with 'oil field' type construction. These wells have steel casing which is cemented the entire length of the well. Geophysical logs reveal the good sandstone layers and the well casing is then perforated to allow water production. Perforated wells produce large quantities of water and are constructed to control water quality. The occasional water quality problem can be corrected in a perforated well. Currently construction techniques of "screened" wells prevents, in most cases, corrective actions to seal off poor quality water zones.

Water wells in the Garber-Wellington Aquifer occasionally experience problems such as: reduced production, reduced well depth, mud or sand and toxic elements in the produced water, and rapid increases in bacterial counts. These problems are usually examined by a traditional engineering firm philosophy. Corrective measures are traditionally to examine the pump and tubing, acidize the well, or blindly reperforate the casing, or dump cement in the bottom of the hole. Such actions rarely eliminated the problem and often resulted in the well being abandoned or plugged. Then, at great expense, other water supply wells are drilled to replace the impaired wells.

Now a combination of subsurface geology and geochemistry, downhole camera videos, and proper interpretation of geophysical logs can provide data to better identify and eliminate most water well problems. When the problem with a well is defined by using these tools and other new technologies, a proper solution to these troubles can be devised.

The use of a downhole camera is the best known method to use for the initial definition of almost any water well problem. While reduced well yield may be due to pump or tubing problems, it is commonly due to incrustation, casing collapse or reduced well depth. Using a downhole camera can allow you to see what is wrong with the well better and cheaper than any other method. The camera can show sediment entry points, perforations and casing crack locations more accurately than any other survey.

Only downhole camera videos can view well incrustacean, help define the type, determine how to remove it and how to impede it's growth in the future. Shallow casing leaks can contaminate a water well. Former, temporary, and present casing leaks can only be seen on the downhole video.

If there is no data on a well the camera can very accurately define: the water well's casing string, casing quality, open perforation locations, static water level, and obstructions or fill in the well casing.

Upon completion of the camera work, geophysical logs can be used to supply data on the materials behind the casing. A Cement bond - Gamma Ray log can be used to determine the extent of cavities behind the casing. This can be valuable in wells producing sediment or toxic elements. The cavities may have formed because of a poor cement job or during sediment flow into the well. Cavities can be a pathway for toxins that were intended to be sealed off from the well bore.

Gamma Ray - Neutron logs can be run through casing and used to define thickness and porosity of the sandstones encountered in the well. Comparisons with the perforation records will show if the best sands were opened to the well for water production. A few precisely placed additional perforations could increase well yield.

Water chemistry problems can be addressed in many ways. If open hole logs were run, zones containing chlorides or sulfates can be defined and avoided or sealed off. If no logs have been run, a salinity log can indicate perforations that are producing saltwater. Other water chemistry problems can be defined by individually sampling each set of perforations. Analysis of each sample will define the source of the contaminants in the well.

Analysis of the camera surveys, geophysical logs, and geochemical data allows a method of correcting the problem to be developed. Perforations or casing leaks producing sediments, toxic elements or biota can be squeezed off with certain packers and special but easily available cements. There are various procedures for removing sediment or junk which is filling water wells and reducing production. Casing incrustaceans can be removed by reaming, brushing or acidizing. A well maintenance program can be developed that will help retard the growth of these various incrustaceans.

Water quality and quantity can be preserved on good wells and improved on deteriorating wells. These alternatives are much cheaper than drilling new water supply wells which may encounter the same problems at some time in the future.

SPATIAL DISTRIBUTION OF CHLORIDES IN DRINKING WATER WELLS IN THE CENTRAL OKLAHOMA AQUIFER

By B.E. Vieux, R.C. Knox, N. Gaur, and J. Black
School of Civil Engineering and Environmental Science
University of Oklahoma, Norman, Okla.

ABSTRACT

Oil and gas exploration and production activities inevitably encounter large volumes of highly concentrated seawater referred to as brine. Produced brines can be reinjected under high pressures as part of a waterflood process during secondary recovery operations. These brines can migrate upward through faults, fractures, abandoned boreholes, or poorly sealed wells to overlying fresh ground-water formations. Casing leaks in injection or production wells can introduce contamination directly into ground-water formations. In addition, poor maintenance and housekeeping procedures at production and injection facilities can lead to surface leaks or spills that can migrate down to ground-water formations.

