NUTRIENTS AND PESTICIDES IN GROUND WATER OF THE OZARK PLATEAUS IN ARKANSAS, KANSAS, MISSOURI, AND OKLAHOMA

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96-4313

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by James C. Adamski

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CONVERSION FACTORS

Multiply	By	To obtain
inch (in.)	25.40	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
inch per year (in/yr)	25.40	millimeter per year
foot per second (ft/s)	0.3048	meter per second
square mile (mi^2)	2.590	square kilometer
gallon per minute (gal/min)	0.06309	liter per second
ton	0.9072	megagram
pound per acre per year	0.1836	kilogram per hectometer per year

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

$$°F = (1.8 \times °C) + 32$$

NUTRIENTS AND PESTICIDES IN GROUND WATER OF THE OZARK PLATEAUS IN ARKANSAS, KANSAS, MISSOURI, AND OKLAHOMA

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ABSTRACT

A total of 229 ground-water samples were collected from 215 sites as part of the Ozark Plateaus study unit of the National Water-Quality Assessment Program. These samples were collected from 1993 through 1995 using a network of springs and wells with three scale-dependent components. The first component, the study-unit survey, consisted of 99 randomly selected springs and domestic wells in the Springfield Plateau and Ozark aquifers. The second component, two land-use studies, consisted of 42 springs and domestic wells in a poultry-dominated agricultural area and 40 springs and domestic wells in a cattle-dominated agricultural area overlying the Springfield Plateau aquifer. The third component, the small-watershed study, consisted of 4 springs, 18 domestic wells, and 11 monitoring wells in a small basin within the poultry land-use study area. Samples were analyzed for major ions, nutrients, dissolved organic carbon, methylene blue active substances, tritium, and 88 pesticides and metabolites.The water-quality data from these samples were analyzed with descriptive and statistical methods.

Nitrite plus nitrate, which was detected more often and in greater concentrations than any of the other nutrients, ranged from less than 0.05 to 25 milligrams per liter as nitrogen. Nitrite plus nitrate concentrations positively correlated to percent agricultural land use around each site. Median nitrite plus nitrate concentrations generally were greater in samples from springs than in samples from wells. Concentrations of nitrite, ammonia, and ammonia plus organic nitrogen were also affected by land use and also by concentrations of dissolved oxygen in the ground water. Concentrations of phosphorus and orthophosphate probably were affected by land use and also by phosphorus solubility.

Pesticides were detected in 80 of 229 samples from 73 of 215 sites. A total of 20 pesticides were detected with a maximum of 5 pesticides detected in any 1 sample. The most commonly detected pesticides were tebuthiuron, atrazine, prometon, desethylatrazine, and simazine. Maximum concentrations ranged from 0.003 to 1.0 microgram per liter. The occurrence and distribution of pesticides were related to land use. Percent agricultural land use was greater for samples with pesticides detected than for samples with no pesticides detected. Pesticides were detected more often in samples from springs than in samples from wells. The occurrence of pesticides also was related to seasonality and chemical characteristics, such as solubility and persistence, of the compounds.

INTRODUCTION

In 1991, the U. S. Geological Survey (USGS) began implementation of the National Water-Quality Assessment (NAWQA) Program to provide a consistent description of the Nation’s ground- and surface-water resources. The NAWQA Program consists of 60 river basins or aquifer systems, referred to as study units, throughout the Nation. The objectives of the NAWQA Program are to 1) determine the general ground- and surface-water quality of the 60 study units, 2) determine the natural and anthropogenic factors affecting the water quality, and 3) determine any changes in water quality with time. Implementation of the study units is on a rotational basis, with the first 20 being implemented in 1991 (Leahy and others, 1990).

The Ozark Plateaus study unit was among the first 20 study units investigated (Freiwald, 1991). The aquifers underlying the karst terrane of the study unit are complex and extremely susceptible to contamination. Furthermore, the study unit has experienced recent growth and will probably experience future growth in population and agricultural land use. Hence, there is concern that the ground-water quality of the study unit will be adversely affected by elevated concentrations of nutrients and pesticides.

Purpose and Scope

The purpose of this report is to describe the ground-water quality of the Ozark Plateaus study unit with regard to nutrients and pesticides. The report contains a brief environmental-setting description of the study unit including climate, physiography, geology, hydrogeology, and major land uses. This report also contains a description of the ground-water sampling network and a summary and interpretation of nutrient and pesticide water-quality conditions determined from 3 years (1993-95) of ground-water sample collection. Natural and anthropogenic factors affecting nutrients and pesticide water-quality conditions as indicated by statistical analyses are also discussed. This report is part of a series of reports on the Ozark Plateaus study unit.

Location

The Ozark Plateaus study unit is approximately 48,000 square miles (mi^2) and includes parts of northern Arkansas, southeastern Kansas, southern Missouri, and northeastern Oklahoma (fig.1). The study unit includes most of the Ozark Plateaus Province and small parts of the Osage Plains section of the Central Lowland Province and the Mississippi Alluvial Plain section of the Coastal Plain Province (Adamski and others, 1995).

Previous Investigations

The NAWQA Program is described in reports by Hirsch and others (1988) and Leahy and others (1990). The objectives of the Ozark Plateaus study unit were described by Freiwald (1991). The objectives and approach of the ground-water data collection network of the study unit were described by Pugh and Adamski (1993).

Previous studies have addressed the ground-water resources of the Ozark Plateaus Province. Regional ground-water flow was simulated by Imes and Emmett (1994). Regional ground-water geochemistry was described by Baker and Leonard (1995). Ground-water geochemistry of Missouri was investigated by Feder (1979). The ground-water resources of southern Missouri and northern Arkansas were investigated by Harvey (1980). The hydrogeology and water quality of northwestern Arkansas were investigated by Lamonds (1972). Steele and Adamski (1987) and Leidy and Morris (1990) determined that ground-water quality was affected by agricultural land use in northwestern Arkansas. Few of these studies investigated the ground-water quality of large parts of the Ozark Plateaus. Furthermore, methods of collecting water-quality data have not been consistent through time, and water-quality data are not available for a wide range of constituents.

Several studies have investigated the ground-water quality in areas adjacent to the Ozark Plateaus. Ground-water samples were collected from near-surface aquifers in all or parts of 12 states (Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin) and analyzed for selected herbicides (Kolpin and others, 1994). Samples were collected in 1991 from 303 wells in areas where at least 25 percent of the land had been planted in corn or soybeans. Atrazine and two of its metabolites were the most commonly detected constituents (22.1 percent of samples); other pesticides detected included alachlor, cyanazine, metolachlor, metribuzin, prometon, and simazine. Maximum concentrations ranged from 0.27 to 2.32 micrograms per liter (μg/L). A reporting limit of 0.05 μg/L was used.

Ground-water samples were collected in four counties in west-central Missouri and analyzed for selected herbicides (Ziegler and others, 1994). Row-crop agriculture accounted for 25 to 38 percent of the land use in the four counties. Results were similar to those of Kolpin and others (1994). Pesticides were detected in 29 of 92 samples (32 percent) collected in 1990 and in 27 of 100 samples collected in 1991. Pesticides detected included alachlor, atrazine, cyanazine,

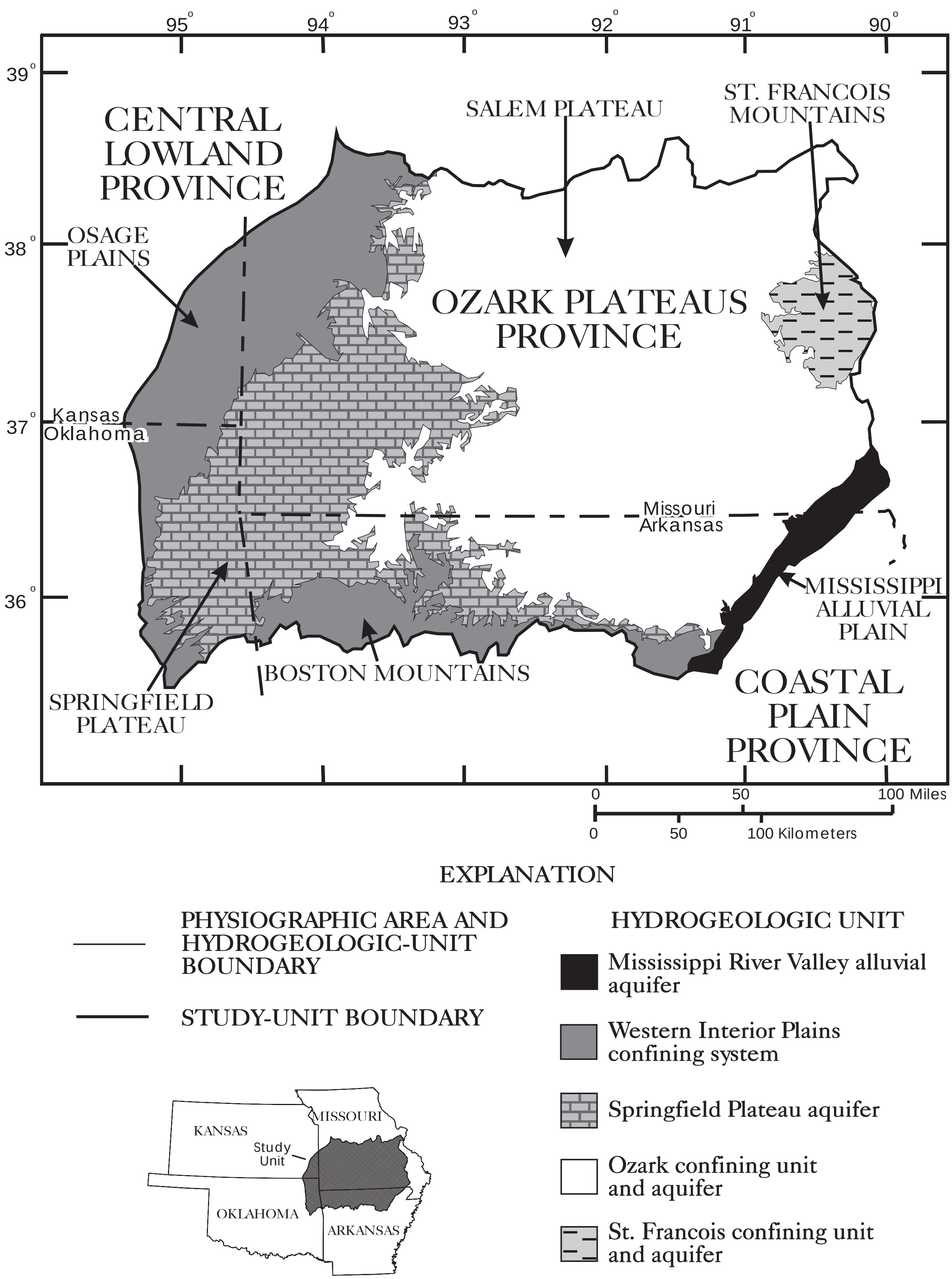

Figure 1. Location of Ozark Plateaus study unit, physiographic areas, and surficial extent of hydrogeologic units.

metolachlor, metribuzin, prometon, propazine, and simazine. Atrazine, the most commonly detected constituent, had concentrations ranging from less than the reporting limit of 0.05 to 8.4 µg/L.

As part of NAWQA Program studies of the Ozark Plateaus, historical nutrient and pesticide data were analyzed to better define the water quality of the study unit (Davis and others, 1995; Bell and others, 1996). These existing data were collected by the USGS and other Federal and State agencies from 1970 to 1992. Nutrient data from 395 ground-water sites were compiled. Results (Davis and others, 1995) indicated that nutrient concentrations, particularly nitrite plus nitrate, in ground water were related to hydrogeology and land use. Median nitrite plus nitrate concentration in ground water was 0.25 milligrams per liter (mg/L) as nitrogen. Fifteen of the samples, collected from sites located primarily in agricultural areas, had nitrite plus nitrate concentrations that exceeded the maximum contaminant level (MCL) of 10 mg/L in drinking water established by the U.S. Environmental Protection Agency (1986). In addition, nitrite plus nitrate concentrations were significantly greater in water samples collected from springs than in water samples collected from wells.

Pesticide data were available for 103 samples collected from 1970 to 1990 from 92 ground-water sites within the study unit (Bell and others, 1996). Ninety-four percent of the sites were located in the Osage Plains or Mississippi Alluvial Plain sections of the study unit. Samples were analyzed for a total of 44 pesticides and metabolites, of which 7 were detected in 31 samples from 18 sites. Pesticides were detected only in samples collected from the Osage Plains section. The most commonly detected pesticides were atrazine, metolachlor, alachlor, and prometon. With the exception of atrazine (8.2 µg/L) and prometon (2.4 µg/L), maximum concentrations of pesticides in the samples were less than 1.0 µg/L (Bell and others, 1996).

Pesticide data collected in 1993 and 1994 and included in this report have previously been evaluated. The results indicated that pesticides were detected more often in samples from the Springfield Plateau aquifer than in samples from the Ozark aquifer. Results also indicated that pesticides were detected more often in samples from springs than in samples from wells (Adamski, 1994; Adamski and Pugh, 1996).

Acknowledgments

The author is grateful to the homeowners and landowners who allowed access to domestic wells and springs. The author expresses appreciation to William Bush and William Prior of the Arkansas Geological Commission for assistance in drilling and installation of monitoring wells. The author also thanks the following individuals for assisting in data-collection activities: Cynthia Brookshire and James Vandike of the Missouri Division of Geology and Land Survey; and Aaron Pugh, Richard Bell, Dale Ferree, David Freiwald, Gerard Gonthier, Phillip Hays, Royce Johnson, Robert Joseph, Valarie Leidy, Gilbert Malone, Christopher O'Dell, Larry Remsing, and Gregory Stanton of the U.S. Geological Survey.

