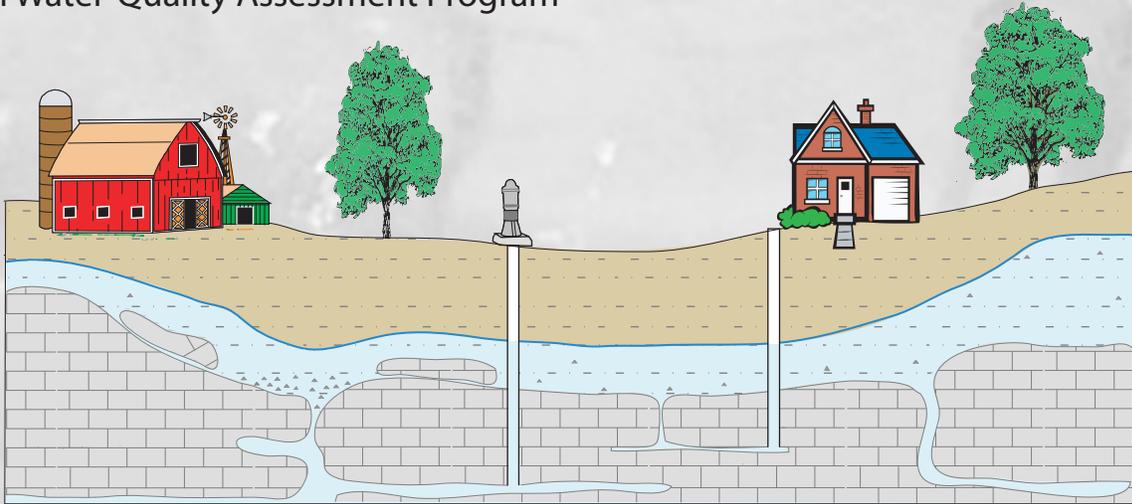


Water Quality of the Mississippian Carbonate Aquifer in Parts of Middle Tennessee and Northern Alabama, 1999

Water-Resources Investigations Report 02-4083
National Water-Quality Assessment Program



Cover illustration: Conceptual diagram depicting ground-water wells completed in the Mississippian carbonate aquifer. Left photograph is a turbine pump at a municipal water supply in northern Alabama. Right photograph is a domestic well near Huntsville, Alabama.

Water Quality of the Mississippian Carbonate Aquifer in Parts of Middle Tennessee and Northern Alabama, 1999

By JAMES A. KINGSBURY and JOHN M. SHELTON

U.S. GEOLOGICAL SURVEY

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Nashville, Tennessee
2002

U.S. DEPARTMENT OF THE INTERIOR
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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. 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.

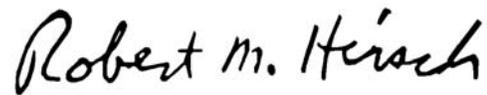
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program 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. 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.

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 AND VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi ²)	2.590	square kilometer
acre	4,047	square meter
gallon per minute (gal/min)	0.06309	liter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second
pound, avoirdupois (lb)	0.4536	kilogram
ton per square mile (ton/mi ²)	0.3503	metric tons per square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$

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

Altitude, as used in this report, refers to distance above or below sea level.

Horizontal datum: 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 ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

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By James A. Kingsbury and John M. Shelton

ABSTRACT

Water-quality data for nitrate, fecal-indicator bacteria, pesticides, and volatile organic compounds collected in parts of Middle Tennessee and northern Alabama indicate that the Mississippian carbonate aquifer in these areas is susceptible to contamination from point and nonpoint sources. Thirty randomly located wells (predominantly domestic), two springs, and two additional public-supply wells were sampled in the summer of 1999 as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. These wells and springs were sampled to characterize the occurrence and distribution of the above constituents in this karst aquifer of Mississippian age and to determine the principal environmental factors related to their occurrence.

Nitrate and fecal indicator bacteria were frequently detected at the sampled sites. Nitrate exceeded the drinking-water maximum contaminant level of 10 milligrams per liter in two samples; the median concentration for all samples was about 1.5 milligrams per liter. Correlation of nitrate concentrations to the amount of cropland near a site and to pesticide detections indicates that fertilizer application is the predominant source of nitrogen to the aquifer. Fecal-indicator bacteria were present in samples from about 40 percent of the sites. The presence of fecal-indicator bacteria is weakly correlated to the depth to ground water but is not correlated to a specific land use near the sites.

