

Cover: Conceptual diagram depicting shallow agricultural land-use monitoring wells and a domestic well completed in the Mississippian carbonate aquifer. Photograph on left side of cover shows a submersible pump in a monitoring well adjacent to a field of winter wheat near Huntsville, Alabama. Photograph on right side of cover is a cotton field in northern Alabama.

Shallow Ground-Water Quality in Agricultural Areas of Northern Alabama and Middle Tennessee, 2000-2001

By James A. Kingsbury

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FOREWORD

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

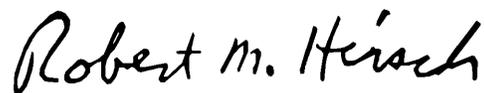
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (<http://water.usgs.gov/nawqa/>). Shaped by and coordinated with ongoing efforts of other Federal, State,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

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

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

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

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



Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS, DATUMS, AND WATER-QUALITY UNITS

	Multiply	By	To obtain
	inch (in.)	2.54	centimeter (cm)
	inch (in.)	25.4	millimeter (mm)
	foot (ft)	0.3048	meter (m)
	mile (mi)	1.609	kilometer (km)
	acre	4,047	square meter (m ²)
	square mile (mi ²)	2.590	square kilometer (km ²)
	gallon per minute (gal/min)	0.06309	liter per second (L/s)
	million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
	pound, avoirdupois (lb)	0.4536	kilogram (kg)
	gallon per minute per foot [(gal/min)/ft]	0.2070	liter per second per meter [(L/s)/m]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = (1.8 × °C) + 32

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Water-quality units

mg/L milligrams per liter

µg/L micrograms per liter

µS/cm microsiemens per centimeter

pg/kg picogram per kilogram

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ABSTRACT

As part of the U.S. Geological Survey National Water-Quality Assessment Program, 32 monitoring wells were installed near cropland in parts of northern Alabama and Middle Tennessee to characterize the effect of row-crop agriculture on shallow ground-water quality. The wells were completed in regolith overlying carbonate bedrock. These geologic units are part of the Mississippian carbonate aquifer, a source of drinking water for domestic and municipal supply in the area. The majority of these wells were sampled in the spring of 2000 for inorganic constituents, nutrients, pesticides, and selected pesticide degradates. Land use and soil characteristics were delineated for a 1,640-foot radius buffer area around each well to relate water quality to environmental factors. A strong association among soil characteristics, land use, and hydrogeology limited the analysis of the effect of these factors on nitrate and pesticide occurrence.

Nitrate and pesticide concentrations generally were low, and no samples exceeded established drinking-water maximum contaminant levels. The maximum concentration of nitrate was about 8 milligrams per liter as nitrogen, and the median concentration was 1 milligram per liter. Nitrate concentrations were strongly correlated to dissolved-oxygen concentrations, and ratios of chloride to nitrate indicate nitrate concentrations were affected by denitrification in about a third of the samples. A pesticide or pesticide degradate was detected at concentrations greater than 0.01 microgram per liter in 91 percent of the samples. Pesticides with the highest use typically

were detected most frequently and at the highest concentrations; however, glyphosate had the highest estimated use but was not detected in any samples. Fluometuron and atrazine, two high-use pesticides, were detected in 83 and 70 percent, respectively, of the samples from wells where the pesticide was applied in the buffer area. Maximum concentrations of fluometuron and atrazine were 2.13 and 1.83 micrograms per liter, respectively. Detection rates of pesticide degradates were similar to parent pesticides, and concentrations of degradates generally were comparable to or greater than the parent pesticide. Pesticide detections were correlated to dissolved-oxygen concentrations, suggesting that pesticides are most likely to be detected at high concentrations where ground-water residence time is short and the rate of recharge is fast.

Nitrate and pesticide data collected in this study were compared to data collected from similar agricultural land-use studies conducted by the National Water-Quality Assessment Program throughout the Nation. Nitrate concentrations generally were lower in this study than in samples from other agricultural areas; however, pesticides were detected more frequently in samples from wells in this study. For example, atrazine and its degradate, deethylatrazine, were detected in 62 and 47 percent, respectively, of water samples in this study but were detected in about 25 percent of the 851 wells sampled for agricultural land-use studies nationwide. In national study areas where atrazine use is greater than in the lower Tennessee River Basin, atrazine was detected in 30 percent of the water samples. Pesticides used on cotton were detected much more frequently in this study,

but many of the study areas nationwide have smaller amounts of cotton acreage than the lower Tennessee River Basin.

Similarities in nitrate concentrations and the pesticides detected frequently in this agricultural land-use study and a network of drinking-water wells in the same area completed in bedrock in the Mississippian carbonate aquifer (sampled in a previous study) indicate the aquifer is susceptible to contamination from nonpoint sources. Nitrate concentrations were not statistically different for the two well networks and were correlated to total pesticide concentrations in both networks. Although detection frequencies and maximum concentrations were higher in the land-use monitoring wells than in the drinking-water wells, the same pesticides were detected frequently, and median concentrations of these pesticides were similar. The similarity in water quality between samples from the shallow land-use and the deeper drinking-water wells is probably the result of the karst hydrology of the aquifer, which allows substantial transport of nonpoint-source contaminants from agricultural areas once water has moved through the regolith to conduits in bedrock.

INTRODUCTION

Nitrate and pesticide contamination of ground water in agricultural areas is an important issue because ground water is often the principal source of drinking water in northern Alabama and Middle Tennessee. Although local, regional, and national reconnaissance studies of nitrate and pesticides in ground water have been conducted, these studies typically have evaluated the quality of water obtained from existing domestic or public-supply wells. These types of wells commonly withdraw water from deep parts of aquifers where the effects of land use on water quality are less evident.

As part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program in the lower Tennessee River Basin (LTEN), a network of shallow land-use monitoring wells was installed in parts of northern Alabama and Middle Tennessee to characterize the quality of recently recharged ground water near agricultural fields (figs. 1 and 2). The data

from these shallow wells represent parts of the aquifer most affected by land-use activities at land surface and serve as a point of comparison for the effects of land use on the drinking-water resource. Wells were installed near agricultural fields in the Eastern Highland Rim, one of nine subunits (fig. 1) that generally correspond to Level III and IV ecoregion boundaries (Griffith and others, 1997; Kingsbury and others, 1999) and into which the LTEN was subdivided. These monitoring wells are nested within a network of predominantly domestic wells in the same subunit that was sampled in the summer of 1999 (Kingsbury and Shelton, 2002).

The Eastern Highland Rim is underlain by carbonate rocks of Mississippian age that make up the Mississippian carbonate aquifer, the most areally extensive and productive aquifer in the LTEN. Estimated ground-water withdrawals from the Mississippian carbonate aquifer for public and domestic supply in the Eastern Highland Rim was about 40 Mgal/d in 1995 (U.S. Geological Survey, 1997). The City of Huntsville, Alabama, is the largest ground-water user, withdrawing about 14 Mgal/d from wells that have a maximum depth of 125 ft. Ground water accounts for about 40 percent of water used in Huntsville. About 25 public water-supply systems rely on ground water from the Mississippian carbonate aquifer in the Eastern Highland Rim. About 5 Mgal/d of the total ground-water withdrawals for 1995 were for domestic use.

Purpose and Scope

This report describes the quality of shallow ground water collected in the spring of 2000 and 2001 from monitoring wells installed near agricultural areas in the Eastern Highland Rim of the LTEN study area. Soil properties, hydrogeology, and land-use data in the area near the monitoring wells are evaluated to determine the principal factors that affect the occurrence of nitrate and pesticides. The occurrence and distribution of nitrate and pesticides in the Mississippian carbonate aquifer are put into a broader context by comparing the results from other NAWQA agricultural land-use studies across the Nation. The nitrate and pesticide data in this study also are compared to data from a network of predominantly domestic wells sampled in 1999 to characterize the effect of agricultural land use on the quality of drinking water in the aquifer.

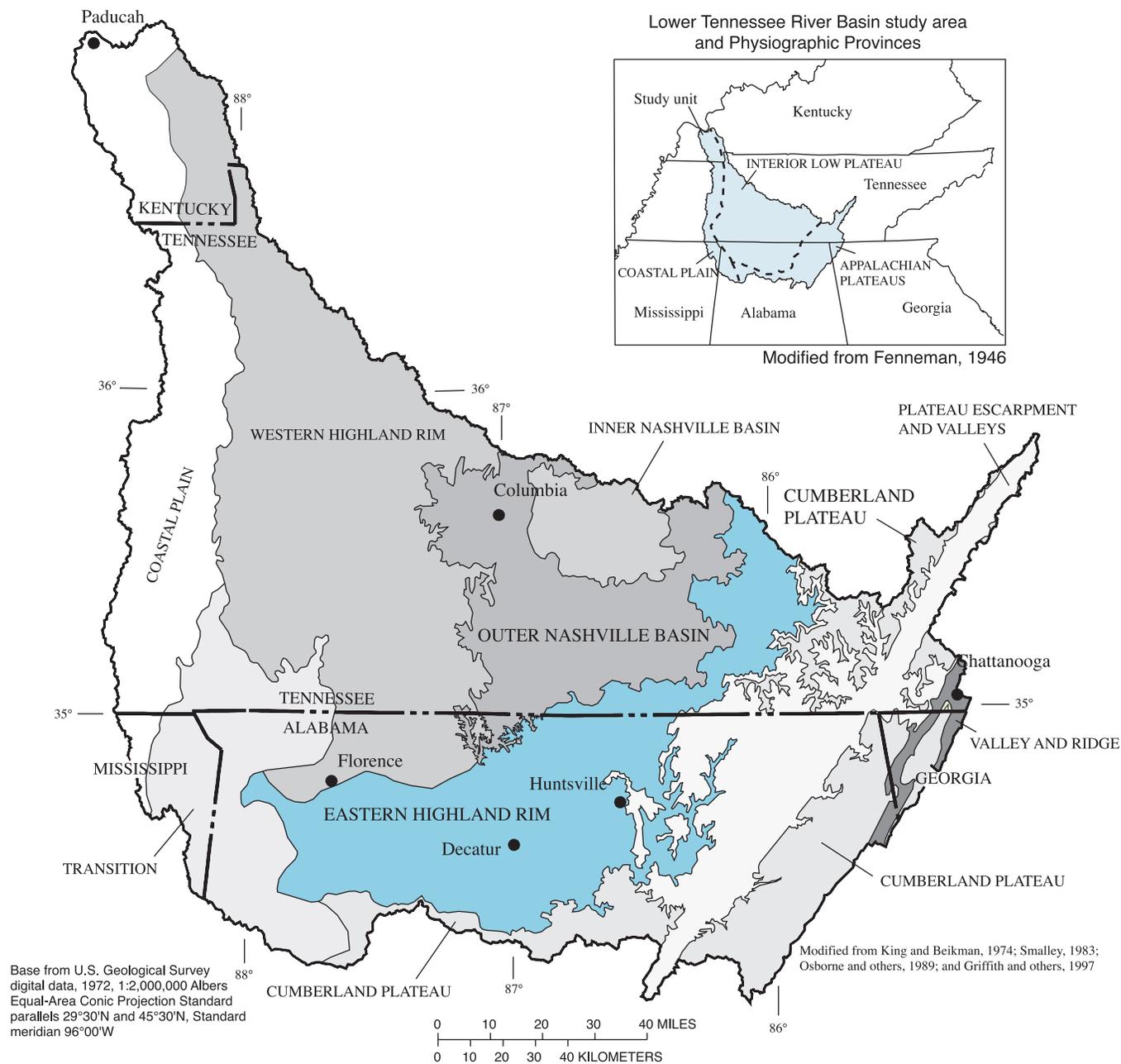


Figure 1. Location of the lower Tennessee River Basin with its delineated subunits, including the Eastern Highland Rim study area.

Acknowledgments

The author thanks the many landowners who permitted access to their land for the installation and sampling of shallow monitoring wells. The following Natural Resources Conservation Service District Conservationists were particularly helpful in locating potential sites for wells: Joe Berry, Madison County, Alabama; Billy Frost, Lawrence County, Alabama;

Kathy Gotcher, Colbert County, Alabama; and Kenneth Swafford, Limestone County, Alabama. The following water departments provided water during drilling: City of Winchester Water, Manchester Water Department, and Lincoln County Water Department in Tennessee; Madison County Water Department, City of Huntsville, Limestone County Water Authority, Tusculum Water, and West Morgan and East Lawrence County Water Authority in Alabama.

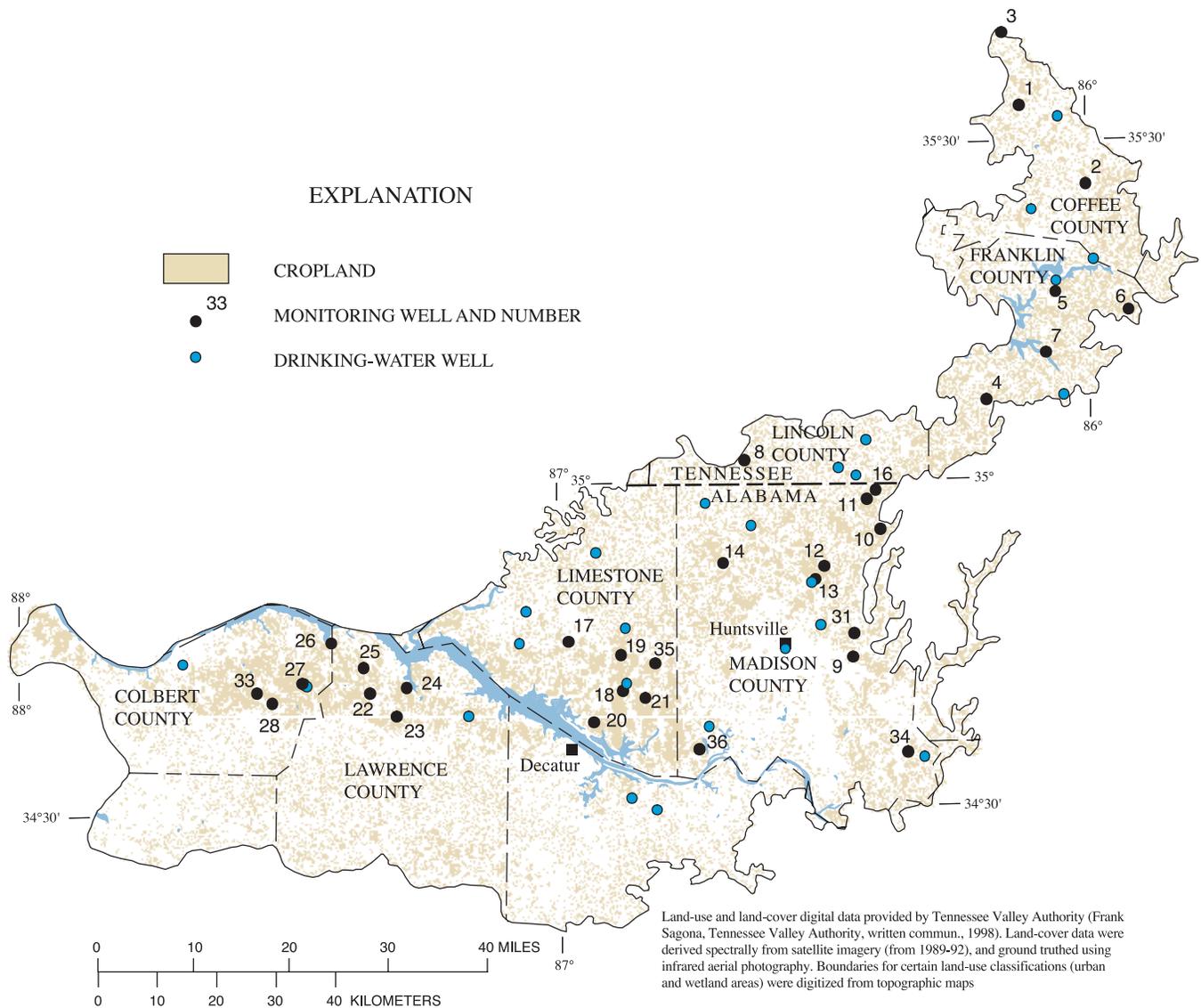


Figure 2. Location of wells sampled and 1992 distribution of cropland in the Eastern Highland Rim.

APPROACH

A network of 32 monitoring wells was established to characterize shallow ground-water quality in the Mississippian carbonate aquifer in agricultural areas in the Eastern Highland Rim (fig. 2). Cropland delineated from 1992 digital land-use data in the Eastern Highland Rim were combined into about 40 equal subareas from which random locations were generated using a geographic information system (GIS) based computer program (Scott, 1990). Suitable sites for monitoring wells within about a mile radius of random points generated by this program were then located. Wells were installed near agricultural fields, usually

along buffer strips adjacent to fields. The direction of ground-water flow was not known, so wells were installed in locations presumed to be downgradient of the fields.

The wells installed for this study were intended for sampling water near the water table to characterize the effect of row-crop agriculture on the quality of recently recharged ground water. Thirty-two wells were drilled using hollow-stem augers and completed with 2-in.-diameter threaded polyvinyl chloride (PVC) casing. The wells were completed in regolith and were drilled in 1999 during October and November when ground-water levels typically are lowest. The top of the well screens generally were within 10 ft of the

water table. Eight of the wells had more than 10 ft of water above the screens, and 12 wells had water levels below the top of the screen at the time of sampling. Well screens were 0.01-in.-diameter slotted 10-ft-long PVC, with the exception of three wells with 5-ft-long screens. Wells ranged from 14 to 79 ft deep, with a median depth of 37.5 ft. A sand pack was placed around the well screens, and a bentonite seal was placed on top of the sand pack at least 2 ft above the top of the screen. The remainder of the annulus was grouted to land surface with a cement-bentonite mixture. Wells were developed several weeks prior to sampling, by pumping or bailing if the well did not produce enough water, typically until the turbidity was less than 10 nephelometric turbidity units.