ENVIRONMENTAL SETTING

This section contains a brief description of the environmental setting of the Ozark Plateaus study unit. Additional information on the environmental and hydrologic setting of the study unit is in Adamski and others (1995).

Climate

The Ozark Plateaus study unit has a humid, temperate climate. Mean annual air temperature ranges from 56 degrees Fahrenheit (^{o}F) in the northeastern part of the study unit to 60 ^{o}F in the southwestern part. Annual precipitation averages about 38 inches per year (in/yr) in the northern part of the study unit to about 48 in/yr near the southern boundary. Precipitation generally is the greatest in mid to late spring (April to June) and least in winter (December to February) (Adamski and others, 1995).

Physiography

The Ozark Plateaus study unit includes most of the Ozark Plateaus Province (Fenneman, 1938). The study unit also contains small parts of the Osage Plains and Mississippi Alluvial Plain, which are sections of the Central Lowland Province and Coastal Plain Province, respectively (Fenneman, 1938; Adamski and others, 1995). Because ground-water samples for this study were collected only from parts of the Ozark Plateaus Province, further discussion of the environmental setting of the study unit will be limited primarily to the Ozark Plateaus Province.

The Ozark Plateaus Province has an area of about 40,000 mi^2 and is subdivided into three distinct physiographic sections--the Salem Plateau, the Springfield Plateau, and the Boston Mountains (fig. 1). The St. Francois Mountains are a subsection of the Salem Plateau (Fenneman, 1938).

Land surface elevations range from a few hundred feet above sea level near the boundary with the Mississippi Alluvial Plain section to more than 2,300 feet (ft) in the Boston Mountains. Topography is from gently rolling to rugged. Most of the rugged topography is located in the Boston Mountains and in parts of the Springfield and Salem Plateaus where deeply incised stream valleys are separated by narrow divides. Local relief can be as much as 500 ft in parts of the Springfield and Salem Plateaus, and as much as 1,000 ft in the Boston Mountains. Karst features, such as caves, sinkholes, and springs, are abundant in many parts of the Springfield and Salem Plateaus (Harvey, 1980; Adamski and others, 1995).

Geology and Hydrogeology

The geology of the Ozark Plateaus Province consists of flat lying to gently dipping sedimentary rocks of Cambrian through Pennsylvanian age. These units overlie crystalline rocks of Precambrian age which crop out in southeastern Missouri forming the St. Francois Mountains (Adamski and others, 1995).

Regional dip of the sedimentary rock units is gentle and generally away from the St. Francois Mountains. Locally, the rocks are jointed. In some areas, the rocks are also faulted or gently folded (Adamski and others, 1995).

These sedimentary and crystalline rocks of the Ozark Plateaus Province compose seven hydrogeologic units--the Western Interior Plains confining system, the Springfield Plateau aquifer, the Ozark confining unit, the Ozark aquifer, the St. Francois confining unit, the St. Francois aquifer, and the Basement confining unit (fig. 1) (Imes and Emmett, 1994; Adamski and others, 1995). Because ground-water samples for this study were collected only from the Springfield Plateau and Ozark aquifers, further discussion of the geology and hydrogeology will be limited to these two aquifers.

The Springfield Plateau aquifer consists of limestones and cherts of Mississippian age that crop out in the Springfield Plateau. These rocks have a combined thickness ranging from less than 100 to 500 ft. The aquifer is unconfined over much of the Springfield Plateau, but is confined in the Boston Mountains and Osage Plains where the aquifer is overlain by shales, sandstones and limestones of late Mississippian through Pennsylvanian age. Well yields average less than 20 gallons per minute (gal/min); however, the aquifer is an important source of domestic and livestock water supplies, particularly where it is unconfined. The Springfield Plateau aquifer is separated from the underlying Ozark aquifer by the Ozark confining unit, which is composed primarily of black shale of Devonian age (Imes and Emmett, 1994; Adamski and others, 1995).

The Ozark aquifer consists of dolomites, cherts, sandstones, limestones, and shales of late Cambrian through Devonian age. These rocks have a combined thickness ranging from 50 to more than 4,000 ft. The Ozark aquifer is unconfined over much of the Salem Plateau, but in the Springfield Plateau and Boston Mountains, the aquifer is confined by rocks of younger age. Well yields average 50 to 100 gal/min and can be as much as 600 gal/min; hence, the Ozark aquifer is an important source of domestic and municipal water supplies even in places where it is confined (Imes and Emmett, 1994; Adamski and others, 1995).

The configuration of the potentiometric surfaces of unconfined portions of both the Springfield Plateau and Ozark aquifers generally mimics the overlying topography. In general, ground water flows laterally from topographic highs and discharges in springs and seeps along streams. The unconfined aquifers are recharged nearly everywhere by precipitation (Imes and Emmett, 1994; Adamski and other, 1995).

Primary porosity and permeability are low for most of the rock units forming the Springfield Plateau and Ozark aquifers. Secondary porosity and permeability result from fracturing and dissolution of the carbonate rocks, causing porosity and permeability distribution to be extremely heterogeneous and vary widely even on a local scale. Hydraulic conductivity ranges from 1×10^{-8} feet per second (ft/s) to more than 1×10^{-3} ft/s in the Ozark aquifer (Imes and Emmett, 1994). Furthermore, regolith thickness, faults, the presence of chert nodules, and spatial variations in lithology and cementation affect ground-water recharge and flow. As a result, the hydrogeology of the aquifers is complex--generally involving a combination of discrete and diffuse flow components. Recharge and ground-water flow can be rapid. Discharge, sediment concentration, and water quality of many springs are affected by rainstorms. Ground-water flow can cross topographic divides; hence determination of contributing areas for wells and recharge basins for springs can be difficult (Adamski and others, 1995).

Soils in the study unit are primarily moderately to strongly weathered alfisols and ultisols composed of kaolinite, illite, and aluminum and iron hydroxides. Chert nodules, weathered from the underlying bedrock, are common in soils of many areas. Soil thickness ranges from several inches to tens of feet. Permeability of the soils can be as much as 6 inches per hour, resulting in a high potential to leach dissolved solids from the surface to the ground water (Adamski and others, 1995).

Land Use

Dominant land use differs between the Salem and Springfield Plateaus. The Salem Plateau is covered primarily (71 percent) by second-growth forest, whereas the Springfield Plateau is covered primarily (58 percent) by agricultural land use (fig. 2) (U.S. Geological Survey, 1990). Dominant agricultural land use in both the Salem and Springfield Plateaus is the raising of livestock including cattle, poultry, and swine. Dairy and beef cattle are raised throughout most of the Springfield Plateau; many confined poultry operations are present in the southern part of the Springfield Plateau in northwestern Arkansas, southwestern Missouri, and northeastern Oklahoma. The large amount of animal wastes generated by cattle and poultry operations is a major source of nutrients. About 358,300 tons of nitrogen and 123,400 tons of phosphorus are generated each year in the study unit, most of which is applied to local pastures as fertilizer (Davis and others, 1995).

Commercial fertilizer use varies widely across the Springfield and Salem Plateaus. Average nitrogen application rates in 1985 for the Springfield and Salem Plateaus were 2.8 and 3.0 tons/mi^2, respectively. Average phosphorus application rates for the Springfield and Salem Plateaus were 0.52 and 0.49 tons/mi^2, respectively (Davis and others, 1995).

Intensive row-crop agriculture is not common in most of the Springfield or Salem Plateaus because the deeply weathered soils are not fertile (Adamski and others, 1995). Nevertheless, pesticides are used in some parts of the study unit for numerous purposes.

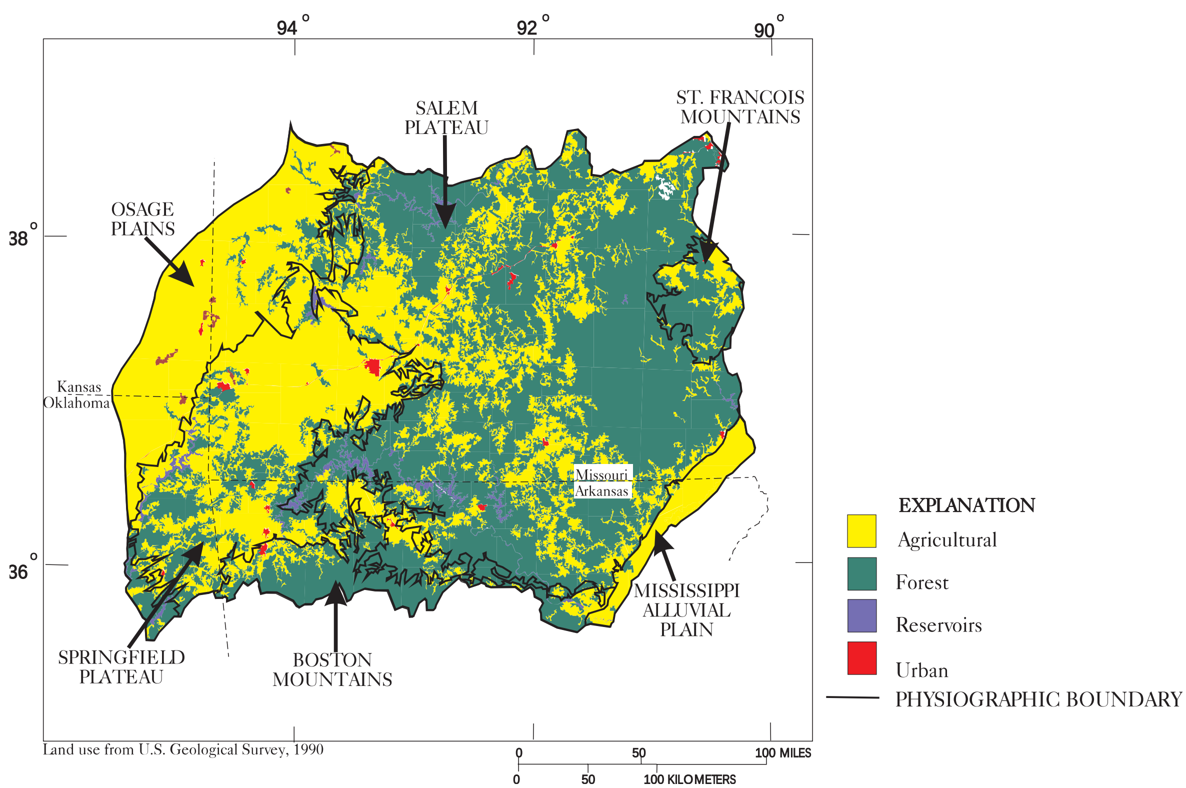

Figure 2. Generalized land use in the Ozark Plateaus study unit.

Pesticide usage includes controlling weeds in pastures, and along fencerows, roads, and utility rights-of-way. Information on 24 pesticides that were applied to parts of the study unit for the period 1982 to 1985 indicated that the six most commonly applied pesticides were 2,4-D, alachlor, atrazine, propanil, trifluralin, and metolachlor (Bell and others, 1996). In general, pesticide use was greater in the Springfield Plateau than in the Salem Plateau. Pesticide use ranged from about 0.01 to 1 pound per acre per year (lb/acre/yr) in the Springfield Plateau and from less than 0.01 to 0.5 lb/acre/yr in the Salem Plateau.

APPROACH

The investigation approach and methods used for ground-water studies were similar among the NAWQA study units to provide consistency and comparability of results. A thorough description of ground-water sample-collection methods for the NAWQA Program is contained in Koterba and others (1995).

Ground-Water Sampling Network

The ground-water sampling network in the Ozark Plateaus study unit was established with three scale-dependent components. The three network components, from largest to smallest in area, are the study-unit survey, the land-use studies, and the small-watershed study.

Water samples were collected from 1993 through 1995 from springs and existing domestic wells, and in 1995 from newly installed monitoring wells. Sampling locations for the study-unit survey and land-use studies were determined using a geographical information system (GIS) based, random-selection program (Scott, 1990); specific wells and springs available for sample collection were identified during field inventory. Stringent criteria were used to select well and spring sites. Criteria for wells required that wells had to be recently drilled, tap the local unconfined aquifer, and have a spigot close to the wellhead. Criteria for springs required that springs had to have minimal improvements and an access to the orifice from which water issued. In a few areas, samples were collected from well and spring sites that did not meet site criteria because no other sites were available. Although sites near point sources of contamination were avoided, in general, land use was not used as a criterion for site selection during the study-unit survey; however land use was a critical criterion during the land-use studies.

Study-Unit Survey

The study-unit survey, approximately 35,400 mi^2 in area, included most of the Springfield and Salem Plateaus (fig. 3). The objective of the study-unit survey was to determine the occurrence and distribution of inorganic and organic chemical constituents in the Springfield Plateau and Ozark aquifers. Water samples were collected from 50 springs and 49 domestic wells in the Springfield Plateau and Ozark aquifers from April through September 1993 (table 1). Depth of wells sampled ranged from 65 to 400 ft, with a median of 170 ft. Discharge of springs sampled ranged from 1 to more than 4,400 gal/min, with a median of 52 gal/min. Figure 4 shows spring discharge and well depth categorized by network component and by aquifers. Agricultural land use was greatest near springs (within probable recharge basin) and wells (within 1-mile radius) in the Springfield Plateau aquifer and least near springs in the Ozark aquifer, where second-growth forest was the predominant land use (fig. 5).