This paper presents a case study of the spatial distribution of chloride concentrations in a segment of the Central Oklahoma aquifer system. During the past five years, a number of residents of a rural area north of Norman, Oklahoma, have had to abandon their private water wells because of increasing dissolved solids concentrations. A suspected source of the increased chloride concentrations is the oil-field production and injection activities in the area. The spatial correlation of increased chloride concentrations with respect to oil production and brine injection facilities is investigated using a Geographic Information System, the Geographic Resource Analysis Support System (GRASS), developed by the U.S. Army Corps of Engineers, Construction Engineering Research Laboratory. Using the Universal Transverse Mercator coordinates of the various water wells and oil-field facilities, along with the reported chloride concentrations in the wells, two-dimensional maps and three-dimensional surfaces are developed. These graphics depict the proximity of the chloride-contamination areas to the probable oil-field facility guiding further investigation, remediation, and analysis.

CONTAMINANT MIGRATION IN THE CENTRAL OKLAHOMA (GARBER-WELLINGTON) AQUIFER: LABORATORY STUDIES

By D. Sabatini, B. Shiau, T. Soerens, and C. Palmer
School of Civil Engineering and Environmental Science
University of Oklahoma, Norman, Okla.

ABSTRACT

The Central Oklahoma (Garber Wellington) Aquifer is a vital ground-water resource. An understanding of the movement of contaminants in this aquifer is important relative to responding to episodes of ground-water contamination as well as in developing strategies for protection of this resource. The research to be presented focuses on the migration of hydrophobic (nonpolar–water disliking), amphiphilic (polar and nonpolar moieties), and ionogenic (weak organic acid) compounds in Garber Wellington media, as observed in laboratory batch and column studies. The hydrophobic chemicals include two pesticides (atrazine and diuron) and two gasoline components (o- and m-xylene), the amphiphilic chemicals include four nonionic surfactants (polyoxyethoxylated alkylphenols), and the ionogenic chemical is rhodamine WT (a common surface and ground-water tracer). The impacts of cosolvents (e.g., acetone and water) on the migration of the rhodamine WT will also be presented; this situation may be experienced in the vicinity of landfills containing organic solvents and contaminants. The use of rhodamine WT as a conservative and sorbing ground-water tracer will also be discussed; ground-water tracing has implications relative to detection of releases, remediation of releases, and delineation of protection zones.

HIGH PERFORMANCE CAPILLARY ELECTROPHORESIS METHODS FOR THE SEPARATION OF PESTICIDES

By Z. El Rassi and J.Cai
Department of Chemistry, Oklahoma State University, Stillwater, Okla.

ABSTRACT

High performance capillary electrophoresis (HPCE) employing sophisticated instrumentation and advanced capillary technology is emerging as a important microseparation technique of high resolving power and unique selectivity. This paper is concerned with expanding the utility of the technique to the analysis of pesticides and herbicides at low level.

Thus far, high performance liquid chromatography (HPLC) and gas chromatography (GC) have been the most widely used analytical techniques for the analysis of organics in water. However, more than 80 percent of organics are not amenable to GC due to their high boiling points. The alternative technique for the analysis of nonvolatile compounds has been HPLC. HPCE is well placed to complement HPLC and to achieve efficiency and detection sensitivity several fold higher than can HPLC in some applications.

We will present preliminary results on the electrophoretic determination and separation of ionic and neutral pesticides and herbicides as well as on the separation of polycyclic aromatic hydrocarbons.

Our initial studies have shown that capillary zone electrophoresis with on-column UV detection and untreated fused-silica capillaries of 50 μm inner diameter is well suited for the separation of cationic herbicides on the time scale of a few minutes. High separation efficiencies were obtained at an applied voltage of 15 kV. The separation medium permitted the baseline resolution of the quaternary ammonium ion herbicides, paraquat and diquat. The two cationic herbicides having the same net charge and similar molecular weights separated on the basis of differences in their molecular shape. The detection limits for paraquat and diquat were 15.4 and 16.8 femtomoles, respectively, with a UV detector.

To further develop capillary zone electrophoresis in the area of herbicides and pesticides, we have made some initial studies on the on-line preconcentration of dilute samples with tandem octadecyl capillaries-capillary zone electrophoresis. The coupled format was investigated with two herbicides, prometryne and prometon. Large volume of samples could be introduced into the capillaries without affecting separation efficiencies, thus permitting the determination of dilute samples.