Samples were collected and processed according to NAWQA ground-water sampling protocols (Koterba and others, 1995). Wells were purged a minimum of three casing volumes; specific conductance, dissolved oxygen, pH, and temperature were monitored until they stabilized prior to sampling. Wells that could not be pumped continuously were pumped dry, and the water level was allowed to recover to 90 percent of the pre-pumping level, at which time the wells were sampled. Samples for inorganic constituents were filtered through a disposable 0.45- μm capsule filter, and samples for cation analysis were preserved with nitric acid. Pesticide samples were filtered through a 0.7- μm disposable glass-fiber filter. Nutrient and pesticide samples were kept chilled and shipped overnight to the U.S. Geological Survey National Water-Quality Laboratory (NWQL) in Denver, Colorado. All sampling equipment was constructed of stainless steel or teflon and was cleaned with three volumes (pump line) of soapy wash, tap-water rinse, and a final rinse with de-ionized water. The aluminum pesticide filtration unit also was rinsed with pesticide-grade methanol.

Analytical Methods

Samples were analyzed using approved U.S. Geological Survey (USGS) methods at the NWQL in Denver, Colorado, and at the USGS Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kansas. Dissolved inorganic constituents were determined by atomic absorption, inductively coupled plasma, ion chromatography, ion specific electrode, and colorimetric methods, as described in Fishman and Friedman (1989) and Fishman (1993).

Two analytical methods were used at the NWQL (Zaugg and others, 1995; Furlong and others, 2001), and one method was used at the ORGL (Kish and others, 2000) to analyze a total of 93 pesticides and 19 pesticide degradates (appendix 1). Pesticides were extracted from samples by pumping filtered samples through solid-phase extraction columns. Extracts from these columns were subsequently analyzed by gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography/mass spectrometry (HPLC/MS). Minimum reporting levels (MRL) range from 0.001 to 0.193 $\mu\text{g/L}$ and are based on method detection limits (MDL) for each pesticide. The MDL represents the lowest concentration at which a constituent can be identified and measured with 99 percent confidence that the concentration was greater than zero (Wershaw and others, 1987) and varies based on the performance of the method for each pesticide. Some concentrations are qualified with an "E" indicating an estimated concentration. These concentrations are estimated because they are either above or below the range in concentration of the calibration standards; the sample matrix interfered with the measurement of the analyte; surrogates added to samples indicated that the method was not performing adequately; or the analyte has systematically had low or inconsistent recoveries throughout the development and implementation of the method and concentrations always are reported as estimates (appendix 1).

Samples were analyzed by the HPLC/MS method before final approval by the USGS Office of Water Quality in April 2001. Although the analytical method did not change following approval, data analyzed before method approval are considered provisional. During initial implementation of this analytical method in 1999, a backlog of samples resulted in a number of samples exceeding the recommended 4-day holding time prior to sample extraction (Furlong and others, 2001). Samples collected from the agricultural monitoring wells in 2000 and 2001 met the recommended holding times, but samples from some of the drinking-water wells presented in this report did not. Degradation of pesticides during extended sample storage is likely, and concentrations and detection frequencies for the pesticides analyzed by this method may be biased low in the samples from the drinking-water wells. Pesticides analyzed by HPLC/MS are shown in italics in appendix 1.

Analyses of fluometuron and norflurazon degradates were conducted by GC/MS at the OGRL.

Analytical methods are described in Kish and others (2000). The MRL for these degradates is 0.05 µg/L (appendix 1). Glyphosate was analyzed by enzyme-linked immunosorbant assay at the OGRL (Lee and others, 2002) and had a MRL of 0.1 µg/L. At the time these samples were analyzed, these analytical methods also were not yet approved, so the results are considered provisional.

Quality Assurance and Quality Control

The low-level concentrations at which pesticides were analyzed in this study necessitated quality-control sampling to demonstrate that equipment cleaning, sample collection and processing, and analytical procedures were noncontaminating and to identify bias in the methods. Field quality-assurance samples made up about 30 percent of all samples analyzed and included blanks, replicates, and pesticide spikes. Data from inorganic constituent and pesticide blanks indicate that equipment cleaning procedures were adequate and that sample collection and processing procedures generally were noncontaminating. Only two pesticides were detected in a total of five blanks. Terbacil was detected in two blanks but was not present in any environmental samples. Diuron was detected at an estimated concentration of 0.01 µg/L in one blank; environmental samples associated with this blank did not contain diuron. Recoveries of spiked pesticides ranged from 5 to 245 percent for all of the pesticides analyzed, and the median recovery was 86 percent. For pesticides detected in this study, the range in recoveries was 52 to 245 percent with a median recovery of 86 percent. Recoveries of several spiked pesticides have had considerable and systematic bias with these analytical methods; deethylatrazine, aldicarb (52 percent) and its degradates, and hydroxyatrazine were biased low. Carbaryl and carbofuran (245 percent), which historically have had poor recoveries with this analytical method (Zaugg and others, 1995), were biased high in spiked samples analyzed.

Delineation of Land Use and Soil Properties Near Wells

Because the rate and direction of ground-water flow generally is not known for monitoring wells installed for the NAWQA Program, a 1,640-ft (500-m) buffer area was used for characterizing land use near

monitoring wells. Based on data from other studies, Koterba (1998) concluded that a buffer area of this size likely would represent at least part of the recharge area for a well in a shallow, unconfined aquifer and should be used in NAWQA ground-water studies. High-resolution black and white aerial photographs at a 1:20,000 scale were used to delineate land use within the buffer area around each well. All of the aerial photographs, with the exception of one which was taken in 1992, were taken between 1997 and 1999 by the National Aerial Photography Program. A mylar overlay was used to delineate land-use areas. Land uses identified from aerial photographs and crops were verified by site visits. The area of each land-use type in buffer areas was determined using a planimeter. Planimeter measurements were made three times and averaged. The sum of the land-use areas was within 2 percent or less of the total buffer area measured with the planimeter for most of the wells. Differences for a few wells were as much as 5 percent because of measurement error associated with the large number and small size of land-use areas delineated. Land-use data also were delineated using the same methodology for a network of existing, predominantly domestic wells, and the relative percentages of land uses in those buffer areas were calculated by using GIS.

These land-use data were used to estimate pesticide use for the 2000 growing season in each of the buffer areas. Information about application rates was provided by local agricultural officials and also were obtained from the national pesticide use database maintained by the National Center for Food and Agricultural Policy (2002). These application rates were multiplied by the percentage of acreage typically treated and by the acreage of a given crop in the buffer areas determined from the aerial photographs.

Soil properties were characterized for the buffer areas around each well. County soil survey maps (scale 1:20,000) were used to delineate soil map units within the buffer areas. Mylar overlays with soil map unit boundaries were scanned and converted into digital coverages. The area of each map unit within the buffer was determined by GIS. Digital soil maps at a scale of 1:24,000 from the National Soil Survey Geographic (SSURGO) database (U.S. Department of Agriculture, 2001a) were available for Limestone and Madison Counties in Alabama. Soil map units in buffers around wells in these counties were delineated from these digital data. Soil attributes for map units were obtained from the National Map Unit Interpretation Record (MUIR) database (U.S. Department of

Agriculture, 2001b). Soil properties were derived for only the first soil layer because not all map units had data for deeper layers and because soil attributes for deeper layers generally were similar to the first soil layer for map units with multiple layers. Minimum, maximum, and mean values were used for soil properties that had ranges. Percentages of sand and silt are not in the MUIR database but were calculated (following Burkart and others, 1999) by subtracting the percentage of material passing through a 0.08-mm and a 50-mm sieve (sand) and the clay percentage from the 0.08-mm sieve (clay). Categorical properties, such as hydrologic group, were converted to continuous variables by using the percentage of the buffer area containing soils in a given group. Soil data were not available for one well, so that well is not included in any data analysis involving soil properties.

Statistical Methods

Several statistical tests were used in this study to evaluate relations between water-quality constituents and environmental factors that could affect constituent concentrations in ground water. The Spearman rank correlation test (Helsel and Hirsch, 1992) was used to evaluate whether nitrate and pesticide concentrations are correlated to other water-quality constituents, site characteristics, and land use. Wilcoxon rank sum tests were used to determine if constituent concentrations are significantly different for two groups of samples. For example, samples from wells with detections were compared to samples from wells without detections to determine whether environmental factors are significantly different for the two groups of wells. Partial correlation analysis (Blalock, 1972) was used to determine whether two colinear variables contribute to the variability in nitrate and pesticide concentrations, or whether one variable explains most of the variability in concentration. Partial correlation analysis determines the strength of the correlation between two variables if a third, correlated variable were to be held constant (Lowry, 2000). A significance level of 5 percent ($p < 0.05$) was used for statistical analysis of the data for this study. A common reporting level of $0.01 \mu\text{g/L}$ was used for computing detection frequencies for pesticides in this report, with the exception of those pesticides analyzed by the OGRL that did not include estimated concentrations below the MDL.

HYDROGEOLOGY

Much of the study area is underlain by the Mississippian-age Tusculumbia Limestone and Fort Payne Chert, a cherty limestone (Osborne and others, 1989). Most of the wells were completed in regolith overlying these formations. In Tennessee, the equivalent units to the Tusculumbia Limestone are the Warsaw and St. Louis Limestones. Two wells were installed in regolith overlying the Monteagle Limestone, which crops out in the southern part of the Eastern Highland Rim. The predominantly carbonate geology of these formations has resulted in the development of karst landforms such as sinkholes, caves, disappearing streams, and springs throughout much of the subunit. The regolith is a layer of residual material derived in place from the weathering of the carbonate bedrock. The regolith consists of a mixture of clay, silt, and clay-sized chert, with some chert gravel and chert interbeds. Gravel is scattered throughout the regolith but typically is more abundant and larger above the contact with bedrock where locally, bedrock cobbles or boulders may be present. Locally, these sediments are reworked and redeposited. The regolith can be as much as 100 ft thick but typically is between 30 and 60 ft thick.

The regolith and underlying bedrock are hydrologically connected, and in this report, the saturated regolith and bedrock are referred to as the Mississippian carbonate aquifer. Ground water in the aquifer typically is under water-table conditions; however, clay layers in the regolith can provide varying degrees of confinement locally. Recharge to the aquifer is largely from precipitation infiltrating and moving through the regolith. Focused recharge also occurs from surface drainage into sinkholes or losing stream reaches that intersect the aquifer.

Most of the wells were screened in parts of the aquifer that remained saturated throughout the year, but nine wells that were completed at the top of bedrock were dry during part of the year. Of these nine wells, some are well connected to ground water in bedrock, and the dry periods represent times of the year when the water level in the aquifer was below the top of bedrock (below the bottom of the well). Other wells were dry for part of the year because they may not be well connected to ground water in bedrock. These wells are analogous to wells completed in perched water-bearing zones in that they are not well connected to the water table and go dry as recharge decreases in the summer as water drains into conduits

in bedrock. Without a nearby water-level measurement in a well completed in bedrock, determining which scenario applies to a given well is difficult. Figure 3 shows a conceptual diagram of the hydrogeology of the Mississippian carbonate aquifer and hydrographs of wells that represent different hydrologic conditions in the regolith. Monthly measurements indicate that water levels fluctuated as much as 20 ft throughout the year (fig. 3) in some wells. Hydrograph A (fig. 3) represents a shallow well (well 18) screened in fine-grained material at the top of bedrock that was dry for parts of the year. Water levels rose in response to rainfall in the winter and spring and declined at about the same rate as they had risen as precipitation decreased and evapotranspiration rates increased. Hydrograph B (fig. 3) represents data from a deeper well (well 11) screened in a gravel zone that remained saturated all year. Water levels responded more slowly to rainfall in the winter and continued to decline through the beginning of February before they began to rise (fig. 3). The rate of water-level decline was slower in well 11 than in well 18, which may represent a contribution of recharge from areas with low permeability or diffuse recharge.

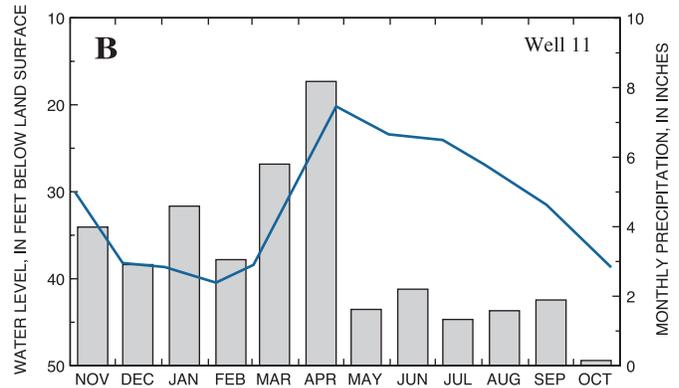
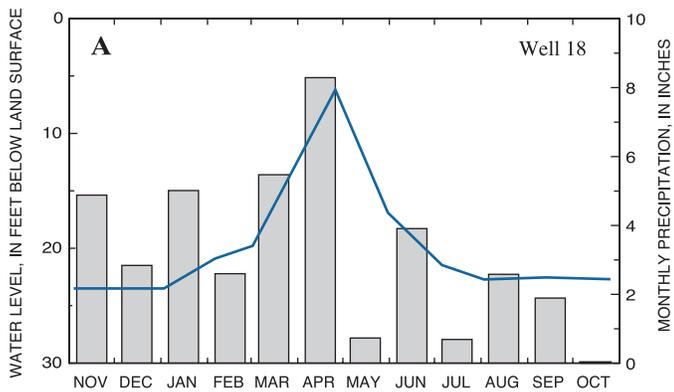
Specific capacities of wells installed for this study generally were low (table 1). Only four of the wells had specific capacities greater than 1 (gal/min)/ft of drawdown; more than half of the wells had specific capacities less than 0.1 (gal/min)/ft of drawdown. These low specific capacities are not surprising considering the predominance of fine-grained material in the regolith and the small diameter of the wells. Lateral movement of ground water in the regolith near these low capacity wells is probably limited, and the principal direction of ground-water flow is downward toward conduits in bedrock; therefore, recharge to these wells likely is localized. Wells intersecting gravel zones have higher specific capacities and likely have larger areas of contribution and a larger component of lateral ground-water flow than wells completed in predominantly fine-grained material in the regolith (fig. 3).

Estimated Age of Ground Water

Chlorofluorocarbons (CFCs) have been used in numerous studies to estimate the recharge age of ground water (Busenberg and Plummer, 1992). The basis of CFC age-dating is that atmospheric concentrations of three CFCs (CFC-11, CFC-12, and CFC-113) increased from about 1945 to the mid 1990s because

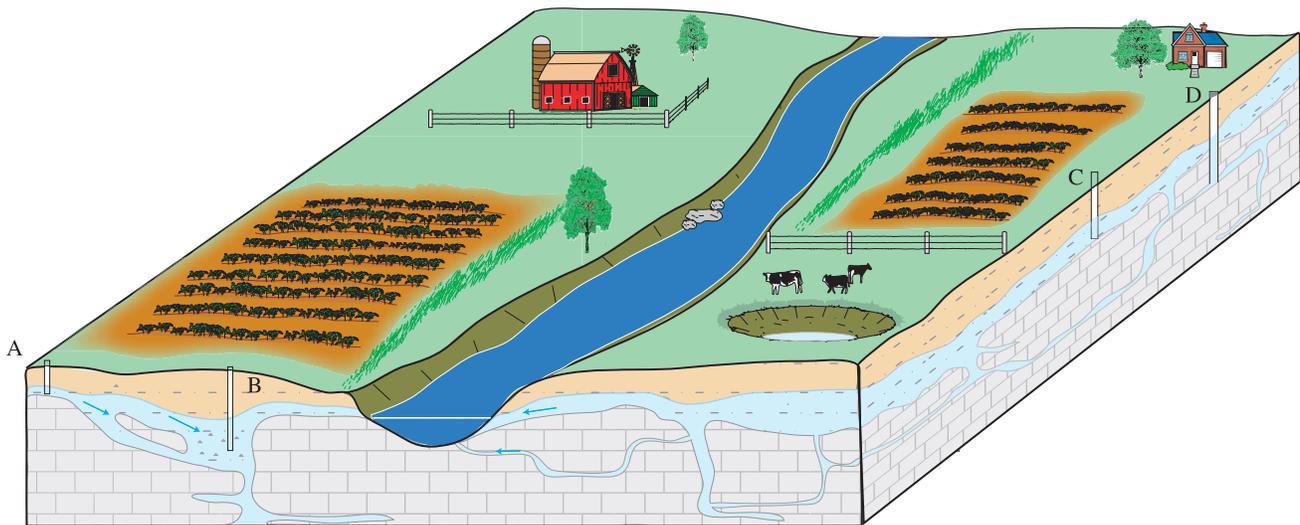
of increases in production of these chemicals. As a result, CFC concentrations in rainfall and recharge water have had corresponding increases in concentrations until the early to mid-1990s. The model recharge date (assuming piston flow) estimated for ground-water recharge represents the time at which infiltrating precipitation (recharge) was isolated from the atmosphere and assumes no modification of CFC concentrations in ground water as a result of degradation or sorption. CFC concentrations greater than atmospheric air and water equilibrium concentrations indicate that ground water is contaminated by a local source of CFCs, and reliable recharge ages cannot be estimated. With no modification of CFC concentrations in the subsurface, all three CFCs should yield the same model recharge date.

A subset of nine wells was analyzed for CFCs to estimate the ground-water age. These nine wells were selected for CFC analysis because they could be pumped without drawing the water level down to the pump intake during sample collection, which would allow air to enter the pump. Introduction of air during sampling could contaminate the sample and affect the apparent age of ground water. Model recharge dates determined for each of the CFCs indicated contamination by CFCs locally as well as some degradation of CFCs (table 1 and appendix 2). In general, CFC-12 is the most stable of the three CFCs and usually provides the most reliable age if local contamination does not occur (Busenberg and Plummer, 1992). CFC-12 model recharge dates for the nine wells ranged from about 1969 to modern (post-1997) with most of the wells having recharge dates between 1992 and 1997 (table 1). Samples collected from wells that are hydraulically connected to the bedrock part of the aquifer likely are mixtures of water with varying residence times in the aquifer. The earlier the model recharge date in samples from these wells, the greater the proportion of "old" water. Samples with model recharge dates prior to 1997 (table 1) indicate that at least some proportion of the water in these wells has a residence time of 3 or more years. Model recharge dates for wells 25 (1969) and 33 (1978) may be overestimates because of degradation of CFCs, which can occur in ground water with low concentrations of dissolved oxygen (Plummer and Busenberg, 2000). Dissolved-oxygen concentrations were 0.4 and 4.7 mg/L, respectively, in these wells. Water from well 33 may represent a mixture of water with low dissolved-oxygen and CFC concentrations with water containing both dissolved oxygen and CFCs.