Table 1. Summary of number and type of ground-water sampling sites for each network component in the Ozark Plateaus study unit

[Springfield, Springfield Plateau aquifer; Ozark, Ozark aquifer; numbers in parentheses are numbers of additional springs previously sampled as part of the study-unit survey]

	Springs	Wells	Total
Study-unit survey			
Springfield	20	16	36
Ozark	30	33	63
Land-use studies			
Poultry land-use study	21 (1)	20	41 (1)
Cattle land-use study	19 (1)	20	39 (1)
Reference sites	3	1	4
Small-watershed study			
	3 (1)	29	32 (1)
Total	96 (3)	119	215 (3)

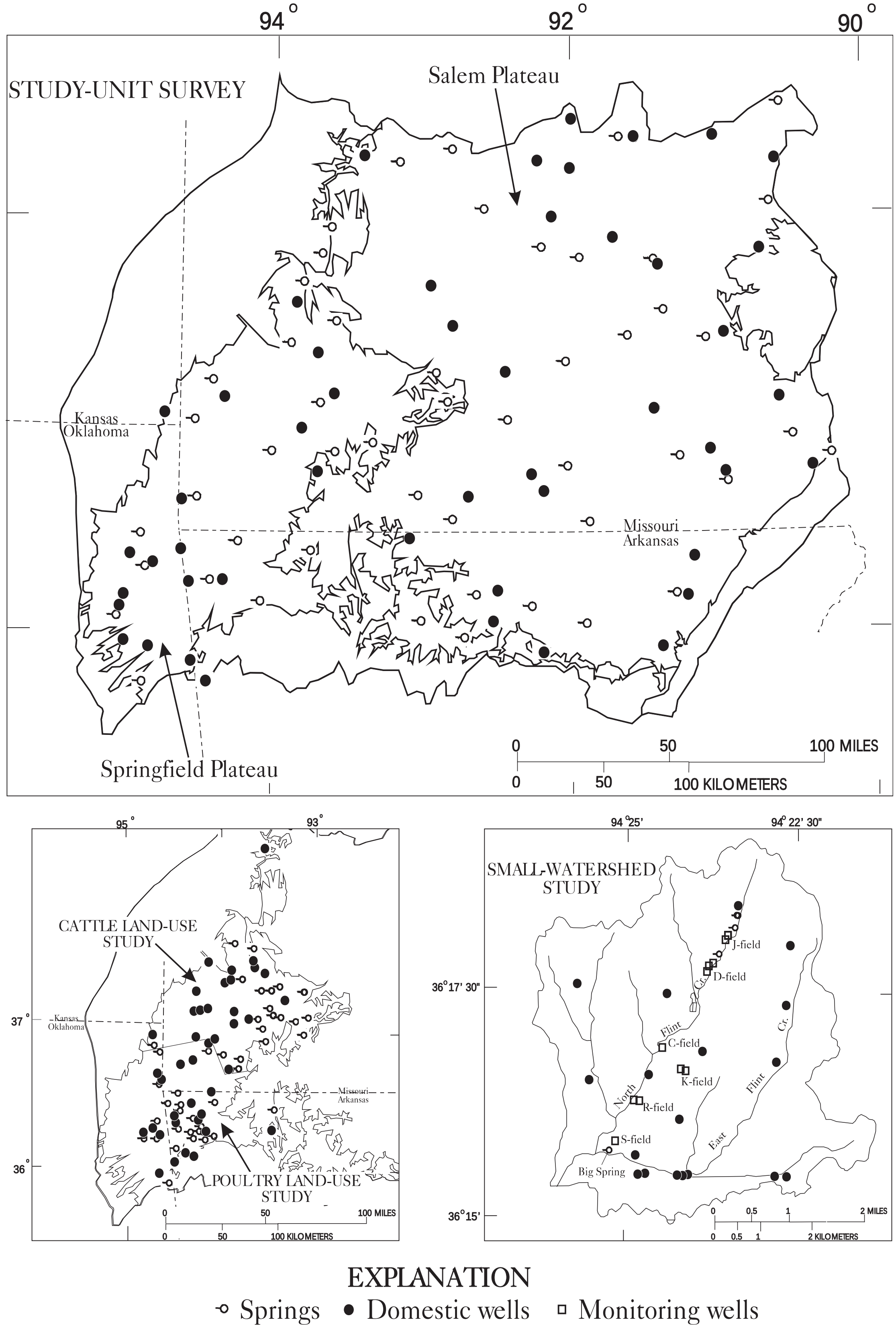

Figure 3. Location of springs and wells in the Ozark Plateaus study unit sampled for the study-unit survey, the poultry and cattle land-use studies, and the small-watershed study.

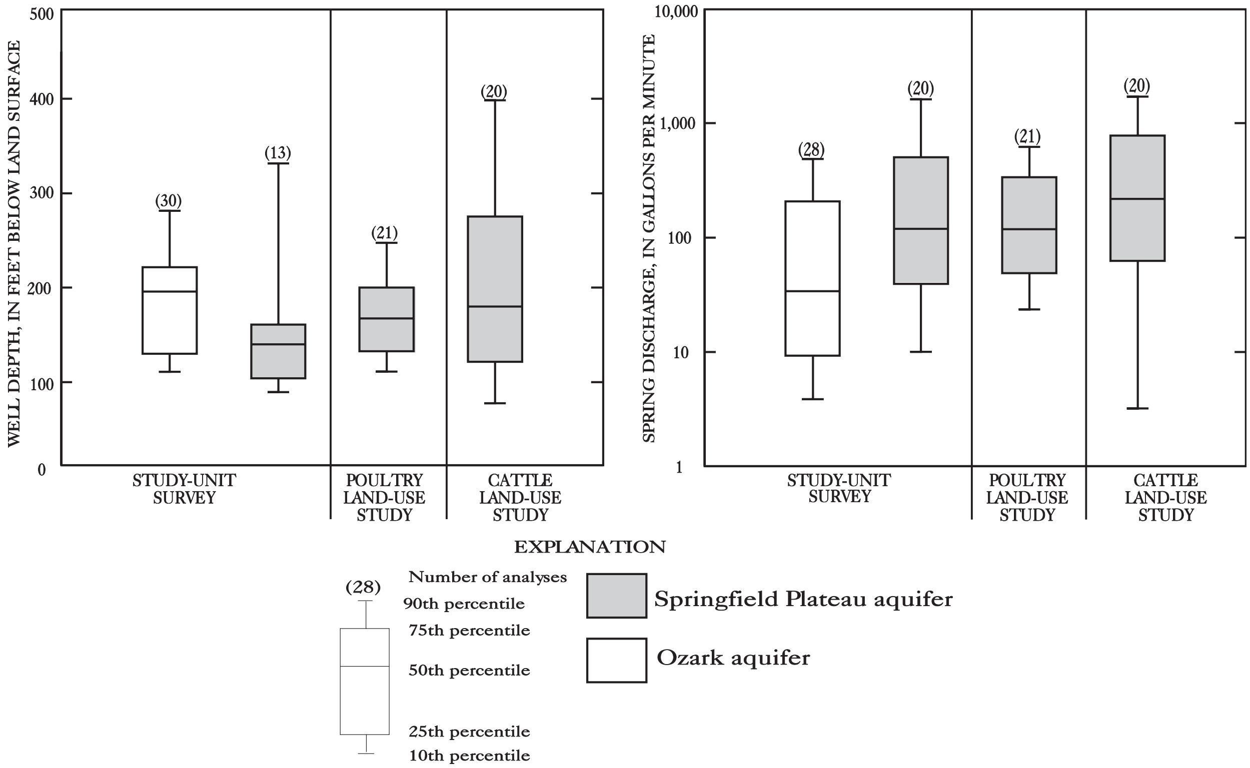

Figure 4. Distribution of spring discharge and well depth of sites sampled for the study-unit survey, and the poultry and cattle land-use studies.

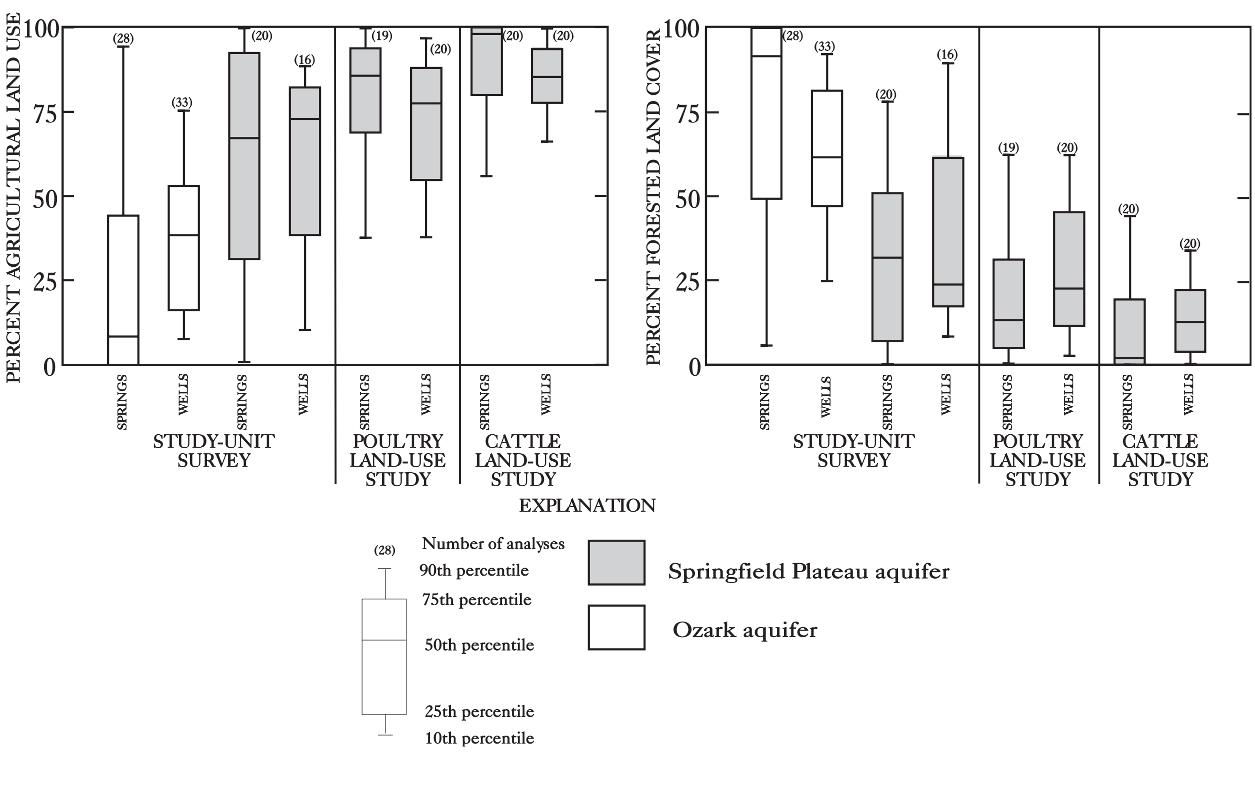

Figure 5. Distribution of agricultural land use and forested land cover within probable recharge basins of springs and within 1-mile radius of wells sampled for the study-unit survey, and the poultry and cattle land-use studies.

Land-Use Studies

Two land-use studies were performed to determine the effect of agricultural practices on the quality of ground water in the Springfield Plateau aquifer, primarily with regard to nutrients and pesticides. Ground-water sites were selected within or adjacent to poultry or cattle agricultural land uses.

The first land-use study was located in the southern part of the Springfield Plateau where pastureland use consists of confined poultry and cattle operations (fig. 3). In this report, the first land-use study will be referred to as the poultry land-use study. Water samples were collected from 20 domestic wells and 22 springs from March to May 1994; 1 of the 22 springs was previously sampled as part of the study-unit survey and resampled during the poultry land-use study (table 1). Well depth ranged from 32 to 275 ft, with a median of 168 ft. Spring discharge ranged from 10 to 898 gal/min, with a median of 117 gal/min (fig. 4).

The second land-use study was located in the northern part of the Springfield Plateau where pastureland use consists primarily of raising cattle (fig. 3). In this report, the second land-use study will be referred to as the cattle land-use study. Water samples were collected from 20 domestic wells and 20 springs from April through May 1995; 1 of the 20 springs was previously sampled as part of the study-unit survey and resampled as part of the cattle land-use study (table 1). Well depth ranged from 45 to 430 ft, with a median of 180 ft. Spring discharge ranged from 2 to 2,210 gal/min, with a median of 219 gal/min (fig. 4).

In addition to samples collected for these two land-use studies, water samples from reference sites were collected from one domestic well and three springs located in forested areas of the Springfield Plateau in June 1995. Data from these samples, along with data from samples collected in forested areas during the study-unit survey, were used to determine maximum background concentrations of nutrients and pesticides in ground water underlying the forested areas of the study unit.

Small-Watershed Study

The objective of the small-watershed study was to define the spatial, both vertical and horizontal, distribution of nutrients and pesticides in the ground water beneath a small part of the Springfield Plateau aquifer. Flint Creek Basin (fig. 3), a 14.7-mi^2 basin located in northwestern Arkansas, was selected for the small-watershed study because (1) the land use was considered representative of the poultry land-use study; (2) Flint Creek was not regulated or influenced by municipal or sewage discharge; and (3) hydrogeologic studies of the basin were concurrently being conducted (J.V. Brahana, U.S. Geological Survey, oral commun., 1994). Land use in the basin is about 70 percent agricultural and 30 percent forest.