In order to expand the utility of CZE to neutral herbicides and pesticides, we have developed novel buffer systems for the separation and quantitative determination of these species by micellar electrokinetic capillary chromatography (MECC), a branch of capillary electrophoresis. In these initial studies we have investigated the potentials of novel micellar pseudo-stationary phases. These phases are based on the complexation of alkylglucoside surfactants and borate ions at high pH. These novel micelles present several advantages over traditionally used ones and expanded the applicability of MECC to difficult to separate neutral organics. The alkylglucosides-borate micelles are characterized by an adjustable surface charge density and balanced hydrophile-lipophile character that allowed more equitable partitioning of the solute between the aqueous phase and the pseudo micellar phase and also the adjustment of the separation window for a particular separation problem.

The various electrophoretic systems developed in these initial studies will be discussed and examples of separation of relevance to water research will be presented.

GROUND WATER QUALITY BENEATH AGRICULTURAL LANDS IN CENTRAL OKLAHOMA

By S.J. Smith, J.W. Naney, and A.N. Sharpley, USDA-ARS, National Agricultural Water Quality Laboratory, Durant, Okla.

ABSTRACT

For more than a decade, part of our research has been to assess the impact of agricultural practices on ground-water quality of watersheds in major land resource areas of Oklahoma and Texas. Presented here are results for 12 shallow wells (<20 meter (m) water table depth) on two cropland and two grassland watersheds in the Reddish Prairie land resource area near El Reno, Oklahoma. Three wells were installed, typically in the direction of flow down the center of each 1.6 hectare (ha), 3 to 4 percent slope, watershed. The wells, sampled seasonally, were bailed one day prior to sampling to ensure samples represented aquifer water. General chemical analyses were conducted according to standard procedures (Smith, et al., 1991). Samples were sent to the Oklahoma Department of Agriculture State Laboratory for pesticide analyses. Environmental Protection Agency publications were used as guides for ground-water quality standards (EPA, 1976; Williams, et al., 1988).

Watershed stratigraphy involved terrace deposits on the Cloudchief and Whitehorse formation of the El Reno group, and the lithology was varied, consisting of sand, shale, and gypsum. The dominant soil was Bethany-Kirkland silt loam (Typic hapludolls). The conventional till watershed was in double-crop wheat/sudangrass management, and the no-till watershed was in wheat. The grass watersheds were in native tall grasses (primarily bluestems), and the improved grass watershed received fertilizer and herbicide (phenoxy and picloram) on an occasional basis (6 of 12 years). Fertilizer and herbicide application rates were in accordance with accepted practice. More detailed information about the watersheds and their management has been given in earlier publications (Smith, et al., 1987; 1991).

A summary of the chemical analyses for the wells is given in Table 1. Analyses include nitrate-N, ammonium-N, soluble phosphorus, pH, and conductivity. The data indicate the main area of water quality concern to be the increased nitrate-N contents associated with the no-till practice. Here, the average N levels were 13.3 milligrams per liter (mg/L), compared to the 10 mg/L acceptable limit for potable water. Moreover, the yearly N levels have increased from 5 mg/L in 1983 to 20 mg/L in 1990. In an effort to ascertain more about the high nitrate levels, the no-till watershed was sampled in 30 centimeter (cm) increments down to the 180 cm soil depth, to determine whether nitrate was accumulating below the root zone. To date, no evidence of a nitrate buildup has been observed. Possibly, some nitrate movement to the ground water is occurring by preferential flow, due to more undisturbed, large pores and a wetter soil profile associated with no-till.

In 1985, well samples from the improved grass watershed were analyzed for phenoxy levels, and in 1991 for both phenoxy and picloram levels. In all cases, levels have been <0.01 μg/L, except for one 0.60 μg/L picloram detection. Present health advisory limits for picloram in ground water are 490 μg/L.

In summary, the major water-quality impact from watershed management practice to date has been with the increased nitrate levels associated with no-till. Because groundwater problems can take several years to become established, we plan a continual periodic monitoring of the watershed wells, in addition to occasional soil profile sampling for possible contamination. Moreover, we plan to determine whether more timely soil testing and more precise placement of N fertilizer may alleviate the nitrate situation with the no-till wells.