EXPLANATION

- PRECIPITATION
- WATER LEVEL
- DIRECTION OF GROUND-WATER FLOW



Note: Three land-use monitoring wells (A-C) and one domestic well (D) are shown. A and C represent wells that do not have a good connection with the bedrock part of the aquifer; recharge is local and the principal ground-water flow direction is toward conduits in bedrock. B represents a well in good connection with the bedrock part of the aquifer and has a larger contributing area than wells A and C. The domestic well D is completed in bedrock and has a larger contributing area than the monitoring wells.

Figure 3. Conceptual model of ground-water flow in the regolith and bedrock of the Mississippi carbonate aquifer and monthly water levels for two wells that show different responses to precipitation.

Table 1. Water level, well depth, and specific capacity of wells installed in regolith in the Mississippian carbonate aquifer and model recharge dates of selected samples, 2000-2001

[NGVD, National Geodetic Vertical Datum; <, less than; --, no data; Modern, model recharge dates that are post-1997]

Well number	Station number	Date	Well Depth, in feet		Elevation, in feet above NGVD 29	Specific capacity, in gallons per minute per foot of drawdown	Model recharge date (data in appendix 2)
			Water level, in feet below land surface	in feet below land surface			
1	353341086074501	05/30/00	12.4	43	1,097	<0.01	--
2	352627086002601	05/30/00	7.91	15	1,098	<0.01	--
3	354014086093401	05/30/00	16.8	43.5	1,250	<0.01	--
4	350709086120701	06/06/00	48.15	51	958	2.13	--
5	351646086040701	05/30/00	34.74	43.5	1,018	<0.01	--
6	351459085555901	06/05/00	13.46	23	1,030	<0.01	--
7	351118086051801	06/05/00	68.95	73.5	950	1.43	1997
8	350203086391701	05/31/00	8.85	29	950	0.01	--
9	344407086273401	06/01/00	35.2	37	760	0.03	--
10	345539086241301	05/31/00	22.4	53	790	0.01	--
11	345822086254001	06/06/00	23.4	50	858	0.13	1996
12	345222086303301	06/07/00	72.76	79	765	7.92	Modern
13	345112086313401	06/01/00	24.6	35	705	0.23	1994
14	345247086415001	05/31/00	26.25	39.5	822	0.02	1992
16	345912086243901	05/31/00	16.55	30	845	0.13	--
17	344553086591301	05/25/00	13.9	38	697	<0.01	--
18	344124086531401	05/24/00	16.9	24	612	0.03	--
19	344439086532001	04/16/01	9.23	23	662	0.02	--
20	343836086562901	05/25/00	22.01	33	580	0.19	1997
21	344042086504301	04/16/01	26.78	32	608	0.05	--
22	344127087212001	05/23/00	3.63	55	593	<0.01	--
23	343919087182201	05/24/00	20.65	43.5	574	<0.01	--
24	344154087171201	05/24/00	5.4	14	565	0.85	--
25	344343087220101	05/24/00	7.05	53	550	0.47	1969
26	344557087253201	04/17/01	28.3	31.5	543	0.08	--
27	344217087283601	04/17/00	43.15	46	585	0.21	--
28	344036087320901	05/22/00	24.2	28	567	<0.01	--
31	344615086272201	06/01/00	19.37	36	663	0.11	--
33	344131087335201	05/22/00	22.97	53	538	0.04	1978
34	343530086213801	06/01/00	10.9	23	595	<0.01	--
35	344348086493401	05/25/00	42.25	53	640	2.85	1997
36	343613086441701	05/25/00	8.2	24.5	560	0.04	--

Land Use and Soils

Cropland accounted for about 16 percent of the land cover in the Eastern Highland Rim in 1992 (Kingsbury and others, 1999), with much of the cropland concentrated along the Tennessee River in northern Alabama (fig. 2). Cotton, corn, soybeans, and winter wheat are the principal crops grown in the Eastern Highland Rim. A total of about 441,000 acres of these crops were harvested in 2000 (U.S. Department of Agriculture, 2001c). Cotton accounted for 43 percent of this acreage. Various cropping systems are used throughout the area, with significant crop rotation occurring; as a result, this study did not target a specific crop with respect to its effect on shallow groundwater quality.

The amount of cropland in buffer areas around the monitoring wells ranged from 20 to 100 percent, with a median of 63 percent (table 2). The majority of monitoring wells had some cotton and corn in the buffer area; however, wells with greater than about 50 percent cropland in the buffer area typically were dominated by cotton (fig. 4). Cotton acreage was more prevalent around wells located in northern Alabama. Winter wheat and soybeans were present in buffer areas surrounding 12 and 7 of the wells, respectively, and typically represented less than 10 percent of the buffer area (table 2). Buffer areas around many of the wells included both conventional till and no-till fields. Only 6 of the 32 wells had buffer areas that included irrigated fields.

Many of the soil characteristics delineated in buffer areas are correlated to one another (table 3). Soils in the study area are predominantly silt loams and cherty silt loams. The soils are moderately well to well-drained, with an average slope of about 3 percent and organic matter content of less than 3 percent. Soil hydrologic group and drainage class, two variables that describe the movement of water through soil, are correlated to clay content and soil pH and are

inversely related to organic matter content (table 3). The percentage of soil hydrologic group B and the percentage of well-drained soil are strongly correlated (table 3), so the amount of well-drained soil in the buffer areas was the principal soil characteristic used for data analysis. Given that the soil characteristics are not independent, discerning the effect of specific soil characteristics on water quality is difficult.

Land use is related to the soil properties near the wells. Most notably, the percentage of cotton, as well as the percentage of cropland, in buffer areas tends to be greater where soils are predominantly well-drained (fig. 4). Although not statistically significant at the 95-percent confidence level, the amount of corn near the wells is inversely related to the amount of well-drained soil in the buffer areas. Soils also are less well drained and have higher organic matter content in areas with larger amounts of forest land. The strong correlations between soil characteristics and land use including the types of crops (and, therefore, the types of pesticides used) confound analysis of the effects of soil properties on nitrate and pesticide occurrence in this area.

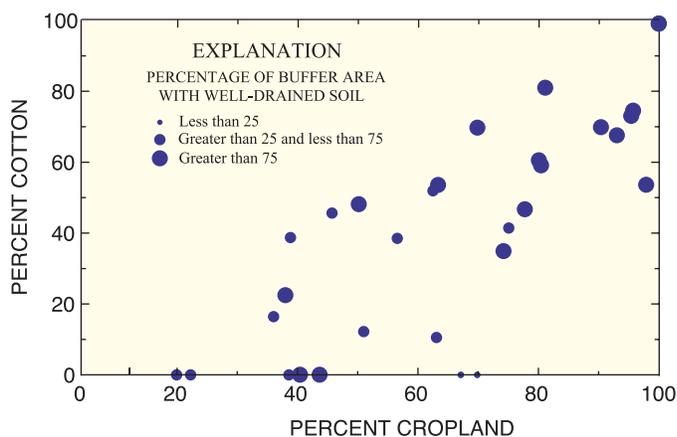


Figure 4. Percentage of cotton, cropland, and well-drained soils in buffer areas around land-use monitoring wells in the Mississippian carbonate aquifer.

Table 2. Summary of major land uses in buffer areas of wells in agricultural areas in the Eastern Highland Rim, 2000

[Values in percent; N, number of wells with a particular land use in the buffer area]

	Cotton	Corn	Soybeans	Winter wheat	Cropland (total)	Hay and pasture	Urban	Forest
Minimum	11	2	7	2	20	3	1	2
Median	50	15	10	8	63	38	8	12
Maximum	100	58	16	41	100	61	43	47
N	24	21	7	12	32	20	21	26

Table 3. Spearman's correlation coefficient, rho, for soil characteristics in buffer areas around wells

[Spearman's rho bolded indicates significance at $p < 0.05$ and italics indicates $p < 0.10$; <, less than]

	Slope	Percent hydro-logic group B	Percent well drained	Percent sand	Percent silt	Percent clay	Available water capacity	Bulk density	Organic matter	Permeability	pH
Slope	1.00	<i>0.30</i>	0.28	0.27	-0.59	0.48	<i>0.35</i>	<i>0.30</i>	0.04	0.07	0.54
Percent hydrologic group B		1.00	0.99	0.20	-0.00	0.44	-0.19	-0.35	-0.50	-0.13	0.48
Percent well drained			1.00	0.22	-0.02	0.46	-0.17	-0.35	-0.50	-0.16	0.53
Percent sand				1.00	-0.58	0.07	-0.20	0.20	0.02	-0.33	0.15
Percent silt					1.00	-0.54	0.67	-0.22	-0.15	0.08	-0.36
Percent clay						1.00	-0.67	-0.28	-0.28	-0.13	0.43
Available water capacity							1.00	0.03	0.06	-0.06	-0.11
Bulk density								1.00	0.46	0.18	0.03
Organic matter									1.00	<i>0.32</i>	-0.10
Permeability										1.00	-0.12
pH											1.00

The specific capacity and depth to water in the monitoring wells also were correlated to soil properties in the buffer areas. In areas with higher percentages of well-drained soils in the buffer areas, the depth to water generally increased as did the specific capacity of water in a well.

SHALLOW GROUND-WATER QUALITY IN AGRICULTURAL AREAS

Wells were sampled for major inorganic constituents, nutrients (nitrogen and phosphorus species), pesticides, and selected pesticide degradates. Nitrate typically is the most important nutrient in ground-water systems because of its potential effects on human health, solubility, and stability in oxic ground water; therefore, discussion of nutrients in this report is limited to nitrate. A large number of pesticides were analyzed in the samples collected (appendix 1); however, not all of them have significant use in the study area. Pesticides that were analyzed and detected, or are used extensively in the study area, are discussed in this report. Most of the wells were sampled in the early summer of 2000 (table 4). Four wells that were dry during the summer of 2000 were sampled in April 2001, and five wells were resampled to evaluate whether constituent concentrations differed significantly between sampling periods. Rainfall for the 12-month period prior to both sampling periods was about 9 inches below the 30-year average annual rainfall

(AWIS Weather Services, Inc., written commun., 2001).

Major inorganic constituents and field properties did not vary substantially for four of the five wells that were resampled in 2001 (table 4). Differences in constituent concentrations between years typically were not greater than the variability associated with sampling and analysis as indicated by replicate samples. Calcium and alkalinity varied by more than 15 percent in the samples collected from well 35 (table 4), but other constituents in these samples did not vary substantially. Given the small amount of variability in major inorganic constituent concentrations between the sample periods, nitrate and pesticide data for the four wells sampled in 2001 are included with the data for the 28 samples from 2000.

About two-thirds of the samples collected were calcium bicarbonate water. In a few samples, particularly in low ionic strength samples (specific conductance less than 100 $\mu\text{S}/\text{cm}$), nitrate and chloride replaced bicarbonate as the dominant anion, and there was not a dominant cation in most of these samples. Samples from wells installed in regolith overlying the Fort Payne Chert had lower specific conductance and lower concentrations of constituents that are contributed from carbonate mineral dissolution, such as calcium and alkalinity, than samples from wells installed in regolith overlying the Tusculumbia Limestone (table 4). These differences for samples from wells in the Fort Payne Chert likely are the result of a greater amount of siliceous material in this formation than in

the Tuscumbia and Monteagle Limestones. The two samples with the highest specific conductance were completed in regolith overlying the Monteagle Limestone (table 4).

Dissolved-oxygen (DO) concentrations for most of the samples were greater than 1 mg/L (table 4) and were correlated to several factors. DO concentrations were positively correlated to the amount of well-drained soil in the buffer areas (Spearman's $\rho=0.31$, $p=0.04$). DO concentrations also tended to increase with depth to water (fig. 5). This somewhat atypical relation between DO and water level likely is a result of the hydraulic connection of water in wells completed in deep regolith to oxic water in the bedrock part of the aquifer. These deep wells generally had the highest specific capacities (table 1). Although the median DO concentration was lower in samples from the Tuscumbia Limestone than from the Fort Payne Chert (table 4), the difference was not statistically significant. DO concentrations were inversely related to the amount of forest land and positively related to the amount of agricultural land (cropland plus pasture) in the buffer area around wells. The inverse relation of DO to the amount of forest land in the buffer area likely is a result of a lower percentage of well-drained soils in forested areas related to greater amounts of respiration by soil microbes in forested areas.

Chloride concentrations were positively correlated with DO (Spearman's $\rho=0.44$, $p=0.01$), indicating that much of the chloride in the aquifer is transported from the surface with recharge rather than originating from dissolution of the carbonate rock. Median chloride concentrations were not statistically different for wells overlying the Tuscumbia Limestone and Fort Payne Chert; however, concentrations were

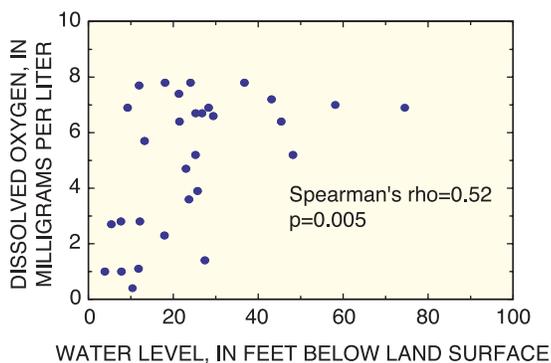


Figure 5. Relation between dissolved-oxygen concentration and water level in agricultural monitoring wells in the Mississippian carbonate aquifer.

considerably higher in the two wells completed in regolith overlying the Monteagle Limestone (table 4). The high concentrations of chloride in these two samples may reflect differences in the composition of this formation. Chloride can be contributed to ground water from numerous sources at land surface. Agricultural sources of chloride that could affect these wells include soil amendments such as potash (KCl) and sodium chlorate, a defoliant used on cotton.

The calcite saturation index is inversely related to DO concentrations, which may indicate relative differences in average ground-water residence times for some samples, particularly from wells completed in the Tuscumbia Limestone (fig. 6). The calcite saturation index relates the concentrations of calcium and

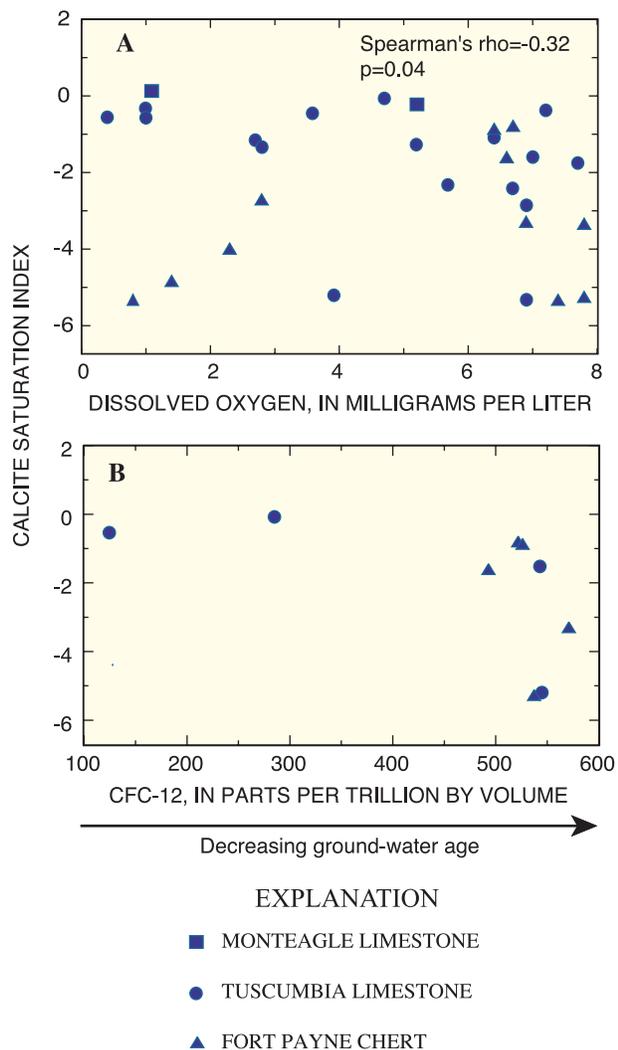


Figure 6. (A) Relation between dissolved-oxygen concentration and calcite saturation index and (B) young model ground-water ages as indicated by CFC-12 concentrations coincided with low calcite saturation indices in samples from the Mississippian carbonate aquifer.