Ground-water samples were collected from 18 domestic wells and 3 springs within the basin from July through August 1994. Additional samples were collected from the fourth spring, Big Spring, in July 1993 as part of the study-unit survey and in July 1994 and July 1995 (table 1). Depth of sampled wells ranged from 17 to 263 ft, with a median of 113 ft. Discharge at three springs ranged from 5 to 50 gal/min, and discharge at Big Spring was 3,620 gal/min.

Eleven monitoring wells were drilled in or adjacent to pastures in the basin from January through March 1995. The monitoring wells generally were drilled as pairs of shallow and deep wells. Depth ranged from 5.3 to 67 ft for the shallow wells and from 50 to 200 ft for the deep wells. Samples were collected from the monitoring wells in April and July 1995.

Collection of Site Information

Site characteristic information, including land-surface elevation, topographic setting, land use, geology, water level in wells, and spring type (cave opening, fracture, or seepage) was collected at all sites either during field inventory or sample collection. Domestic-well depth and casing data were obtained, when available, from either the owner or drilling reports from the Arkansas Geological Commission or the Missouri Division of Geology and Land Survey. All domestic wells chosen for sampling had 6-inch (in.)-diameter steel or polyvinyl chloride (PVC) casing that extended down to or just below the bedrock, with the remainder of the borehole open. Monitoring wells were constructed with 2-in.-diameter PVC casing with a bentonite seal in the annulus above the target aquifer and 2 to 20 ft of 2-in.-diameter PVC well screen near the bottom of the hole in the target aquifer.

The aquifer contributing water to springs was determined from site location and surficial bedrock geology. The aquifer contributing water to wells was determined from site location, surficial bedrock geology, well depth and casing length, and concentrations of major ions detected in the water samples.

Generally, springs were selected that had minimal improvements. Discharge was measured either volumetrically or with a current meter at most springs during sample collection. At a few springs, improvements precluded accurate measurements of discharge. The size of the recharge basins of springs was estimated by using local recharge rates and discharge (Vandike, 1994). Topography, surficial geology, and previous dye-tracing studies were used to approximate probable boundaries of the recharge basins of springs.

Land use was determined within a 1-mile radius of all well sites and within the probable recharge basins of most springs. Land use was initially described during site visits, facilitated by the use of topographic maps. Land use was further quantified at all sites using the Geographical Information Resources Analysis System (GIRAS) land use and land cover data (U.S. Geological Survey, 1990) to determine the percent and area of each land-use category (agricultural, forested, urban, and water) around each well site and in each spring basin.

Ground-Water Sample Collection and Analysis

A total of 229 ground-water samples were collected from 215 sites. Water samples were analyzed for major ions (calcium, magnesium, sodium, potassium, chloride, sulfate, fluoride, and bromide), silica, nutrients (nitrite, nitrite plus nitrate, ammonia, ammonia plus organic nitrogen, phosphorus, and orthophosphate), dissolved organic carbon (DOC), methylene blue active substances, and 88 pesticides and metabolites. Water samples from 183 sites were analyzed for tritium.

Field measurements (water temperature, specific conductance, dissolved oxygen, pH, and alkalinity) were made at all sites. Water samples from the springs were collected at or near the orifice using a FEP hose and pump equipped with a PTFE diaphragm head. Samples were collected and processed directly from the discharge end of the hose.

Water samples were collected from domestic wells using the existing submersible pumps, and from monitoring wells with a portable stainless-steel submersible pump. Samples were collected and processed directly from the discharge end of a FEP hose, which was attached to a spigot near the domestic wellhead or to the stainless-steel submersible pump. Sample collection began after purging wells of three well volumes (generally) and stabilization of all field measurements (Koterba and others, 1995). The low yield of some wells made it difficult to purge three well volumes prior to sample collection. However, the continual use of those wells for domestic supply and the generally rapid stabilization of field measurements indicate that the wells were receiving fresh aquifer water at the time of sample collection.

Samples collected for major-ion and nutrient analyses were filtered either with a 142-millimeter (mm) acrylic plate filter equipped with a 0.45-micrometer (µm) pore-size cellulose nitrate filter membrane, or with a 0.45-µm pore-size disposable capsule filter. Samples collected for cation analyses were preserved with nitric acid to adjust the sample pH to less than 2. Samples for nutrient analyses collected before October 1994 were preserved with mercuric chloride and chilled to 4 degrees Celsius (^{o}C). Samples for nutrient analyses collected after October 1, 1994, were simply chilled to 4 ^{o}C. No preservative was added to samples collected for anion analyses (Koterba and others, 1995). Samples were analyzed at the USGS National Water-Quality Laboratory (NWQL).

Samples collected for DOC analysis were filtered with a 47-mm stainless-steel pressure filtration funnel equipped with 0.45-µm pore-size silver filters (pressured with nitrogen gas to no more than 15 pounds per square inch), and chilled to 4 ^{o}C. Samples collected for pesticide analysis were filtered using a 142-mm aluminum filter plate equipped with a 0.7-µm pore-size baked glass-fiber filter. Filtered samples were collected in 1-L baked amber glass bottles, chilled to 4 ^{o}C, and delivered overnight for solid phase extraction (SPE) and analysis (Koterba and others, 1995). Samples were analyzed at NWQL.

Samples collected for tritium analysis were collected in 1-L polypropylene bottles. Samples were not filtered or preserved (Koterba and others, 1995). Samples were shipped to NWQL for analysis.

Risk of sample contamination was minimized during collection and processing through consistent use of trace-level sampling protocols. Collection and preservation were done using dedicated environmental chambers consisting of polypropylene bags stretched over PVC frames; the bags were replaced between sites. Between sites, all equipment was thoroughly cleaned with a non-phosphatic detergent and thoroughly rinsed with deionized water. Equipment used to collect samples for inorganic analyses was additionally rinsed with a 3-percent hydrochloric-acid solution and finally rinsed with trace-element-grade laboratory water. Equipment used to collect samples for pesticide analysis was additionally rinsed with pesticide-grade methanol and pesticide-grade laboratory water. The stainless-steel filtration funnel used to collect samples for DOC analysis was rinsed only with deionized and pesticide-grade laboratory water (Koterba and others, 1995).

Quality-assurance samples were collected at 37 sites. Quality-assurance samples included field-equipment and source-solution blanks collected at 14 sites, and replicate samples collected at 14 sites. In addition, three samples from each of nine sites were spiked with pesticide solutions. Two of the samples from each site were spiked in the field, whereas the third sample was spiked at the laboratory prior to solid phase extraction.

Statistical Methods of Data Analysis

Data were statistically analyzed for quality assurance. Field measurements were determined to be stabilized if temperature, pH, and specific conductance did not significantly vary during three successive measurements taken at 5-minute intervals. Agreement within 10 percent between duplicate alkalinity analyses at each site was verified. Percent ion-balance errors were determined to be within acceptable limits. Depending on the specific conductance of the ground-water sample, the acceptable limits of ion-balance errors ranged from 5 to 10 percent. Data from blank samples indicated that decontamination procedures generally were adequate to prevent cross contamination of samples. Data from replicate samples agreed well with data from environmental samples at the same sites which verified the accuracy and precision of analytical methods. Finally, results of field and laboratory pesticide-spiked samples generally were comparable indicating good recoverability of most constituents.

Data were statistically analyzed (Helsel and Hirsch, 1992) to identify factors affecting nutrient concentrations and pesticide occurrences in ground-water samples. Data analyzed for this report primarily were those collected during the study-unit survey and land-use studies because these data represent large areas of the Ozark Plateaus study unit and provide a statistically significant sample size. Data from the small-watershed study were used to describe local-scale processes. Spearman's rho rank order correlation coefficient was used to measure the monotonic association among nutrient concentrations, other water-quality constituents, and site characteristics such as well depth or spring discharge. The nonparametric Kruskal-Wallis test was used to indicate differences in the medians of two or more groups of data. For example, the Kruskal-Wallis test was used to determine if median spring discharge was significantly different between samples with detectable pesticides and samples with no detectable pesticides. The medians of the groups are assumed to be significantly different from one another if the probability (p-value) is less than 5 percent (<0.05) that the observed difference occurs by chance. Contingency tables were used to determine if the number of pesticide detections were related to characteristics such as network components (study-unit survey and land-use studies), site type (wells and springs), or aquifer.

NUTRIENTS AND PESTICIDES IN GROUND WATER

The occurrence and distribution of nutrients and pesticides in ground water of the Springfield Plateau and Ozark aquifers are discussed in the following sections. The relation between nutrients and pesticides, and factors such as land use, hydrogeology, site characteristics, and other water-quality constituents also are analyzed to provide evidence of the factors that affect nutrient and pesticide occurrence in ground water.

Nutrients

Nutrients considered in this report are species of nitrogen and phosphorus. Ground-water samples collected for this study were analyzed for nitrite, nitrite plus nitrate, ammonia, ammonia plus organic nitrogen, phosphorus, and orthophosphate. Summary statistics of nutrient data for all the ground-water samples collected during this study are listed in table 2.

Background concentrations of nutrients in ground water of the Springfield Plateau and Ozark aquifers, determined from concentrations in samples from reference sites and forested areas, were below detection limits in many samples. In samples collected from 25 relatively pristine sites (forest cover greater than or equal to 90 percent), the 90th-percentile concentrations (assumed to represent maximum background concentrations) for nutrients were as follows: nitrite was less than 0.01 mg/L; nitrite plus nitrate was 0.98 mg/L; ammonia was 0.02 mg/L; ammonia plus

Table 2. Statistical summary of nutrient data for filtered ground-water samples in the Ozark Plateaus study unit collecting during 1993-95

[All units are in milligrams per liter; N, nitrogen; P, phosphorus; <, less than]

Constituent	Number of analyses	Number of detections	Minimum concentration	Concentration at indicated percentile					Maximum concentration
				10	25	50 (median)	75	90	
Nitrite as N	228	40	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	1.4
Nitrite plus nitrate	228	212	<.05	.08	.39	1.6	3.0	5.1	25
Ammonia as N	227	178	<.01	<.01	.01	.02	.02	.04	1.2
Ammonia plus organic nitrogen	227	15	<.20	<.20	<.20	<.20	<.20	<.20	4.9
Phosphorus	227	103	<.01	<.01	<.01	<.01	.02	.04	.17
Orthophosphate as P	227	103	<.01	<.01	<.01	<.01	.02	.02	.16

organic nitrogen was less than 0.20 mg/L; phosphorus was 0.02 mg/L; and orthophosphate was 0.01 mg/L.

Nitrite

Nitrite concentrations generally were low in ground-water samples (table 2). In 188 of 228 samples, nitrite concentrations were less than the detection limit of 0.01 mg/L as nitrogen. Only 11 samples had nitrite concentrations greater than 0.02 mg/L as nitrogen; 7 of these samples were from monitoring wells in the small-watershed study.

The source of nitrite in ground water of the Springfield Plateau and Ozark aquifers appears to be related to land use. Results of Kruskal-Wallis testing indicate that percent agricultural land use was greater around sites where nitrite was detected than around sites where nitrite was not detected (p less than 0.01).

Median nitrite concentration was greater in samples collected from the monitoring wells (0.01 mg/L) in the small-watershed study than in samples from springs (less than 0.01 mg/L) or domestic wells (less than 0.01 mg/L; p less than 0.01). The maximum nitrite concentration (1.4 mg/L) was in a sample from a shallow monitoring well at S-field directly downgradient from a large dairy operation (table 3).

Nitrite concentrations in samples inversely correlated with dissolved oxygen, particularly for wells in the Springfield Plateau aquifer (Spearman's rho=0.333, p less than 0.01). Dissolved oxygen in most samples was high, ranging from less than 0.1 to 12 mg/L, with a median of 6.8 mg/L. Nitrite is unstable in aerated water (Hem, 1989); hence, most of the nitrite in ground water of the Springfield Plateau and Ozark aquifers probably oxidizes rapidly to nitrate.

Nitrite probably is more common, and more stable, in deep parts of the aquifers than in shallow parts. Nitrite concentrations in samples from three of the deep monitoring wells in the small-watershed study were greater than 0.1 mg/L, whereas nitrite concentrations in samples from all but one of the shallow monitoring wells were less than 0.04 mg/L (table 3). In addition, nitrite was detected more often in samples from wells than in samples from springs, and median nitrite concentrations were greater in samples from wells than in samples from springs in the cattle land-use study.

Median nitrite concentrations were not significantly different between samples from the Springfield-Plateau and Ozark aquifers. Nitrite concentrations were

Table 3. Concentrations of nitrite, nitrite plus nitrate, ammonia, and ammonia plus organic nitrogen in filtered samples collected from monitoring wells in April and July 1995 during the small watershed study

[mg/L as N, milligrams per liter as nitrogen; <, less than]

Well identifier	Well depth (feet below land surface)	Nitrite (mg/L as N)	Nitrite plus nitrate (mg/L as N)	Ammonia (mg/L as N)	Ammonia plus organic nitrogen (mg/L as N)
C-field	5.3	<0.01 - 0.01	0.09 - 0.11	0.14 - 0.22	0.2 - 0.4
D-field, 1	34	<.01	3.4	<.015	<.20
D-field, 2	35	<.01	3.3 - 3.5	<.015 - .02	<.20
D-field, 3	120	<.01 - .78	.80 - .94	.08 - .18	.20 - .30
J-field, 1	30	<.01	2.4	<.015 - .03	<.20
J-field, 2	120	.01 - .66	1.2 - 2.4	.02 - .08	<.20 - .40
K-field, 1	67	.02	.11	.49	3.7
K-field, 2	200	.35 - .88	.57 - 1.3	.06 - .16	.40
R-field, 1	9.6	.03 - .04	16 - 24	.26 - .51	.40 - .70
R-field, 2	50	<.01 - .02	.13 - .56	<.015 - .04	<.20
S-field	16	.02 - 1.4	.22 - 18	.18 - 1.2	1.0 - 4.9

not related to domestic-well depth, spring discharge, or any other site characteristics. Nitrite concentrations were not related to other field measurements or general water-quality constituents.