Pesticides and pesticide breakdown products (metabolites) were detected at 74 percent of the sites sampled. Concentrations generally were

less than 1 microgram per liter and no pesticide detections exceeded drinking-water maximum contaminant levels. The maximum total pesticide concentration measured was about 4 micrograms per liter. Intensity of pesticide use, proximity of sites to areas of pesticide application, and soil hydrologic group were the primary factors affecting the occurrence of pesticides.

Volatile organic compounds were detected at generally low concentrations at about 81 percent of the sites sampled. Concentrations of trichloroethylene, tetrachloroethylene, and 1,2-dichloropropane at three sites equalled or exceeded drinking-water maximum contaminant levels. The maximum concentration measured was 7.5 micrograms per liter of trichloroethylene. The presence of volatile organic compounds in the Mississippian carbonate aquifer was not related to hydrogeology, soil properties, or land use near the sites; although higher total volatile organic compound concentrations and greater numbers of compounds in samples generally were associated with a higher percentage of urban land use near a site. Chloroform was the most frequently detected compound, and correlation of low-level detections to the amount of wetlands near sites having these detections may indicate biogenic formation of chloroform.

The relation between land use and water quality was stronger for constituents that are contributed to the environment systematically (fertilizer and pesticide applications), than those contributed inadvertently (leaking septic tanks or chemical spills or leaks). Land use and soils characterized in circular buffer areas near sites

sampled in this karst aquifer explained some of the variation in nitrate concentration and presence of pesticides. Use of land use and soil data with greater detail than the large scale data used in this analysis and buffer areas based on well capacities and ground-water withdrawals might strengthen this type of analysis.

INTRODUCTION

The lower Tennessee River Basin (LTEN) is one of more than 50 river basins and aquifer systems in which water-quality assessments are being conducted across the Nation (fig. 1) as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. The purpose of these assessments is to characterize the quality of a large percentage of the freshwater resources of the Nation and to determine if the quality of water is changing over time. These goals are achieved, in part, by using consistent study designs, sampling procedures, and analytical techniques for all of the study areas across the Nation. One component of the NAWQA program is to characterize the occurrence and distribution of nutrients, pesticides, volatile organic compounds (VOCs), and trace elements in shallow ground water across the Nation.

The LTEN extends from Chattanooga, Tennessee, to near Paducah, Kentucky (fig. 1), and encompasses about 19,500 square miles (mi²). The LTEN comprises parts of three physiographic provinces (fig. 1) and a variety of geologic materials including carbonate rocks, sandstones, and unconsolidated sediments. The LTEN was subdivided into nine subunits (fig. 1) that generally correspond to Level III and IV ecoregion boundaries (Griffith and others, 1997; Kingsbury and others, 1999). These subunits represent areas of relative lithologic and geomorphic homogeneity and provide a framework in which water quality can be evaluated. NAWQA ground-water sampling networks typically consist of randomly located sites in a given subunit.

The Eastern and Western Highland Rim subunits (fig. 1) are underlain by carbonate rocks of predominantly Mississippian age. Ground water in these carbonate rocks is an important drinking-water source in the Eastern Highland Rim subunit. Estimated ground-water withdrawals for public and domestic supply in the Eastern Highland Rim subunit was about 40 million gallons per day (Mgal/d) in 1995 (U.S. Geological Survey, unpublished data, 1997). About

5 Mgal/d of the total ground-water withdrawals for 1995 were for domestic use (U.S. Geological Survey, 1997). The City of Huntsville, Alabama, is the largest ground-water user, withdrawing about 14 Mgal/d from shallow wells (maximum depth 125 feet). Ground water accounts for about 40 percent of water use for Huntsville. About 25 public water-supply systems rely on ground water in the Eastern Highland Rim subunit.

In summer 1999, 30 randomly located wells (predominantly domestic wells), two springs, and two additional public-supply wells (fig. 2) were sampled for major and trace inorganic constituents, nutrients, dissolved organic carbon, fecal-indicator bacteria, VOCs, and pesticides to characterize the water quality in the Eastern Highland Rim subunit.

Purpose and Scope

This report describes the occurrence and distribution of nutrients, fecal-indicator bacteria, pesticides, and VOCs from 34 ground-water sites sampled in the Eastern Highland Rim subunit of the LTEN. In addition to summarizing data for these constituents, the purpose of this report is to qualitatively characterize the susceptibility of ground water in the study area to contamination by comparing these data to data collected for similar NAWQA studies across the Nation. This report also describes the effects of natural setting (site characteristics, hydrogeology, and soil properties) and human activities (land use) on ground-water quality.