Table 4. Water-quality properties and major inorganic constituent concentrations in samples from 32 wells in the Mississippian carbonate aquifer, 2000-2001

[$\mu\text{S/cm}$, microsiemens per centimeter; $^{\circ}\text{C}$, degrees Celsius; mg/L , milligrams per liter; $\mu\text{g/L}$, micrograms per liter; <, less than; E, estimated; --, no data; median values by geologic units do not include the second sample for wells with two samples]

Well number	Date sampled	Field pH (standard units)	Field specific conductance ($\mu\text{S/cm}$ at 25°C)	Dissolved oxygen (mg/L)	Field alkalinity (mg/L as CaCO_3)	Solids residue at 180°C dissolved (mg/L)	Hardness, total (mg/L as CaCO_3)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Silica, dissolved (mg/L as SiO_2)	Iron, dissolved ($\mu\text{g/L}$ as Fe)	Manganese, dissolved ($\mu\text{g/L}$ as Mn)	Nitrate, dissolved (mg/L as N)	Calcite saturation index
Fort Payne Formation																		
1	05/30/00	6.4	137	2.8	69	79	8	2.3	0.44	14	18	0.7	3.7	5.9	<10	5,060	< 0.05	-2.75
3	05/30/00	5.5	38	2.3	17	22	12	3.5	0.67	0.7	0.6	0.6	E0.3	9.4	600	1,430	0.25	-4.03
8	05/31/00	4.8	45	0.8	7	23	7	1.7	0.62	4.0	0.4	3.8	2.4	9.3	1,220	373	0.72	-5.36
10	05/31/00	5.3	32	1.4	7	18	7	2.0	0.48	1.5	0.4	3.8	E0.2	9.3	760	61	0.18	-4.87
11	06/06/00	4.6	66	7.8	4	61	20	5.1	1.7	1.9	0.9	4.3	0.4	7.7	E10	44	5.0	-5.30
11	04/19/01	4.9	67	7.7	8	58	20	5.2	1.8	1.7	1.1	4.4	0.3	7.8	<10	40	4.8	-4.82
12	06/07/00	5.6	93	6.9	26	69	36	10	2.7	1.2	2.2	2.8	E0.3	8.7	<10	151	3.8	-3.33
13	06/01/00	7.1	248	6.7	96	140	120	28	12	1.1	0.5	5.7	0.5	8	<10	108	3.3	-0.83
13	04/18/01	6.8	215	7.2	91	110	110	25	11	1.5	0.4	5.1	0.5	8.1	<10	E2	3.2	-1.28
14	05/31/00	6.7	123	6.6	54	72	58	17	3.8	1.4	E0.2	2.9	1	7.6	<10	E2	0.81	-1.63
16	05/31/00	5.5	104	7.8	23	74	41	14	1.7	1.4	0.5	5.0	4.8	8	<10	239	3.2	-3.39
31	06/01/00	4.9	60	7.4	4	42	14	2.9	1.7	4.4	0.8	5.6	1.7	8.1	<10	83	3.3	-5.37
31	04/18/01	5.1	60	6.9	9	52	16	3.3	1.8	3.4	1	5.5	1.1	8.3	<10	83	3.5	-4.77
35	05/25/00	6.7	295	6.4	136	170	140	47	5.6	1.7	1	2.9	1.2	8.2	<10	3	2.7	-0.89
35	04/17/01	6.9	220	7.9	92	131	110	35	4.5	1.6	0.7	2.7	0.9	8	<10	3	3.1	-1.03
Median of 11 samples		5.5	93	6.6	23	69	20	5.14	1.72	1.5	0.6	3.8	1	8.1	<10	108	2.71	-3.39
Tuscumbia Limestone																		
2	05/30/00	6.1	131	5.7	50	82	64	19	4.1	1.6	1.1	3.0	4	6.8	E10	94	2.2	-2.31
4	06/06/00	6.6	245	5.2	106	140	110	34	7.0	1.5	0.5	4.2	4	7.6	<10	5	2.6	-1.25
5	05/30/00	7.0	264	--	115	158	130	48	2.0	4.7	0.8	1.2	7.6	8.4	<10	71	0.12	-0.66
6	06/05/00	6.8	178	7.7	39	127	70	17	6.7	4.1	0.7	9.7	2	8.4	<10	3	8.5	-1.74
7	06/05/00	6.2	263	7	99	162	120	39	4.5	1.7	0.7	6.9	2.7	6.9	<10	7	4.8	-1.58

Table 4. Water-quality properties and major inorganic constituent concentrations in samples from 32 wells in the Mississippian carbonate aquifer, 2000-2001—Continued

Well number	Date sampled	Field pH (standard units)	Field specific conductance ($\mu\text{S}/\text{cm}$ at 25 °C)	Dis-solved oxygen (mg/L)	Field alkalinity (mg/L as CaCO_3)	Solids residue at 180 °C dis-solved (mg/L)	Hardness, total (mg/L as CaCO_3)	Calcium, dis-solved (mg/L as Ca)	Magnesium, dis-solved (mg/L as Mg)	Sodium, dis-solved (mg/L as Na)	Potassium, dis-solved (mg/L as K)	Chloride, dis-solved (mg/L as Cl)	Sulfate, dis-solved (mg/L as SO_4)	Silica, dis-solved (mg/L as SiO_2)	Iron, dis-solved ($\mu\text{g}/\text{L}$ as Fe)	Manganese, dis-solved ($\mu\text{g}/\text{L}$ as Mn)	Nitrate, dis-solved (mg/L as N)	Calcite saturation index	
Tuscumbia Limestone—Continued																			
9	06/01/00	6.3	156	--	51	94	73	16	8.2	1.8	0.5	5.6	1.2	6.3	<10	117	5.7	-2.33	
17	05/25/00	7.2	122	2.8	50	72	53	15	4.0	2.4	0.6	1.2	9.8	5.3	<10	2,590	0.07	-1.34	
18	05/24/00	6.6	258	6.4	115	150	120	43	3.7	1.4	0.8	2.0	3.4	6.5	<10	<2	3.37	-1.05	
19	04/16/01	5.1	22	6.9	6	28	5	1.1	0.55	1.7	0.3	4.0	0.2	9.7	10	45	0.15	-5.35	
20	05/25/00	5.0	39	3.9	8	36	12	3.3	1.0	1.4	0.7	1.3	2.8	8.6	E10	437	1.0	-5.20	
21	04/16/01	6.1	147	6.7	35	99	64	20	3.3	2.1	0.7	2.8	1.7	8.2	E10	12	7.7	-2.41	
22	05/23/00	7.2	455	1	207	265	240	85	6.4	4.8	0.5	0.8	5.6	8.1	40	438	< 0.05	-0.34	
23	05/24/00	7.0	312	3.6	153	201	170	60	4.0	5.1	0.4	1.4	11	8.4	<10	9	0.56	-0.47	
24	05/24/00	6.5	273	2.7	135	158	140	51	3.0	1.6	2.5	2.8	3.1	4.1	<10	67	0.87	-1.16	
25	05/24/00	7.0	351	0.4	165	206	190	68	3.7	2.1	0.5	3.7	2.9	8.1	<10	177	0.32	-0.54	
26	04/17/01	5.9	76	6.9	38	63	37	11	2.2	0.9	0.4	1.5	0.2	9	30	63	0.44	-2.84	
27	04/17/01	7.0	423	7.2	172	257	200	76	2.7	5.0	0.9	19	0.9	9.5	<10	3	4.1	-0.35	
33	05/22/00	7.6	259	4.7	118	162	120	46	1.7	1.7	0.5	3.0	1.9	8.7	<10	E2	3.7	-0.07	
33	04/18/01	7.4	263	4.9	113	179	130	50	1.7	1.7	0.5	3.3	0.9	9	<10	3	4.5	-0.31	
36	05/25/00	6.5	478	1	276	281	260	95	5.2	2.1	0.5	1.5	1.1	7.6	20	1,130	< 0.05	-0.57	
Median of 19 samples		6.6	258	5.2	106	150	120	39	3.6	1.8	0.6	2.8	2.85	8.1	<10	63	1.01	-1.25	
Monteagle Limestone																			
28	05/22/00	6.6	714	5.2	340	402	340	123	8.5	19	0.4	20	6	8.2	<10	4	0.48	-0.23	
34	06/01/00	7.1	816	1.1	366	490	340	122	8.5	40	0.7	26	41.4	13.5	<10	64	0.10	0.16	

carbonate ions in solution to the solubility of calcite. The calcite saturation index is expressed as the logarithm of the ion activity product of bicarbonate and calcium divided by the solubility constant for calcite. Saturation indices were calculated using the geochemical modeling code PHREEQC (Parkhurst and Appelo, 1999). Saturation indices close to zero indicate water is near to saturation with respect to calcite. The degree of calcite saturation is a qualitative indicator of the contact time between the ground water and carbonate aquifer material. A small saturation index may indicate a short amount of contact time between the water and carbonate rock. As DO concentrations decrease, the calcite saturation index tends to be higher (fig. 6). As previously noted, differences in saturation indices also can be attributed to differences in the composition of bedrock as well as to ground-water residence time. Chert in both the Fort Payne Chert and the Tusculumbia Limestone could affect this relation and may account for the low calcite saturation indices for several samples also having low DO concentrations (fig. 6). For the small number of samples with CFC-12 age dates, a relation seems to exist between ground-water age and the calcite saturation index (fig. 6).

Nitrate

Nitrate concentrations generally were low with no samples exceeding the drinking-water maximum contaminant level (MCL) of 10 mg/L. The maximum concentration of nitrate (as N) was 8.4 mg/L, and the median concentration was about 1 mg/L. Nitrate and DO concentrations were strongly correlated (fig. 7); therefore, nitrate concentrations were correlated to many of the same variables to which DO was correlated. For example, nitrate concentrations increase with the depth to ground water in the wells as did DO concentrations. This relation contrasts with the typical relation of decreasing nitrate concentrations with increasing depth to the water table documented in other ground-water studies (Hallberg and Keeney, 1993). In this setting, increased depth to water in these regolith wells may reflect a hydraulic connection to oxic ground water in bedrock. These parts of the aquifer represent the active part of the flow system, where nitrate likely is more stable. Partial correlation analysis of variables related to both nitrate and DO indicates that DO concentration accounts for most of the variation in nitrate concentrations in ground water. Nitrate concentrations in four of the five wells sampled twice

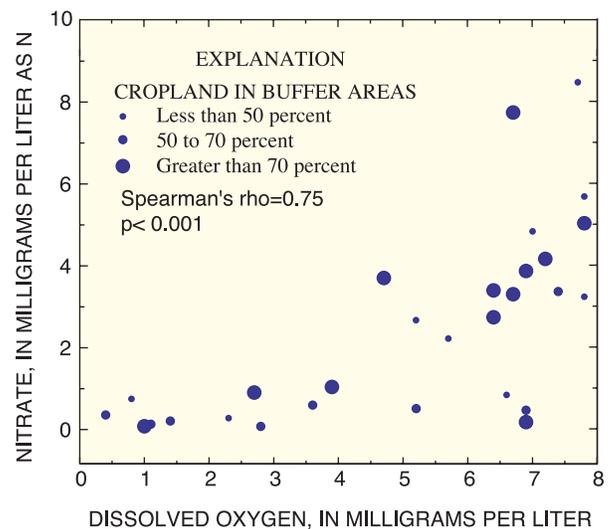


Figure 7. Nitrate and dissolved-oxygen concentrations for samples and cropland in buffer areas around wells in the Mississippian carbonate aquifer, 2000.

varied less than 5 percent (table 4), similar to the amount of variability between replicate samples. Nitrate concentrations were about 10 percent different in the two samples from well 33 (table 4).

The correlation of nitrate to DO suggests that nitrate concentrations are affected by denitrification and are low where either the average ground-water residence time is long or where recharge is slow as indicated by low DO concentrations. Nitrate and chloride concentrations are correlated and appear to be contributed to the aquifer predominantly from activities at land surface. Given that chloride is conserved in ground-water systems, the ratio of chloride to nitrate ($\text{Cl}:\text{NO}_3$) may indicate whether nitrate concentrations in samples are affected by denitrification. Samples with nitrate concentrations greater than 2 mg/L generally had DO concentrations greater than 6 mg/L and $\text{Cl}:\text{NO}_3$ ratios less than 2 (fig. 8). In contrast, samples with nitrate concentrations less than 1 mg/L tended to have lower DO concentrations and higher $\text{Cl}:\text{NO}_3$ ratios. Two samples with high $\text{Cl}:\text{NO}_3$ ratios were from wells completed in the Monteagle Limestone, and the elevated chloride in these samples may be from natural sources. Samples with nitrate concentrations less than 1 mg/L and a $\text{Cl}:\text{NO}_3$ greater than about 5 (fig. 8) likely represent samples from areas where denitrification is occurring. About a third of the samples fit these criteria. In addition, nitrate concentrations were inversely related to manganese concentrations (Spearman's $\rho=-0.5$, $p=0.002$). Dissolved manganese concentrations are greatly affected by the oxidation-reduction (redox) state of ground

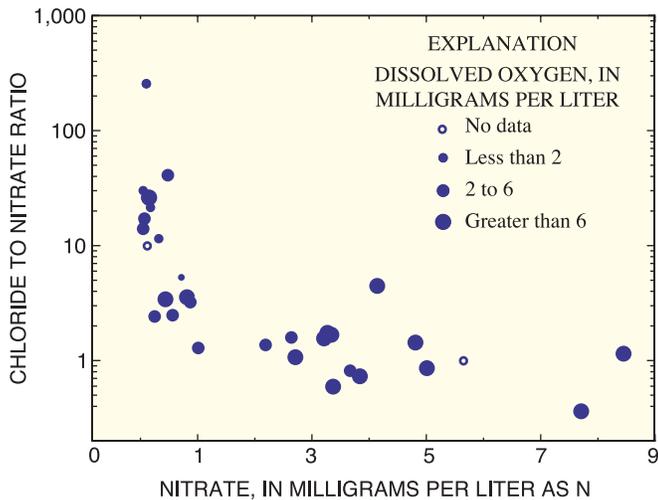


Figure 8. Relation between ratio of chloride to nitrate and nitrate concentrations in samples collected from the Mississippian carbonate aquifer.

water. The reactions that reduce manganese oxides to the soluble ionic form (Mn^{+2}) follow denitrification in the sequence of redox reactions (Stumm and Morgan, 1996). The inverse relation between nitrate and manganese concentration indicates that where nitrate concentrations are low, the redox conditions were favorable to denitrification.

Nitrate concentrations in the Eastern Highland Rim were lower than in other agricultural areas across the Nation. The median nitrate concentration for samples collected from 848 monitoring wells installed in agricultural areas in 30 NAWQA study areas across the Nation (fig. 9) was 2.3 mg/L compared to a median of about 1 mg/L for wells in this study (fig. 10). The NAWQA wells nationwide were sampled between 1991 and 2001 and ranged in depth from 7 to 200 ft with a median depth of 25 ft, compared to a median depth of 37.5 ft for the wells in this study. However, the interquartile range in nitrate concentration generally is comparable for the two data sets, and the nitrate concentration distributions are not statistically different (fig. 10). The maximum nitrate concentration measured in this study was equal to the 75th percentile in the NAWQA wells nationwide. About 21 percent of the samples from the wells nationwide equaled or exceeded the drinking-water MCL of 10 mg/L. No samples from the monitoring wells in the Mississippian carbonate aquifer exceeded the MCL.

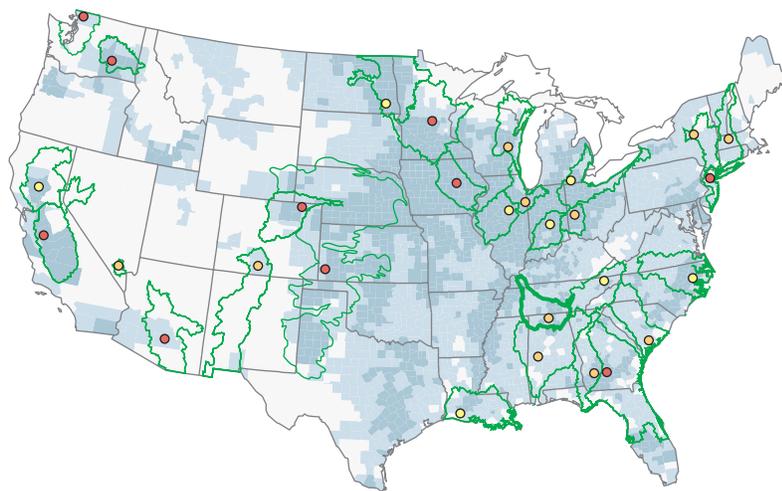
Pesticides

Pesticides have increased the productivity of agricultural land in the Nation by controlling weeds,

fungi, insects, and nematodes, all of which can lower crop yields. Despite the increases in agricultural productivity and the associated economic benefits, a general concern exists about the effects of dispersing large quantities of potentially harmful pesticides into the environment. The fate of pesticides in the environment is influenced by many factors such as the method of application, physical and chemical properties of each pesticide, and numerous environmental factors. Pesticides typically are designed to degrade in a few days or weeks after application under ideal conditions. Degradation occurs by several processes including photolysis, hydrolysis, and biologically mediated reactions. Most of these processes occur more rapidly in the near-surface soil environment than in ground water. Movement of pesticides into ground-water systems may reduce the rate at which pesticides degrade, and pesticide residues may persist in ground water longer than in the soil zone. During the 1990s, numerous studies documented the importance of pesticide degradates in ground water (for example, Kolpin and others, 1998).

Of the 32 wells sampled, 29 (91 percent) contained one or more pesticides or pesticide degradates (fig. 11). Thirty-five different pesticides and pesticide degradates were detected (appendix 1), but 11 of them were detected in only one sample at concentrations below 0.01 $\mu\text{g/L}$, and are not included in the summary of detections (table 5). Atrazine, fluometuron, norflurazon, and their degradates were detected frequently and at the highest concentrations (table 5). No pesticide concentrations exceeded established MCLs for drinking water, but 32 of the 35 pesticides detected do not have MCLs. Degradates generally do not have MCLs. More than half of the samples contained 5 or more pesticides (fig. 11), and the maximum number of pesticides detected in a single sample was 13. The maximum concentration of a single pesticide was 3.21 $\mu\text{g/L}$ for demethylnorflurazon, a degradate of the cotton herbicide norflurazon (table 5). About half of the samples had a total pesticide concentration of 1 $\mu\text{g/L}$ or more (fig. 11), and the maximum total pesticide concentration measured in a sample was 7.2 $\mu\text{g/L}$.