Nitrite Plus Nitrate

Nitrite plus nitrate was detected in ground-water samples more often and in greater concentrations than any other form of nitrogen (table 2). Because nitrite was below detection limit in most samples, nitrite plus nitrate in ground-water samples consisted primarily of nitrate.

Nitrite plus nitrate concentrations in the Springfield Plateau and Ozark aquifers commonly exceeded background levels (figs. 6 and 7). Nitrite plus nitrate concentrations were greater than 0.98 mg/L as nitrogen in 45 of 98 samples collected for the study-unit survey, in 31 of 42 samples collected for the poultry land-use study, and in 27 of 40 samples collected for the cattle land-use study. Nitrite plus nitrate concentrations in samples from four sites--two shallow monitoring wells in the small watershed study (table 3) and two wells in the cattle land-use study--exceeded the MCL of 10 mg/L as nitrogen for nitrate in drinking water. These results indicate that elevated concentrations of nitrite plus nitrate in ground water of the Springfield Plateau and Ozark aquifers are widespread, particularly in areas where land use is predominantly agricultural, and that ground water in both aquifers is vulnerable to surface contamination. Susceptibility of the aquifers could result from the fractures and solution openings in the bedrock and permeable soils that allow rapid recharge of the ground water.

Agricultural land use is a significant factor affecting nitrite plus nitrate concentrations in ground water of the Ozark Plateaus. Nitrite plus nitrate concentrations in samples were positively correlated to percent agricultural land use around each site (fig. 8a; rho= 0.58) and negatively correlated to percent forest cover around each site (fig. 8b; rho=0.59). These correlations are strong considering the complexities of the hydrogeology and subsequently the difficulty and potential degree of error in determining recharge areas to springs and contributing areas to wells. These results indicate that concentrations of nitrite plus nitrate in ground

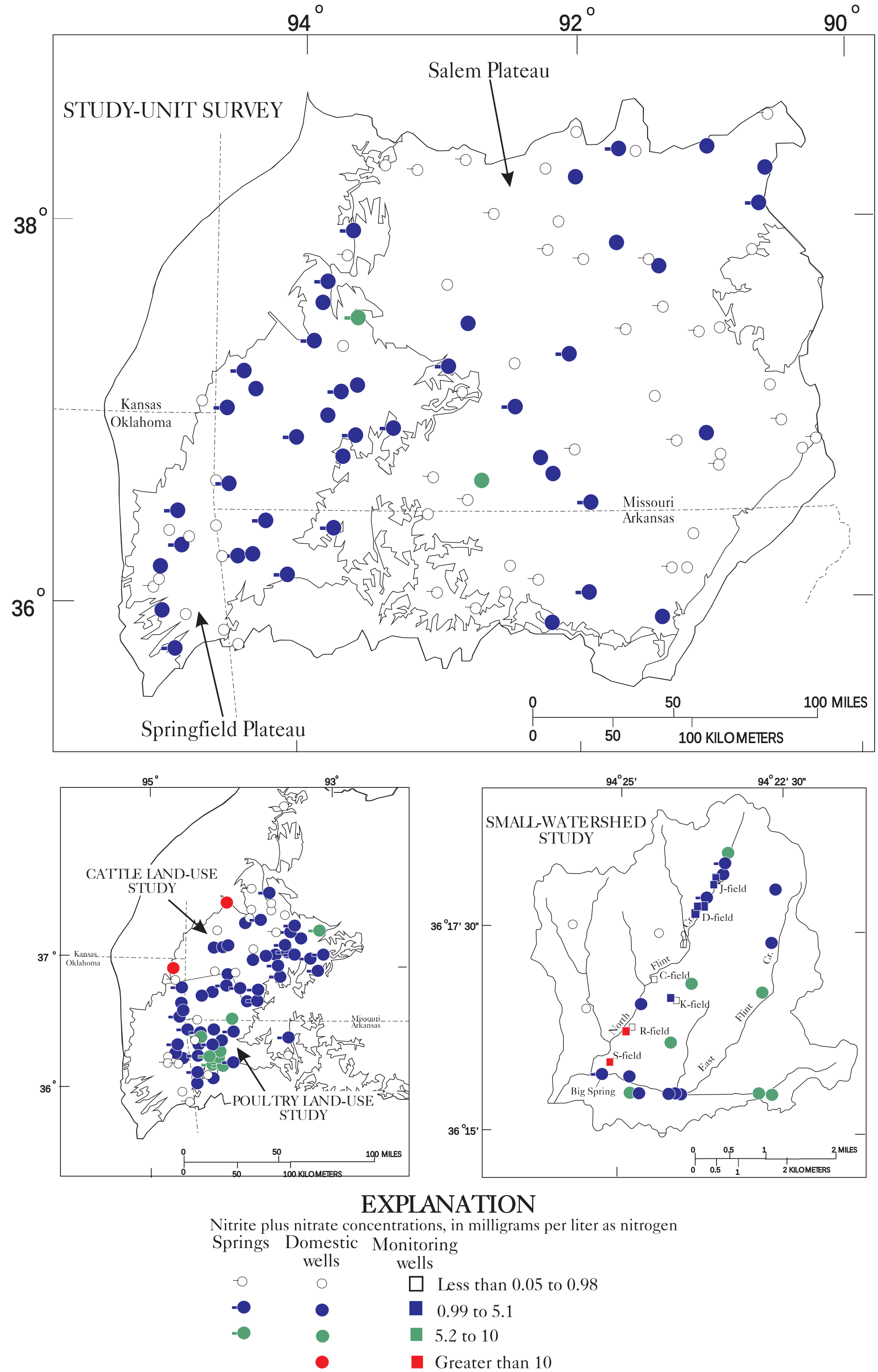

Figure 6. Concentrations of nitrite plus nitrate in ground-water samples collected from springs, domestic wells, and monitoring wells.

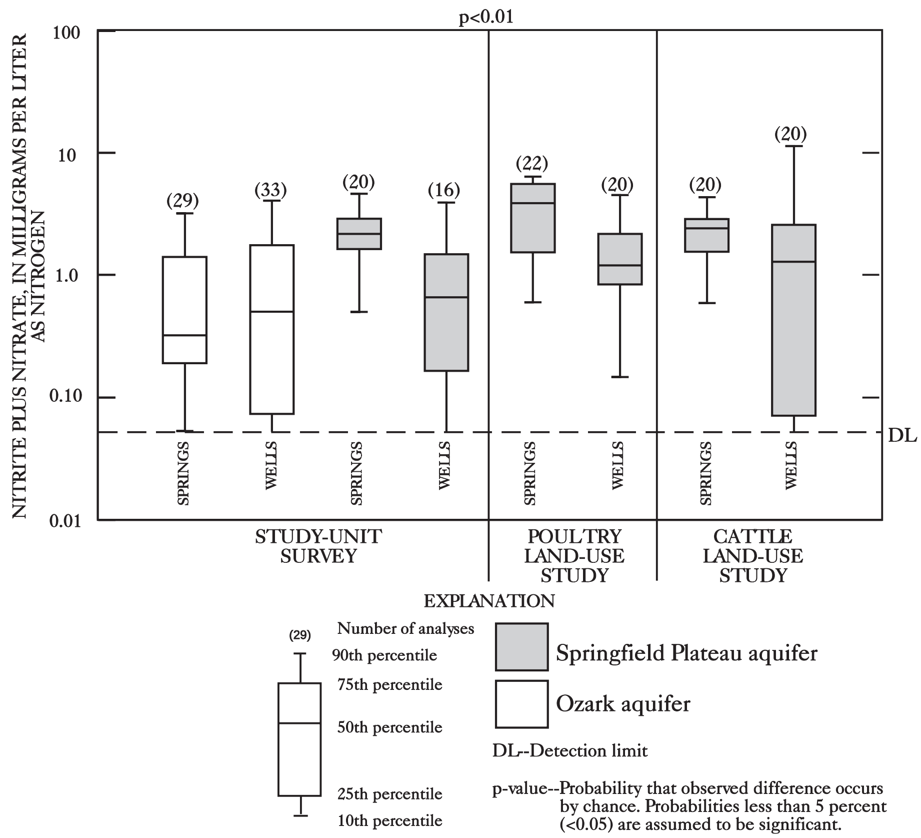

Figure 7. Distribution of nitrite plus nitrate concentrations in ground-water samples collected for the study-unit survey, and the poultry and cattle land-use studies.

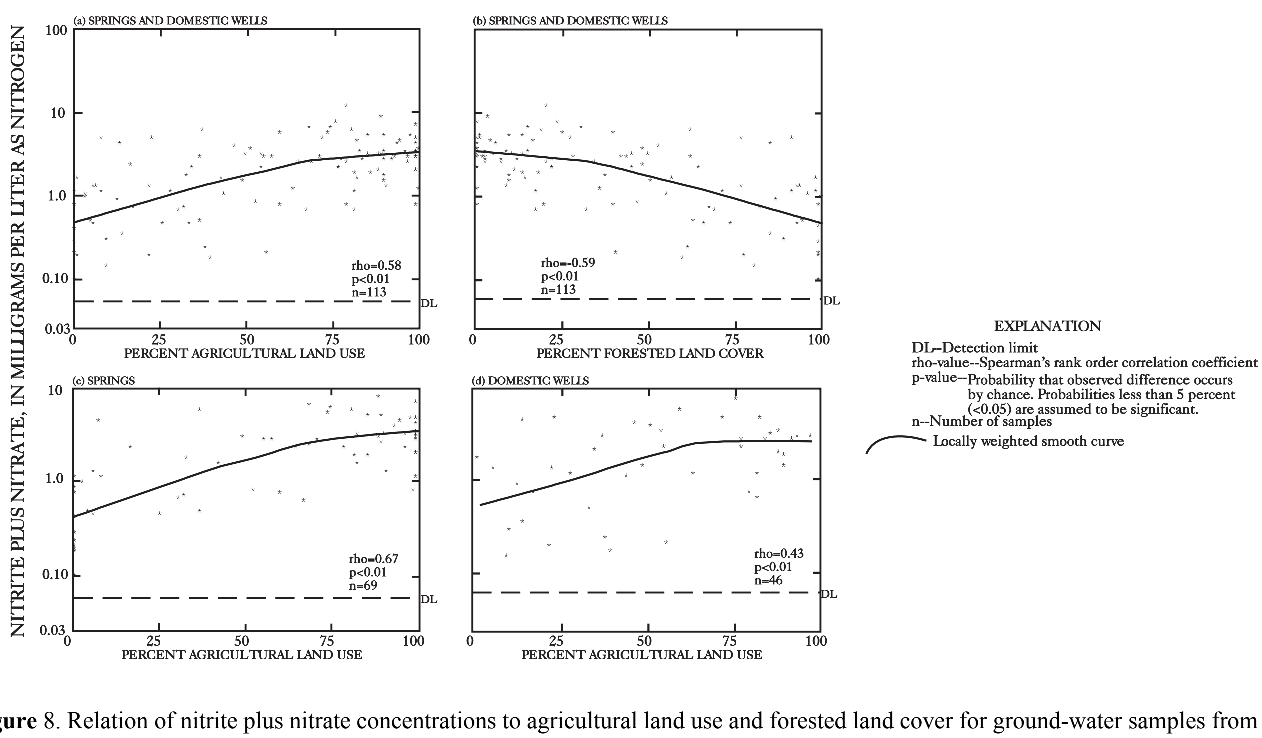

Figure 8. Relation of nitrite plus nitrate concentrations to agricultural land use and forested land cover for ground-water samples from (a) springs and domestic wells, (b) springs and domestic wells, (c) springs, and (d) domestic wells.

water increase as percent of agricultural land use overlying the aquifer increases. The relation was stronger for samples from springs (fig. 8c; rho=0.67) than for samples from wells (fig. 8d; rho=0.43).

Median concentration of nitrite plus nitrate was statistically greater in samples collected from springs in the Springfield Plateau aquifer than in samples collected from springs in the Ozark aquifer (fig. 7). These results probably are related to the significantly greater agricultural land use overlying the Springfield Plateau aquifer compared to the Ozark aquifer (fig. 2). Median agricultural land use around spring sites in the Springfield Plateau aquifer was 67 percent compared to 9 percent agricultural land use around spring sites in the Ozark aquifer (fig. 5).

Median nitrite plus nitrate concentrations were statistically greater in samples collected for the two land-use studies than in samples collected from the Springfield Plateau aquifer for the study-unit survey (p less than 0.01) (fig. 7). These results also indicate a relation of nitrite plus nitrate concentrations to land use. Median agricultural land use was 82 and 89 percent around sites in the poultry land-use study and cattle land-use study, respectively. Median agricultural land use around sites in the study-unit survey, which were selected without regard to land use, was 69 percent (fig. 5).

Hydrogeology also affects nitrite plus nitrate concentrations in ground water. Median nitrite plus nitrate concentration was greater in samples collected from springs (2.6 mg/L) than in samples collected from wells (1.0 mg/L) in the Springfield Plateau aquifer (p less than 0.01) (fig. 7). Land use around well and spring sites was not statistically different within each network component. Water from springs is more susceptible to surface contamination, in general, than is water from wells. Field measurements (specific conductance, alkalinity, and dissolved oxygen) indicate that water issuing from springs generally interacts less with the aquifer, and follows more shallow flowpaths along fractures and solution openings, than water from wells. In general, specific conductance and alkalinity, which are related to ionic concentrations resulting from dissolution of the rock (Hem, 1989), were greater in samples from wells than in samples from springs; however, dissolved oxygen, which is supplied by recharge (Hem, 1989), is greater in samples from springs than in samples from wells.