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Table 1. *Analyses of watershed wells (1979–83 through 1990)*

Management	NO_3-N		NH_4-N		SP		pH		Conductivity	
	$\overline{X}$	range	$\overline{X}$	range	$\overline{X}$	range	$\overline{X}$	range	$\overline{X}$	range
	- - - - - -	- - -mg/L- - -	- - - - - -	- - - - - -	- - - - - -	- - - - - -			- - -µmho/cm- - -	
Convent. Till	1.4	0.05–8.8	0.13	0.0–1.4	0.03	0.0–0.08	8.0	6.4–8.4	1057	273–4060
No-Till	13.3	1.5–34.4	0.04	0.0–0.2	0.03	0.0–0.45	7.9	6.5–8.4	1597	1050–4330
Grass	1.5	0.0–6.6	0.33	0.0–5.9	0.10	0.0–0.34	7.6	6.6–8.4	1485	140–4022
Imp. Grass	1.1	0.0–9.8	0.05	0.0–0.2	0.02	0.0–0.12	7.8	6.4–8.4	1496	196–4239

FACTORS RELATED TO GROUND-WATER QUALITY IN THE OKLAHOMA CITY URBAN AREA

By Alan Rea and Scott Christenson
U.S. Geological Survey
Oklahoma City, Okla.

ABSTRACT

The Central Oklahoma aquifer underlies about 8,000 square kilometers of central Oklahoma, where the aquifer is used extensively for municipal, industrial, commercial, and domestic water supplies. The aquifer was selected for study as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program, and an investigation of the quality of ground water under the Oklahoma City urban area was undertaken as part of the study.

Sampling networks were established to investigate the quality of the ground water under the Oklahoma City urban area and the overall water quality of the Central Oklahoma aquifer. An urban network was established in the central part of the urban area. Two low-density survey sampling networks were established to assess the overall water quality of Permian-age geologic units and alluvium and terrace geologic units. Wells included in all networks were randomly selected. All wells sampled were existing water-supply wells, mostly but not exclusively domestic supply wells. Water samples were collected and analyzed for 56 inorganic constituents, 44 volatile organic compounds, and 44 pesticides, using standard methods.

Pesticides were detected only in wells that had detectable concentrations of tritium. Tritium is thus a directly measurable indicator of a well's vulnerability to pesticide contamination. Organic pesticides were not commonly used in the United States until about the time tritium concentrations became elevated due to atmospheric nuclear testing between 1952 and the mid-1960's. The presence of detectable tritium does not indicate that a well will be contaminated with pesticides; rather, detectable tritium indicates that there are flowpaths to the well by which post-1952 recharge water is entering the well. The absence of detectable tritium indicates that the well is not receiving significant quantities of post-1952 recharge water.

A contingency table analysis indicated that the geologic unit in which the wells were completed did not affect the proportion of wells with detectable concentrations of volatile organic compounds or pesticides. This result was unexpected because the Permian-age geologic units are geologically very different from the alluvium and terrace deposits.

Several different methods were used to categorize land use at the sampled wells as either urban or nonurban. These methods included: the sampling network (all wells in the low-density survey sampling networks were categorized as nonurban); field sheets completed by project personnel visiting the wells; and overlays on land-use and sewered-area maps using point-in-polygon overlays, buffer overlays, and a particle-tracking analysis.

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

A contingency table analysis indicated that the proportion of wells with detectable pesticides or volatile organic compounds may or may not be significantly different between urban and nonurban land uses, depending on the method used to categorize urban land and how the volatile organic compounds are grouped. Based on the results of statistical tests and field work, there is evidence that the sources of organic contaminants often are near the wellhead. This may indicate that the shallow seals and gravel packs common to well construction in the area are providing pathways for contaminants to enter the wells.

An important result of this investigation is that the comparisons between sampling networks (which represent the basis of the sampling design) consistently showed that the presence or absence of organic constituents, as well as the concentrations of many of the inorganic constituents, were significantly different between urban and nonurban wells. Additionally, the median concentrations of inorganic constituents that were significantly different were larger in the urban wells than in nonurban wells, except fluoride, cadmium, and chromium. For the land-use categorizations that showed significant differences, median concentrations of fluoride were smaller in the urban wells, and the median concentrations of cadmium and chromium were equal between urban and nonurban wells. The median concentrations of cadmium and chromium were less than the minimum reporting level, but the upper ends of the distributions showed significant differences. The proportion of wells with detectable organic compounds was higher in the urban network than in the other networks.

Potential causes of inorganic and organic contamination include changes in recharge, lawn watering, leakage from municipal water and sewer lines, road salt, fertilizers, oil-field brines, pesticide usage, manufacturing, and leaking underground storage tanks. The observed contamination probably results from multiple sources; the dominant sources could not be determined. Although only samples from wells completed in the Garber Sandstone and Wellington Formation were compared, the possibility cannot be completely discounted that differences within these geologic units may account for the differences in concentrations of inorganic constituents.

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