The frequency of detection and magnitude of concentrations was related to the estimated use of pesticides (table 5). Atrazine, fluometuron, and norflurazon are among the most heavily used pesticides in the study area and were detected more frequently than pesticides with lower estimated use. Aldicarb, which



EXPLANATION

AVERAGE ANNUAL TOTAL NITROGEN INPUT—
in pounds per acre, by county, for 1995-98.
Inputs are from fertilizer, manure, and the
atmosphere

- Greater than 25 pounds per acre
- 6 to 25 pounds per acre
- Less than 6 pounds per acre

— NATIONAL WATER-QUALITY ASSESSMENT
PROGRAM AGRICULTURAL LAND-USE
STUDY-AREA BOUNDARY

MEDIAN CONCENTRATION OF NITRATE,
IN MILLIGRAMS PER LITER

- Less than 1
- 1 to 5
- Greater than 5

Figure 9. Distribution of selected National Water-Quality Assessment Program agricultural land-use study areas, median nitrate concentration, and estimated average annual nitrogen input across the Nation. (Modified from U.S. Geological Survey, 1999.)

had comparable estimated use to fluometuron and also is used on cotton, was not detected, and its degradates were detected less frequently and at lower concentrations than fluometuron (table 5). The physical and chemical properties of these two pesticides are similar; however, the field dissipation half-life of fluometuron is about twice as long as that of aldicarb (Wauchope and others, 1992). Glyphosate, the exception to the relation between use and detection frequency, had the highest estimated use and was applied within the buffer areas of all of the wells but was not detected (table 5). The analytical method for glyphosate had a higher MRL (0.1 $\mu\text{g/L}$) than many of the other pesticides (table 5), but that probably does not account for the lack of detections. Median concentrations of

fluometuron and atrazine detections were 0.41 and 0.12 $\mu\text{g/L}$, respectively (greater than the MRL for glyphosate), even though fluometuron and atrazine applications were about a third of the estimated amount of glyphosate applied. Glyphosate has a soil sorption coefficient two orders of magnitude higher than atrazine and fluometuron, and the aerobic soil half-life of glyphosate is 47 days compared to 146 and 189 days for atrazine and fluometuron, respectively (U.S. Department of Agriculture, 2002). Degradates of glyphosate were not analyzed in this study.

Fluometuron and atrazine generally were detected in samples from wells where these pesticides were applied in the buffer area (fig. 12). Fluometuron was detected in samples from 83 percent of wells with buffer areas that had estimated use during 2000 (fig. 12). Three of the four samples in which fluometuron was not detected had low DO concentrations (less than 1.5 mg/L), indicating long average ground-water residence times at these wells, slow rates of recharge, or some degree of confinement in the regolith (the fourth well could not be pumped continuously and did not have a DO measurement). Atrazine was detected in about 70 percent of the wells where it was applied in the buffer area in 2000; and, like fluometuron,

five of the six samples from wells with estimated use in which atrazine was not detected had DO concentrations less than 1.5 mg/L (the sixth sample did not have a DO measurement). Fluometuron was detected only in samples from wells where it was applied in the buffer area during the 2000 growing season; however, atrazine was detected at concentrations between 0.014 and 0.21 $\mu\text{g/L}$ in samples from six monitoring wells where no atrazine was applied in the buffer area during the 2000 growing season (fig. 12). These low-level detections of atrazine indicate either that residues persist in the subsurface for periods greater than a year, or that the contributing area for these wells includes areas not accounted for by the buffer areas.

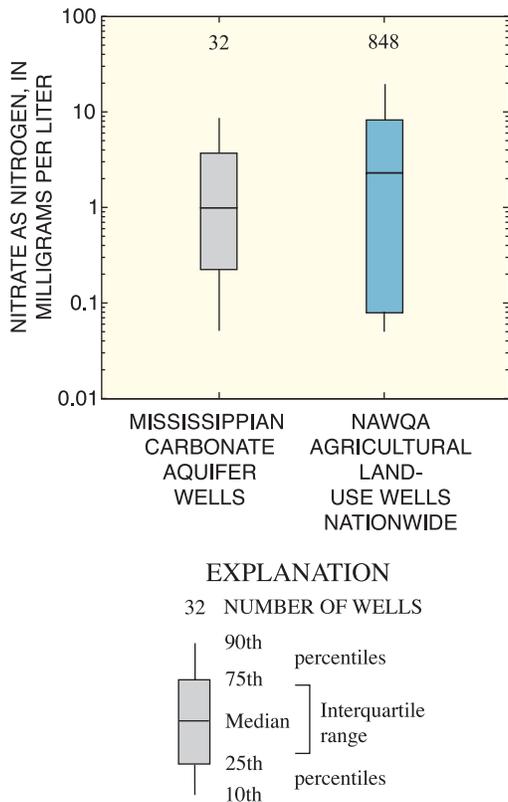


Figure 10. Nitrate concentrations in samples from the Mississippiian carbonate aquifer and from National Water-Quality Assessment Program agricultural land-use wells across the Nation.

Pesticide degradates represented 38 percent of the pesticides detected at concentrations greater than 0.01 $\mu\text{g/L}$; however, degradates accounted for only 17 percent of the pesticides analyzed. Nine of the 12 most frequently detected pesticides were degradates (table 5). The occurrence of degradates generally coincided with detection of the parent pesticide. Atrazine, fluometuron, and norflurazon degradates were commonly detected at concentrations comparable to or greater than the parent pesticide (table 5 and fig. 13). In some samples, the parent pesticide was not detected. Aldicarb sulfone and sulfoxide (degradates of the cotton insecticide aldicarb) were detected at concentrations less than 0.2 $\mu\text{g/L}$ (table 5) in about 22 percent of the samples, but aldicarb was detected only once at a concentration of 0.004 $\mu\text{g/L}$. Not all degradates analyzed were detected. Although carbofuran was detected in two samples at low concentrations (less than 0.03 $\mu\text{g/L}$), two degradates analyzed (3-ketocarbofuran and 3-hydroxycarbofuran) were not detected. The MRLs for these degradates are 0.072 and 0.062 $\mu\text{g/L}$, respectively.

Concentrations of the degradates of fluometuron generally were less than the fluometuron concentration, in contrast to norflurazon and atrazine degradates, which typically were detected at higher concentrations than norflurazon and atrazine (fig. 13). The lower relative concentrations of fluometuron degradates compared with atrazine and norflurazon may be the result of additional applications of fluometuron later in the growing season or may reflect slower rates of degradation for fluometuron. The principal degradate of fluometuron detected was demethylfluometuron (41 percent of samples, table 5). The degradate 3-(trifluoromethyl) aniline (TFMA) forms from degradation of fluometuron or demethylfluometuron and was detected in 19 percent of the samples; 3-phenylurea, the degradate of demethylfluometuron was not detected. TFMA concentrations typically were low (median was 0.07 $\mu\text{g/L}$) and were less than demethylfluometuron concentrations; however, in the two samples from well 33, TFMA concentrations were considerably higher (0.24 and 0.42 $\mu\text{g/L}$), and demethylfluometuron concentrations were less than TFMA concentrations (< 0.05 and 0.18 $\mu\text{g/L}$). Samples from this well had a calcite saturation index near zero (table 4), indicating a longer average ground-water residence time than for other samples. Estimated recharge dates from CFC data for this well were in the mid- to late-1970s. The relatively high TFMA concentrations may be the result of the longer average residence time for ground water at this well, allowing more degradation to occur than at the other wells.

The deethylatrazine to atrazine ratio (DAR) has been used as a qualitative indicator of the pathways through which water and atrazine move into the subsurface (Adams and Thurman, 1991). Deethylatrazine forms from the breakdown of atrazine by microbes in the soil environment. A DAR less than 1 may indicate rapid transport to the subsurface with short residence times for water and atrazine in the soil zone. In the Eastern Highland Rim, sinkholes in addition to soil macropores could provide pathways for rapid movement of water and pesticides into the ground water. The majority of atrazine concentrations were less than 0.25 $\mu\text{g/L}$. The five samples with atrazine concentrations greater than 0.75 $\mu\text{g/L}$ had DARs less than 1 (fig. 14), suggesting that these high atrazine concentrations are the result of rapid recharge to the aquifer with a short residence time in the soil zone. The few detections of metolachlor, which has a shorter aerobic soil half-life than atrazine (U.S. Department of

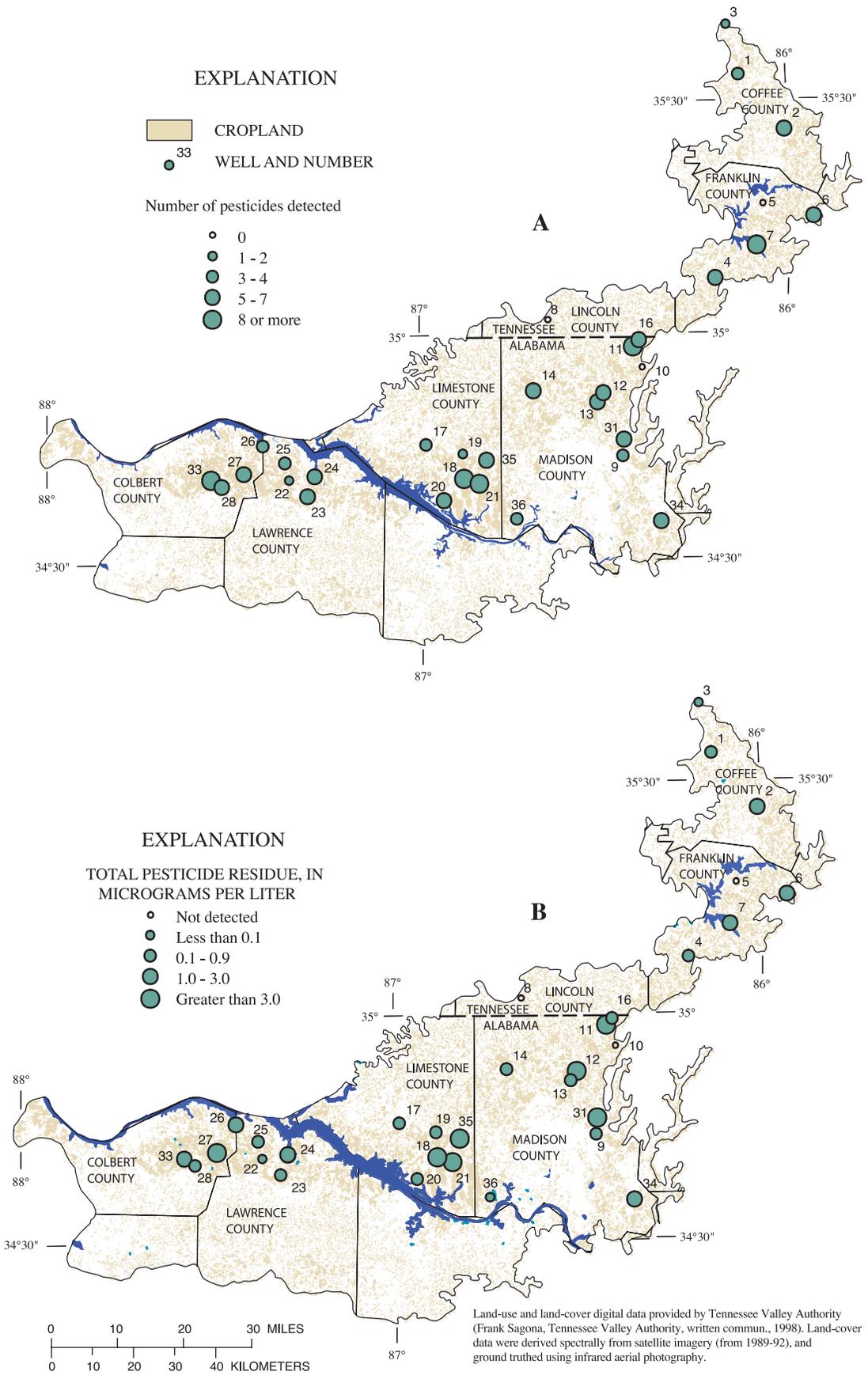


Figure 11. (A) Number of pesticides detected and (B) total pesticide concentration in samples from the Mississippian carbonate aquifer.

20 Shallow Ground-Water Quality in Agricultural Areas of Northern Alabama and Middle Tennessee, 2000-2001

Table 5. Summary statistics for pesticides detected at concentrations equal to or greater than 0.01 microgram per liter in samples from the Mississippian carbonate aquifer and estimated use of selected pesticides in buffer areas around wells

[F, fungicide; H, herbicide; I, insecticide; Degr., pesticide degradate; E, estimated value; --, no data; NA, not applicable; MRL, minimum reporting level; µg/L, micrograms per liter; lbs, pounds]

Pesticide	Detection frequency (percent)	Number of detections	Maximum concentration (µg/L)	Median detection (µg/L)	MRL	Pesticide type	Median estimated use (lbs)	Number of
								buffer areas with use during 2000
Atrazine	62	20	1.83	0.12	0.007	H	36	21
Fluometuron	59	19	2.13	0.41	0.062	H	27	24
Deethyldeisopropylatrazine	59	19	0.071 E	.022 E	0.06	Degr.	NA	NA
Norflurazon	53	17	0.71	0.081	0.077	H	8	24
Hydroxyatrazine	50	16	0.168 E	.035 E	0.193	Degr.	NA	NA
Demethylnorflurazon	47	15	3.21	0.41	0.05	Degr.	NA	NA
Deethylatrazine	47	15	0.71 E	.19 E	0.002	Degr.	NA	NA
Deisopropylatrazine	47	15	0.1 E	.034 E	0.074	Degr.	NA	NA
Demethylfluometuron	41	13	1.85	0.39	0.05	Degr.	NA	NA
Aldicarb sulfone	22	7	0.16 E	.12 E	0.160	Degr.	NA	NA
3-(trifluoromethyl) aniline (TFMA)	19	6	0.42	0.07	0.05	Degr.	NA	NA
Aldicarb sulfoxide	16	5	0.085 E	.029 E	0.027	Degr.	NA	NA
Metolachlor	12	4	0.92	0.19	0.002	H	5	22
Prometon	9	3	0.17	0.02	0.018	H	--	--
Diuron	9	3	0.14	.016 E	0.079	H	11	24
Imazethapyr ¹	7	2	0.056 E	NA	0.088	H	< 0.5	15
Metalaxyl	6	2	0.022 E	NA	0.057	F	4.3	24
Carbofuran	6	2	0.028	NA	0.003	I	0.8	21
Simazine	6	2	0.021	NA	0.005	H	0.5	21
Acetochlor	3	1	0.057	NA	0.002	H	5	21
Metribuzin	3	1	0.015	NA	0.004	H	3	24
Pendimethalin	3	1	0.059	NA	0.004	H	3.5	21
2,4-D methyl ester	3	1	0.025 E	NA	0.086	H	--	--
Diphenamid	3	1	0.014 E	NA	0.058	H	--	--
Glyphosate ²	0	0	--	NA	0.1	H	127	32
Aldicarb	0	0	--	NA	0.082	I	28	24
Carbaryl	0	0	--	NA	0.003	I	2.7	21
Prometryn	0	0	--	NA	0.05	H	4.7	24

¹Analyzed in 28 samples

²Analyzed in 17 samples

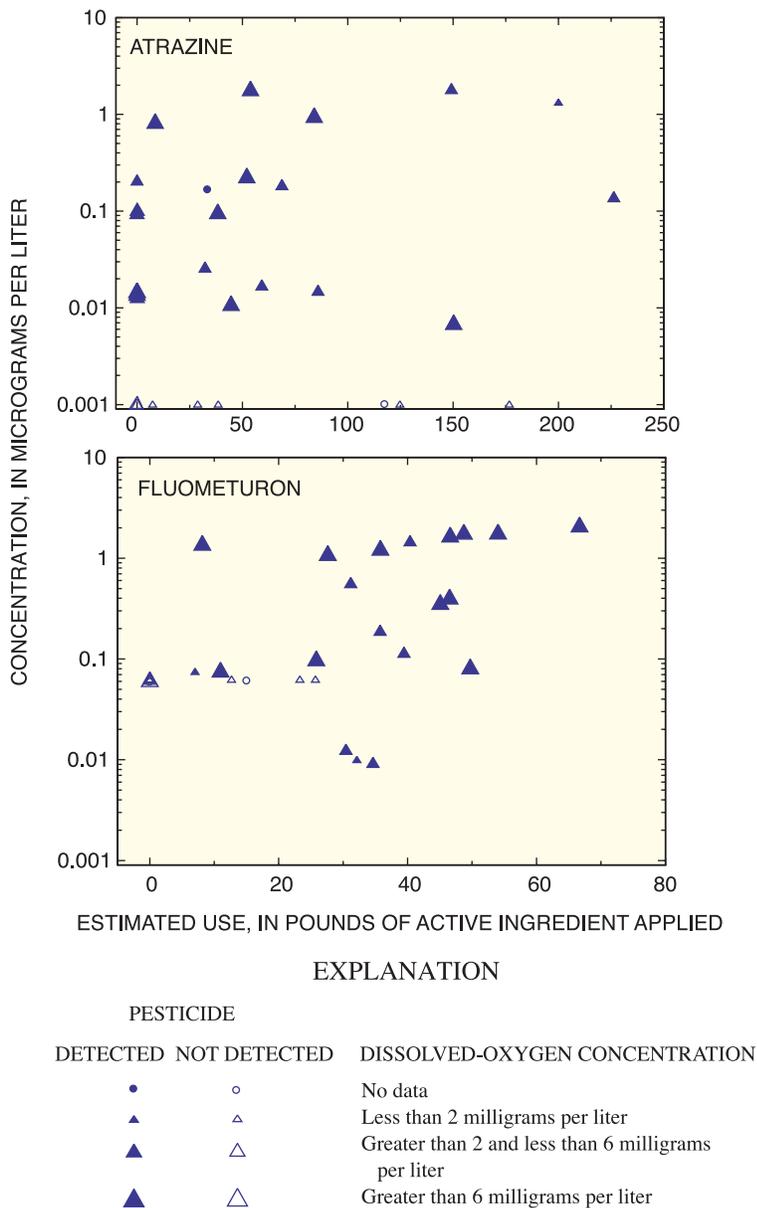


Figure 12. Concentrations of atrazine, fluometuron, and dissolved oxygen and estimated use of atrazine and fluometuron in buffer areas around wells in the Mississippian carbonate aquifer.

Agriculture, 2002), at high concentrations predominantly in samples with DARs less than 1 (fig. 14), supports the interpretation that high concentrations of atrazine result from rapid infiltration of recharge.