Median nitrite plus nitrate concentrations were not statistically different between samples from wells and samples from springs in the Ozark aquifer. Median nitrite plus nitrate concentrations for samples from both springs and wells were less than 1 mg/L (fig. 7), which is within background levels, because most sites, particularly springs, have a large percent of forest cover associated with them (fig. 5).

Nitrite plus nitrate concentrations were positively correlated to dissolved oxygen in ground-water samples from domestic wells (rho=0.53, p less than 0.01) (fig. 9). As with springs, a relatively high concentration of dissolved oxygen in water from wells would indicate a shallow source or short flowpath for the water, increasing susceptibility to surface contamination.

Nitrite plus nitrate concentrations were not related to other field measurements or water-quality constituents in samples. Spearman's rho indicates that nitrite plus nitrate concentrations were not related to well depth, spring discharge, or other site characteristics. Because the wells had open-borehole construction, well depth and casing length are not good indicators of the depth of the source(s) of water entering the well. Similarly, discharge alone is not a good indicator of depth of flow, or susceptibility to surface contamination of water issuing from a spring.

Ammonia

As with nitrite, ammonia concentrations in most ground-water samples were low (table 2). In 49 of 227 samples, ammonia concentrations were less than the detection limit of 0.01 mg/L as nitrogen. Ammonia concentrations were less than or equal to background concentration of 0.02 mg/L as nitrogen in 172 of 227 samples.

As with nitrite and nitrite plus nitrate, the source of ammonia in ground-water samples probably was related to land use. Of 30 samples with ammonia concentrations greater than 0.03 mg/L, 8 samples were collected for the land-use studies and 16 samples were collected for the small-watershed study. However, concentrations of ammonia in samples did not directly correlate with percent agricultural land use around sites.

Median ammonia concentration was statistically greater in samples collected from monitoring wells (0.08 mg/L) for the small-watershed study than in samples from springs (0.02 mg/L) or domestic wells (0.02 mg/L) for any of the network components (p less than 0.01) (fig. 10). The maximum ammonia concentration (1.2 mg/L) was in a sample collected from the monitoring well at S-field that also yielded the sample with the

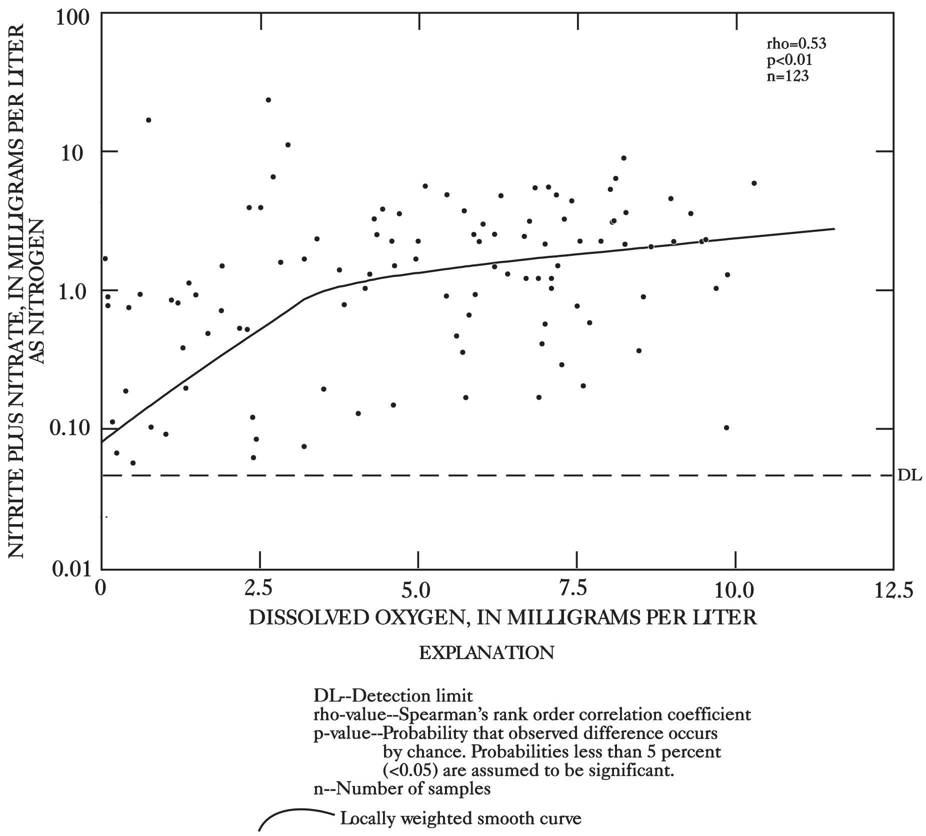

Figure 9. Relation of nitrite plus nitrate concentrations and dissolved oxygen in ground-water samples from domestic wells.

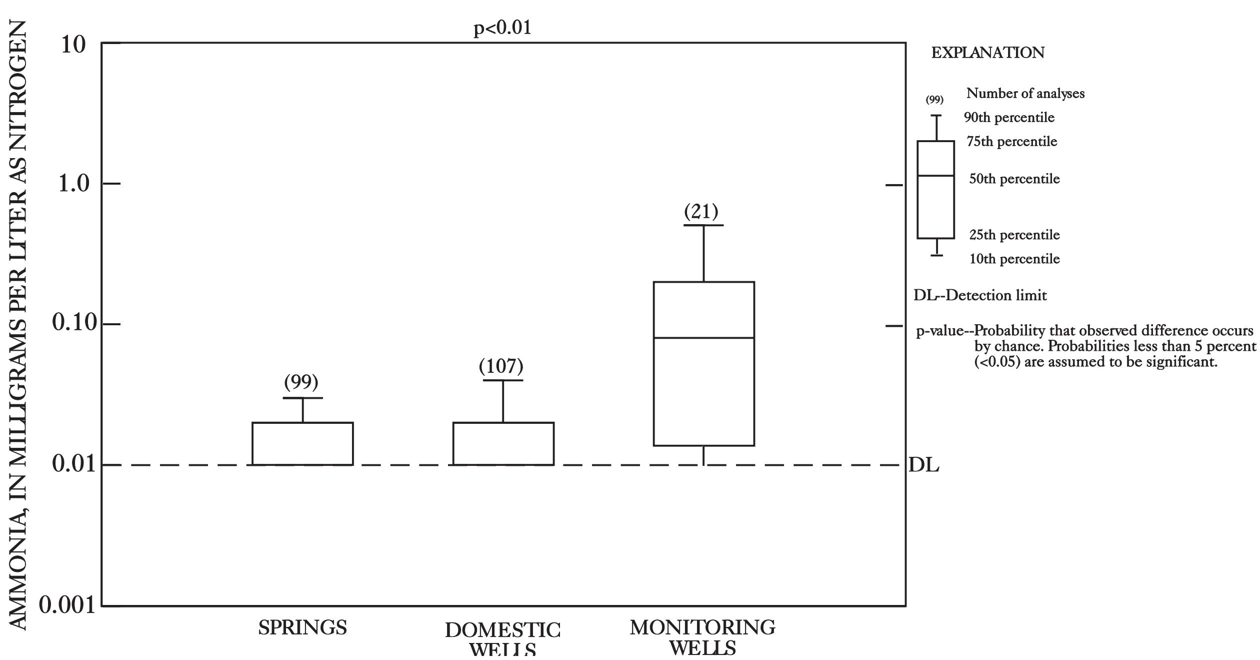

Figure 10. Distribution of ammonia concentrations in ground-water samples collected from springs, domestic wells, and monitoring wells.

maximum nitrite concentration (table 3). Most of these monitoring wells are located in or downgradient from pastures with large influxes of animal waste, a source of nitrogen.

As with nitrite, ammonia in ground water of the Springfield Plateau and Ozark aquifers negatively correlated to dissolved oxygen for the monitoring wells (rho=-0.654, p less than 0.01). Hence, ammonia in ground water probably is oxidized to nitrate.

Spearman's rho indicates ammonia concentrations in samples were not related to well depth, spring discharge, or other site characteristics. Ammonia concentrations in samples were not related to other field measurements or water-quality constituents.

Ammonia Plus Organic Nitrogen

As with nitrite and ammonia, concentrations of ammonia plus organic nitrogen in ground-water samples were low (table 2). Ammonia plus organic nitrogen was detected in 15 of 227 samples. Twelve of the 15 samples were from 7 of the monitoring wells in the small-watershed study. The maximum concentration of ammonia plus organic nitrogen, 4.9 mg/L as nitrogen, was in a sample from the shallow monitoring at S-field that also yielded samples with the maximum nitrite and ammonia concentrations (table 3).

Ammonia plus organic nitrogen in these 15 ground-water samples consisted primarily of organic nitrogen. Organic nitrogen ranged from 27 to 98 percent of the concentration, with a median of 75 percent. The presence of organic nitrogen in water indicates contamination by sewage or other organic wastes (Hem, 1989). Because most of these samples were from sites near pastures and livestock operations, the source of organic nitrogen in the samples probably was animal wastes.

Like nitrite and ammonia, organic nitrogen is unstable in water with high concentrations of dissolved oxygen (Hem, 1989) and is probably oxidized rapidly to nitrate. Samples from springs and domestic wells, even sites located in or near pastures, commonly had concentrations of nitrite, ammonia, and organic nitrogen less than the detection limit, consistent with the high dissolved-oxygen concentrations common in samples from these sites. High dissolved-oxygen concentrations in samples from springs and domestic wells appear to indicate that oxic conditions are widespread throughout most of the Springfield Plateau and Ozark aquifers. However, samples from the monitoring wells indicate that locally anoxic conditions can exist resulting in high concentrations of nitrite, ammonia, and organic nitrogen.

Phosphorus and Orthophosphate

Concentrations of phosphorus and orthophosphate were low in ground-water samples (table 2). In 93 of 227 samples, phosphorus and orthophosphate were less than the detection limit of 0.01 mg/L as phosphorus; in 159 of 227 samples, either phosphorus or orthophosphate was less than 0.01 mg/L. Phosphorus was greater than the background concentration of 0.02 mg/L in 33 samples; orthophosphate was greater than the background concentration of 0.01 mg/L as phosphorus in 66 samples. Twenty-one samples had phosphorus or orthophosphate concentrations greater than or equal to 0.05 mg/L as phosphorus.

Phosphorus concentrations in samples were the sum of all phosphorus species present and included orthophosphate. The median of the differences between phosphorus and orthophosphate concentrations in samples was less than 0.01 mg/L as phosphorus; hence, with few exceptions, phosphorus in samples consisted primarily of orthophosphate.

Median orthophosphate concentrations (fig. 11) were statistically greater in spring samples from the Springfield Plateau (0.02 mg/L) than in spring samples from the Ozark aquifer (0.01 mg/L; p less than 0.01). As with nitrite plus nitrate, the differences in orthophosphate concentrations between samples from the two aquifers probably resulted from differences in land use overlying the aquifers.

Median phosphorus and orthophosphate concentrations were statistically different between samples from springs (0.02 mg/L) and samples from domestic wells (less than 0.01 mg/L) in the Springfield Plateau aquifer (p less than 0.01) (fig. 11). The results, which agree with the results of nitrite plus nitrate analyses, indicate that water from springs generally is more susceptible to surface contamination than water from wells.

The solubility of phosphorus is affected by pH and concentrations of other ions in the water. Phosphorus can form insoluble residues with calcium and with aluminum and iron hydroxides. Phosphorus also can be sorbed onto clay minerals such as kaolinite (Brady, 1984). Hence, most of the phosphorus applied to pastures in the study unit could remain in the soil or be transported with particulates in the water. Further study would help to quantify the fate of phosphorus in the study unit.

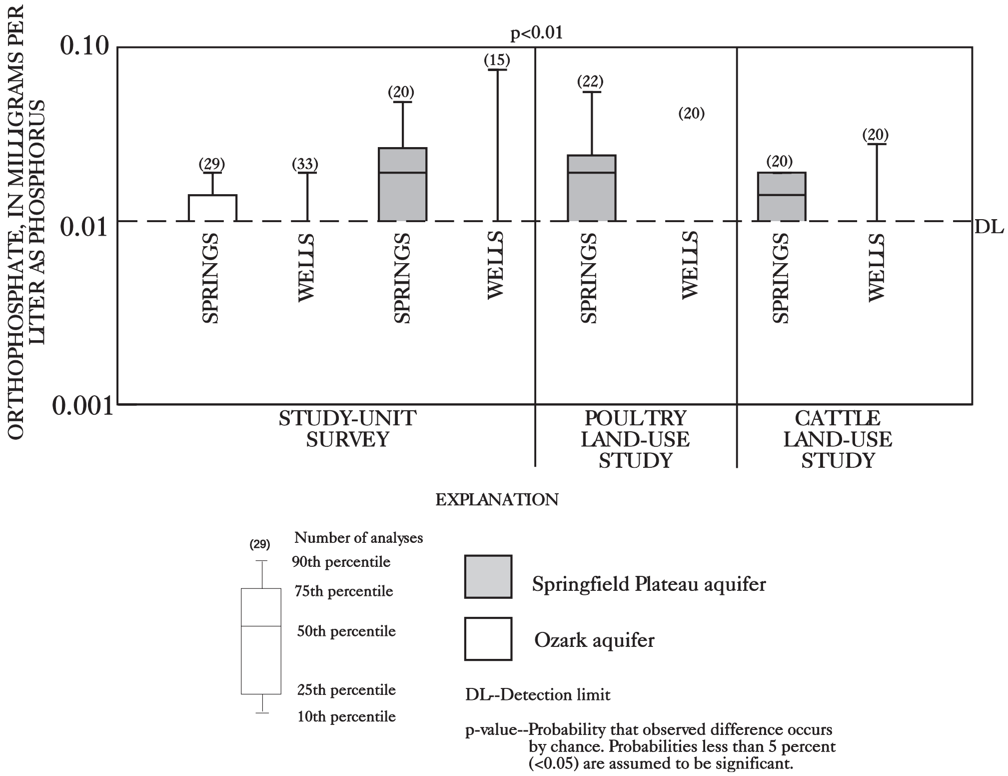

Figure 11. Distribution of orthophosphate concentrations in ground-water samples collected for the study-unit survey, and the poultry and cattle land-use studies.

Pesticides

Pesticides are chemicals, primarily synthetic organic compounds that are not naturally present in water, used to control unwanted plants or animals (Ware, 1989). Pesticides considered in this report include a wide range of classes of herbicides and insecticides. The list of pesticides is consistent with pesticides analyzed by other study units across the Nation. Many, but not all, of the pesticides on the list currently or historically have been used in the Ozark Plateaus study unit.

Pesticides were detected in 80 of 229 (35 percent) ground-water samples from 73 of 215 sites (fig. 12). Pesticides were detected in samples from 21 springs and 11 wells for the study-unit survey, 8 springs and 2 wells for the poultry land-use study, 10 springs and 7 wells for the cattle land-use study, and 4 springs, 3 domestic wells, and 7 monitoring wells for the small-watershed study.

Twenty pesticides were detected (table 4), with a maximum of five pesticides detected in any one sample. The most commonly detected pesticides were tebuthiuron (31), atrazine (30), prometon (25), desethylatrazine, a metabolite of atrazine (19), and simazine (18). These compounds are herbicides that are commonly used on pastures and non-crop areas. Atrazine is commonly used to control weeds in corn fields (Thomson, 1989). All other pesticides were detected in 10 or fewer samples. Alachlor and 2,4-D, two of the most commonly used pesticides in the study unit (Bell and others, 1996), were not detected in any samples.

Maximum pesticide concentrations ranged from 0.003 (benfluralin, metolachlor, p,p'-DDE, and trifluralin) to 1.0 µg/L (atrazine). No pesticide exceeded MCLs or health advisory levels for drinking water set by the U.S. Environmental Protection Agency (Nowell and Resek, 1994).

Concentrations of 12 pesticides and metabolites were estimated in one or more of the samples in which they were detected (table 4) for the following reasons: 1) three compounds (desethylatrazine, carbaryl, and carbofuran) demonstrated small or variable recovery primarily because of poor retention during the analyte extraction process, or 2) pesticide concentrations determined in some samples were less than the designated

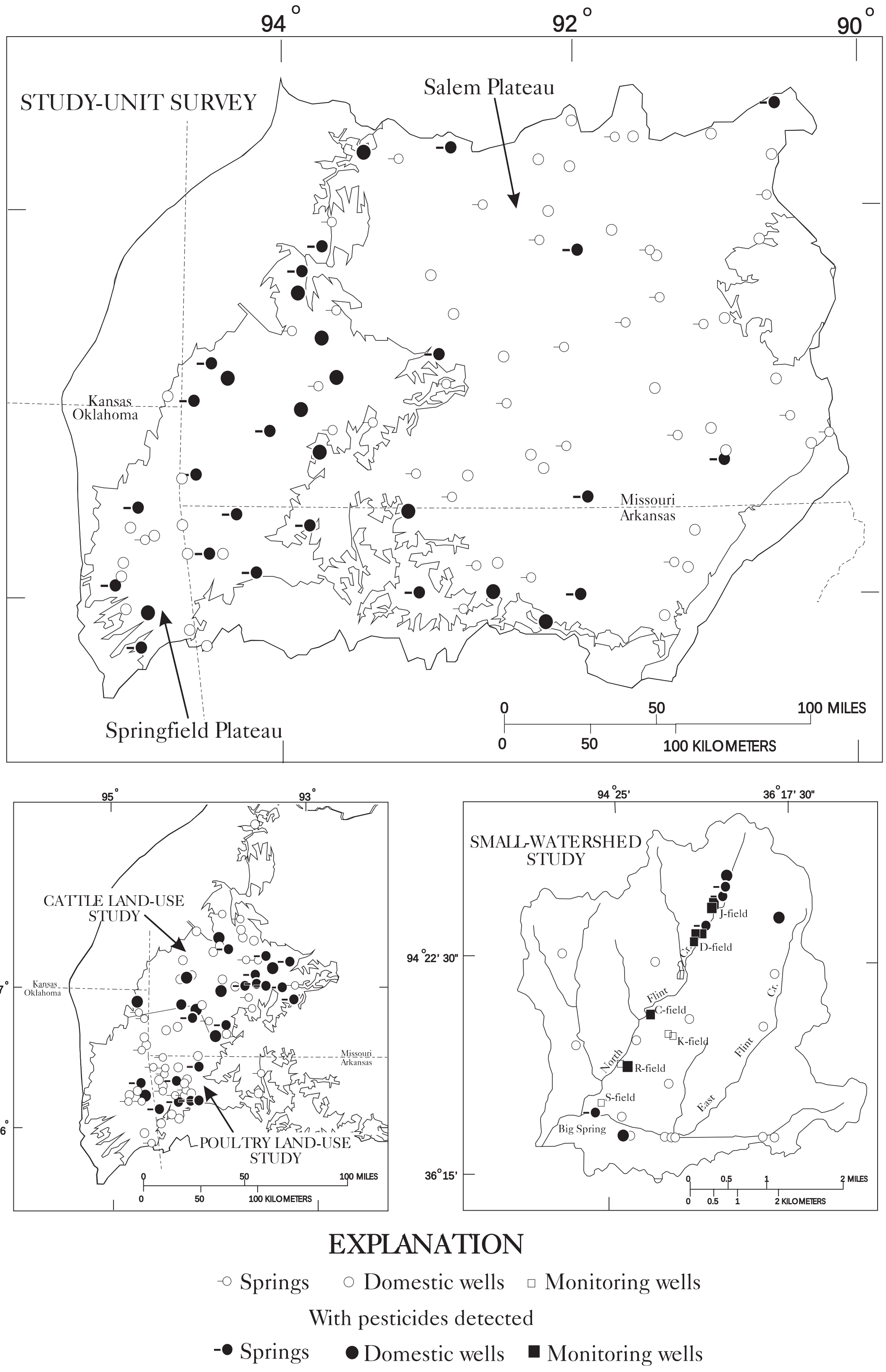

Figure 12. Locations of sampled springs, domestic wells, and monitoring wells with detectable concentrations of pesticides.

Table 4. Number of pesticide detections and range of concentrations

[µg/L, micrograms per liter; number in parentheses, number of total detections for which the reported concentration was an estimated value]

Pesticide	Study-unit survey (99 analyses)	Poultry land-use study (42 analyses)	Cattle land-use study (40 analyses)	Small water-shed study (44 analyses)	Total number of detections (225 analyses)	Range of concentrations (µg/L)	Use
Atrazine	14	7	6 (5)	3 (1)	30 (6)	0.001 - 1.0	Herbicide
Benfluralin	1	0	0	0	1	.003	Herbicide
Carbaryl	2 (2)	2 (2)	0	0	4 (4)	.012 - .03	Insecticide
Carbofuran	0	2 (2)	0	0	2 (2)	.007 - .016	Insecticide
Chlorpyrifos	2 (1)	0	0	0	2 (1)	.003 -.013	Insecticide
DCPA	1	2	0	0	3	.002 .014	Herbicide
Desethylatrazine	8(8)	7 (7)	3 (3)	1 (1)	19 (19)	.002 - 0.35	None (metabolite)
Dieldrin	1	0	1	0	2	.025 - .057	Insecticide, banned
Diuron	0	0	1 (1)	1 (1)	2 (2)	.01 - .18	Herbicide
Lindane	2	0	0	0	2	.028 -.032	Insectide
Linuron	0	1	0	0	1	.016	Herbicide
Metolachlor	3	0	1	1	5	.002 -.003	Herbicide
Metribuzin	0	0	0	3 (1)	3 (1)	.004 - .14	Herbicide
p,p'-DDE	7 (7)	2 (2)	1 (1)	0	10 (10)	.001 -.003	None (metabolite)
Prometon	1 (7)	2 (2)	2 (6)	0	25 (15)	.002-.88	Herbicide
Propanil	2	0	0	0	2	.007 -.012	Herbicide
Propargite	(1)	0	0	0	(1)	.008	Acaricide
Simazine	7 (6)	7 (5)	4 (1)	0	18 (13)	.001 -.026	Herbicide
Tebuthiuron	7 (2)	1	9 (7)	14	31 (9)	.005 -.24	Herbicide
Trifluralin	1	0	0	0	1	.003	Herbicide

method detection limit (Zaugg and others, 1995). Although the concentrations were estimated, the occurrence of these pesticides in samples was not uncertain.

The presence of pesticides in the ground water of the Ozark Plateaus study unit was somewhat unexpected, even at the relatively low concentrations as compared to those from adjacent physiographic areas (Kolpin and others, 1994; Ziegler and others, 1994), because pesticide usage is relatively low throughout most of the study unit (Bell and others, 1996). The occurrence of pesticides in ground water of the Springfield Plateau and Ozark aquifers confirms the vulnerability of those aquifers to surface contamination.

Results of contingency tables indicate pesticides were detected statistically more often in samples collected from the Springfield Plateau aquifer than in samples from the Ozark aquifer (p less than 0.01) (fig. 12). Pesticides were detected in 18 of 36 (50 percent) samples from the Springfield Plateau aquifer and in 14 of 63 (22 percent) samples from the Ozark aquifer collected for the study-unit survey. The relation between pesticide occurrence and aquifer probably results from greater percent agricultural land use around sites in the Springfield Plateau aquifer compared to sites in the Ozark aquifer.

Pesticide detections were related to land use in samples with tritium activities greater than 2.5 picocurie per liter (pCi/L). Tritium activities greater than 2.5 pCi/L in ground water indicate that some portion of the water was recharged to the ground-water system within the past 40 years (Plummer and others, 1993); therefore, the water could be affected by relatively recent land-use activities.

Percent agricultural land use was statistically greater for sites with samples that had detectable pesticide concentrations than for sites with samples that had no detectable pesticides (p less than 0.01) (fig. 13). Conversely, percent forest cover was statistically less for sites with samples that had detectable pesticide concentrations than for sites with samples that had no detectable pesticides (p less than 0.01).

Contingency tables indicate that the number of pesticide detections in ground-water samples was not statistically different between the poultry and cattle land-use studies (p=0.072). Furthermore, atrazine, desethylatrazine, p,p'-DDE, prometon, simazine, and tebuthiuron were detected in samples from both land-use studies. These results indicate a similarity, between the two land-use study areas, of pesticide usage and ground-water vulnerability to surface contamination.

Pesticides were detected statistically more often in samples from springs than in samples from domestic wells (p less than 0.01). Pesticides were detected in samples collected from 41 of 88 (47 percent) springs and 20 of 89 (22 percent) wells during the study-unit survey and two land-use studies combined. The results, which agree with the results from the nutrient analyses, indicate that water from springs generally is more susceptible to surface contamination than water from wells.

Median spring discharge and recharge area were statistically greater for samples with detectable pesticide concentrations than for samples with no detectable pesticide concentrations (p=0.035). For sites in the Springfield Plateau aquifer surrounded by predominantly agricultural land use, median spring discharge and recharge area for samples with pesticide detections were 294 gal/min (fig. 14) and 1.2 mi^2, respectively; whereas median spring discharge and recharge area for samples with no pesticide detections were 90 gal/min (fig. 14) and 0.39 mi^2, respectively. A large recharge basin is more likely than a small basin to encompass areas of pesticide use and potential sources of surface contamination.

Pesticide detections were related to nitrite plus nitrate and phosphorus concentrations in samples from sites in agricultural areas (greater than 80 percent) of the Springfield Plateau aquifer. Median nitrite plus nitrate and phosphorus concentrations were statistically greater (p less than 0.011 for nitrite plus nitrate; p=0.024 for orthophosphate) in samples with detectable pesticide concentrations (median nitrite plus nitrate = 3.0 mg/L as nitrogen; median phosphorus = 0.02 mg/L) than in samples with no pesticides detected (median nitrite plus nitrate = 1.6 mg/L as nitrogen; median phosphorus <0.01 mg/L). These results indicate that the hydrogeologic and land-use conditions that allow elevated concentrations of nitrite plus nitrate and phosphorus in ground water also allow pesticides to occur in ground water.