Given that pesticides used in buffer areas of wells differed, the total pesticide concentration (sum of all pesticide and pesticide degradates in a sample), in addition to the amount of cropland near a well, was used to evaluate which factors were related to pesticide occurrence. Because soil properties are directly correlated to land use, discerning the influence of dif-

ferences in soil properties on the occurrence of pesticides in this setting is not possible. The total pesticide concentration was correlated to DO concentration and, in turn, related to factors correlated to DO concentrations. Although DO is positively correlated to nitrate concentration, partial correlation analysis indicates that nitrate and DO account for some of the variation in total pesticide concentration. Given the predominance of cropland near these wells and the relation between total pesticide and nitrate concentrations, fertilizer application to cropland is the probable source of nitrate to these wells. The relation between DO and total pesticide concentration indicates that pesticides are more likely to be detected at high concentrations where ground-water residence time is short and the rate of recharge is fast. Although the relation between total pesticide concentration and the calcite saturation index was not statistically significant, samples with the highest total pesticide concentrations were associated with wells having ground water with a short residence time based on DO and the saturation index (fig. 15).

Pesticides were detected more frequently in samples from monitoring wells in this study than in samples from other agricultural areas across the Nation. Atrazine and its degradate, deethylatrazine, were detected in 62 and 47 percent, respectively, of samples collected from the Mississippian carbonate aquifer (fig. 16). Atrazine and deethylatrazine were detected in about 25 percent of the monitoring wells sampled between 1991 and 2001 as part of agricultural land-use studies conducted by the NAWQA Program (U.S. Geological Survey, 2002a) and were the most frequently detected pesticides nationwide. The greater frequency of

detection in this study could reflect greater atrazine use in the LTEN than in the areas sampled in the national data set; however, about half of the wells in the national data set were in areas that had greater estimated use of atrazine than in the LTEN (Thelin and Gianessi, 2000) (fig. 17). The average detection frequency of atrazine in samples from areas nationwide with atrazine use greater than the LTEN was about 30 percent, much lower than the 62 percent detection frequency in samples collected for this study. Metolachlor was the third most frequently detected pesticide

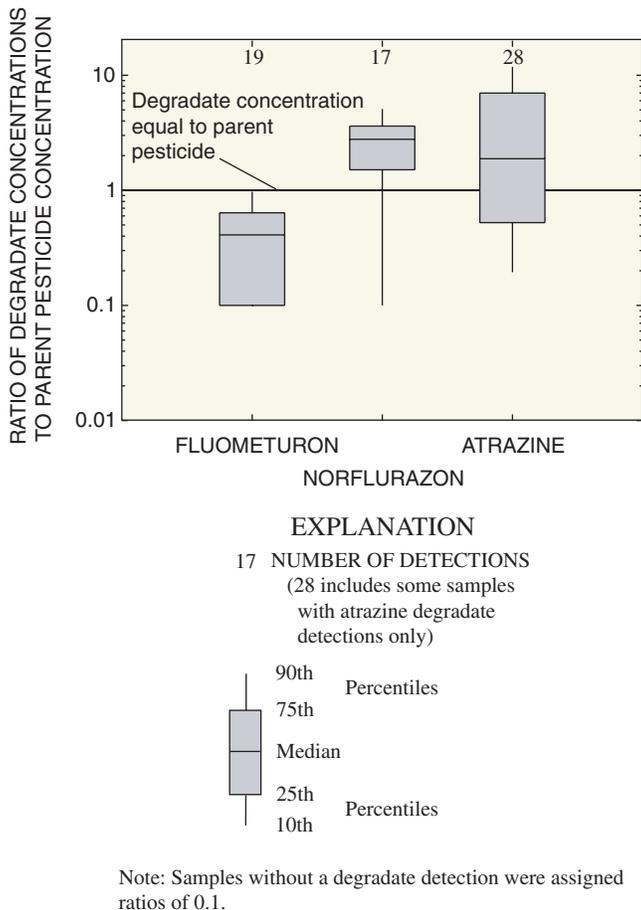


Figure 13. Ratios of degradate to parent pesticide concentration for fluometuron, norflurazon, and atrazine in samples from the Mississippian carbonate aquifer.

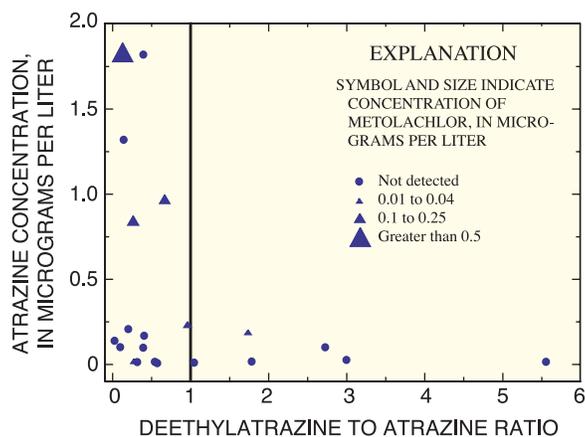


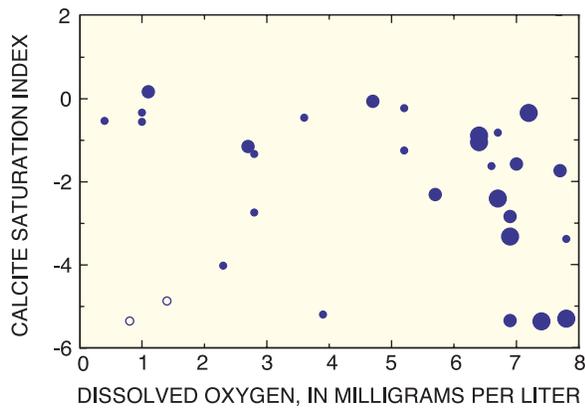
Figure 14. Relation between deethylatrazine to atrazine ratios (less than 1) and concentrations of atrazine and metolachlor in water samples from the Mississippian carbonate aquifer.

nationwide and was the fourth most frequently detected pesticide in this study (not including degradates). Median concentrations of atrazine, deethylatrazine, and metolachlor were not statistically different between the data sets, but tended to be slightly higher in samples collected for this study than in samples collected nationwide (fig. 16).

The cotton herbicides fluometuron and norflurazon also were detected more frequently in this study than in samples from agricultural land-use studies across the Nation (fig. 16). Fluometuron and norflurazon were detected in 59 and 53 percent, respectively, of samples in this study compared to 2 and 1 percent, respectively, of samples from the other study areas. These herbicides had limited use in the areas of the country represented by the national data (fig. 17, Theilin and Gianessi, 2000), which may explain the lower detection frequency. Median concentrations of fluometuron and norflurazon were 0.41 and 0.08 $\mu\text{g/L}$, respectively, in this study, compared to median concentrations of 0.1 and 0.07 $\mu\text{g/L}$, respectively, for the national data (fig. 16).

Implications for Drinking-Water Quality of the Mississippian Carbonate Aquifer

Water-quality data collected for this land-use study and from a previous study of drinking-water wells located in the Eastern Highland Rim (Kingsbury and Shelton, 2002) indicate that the Mississippian carbonate aquifer is susceptible to contamination from nonpoint sources and that the water quality throughout much of the aquifer has been affected by activities associated with crop production. In the summer of 1999, water samples from a network of drinking-water wells (predominantly domestic wells completed in bedrock) were analyzed for a broad range of constituents to characterize the quality of water in the aquifer (Kingsbury and Shelton, 2002). Domestic and public-supply wells in the Eastern Highland Rim typically withdraw ground water from the bedrock in the Mississippian carbonate aquifer. The water-quality data collected from the shallow monitoring wells in this study represent water in the aquifer that should be most affected by activities associated with agricultural land use. Much of the recharge to the bedrock part of the aquifer is from water moving through the regolith. The monitoring well data are compared to data collected from 25 of the drinking-water wells that are completed in the Fort Payne Chert, Tuscomb Limestone, and



EXPLANATION

TOTAL PESTICIDE CONCENTRATION, IN MICROGRAMS PER LITER

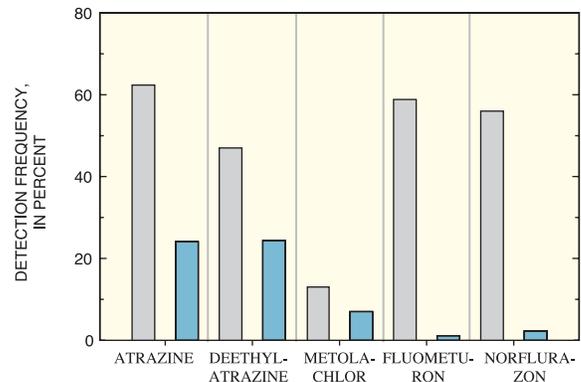
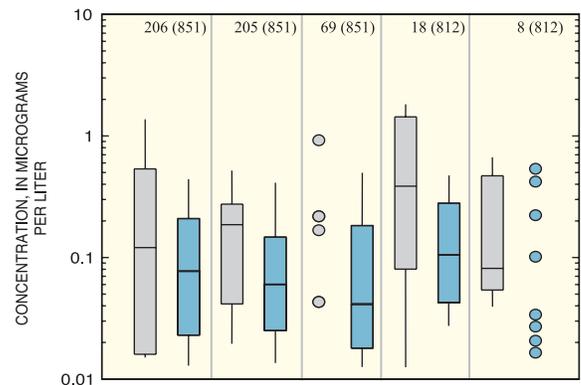
- Not detected
- Less than 1
- 1 to 3
- Greater than 3

Figure 15. Relation between dissolved-oxygen concentration, calcite saturation index, and total pesticide concentration for samples from the Mississippian carbonate aquifer.

Monteagle Limestone to characterize the effect of cropland on parts of the Mississippian carbonate aquifer used for water supply. These drinking-water wells ranged from 44 to 157 ft deep, with a median depth of 87 ft (Kingsbury and Shelton, 2002).

Concentrations of inorganic constituents in the agricultural land-use monitoring wells are similar to concentrations in the drinking-water wells from the previous study. Although drinking-water wells are completed in bedrock and generally are deeper than the monitoring wells, both groups of wells have similar ranges in DO, pH, and specific conductance (fig. 18). With the exception of a slightly higher median concentration of potassium in samples from the land-use monitoring wells, the land-use monitoring wells and the drinking-water wells are not statistically different with respect to major inorganic constituent concentrations. Potassium is a plant nutrient and is applied to agricultural lands, which may account for the slightly higher median concentration for samples from the land-use monitoring wells.

Nitrate concentrations generally were low in both well networks; the median nitrate concentration for the drinking-water wells was about 1.5 mg/L compared to 1 mg/L for the monitoring wells (fig. 19). Nitrate concentrations greater than 5 mg/L were infrequent in both networks (fig. 19). The drinking-water wells had two samples that exceeded the maximum



EXPLANATION

8 (812) NUMBER OF DETECTIONS (Number of samples)

90th Percentiles
75th
Median
25th
10th Percentiles

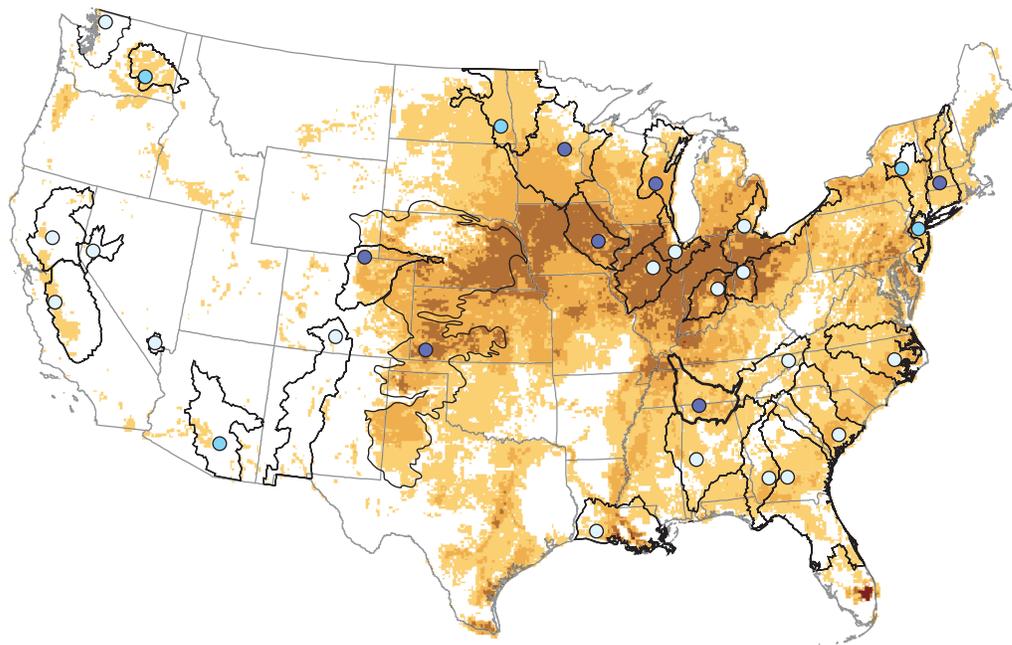
MISSISSIPPIAN CARBONATE AQUIFER (32 wells)

NATIONAL DATA (851 wells)

○ OBSERVATION

Figure 16. Detection frequencies and concentrations of selected pesticides at or above 0.01 microgram per liter in samples collected from the Mississippian carbonate aquifer and from selected National Water-Quality Assessment Program agricultural land-use wells across the Nation.

contaminant level of 10 mg/L. Point sources of nitrate (an animal feedlot and a small cooperative fertilizer storage facility) near these wells may have contributed to these high concentrations (Kingsbury and Shelton, 2002). The generally low concentrations of nitrate in samples from the land-use monitoring wells support



EXPLANATION

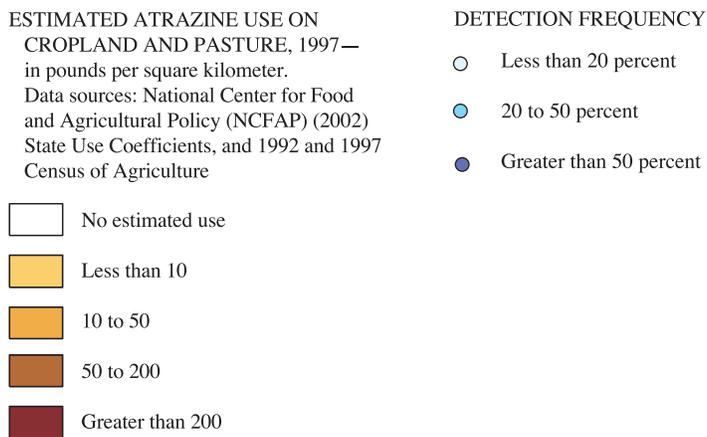


Figure 17. Estimated atrazine use across the Nation and detection frequency of atrazine for selected National Water-Quality Assessment Program agricultural land-use studies. (Modified from U.S. Geological Survey, 2002b.)

the interpretation that point sources and rapid transport of nitrate to the bedrock part of the aquifer likely contributed to these high concentrations (greater than 13 mg/L).

Although the amount of cropland in buffer areas around the drinking-water wells was less than around the land-use monitoring wells (fig. 20), pesticides detected frequently in samples from the land-use monitoring wells corresponded to those detected frequently in the samples from the drinking-water wells (fig. 21). The most frequently detected pesticides in both networks were atrazine and its degradates, fluo-

meturon, and norflurazon (fig. 21). The degradates of fluometuron and norflurazon were not analyzed in samples collected from the drinking-water wells. Metolachlor, deethylatrazine, and the degradates of aldicarb had similar detection frequencies in samples from both networks. Although several pesticides were detected more frequently in the land-use monitoring wells than in the drinking-water wells, median concentrations for several pesticides were similar (fig. 21). The higher detection frequencies in samples from the land-use monitoring wells may be related to the higher percentage of cropland in buffer areas around the wells

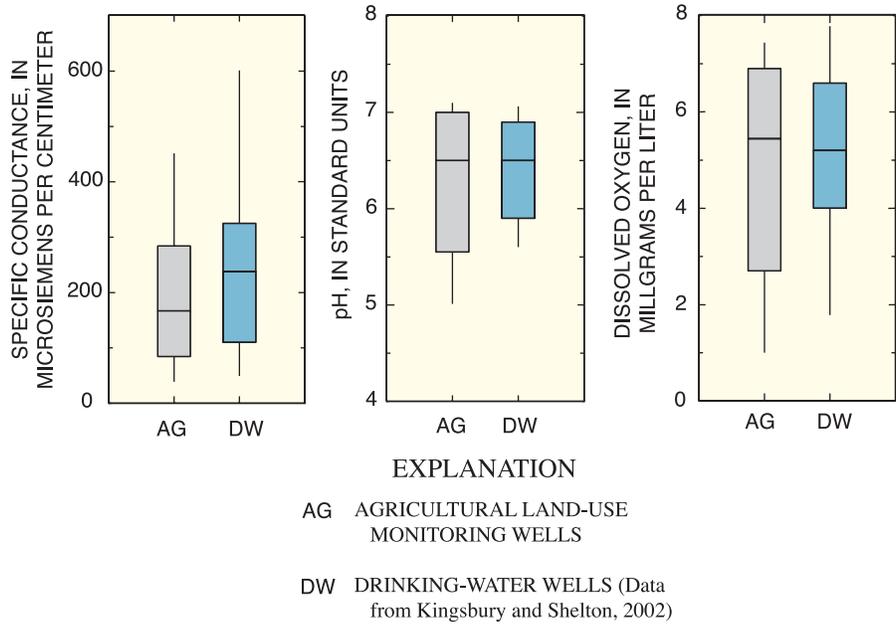


Figure 18. Specific conductance, pH, and dissolved-oxygen concentrations for samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippi carbonate aquifer.

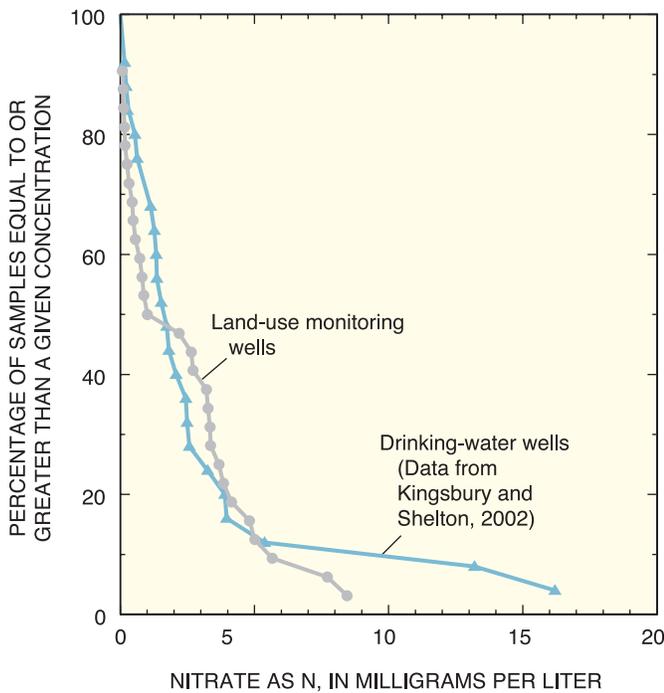


Figure 19. Nitrate concentrations in samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippi carbonate aquifer.

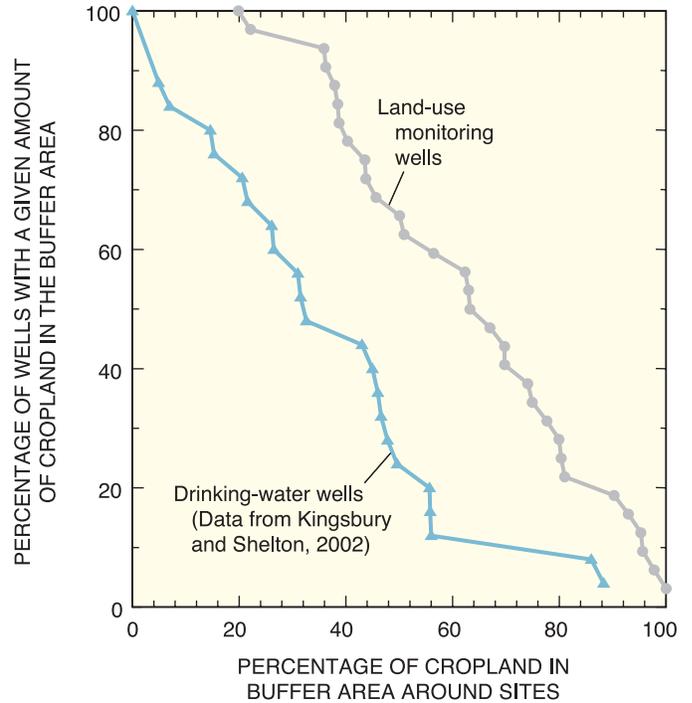


Figure 20. Amount of cropland in buffer areas around agricultural land-use monitoring wells and drinking-water wells in the Mississippi carbonate aquifer.

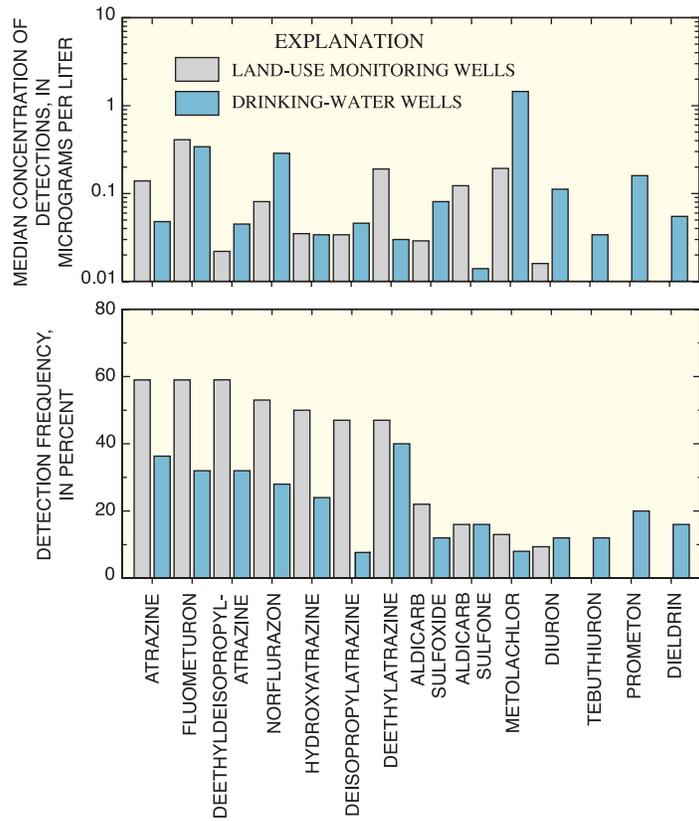


Figure 21. Detection frequency and median concentrations of selected pesticides and degradates detected at concentrations equal to or greater than 0.01 microgram per liter.

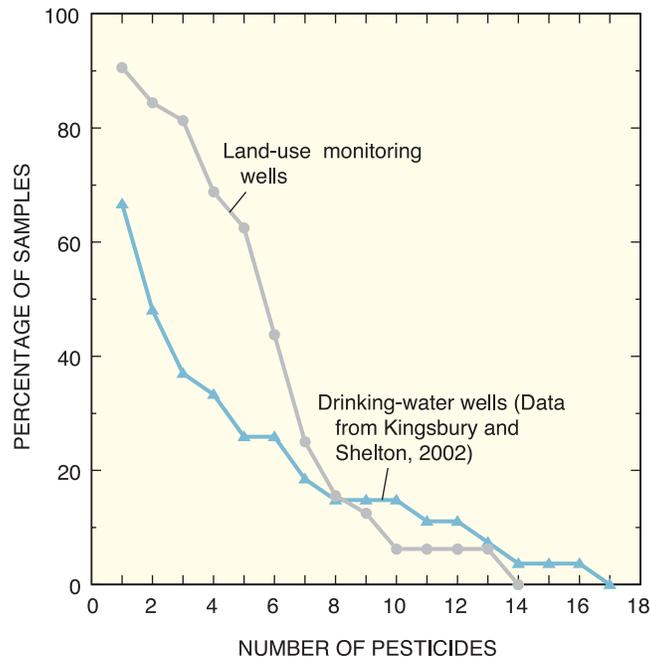


Figure 22. Number of pesticides detected in samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aquifer.

(fig. 20). A number of the samples analyzed for pesticides by HPLC/MS (fluometuron, norflurazon, and aldicarb degradates) from the drinking-water wells exceeded the sample holding time. The concentrations and detection frequencies for these pesticides may be biased low, and the holding time exceedances could contribute to the lower detection frequencies in samples from the drinking-water wells than detection frequencies in samples from the land-use monitoring wells.

Tebuthiuron, prometon, and dieldrin, which have non-agricultural uses, were detected in samples from the drinking-water wells but were not detected above 0.01 µg/L in samples from the land-use monitoring wells. The concentrations of these pesticides were comparable to the concentrations of the pesticides detected that are used on cropland; however, their detection frequency is somewhat lower (fig. 21). Tebuthiuron and prometon are herbicides that are used predominantly for weed control along rights-of-way and roadsides, and they were detected in samples from drinking-water wells having large amounts of urban land use in the buffer areas or that were near railroads and highways (Kingsbury and Shelton, 2002). Although dieldrin had agricultural use until the 1970s, detections only in samples from the drinking-water wells suggest that the principal source of dieldrin to the aquifer is residue remaining from its use for termite control around homes.

No individual pesticide concentrations from either well network exceeded drinking-water standards, but drinking-water standards typically do not exist for degradates, which may have toxicological characteristics similar to the parent pesticide. The potential health effects of mixtures of low-level pesticides and their degradates are not known. A high percentage of samples from both networks contained at least one pesticide. More than 60 percent of samples from the land-use monitoring wells and about 25 percent of samples from the drinking-water wells had five pesticide or pesticide-degradate detections (fig. 22). The high percentage of samples with multiple pesticide detections is a result of the co-occurrence of fluometuron, norflurazon, aldicarb degradates (cotton pesticides), and atrazine and its degradates. Few samples from either network (about 15 percent) had more than eight pesticides in a sample, but the frequency of samples with a large number of detections was greater in the drinking-water wells (fig. 22). The higher percentage of samples with eight or more pesticides and

the greater number of pesticides detected in samples from the drinking-water wells may be a result of the larger contributing areas for these wells than for the land-use monitoring wells. The larger contributing areas for the drinking-water wells likely integrate more land uses and crop types, which increases the maximum number of pesticides detected but generally lowers concentrations (fig. 23).

The total pesticide concentration was more than an order of magnitude higher in the land-use monitoring wells than in the drinking-water wells for 50 percent of samples (fig. 23). The total pesticide concentration was less than 1 µg/L in 60 percent of the land-use monitoring wells and in about 80 percent of the drinking-water wells (fig. 23). Similar to the number of pesticides detected in a sample, the total pesticide concentration for the two networks converge for about the upper 15 percent of samples. The likelihood of a well having a total pesticide concentration greater than 2 µg/L (not including the cotton herbicide degradates) was about the same for both networks.

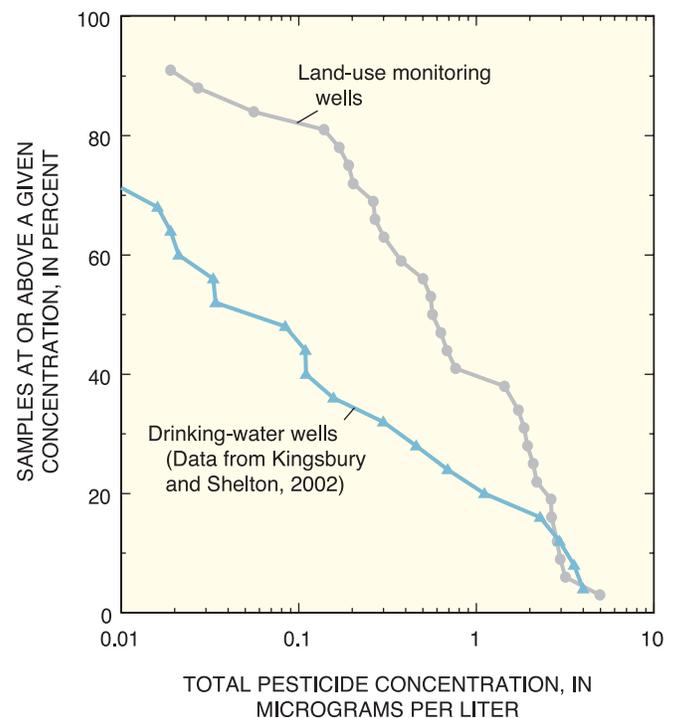


Figure 23. Total pesticide concentration for samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aquifer.

SUMMARY AND CONCLUSIONS

Thirty-two monitoring wells were installed in regolith in the Mississippian carbonate aquifer and sampled for major inorganic constituents, nutrients, and selected pesticides and pesticide degradates to characterize the effect of row-crop agriculture on the quality of recently recharged ground water. Land use and soil characteristics within a 1,640-ft radius buffer area around each well were delineated, and pesticide use was estimated based on crop acreages. A close association among land use, soil characteristics (cropland in areas with well-drained soils), and hydrology in this area limited the analysis of how these factors affect nitrate and pesticide occurrence. The interdependence of these variables in this study suggests that ground-water reconnaissance studies that attempt to relate ground-water quality to factors such as soil properties without considering possible correlation between soil properties and land use may attribute movement of pesticides into ground water to differences in soils, when in fact, differences in land use and pesticide use are related to soil characteristics.

Nitrate concentrations in the land-use monitoring wells generally were low, with a maximum concentration of about 8 mg/L and a median of 1 mg/L. The principal factor affecting nitrate concentrations was dissolved-oxygen concentrations. Low dissolved-oxygen concentrations in wells likely indicate longer average ground-water residence times, slow rates of recharge, or some degree of confinement in the regolith. Ratios of chloride (which is conserved in ground water) to nitrate suggest that nitrate concentrations in at least a third of the samples were affected by denitrification. Although nitrate concentrations were not correlated to the amount of cropland in the buffer areas, a correlation between nitrate and total pesticide concentrations suggests that cropland is the probable source of nitrate to these wells. Nitrate concentrations in this study generally were lower than concentrations measured in similar agricultural land-use well networks sampled for the National Water-Quality Assessment Program throughout the Nation.

Agricultural land in the Eastern Highland Rim typically occurs in areas with well-drained soils and low organic matter content, which likely contributes to the frequent detection of the most heavily used pesticides in the land-use monitoring wells. With the exception of glyphosate, which sorbs tightly to soil, pesticides with the highest use, such as fluometuron, atrazine, and their degradates, were detected most fre-

quently and at the highest concentrations. Fluometuron and atrazine were detected in 83 and 70 percent, respectively, of the samples from wells that had applications of these pesticides in the surrounding buffer areas. Those samples without atrazine and fluometuron detections, but with estimated use in buffer areas, were from wells with dissolved-oxygen concentrations less than 1.5 mg/L. Generally, pesticide concentrations were less than 1 µg/L, and the maximum concentration measured was 3.21 µg/L of demethylnorflurazon, a degradate of the cotton herbicide norflurazon. The highest concentrations of pesticides generally were associated with short average ground-water residence time as indicated by high dissolved-oxygen concentrations and low calcite saturation indices. Pesticide degradates usually were detected in association with the parent pesticide, and concentrations generally were comparable to or greater than the parent pesticide concentrations.

Nitrate concentrations in samples in this study generally were lower than in samples from similar well networks in agricultural areas across the country; however, pesticides were detected more frequently in samples in this study. For example, atrazine and its degradate, deethylatrazine, were detected in 62 and 47 percent, respectively, of samples in this study and were detected in about 25 percent of the 851 wells sampled for agricultural land-use studies conducted by the National Water-Quality Assessment Program. In those study areas with atrazine use greater than in the lower Tennessee River Basin, atrazine was detected in about 30 percent of the samples. Cotton pesticides were detected much more frequently in this study, but many of the study areas nationwide had small amounts of cotton acreage.

Similar nitrate and pesticide concentrations in samples from these shallow monitoring wells and samples collected in an earlier study from deeper drinking-water wells completed in bedrock indicate that the Mississippian carbonate aquifer is susceptible to nonpoint-source contamination associated with cropland. Nitrate concentrations generally were low in both well networks, and concentrations greater than 5 milligrams per liter were infrequent. The fine-grained texture of the regolith likely slows the rate of nitrate transport throughout much of the area and allows for some denitrification to occur, keeping concentrations low. Pesticide detection frequencies and maximum concentrations were higher in the land-use monitoring wells than in the drinking-water wells; however, the median concentrations of pesticides

detected in both networks were similar. The lower frequency of detection in the drinking-water wells may result from a smaller percentage of cropland in the contributing areas of these wells. Pesticides with non-cropland uses were detected in the drinking-water wells at lower frequencies than pesticides used on cropland, but at similar concentrations. Similarities in water quality of ground water collected from the land-use monitoring wells and the drinking-water wells probably reflect the karst hydrology of the aquifer, which allows for substantial movement of nonpoint-source contaminants away from agricultural areas once water has moved through the regolith to conduits in bedrock. Rapid movement of nonpoint-source contaminants also can occur when recharge enters the conduit flow system through sinkholes or macropores where the regolith is thin.

REFERENCES

- Adams, C.D., and Thurman, E.M., 1991, Formation and transport of deethylatrazine in the soil and vadose zone: *Journal of Environmental Quality*, v. 20, no. 3, p. 540-547.
- Blalock, H.M., 1972, *Social statistics* (2d ed.): New York, McGraw-Hill, 583 p.
- Burkart, M.R., Kolpin, D.W., Jaquis, R.J., and Cole, K.J., 1999, Agrichemicals in ground water of the Midwestern USA: Relations to soil characteristics: *Journal of Environmental Quality*, v. 28, no. 6, p. 1908-1915.
- Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl₃F and CCl₂F₂) as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma: *Water Resources Research*, v. 28, no. 9, p. 2257-2283.
- Fenneman, N.M., 1946, *Physical divisions of the United States*: U.S. Geological Survey map, scale 1:7,000,000.
- Fishman, M.J., ed., 1993, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of inorganic and organic constituents in water and fluvial sediments*: U.S. Geological Survey Open-File Report 93-125, 217 p.
- Fishman, M.J., and Friedman, L.C., eds., 1989, *Methods for determination of inorganic substances in water and fluvial sediments* (3d ed.): *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, book 5, chap. A1, 545 p.
- Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry*: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p.
- Griffith, G.E., Omernik, J.M., and Azevedo, S.H., 1997, *Ecoregions of Tennessee*: Corvallis, Oreg., U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, EPA/600/R-97/022, 51 p.
- Hallberg, G.R., and Keeney, D.R., 1993, Nitrate, in Alley, W.M., ed., *Regional ground-water quality*: New York, Van Nostrand Reinhold, p. 297-322.
- Helsel, D.R., and Hirsch, R.M., 1992, *Statistical methods in water resources*: New York, Elsevier, 522 p.
- King, P.B., and Beikman, H.M., 1974, *Geologic map of the United States*: U.S. Geological Survey special map, 2 sheets, scale 1: 2,500,000.
- Kingsbury, J.A., Hoos, A.B., and Woodside, M.D., 1999, *Environmental setting and water-quality issues in the lower Tennessee River Basin*: U.S. Geological Survey Water-Resources Investigations Report 99-4080, 44 p.
- Kingsbury, J.A., and Shelton, J.M., 2002, *Water quality of the Mississippian carbonate aquifer in parts of Middle Tennessee and northern Alabama, 1999*: U.S. Geological Survey Water-Resources Investigations Report 02-4083, 36 p.
- Kish, J.L., Thurman, E.M., Scribner, E.A., and Zimmerman, L.R., 2000, *Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of selected herbicides and their degradation products in water using solid-phase extraction and gas chromatography/mass spectrometry*: U.S. Geological Survey Open-File Report 00-385, 13 p.
- Kolpin, D.W., Thurman, E.M., and Linhart, S.M., 1998, The environmental occurrence of herbicides: the importance of degradates in ground water: *Archives of Environmental Contamination and Toxicology*, v. 53, no. 3, p. 385-390.
- Koterba, M.T., 1998, *Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: collection, documentation, and compilation of required site, well, subsurface, and landscape data for wells*: U.S. Geological Survey Water-Resources Investigations Report 98-4107, 91 p.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, *Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: collection and documentation of water-quality samples and related data*: U.S. Geological Survey Open-File Report 95-399, 113 p.
- Lee, E.A., Zimmerman, L.R., Bhullar, B.S., and Thurman, E.M., 2002, *Linker-assisted immunoassay and liquid chromatography/mass spectrometry for the analysis of glyphosate*: *Analytical Chemistry*, v. 74, p. 4937-4943.
- Lowry, Richard, 2000, *Concepts and applications of inferential statistics*: accessed June 21, 2002, at <http://vassun.vassar.edu/~lowry/webtext.html>