Pesticide occurrences in ground-water samples probably were related to seasonality and to chemical properties of the compounds such as solubility and persistence in the environment. Three springs and ten of the monitoring wells had samples collected two or three times; pesticides were detected in at least one sample from nine of these sites. Desethylatrazine, diuron, metolachlor, and metribuzin were not consistently detected in multiple samples. For example, metribuzin was not detected in any of the samples collected from

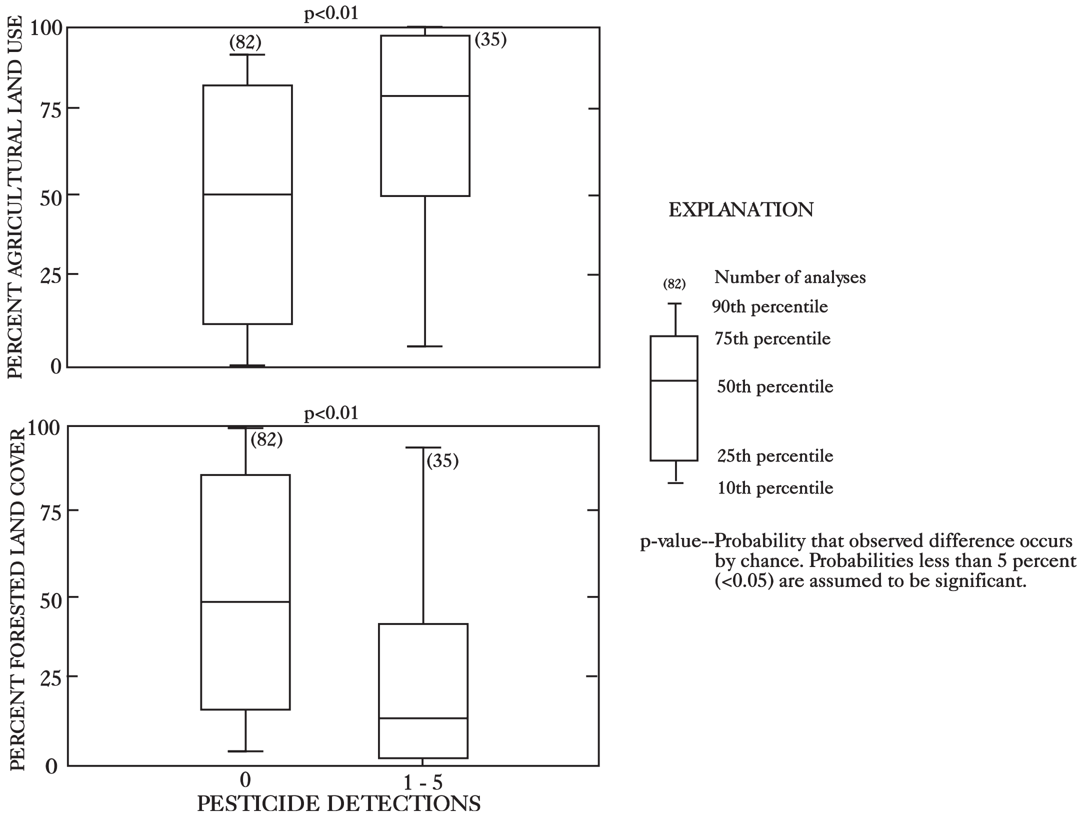

Figure 13. Relation of agricultural land use and forested land cover to pesticide detections in ground-water samples.

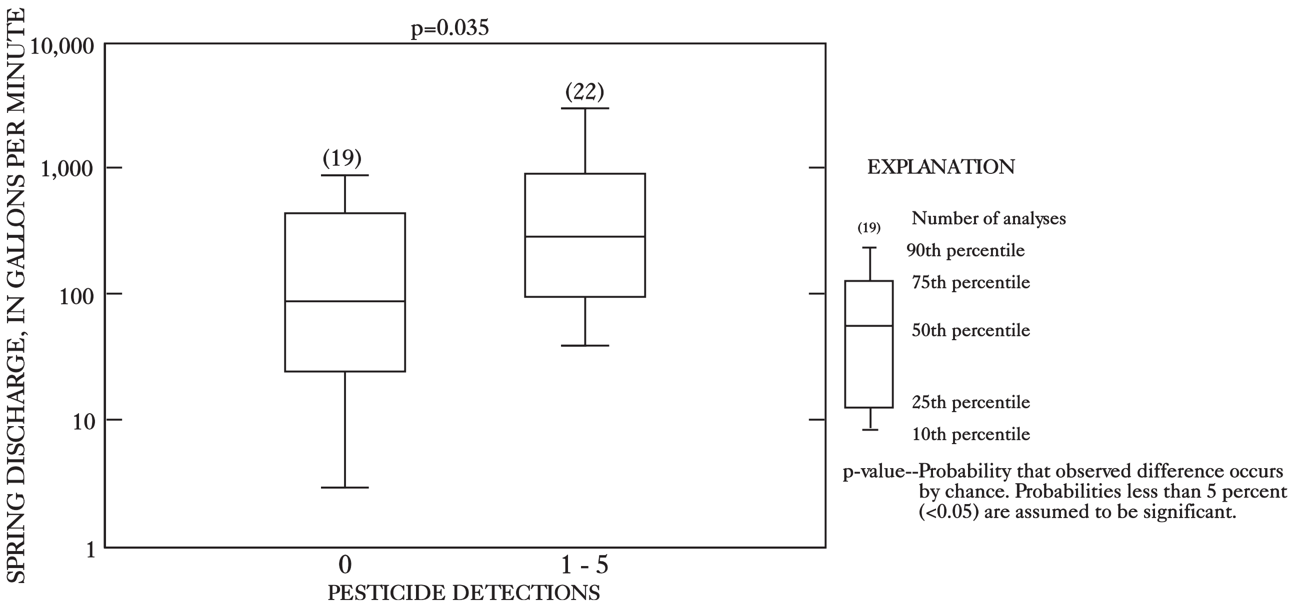

Figure 14. Relation of spring discharge to pesticide detections in ground-water samples from agricultural areas overlying the Springfield Plateau aquifer.

the monitoring wells in April 1995, but was detected in samples collected from three of the same monitoring wells in July 1995. Metribuzin is a selective herbicide with high (1,200 mg/L) solubility (Thomson, 1989). Metribuzin probably was applied after samples were collected in April 1995, and was rapidly transported to the aquifer system before samples were collected in July 1995. These results indicate that there is a high degree of temporal variability of pesticide concentrations in ground water.

In contrast, tebuthiuron, atrazine, prometon and simazine appear to be persistent. Tebuthiuron was detected in multiple samples from five sites; atrazine was detected in two samples from each of two sites; and prometon and simazine were detected in two samples from one site. In addition, the concentrations of these compounds, particularly tebuthiuron, were comparable between samples collected at different times from the same site. Samples collected repeatedly from the same sites during different seasons and different hydrologic conditions would help identify temporal variability or verify persistence of pesticides and further aid in characterizing pesticides in the aquifer.

p,p'-DDE and dieldrin were detected in 10 and 2 samples, respectively. The U.S. Environmental Protection Agency banned DDT in 1973 and dieldrin in 1984 (Ware, 1989). The occurrence of p,p'-DDE, a metabolite of DDT, and dieldrin in ground-water samples indicates the great stability and persistence of these compounds in the environment.

Pesticides in samples were not related to well depth or any other site characteristic. Pesticides in samples were not related to field measurements or any other water-quality constituents.

SUMMARY

In 1991, the U.S. Geological Survey began implementation of the National Water-Quality Assessment Program. The Ozark Plateaus study unit, 1 of 60 study units, is approximately 48,000 square miles in area and includes parts of northern Arkansas, southern Missouri, northeastern Oklahoma, and southeastern Kansas. The study unit includes most of the Ozark Plateaus Province (Salem Plateau, Springfield Plateau, and Boston Mountains sections) and parts of the Osage Plains section of the Central Lowland Province and the Mississippi Alluvial Plain section of the Coastal Plains Province. Dominant land use in the Salem Plateau is forest cover; dominant land use in the Springfield Plateau is livestock agriculture.

The study unit contains flat-lying to gently-dipping sedimentary rocks of Cambrian through Pennsylvanian age that overlie crystalline rocks of Precambrian age. These rocks form seven major hydrogeologic units, two of which--the Springfield Plateau and Ozark aquifers--were investigated as part of this study.

A ground-water sampling network was established with three scale-dependent components--the study-unit survey, the land-use studies, and the small-watershed study. The study-unit survey was largest in area and consisted of collecting samples from 50 springs and 49 wells in the Springfield Plateau and Ozark aquifers. The land-use studies consisted of collecting samples from 22 springs and 20 wells in a poultry-dominated agricultural area overlying the Springfield Plateau aquifer and 20 springs and 20 wells in a cattle-dominated agricultural area also overlying the Springfield Plateau aquifer. The small-watershed study was smallest in area and consisted of collecting samples from 4 springs, 18 domestic wells, and 11 monitoring wells in Flint Creek Basin.

A total of 229 ground-water samples was collected from 215 springs and wells from 1993 through 1995. Samples were analyzed for major ions (calcium, magnesium, sodium, potassium, chloride, sulfate, fluoride, and bromide), silica, nutrients (nitrite, nitrite plus nitrate, ammonia, ammonia plus organic nitrogen, phosphorus, and orthophosphate), dissolved organic carbon, methylene blue active substances, tritium, and 88 pesticides and metabolites. Nutrient and pesticide water-quality conditions were the focus of this report.

Background concentrations of nutrients in the Springfield Plateau and Ozark aquifers are low. Nutrient concentrations were below detection limits in many samples collected from sites in pristine (forest cover greater than or equal to 90 percent) areas.

Nitrite plus nitrate was detected in samples more often, and in greater concentrations, than any other nutrient. Nitrite plus nitrate, which ranged in concentration from less than 0.05 to 25 milligrams per liter as nitrogen with a median of 1.6 milligrams per liter, was greater than background concentrations in many samples from the Springfield Plateau and Ozark aquifers. These results indicate that both aquifers are susceptible to surface contamination. Susceptibility of the aquifers could result from the fractures and solution openings in the bedrock and permeable soils that allow rapid recharge of the ground water.

Nitrite, ammonia, and ammonia plus organic nitrogen are sometimes present locally in the aquifers; however, these nitrogen species probably are rapidly oxidized to nitrate as a result of the relatively high concentrations of dissolved oxygen, common in samples from springs and domestic wells. The concentration of phosphorus and orthophosphate probably was related to solubility, which is affected by calcium, aluminum and iron hydroxides, and clay minerals such as kaolinite present in the soil. Further study would help to quantify the fate of phosphorus in the study unit.

Results indicate that nutrients in ground water were related to land use. Median concentrations of nutrients were greater in samples from the Springfield Plateau aquifer, which is overlain predominantly by agricultural land use, than in samples from the Ozark aquifer, which is overlain predominantly by forested land cover. Nitrite plus nitrate concentrations positively correlated to percent agricultural land use around each site. The presence of organic nitrogen in 15 samples indicates contamination by organic, possibly animal, wastes. Finally, nutrients were detected more often in samples from the land-use and small-watershed studies than in samples from the study-unit survey, which contained a higher proportion of forest.

Hydrogeology also affects nutrient concentrations in samples. Median concentrations of nutrients generally were greater in samples from springs than in samples from wells. Water issuing from springs appears to have a more shallow source, and hence more susceptible to surface contamination than water from wells.

Pesticides were detected in 80 of 229 samples from 73 of 215 sites. Twenty pesticides were detected with a maximum of 5 pesticides detected in any one sample. The most commonly detected pesticides were tebuthiuron, atrazine, prometon, desethylatrazine, a metabolite of atrazine, and simazine. Maximum concentrations of pesticides ranged from 0.003 (benfluralin, metolachlor, p,p'-DDE, and trifluralin) to 1.0 (atrazine) microgram per liter. The presence of pesticides in ground water of the Ozark Plateaus study unit, which was somewhat unexpected because of the relatively low pesticide usage throughout most of the study unit, indicates that water in both aquifers is susceptible to surface contamination.

As with nutrient concentrations, pesticide detections were related to land use. Tebuthiuron, atrazine, and prometon are commonly used to control weeds in pastures and non-crop areas. Atrazine is commonly used to control weeds in corn fields. Pesticides were detected more often in samples from the Springfield Plateau aquifer than in samples from the Ozark aquifer. In addition, percent agricultural land use was greater for samples with pesticides detected than for samples with no pesticides detected. Concentrations of nitrite plus nitrate and phosphorus were greater in samples with pesticide detections than in samples with no pesticides detected.

Pesticides were detected more often in samples from springs than in samples from wells. These results agree with the results of nutrient analyses and indicate that water from springs generally is more susceptible to surface contamination than water from wells. In addition, pesticide detections were related to spring discharge; spring discharge was significantly greater for samples with pesticides detected than for samples with no pesticides detected.

The occurrence of pesticides in ground-water samples probably also was related to seasonality and chemical properties of the compounds. Desethylatrazine, diuron, metolachlor, and metribuzin were not consistently detected in samples from the same sites. These results indicate that there is a high degree of temporal variability in pesticide concentrations. In contrast, tebuthiuron, atrazine, prometon, and simazine appear to be persistent, having been detected in multiple samples from the same sites collected in different seasons. Furthermore, p,p'-DDE, a metabolite of DDT, and dieldrin detections indicate the persistence of these compounds in the environment. DDT was banned in the United States in 1973, and dieldrin was banned in the United States in 1984.

In conclusion, the ground-water quality of both aquifers is susceptible to surface contamination and is being affected by increased concentrations of nutrients, particularly nitrite plus nitrate, and the presence of pesticides. The occurrence of nutrients and pesticides in ground water of both aquifers appears to be related to agricultural land use and hydrogeological factors such as site type (wells and springs), soil composition (such as aluminum and iron hydroxides and kaolinite), and oxidation conditions of the ground water. The presence of pesticides in ground water probably also is related to seasonality and to solubility and persistence of the compounds. Samples collected repeatedly during different seasons and different hydrologic conditions would help identify temporal variability or verify persistence of pesticides and further aid in characterizing pesticide occurrence in the aquifers.

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