- National Center for Food and Agricultural Policy, 2002, National pesticide use database: accessed May 17, 2002, at <http://www.ncfap.org/database/ingredient/default.asp>
- Osborne, W.E., Szabo, M.W., Copeland, C.W., Jr., and Neathery, T.L., comps., 1989, Geologic map of Alabama: Geological Survey of Alabama Special Map 221, 1 sheet, scale 1:500,000.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- Plummer, L.N., and Busenberg, Eurybiades, [2000], Chlorofluorocarbons: tools for dating and tracing young groundwater, *in* Cook, P.G., and Herczeg, A.L., eds., *Environmental tracers in subsurface hydrology*: Boston, Kluwer Academic Publishers, chap. 15, p. 441-478.
- Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90-4101, 109 p.
- Smalley, G.W., 1983, Classification and evaluation of forest sites on the Eastern Highland Rim and Pennyroyal: New Orleans, U.S. Department of Agriculture, Forest Service, Southern Forest Experiment Station, General Technical Report SO-43, 123 p.
- Stumm, Werner, and Morgan, J.J., 1996, *Aquatic chemistry: chemical equilibria and rates in natural waters* (3d ed.): New York, John Wiley & Sons, 1022 p.
- Thelin, G.P., and Gianessi, L.P., 2000, Methods for estimating pesticide use for county areas of the conterminous United States: U.S. Geological Survey Open-File Report 00-250, 62 p.
- U.S. Department of Agriculture, 2001a, National soil survey geographic (SSURGO) database: accessed March 21, 2001, at http://www.ftw.nrcs.usda.gov/ssur_data.html
- 2001b, National Map Unit interpretation records (MUIR) database: accessed January 18, 2001, at <http://ortho.ftw.nrcs.usda.gov/muir/>
- 2001c, Agricultural statistics data base: accessed August 14, 2001, at <http://www.nass.usda.gov/ipedb/>
- 2002, The ARS pesticide properties database: accessed September 25, 2002, at <http://wizard.arsusda.gov/acsl/ppdb.html>
- U.S. Geological Survey, 1997, Aggregated water-use data systems, database—1995 water-use data: Data on file at the U.S. Geological Survey, Water Resources Division, Nashville, Tennessee.
- 1999, The quality of our Nation's waters—nutrients and pesticides: U.S. Geological Survey Circular 1225, 82 p.
- 2002a, USGS National Water-Quality Assessment Program data warehouse, accessed May 12, 2002, at <http://water.usgs.gov/nawqa/data>
- 2002b, Annual pesticide use maps, accessed 2002, at <http://ca.water.usgs.gov/pnsp/use92>
- Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., and Burt, J.P., 1992, The SCS/ARS/CES pesticide properties database for environmental decision-making: *Reviews of Environmental Contamination and Toxicology*, v. 123, p. 1-156.
- Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, *Methods for the determination of organic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the U.S. Geological Survey*, book 5, chap. A3, 80 p.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with select-ion monitoring*: U.S. Geological Survey Open-File Report 95-181, 49 p.

APPENDIXES

Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use

[MRL, minimum reporting level; µg/L, micrograms per liter; CAS, chemical abstracts reference number; H, herbicide; I, insecticide; F, fungicide; Degr., pesticide degradate; N/A, not applicable; --, no CAS number; pesticides in italics were analyzed before analytical method approval, and data in this report are provisional; *, pesticides denoted with an asterisk have had low or inconsistent recoveries throughout method development, and concentrations always are reported as estimated; pesticides denoted with a "+" were analyzed at the U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kansas]

Compound	Common name	MRL, in µg/L	CAS number	Use
Pesticides detected				
<i>2,4-D methyl ester</i>	N/A	0.086	1928-38-7	H
<i>3(4-chlorophenyl) methyl urea</i>	N/A	0.092	1897-46-6	H-Degr.
Acetochlor	Acenit, Guardian, Harness	0.002	34256-82-1	H
<i>Aldicarb*</i>	Temik	0.082	116-06-3	I
<i>Aldicarb sulfone*</i>	Standak, aldoxycarb	0.16	1646-88-4	I-Degr.
<i>Aldicarb sulfoxide*</i>	Temik sulfoxide	0.027	1646-87-3	I-Degr.
Atrazine	Aatrex	0.001	1912-24-9	H
Deethylatrazine*	N/A	0.002	6190-65-4	H-Degr.
<i>Deisopropylatrazine*</i>	N/A	0.074	1007-28-9	H-Degr.
<i>Deethyldeisopropylatrazine*</i>	N/A	0.06	3397-62-4	H-Degr.
<i>Hydroxyatrazine</i>	N/A	0.193	2163-68-0	H-Degr.
<i>Bentazon*</i>	Basagran, Adagio, Galaxy, Storm	0.019	25057-89-0	H
Carbaryl*	Sevin	0.003	63-25-2	I
Carbofuran*	Furadan	0.003	1563-66-2	I
<i>Diphenamid</i>	Dymid, Enide, Rideon, Dyfen	0.058	957-51-7	H
<i>Diuron</i>	DCMU, Diurex, Aguron, Karmex	0.079	330-54-1	H
<i>Fluometuron</i>	Cortoran, Lanex, Cottonex, Flo-met	0.062	2164-17-2	H
<i>Demethylfluometuron+</i>	N/A	0.05	--	H-Degr.
<i>3-(trifluoromethyl) aniline (TFMA)+</i>	N/A	0.05	--	H-Degr.
<i>Imazethapyr*</i>	Pursuit, Pursuit DG	0.088	81335-77-5	H
<i>Metalaxyl</i>	Apron, Subdue, Ridomil	0.057	94-81-5	F
<i>Methiocarb*</i>	Draza, Mesurol, Slug-geta	0.08	57837-19-1	I
Metolachlor	Dual, Pennant	0.002	51218-45-2	H
<i>Methomyl*</i>	Nudrin, Lannate, Lanox	0.077	2032-65-7	I
Metribuzin	Sencor, Lexone	0.004	21087-64-9	H
p,p'-DDE	N/A	0.006	72-55-9	I-Degr.
<i>Norflurazon</i>	Solicam, Telok, Evital, Zorial	0.077	27314-13-2	H
<i>Demethylnorflurazon+</i>	N/A	0.05	--	H-Degr.
Pendimethalin	Prowl, Stomp	0.004	40487-42-1	H
Prometon	Pramitol, Princep	0.018	1610-18-0	H
Trifluralin	Treflan, Gowan	0.002	1582-09-8	H
<i>Siduron</i>	Tupersan, Trey	0.093	1982-49-6	H
Simazine	Princep	0.005	122-34-9	H
<i>Sulfometuron-methyl</i>	Oust, DPX-T5648	0.039	74222-97-2	H

Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use—Continued

Compound	Common name	MRL, in µg/L	CAS number	Use
Pesticides not detected				
<i>2,4-D</i>	Aqua Kleen, Weedone-2,4-DP	0.077	94-75-7	H
2,6-Diethylaniline	N/A	0.003	579-66-8	H-Degr.
<i>3-Hydroxycarbofuran</i>	N/A	0.062	16655-82-6	I-Degr.
<i>3-Ketocarbofuran*</i>	N/A	0.072	16709-30-1	I-Degr.
<i>3-(trifluoromethyl)phenylurea (TFMPU)+</i>	N/A	0.05	--	H-Degr.
<i>2,4-DB</i>	Butyrac, Butoxone, Legumex D	0.054	94-82-6	H
<i>Acifluorfen, sodium salt</i>	Tackle, Blazer	0.062	62476-59-9	H
Alachlor	Lasso, Bronco	0.002	15972-60-8	H
alpha-BHC	HCH-alpha	0.002	319-84-6	I
<i>Bendiocarb</i>	Ficam, Tattoo	0.061	22781-23-3	I
Benfluralin	Balan, Benefin	0.002	1861-40-1	H
<i>Benomyl</i>	Benlate	0.022	17804-35-2	F
<i>Bensulfuron-methyl</i>	Londax	0.048	83055-99-6	H
<i>Bromacil*</i>	Bromax, Hyvar, Uragon	0.081	314-40-9	H
<i>Bromoxynil*</i>	Bromanil, Buctril, Torch	0.057	1689-84-5	H
Butylate	Sutan +	0.002	2008-41-5	H
<i>Chloramben methyl ester*</i>	Amiben, methyl ester	0.114	7286-84-2	H
<i>Chlorimuron-ethyl</i>	Classic	0.037	90982-32-4	H
<i>Chlorothalonil*</i>	Bravo, Forturf	0.048	1897-45-6	H
Chlorpyrifos	Lorsban, Dursban	0.004	2921-88-2	I
<i>Clopyralid</i>	Stinger, Lontrel	0.041	1702-17-6	H
Cyanazine	Bladex	0.004	21725-46-2	H
<i>Cyanazineamide+</i>	N/A	0.05	--	H-Degr.
<i>Cycloate*</i>	Ro-Neet, Marathon	0.054	1134-23-2	H
<i>Dacthalmonoacid</i>	DCPA Monoacid	0.072	887-54-7	H-Degr.
DCPA	Dacthal	0.002	19719-28-9	H
Diazinon	Spectracide	0.002	333-41-5	I
<i>Dicamba</i>	Banvel, Marksman, Clarity	0.096	1918-00-9	H
<i>Dichlorprop</i>	Seritox 50, Weedone	0.05	120-36-5	H
Dieldrin	Dieldrin, Panoram D-31	0.001	60-57-1	I
<i>Dimethenamid</i>	Frontier	0.05	87674-68-8	H
<i>Dinoseb</i>	DNPB, Caldon, Dynamite	0.043	88-85-7	H
Disulfoton	Di-Syston	0.017	298-04-4	I
EPTC	Eradicane, Eptam	0.002	759-94-4	H
Ethalfuralin	Sonalan	0.004	55283-68-6	H
Ethoprop	Mocap	0.003	13194-48-4	I
<i>Fenuron</i>	Beet-Klean, Fenidim	0.074	101-42-8	H

Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use—Continued

Compound	Common name	MRL, in µg/L	CAS number	Use
Pesticides not detected—Continued				
<i>Flumetsulam*</i>	DE 498, XRD 498	0.087	98967-40-9	H
Fonofos	Dyfonate	0.003	944-22-9	I
<i>Glyphosate+</i>	Round-up	0.1	1071-83-6	H
<i>Imazaquin*</i>	Image 1.5LC; Scepter 1.5L	0.103	81335-37-7	H
<i>Imidacloprid</i>	Admire, Gaucho, Merit	0.106	105827-78-9	I
Lindane	Isotox	0.004	58-89-9	I
Linuron	Lorox	0.002	330-55-2	H
Malathion	Cythion	0.005	121-75-5	I
<i>MCPA</i>	Bordermaster, Metaxon, Rhomene	0.058	86-50-0	H
<i>MCPB*</i>	Tropotox, Can-Trol, PDQ	0.062	94-74-6	H
<i>Methomyl oxime*</i>	N/A	0.01	16752-77-5	I-Degr.
Azinphos-methyl*	Guthion	0.001	13749-94-5	I
Methyl parathion	Penncap-M	0.006	298-00-0	I
<i>Metsulfuron-methyl *</i>	Escort, Gropper, Ally	0.114	74223-64-6	H
Molinate	Ordram	0.004	2212-67-1	H
Napropamide	Devrinol	0.003	15299-99-7	H
<i>Neburon</i>	Granurex, Herbalt, Kloben	0.075	555-37-3	H
<i>Nicosulfuron</i>	Accent, Accent DF	0.065	111991-09-4	H
<i>Oryzalin</i>	Ryzelan, Surfian, Dirimal	0.071	19044-88-3	H
<i>Oxamyl</i>	Vydate L, Thioxamyl	0.016	23135-22-0	I
<i>Oxamyl oxime*</i>	N/A	0.064	30558-43-1	I-Degr.
Parathion	Phoskil	0.004	56-38-2	I
Pebulate	Tillam	0.004	1114-71-2	H
cis-Permethrin	Pounce, Ambush	0.005	54774-45-7	I
Phorate	Thimet	0.002	298-02-2	I
<i>Picloram</i>	Tordon, Amdon, Grazon	0.071	191802-1	H
<i>Prometryn+</i>	Caparol	0.05	7287-19-6	H
Pronamide	Kerb	0.003	23950-58-5	H
Propachlor	Ramrod	0.007	1918-16-7	H
Propanil	Stam, Stampede	0.004	709-98-8	H
Propargite	Comite	0.013	2312-35-8	I
<i>Propiconazole</i>	Tilt, Orbit, Banner, Proconazole, Wocosin	0.064	60207-90-1	F
<i>Propoxur</i>	Baygon, PHC, Suncide, Unden	0.059	114-26-1	I
Tebuthiuron	Graslan, Spike, Perflan	0.01	34014-18-1	H
Terbacil*	Sinbar, DPX-D732, Geonter	0.007	5902-51-2	H
Terbufos	Counter	0.013	13071-79-9	I
Thiobencarb	Bolero	0.002	28249-77-6	H
Triallate	Far-Go	0.001	2303-17-5	H
<i>Tribenuron-methyl*</i>	Express, tribenuron methyl ester, DPX-L5300	0.068	101200-48-0	H
<i>Triclopyr</i>	Garlon, Curtail, Redeem, Remedy	0.101	55335-06-3	H

Appendix 2. Chlorofluorocarbon concentrations, calculated atmospheric partial pressures, and model recharge dates for sampled wells

[temp., temperature; °C, degrees Celsius; pg/kg, picograms per kilogram; pptv, parts per trillion by volume; CFC, chlorofluorocarbon; Contam., CFC concentrations in samples were greater than air-water atmospheric equilibrium concentrations; Modern, CFC concentrations indicative of 2000 atmospheric concentrations]

Well number	Sampling date	Time	Recharge temp. (°C)	Elev. (feet above NGVD 29)	Concentration in solution, in pg/kg			Calculated Atmospheric partial pressure, in pptv			Model CFC recharge dates, in years		
					CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
35	05/25/00	1450	16.2	640	546.5	261.5	64.9	270.2	546.8	78.6	1990.5/1998.0	1997.0	1990.5
35	05/25/00	1515	16.2	640	542.3	245.2	67.2	268.2	512.7	81.5	1990.0/1998.5	1992.5	1991.0
35	05/25/00	1525	16.2	640	539.3	251.8	66.9	266.6	526.5	81.1	1989.5	1994.0	1991.0
14	05/31/00	1555	13.8	822	525.3	261.0	62.4	231.6	493.0	66.7	1986.5	1990.5	1988.5
14	05/31/00	1615	13.8	822	527.1	267.8	64.5	232.4	505.8	68.9	1986.5	1991.5	1988.5
14	05/31/00	1620	13.8	822	518.9	241.9	62.5	228.8	456.8	66.7	1986.0	1988.0	1988.5
11	06/06/00	1635	14.8	860	976.5	320.0	74.5	453.8	633.6	84.3	Contam.	Contam.	1992.0/1997.0
11	06/06/00	1640	14.8	860	544.2	269.4	66.8	252.9	533.4	75.6	1988.0	1994.5	1989.5
11	06/06/00	1700	14.8	860	547.9	271.3	66.2	254.6	537.2	74.9	1988.0	1995.5	1989.5
7	06/05/00	1450	13.7	950	655.1	301.2	95.3	288.7	569.0	101.7	Modern	Modern	Contam.
7	06/05/00	1510	13.7	950	649.3	289.8	94.7	286.2	547.5	101.0	Modern	1997.0	Contam.
7	06/05/00	1520	13.7	950	639.4	266.4	88.8	281.8	503.2	94.7	Modern	1991.5	Modern
25	05/24/00	1100	17.5	550	24.2	56.4	0.0	12.7	124.5	0.0	1961.0	1969.5	<1955
25	05/24/00	1115	17.5	550	23.3	50.3	0.0	12.2	111.0	0.0	1960.5	1968.5	<1955
25	05/24/00	1120	17.5	550	23.5	52.1	0.0	12.4	115.0	0.0	1960.5	1969.0	<1955
20	05/25/00	1015	14.7	580	520.4	295.4	71.1	238.1	576.2	79.2	1987.0	Modern	1990.5
20	05/25/00	1030	14.7	580	4,010.7	279.4	67.7	1,835.3	544.9	75.3	Contam.	1997.0	1989.5
20	05/25/00	1050	14.7	580	1,384.0	306.6	73.3	633.3	598.1	81.6	Contam.	Contam.	1991.0
12	06/07/00	1220	15.1	765	750.1	285.6	63.3	352.7	571.2	72.6	Contam.	Modern	1989.0
12	06/07/00	1250	15.1	765	849.6	348.1	79.0	399.5	696.2	90.6	Contam.	Contam.	Modern
12	06/07/00	1300	15.1	765	909.2	301.6	74.9	427.5	603.2	85.9	Contam.	Contam.	1994.0
13	06/01/00	1445	15.0	705	560.0	260.2	69.8	261.4	516.9	79.3	1989.0	1992.5	1990.5
13	06/01/00	1455	15.0	705	562.2	266.2	71.8	262.4	528.8	81.7	1989.0	1994.0	1991.0
13	06/01/00	1500	15.0	705	567.3	262.7	70.2	264.8	521.8	79.8	1989.5	1993.5	1990.5
33	05/22/00	1530	13.4	540	215.0	155.3	25.4	91.9	284.9	26.3	1973.0	1978.0	1981.0
33	05/22/00	1550	13.4	540	219.8	129.5	23.7	93.9	237.6	24.4	1973.0	1975.5	1980.0
33	05/22/00	1600	13.4	540	229.3	133.4	26.2	98.0	244.7	27.0	1973.5	1976.0	1981.0