Description of the Study Area

The Eastern Highland Rim subunit encompasses an area of about 3,400 mi² in the Interior Low Plateau Physiographic Province (Fenneman, 1938). Land-surface altitudes range from about 500 feet above sea level near the Tennessee River to about 1,300 feet above sea level in the northern part of the subunit. The average annual precipitation is about 55 inches per year; spring (March through May) is the wettest part of the year, and late summer (August through October) is the driest part of the year. Rainfall for the 12-month period prior to this sampling (May 1998 to May 1999) was about 10 inches below normal (National Oceanic and Atmospheric Administration, written commun., 2000).

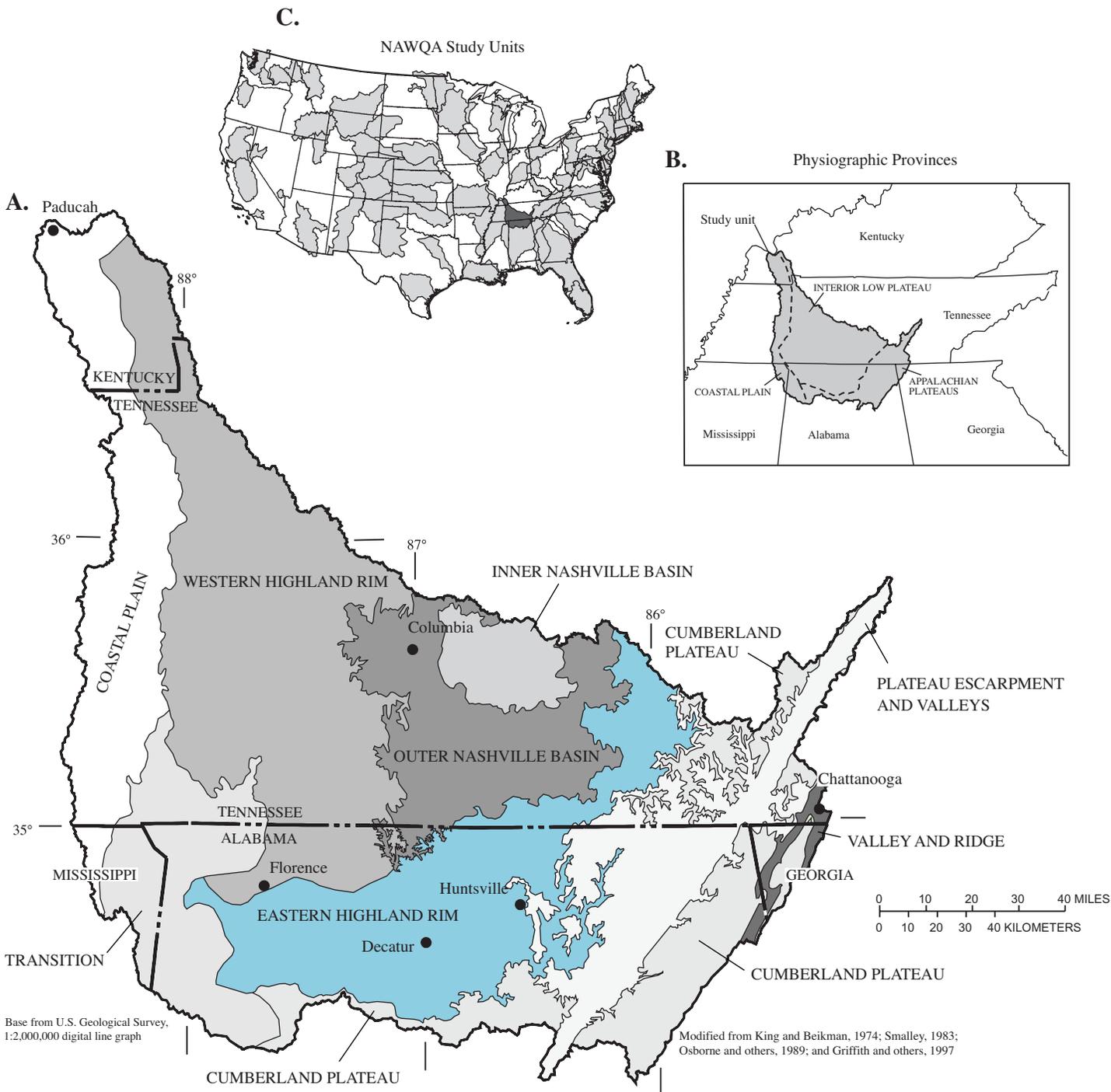


Figure 1. (A) Location of the lower Tennessee River Basin and delineated subunits, (B) physiographic provinces in the study unit, and (C) National Water-Quality Assessment (NAWQA) Program study units nationwide.

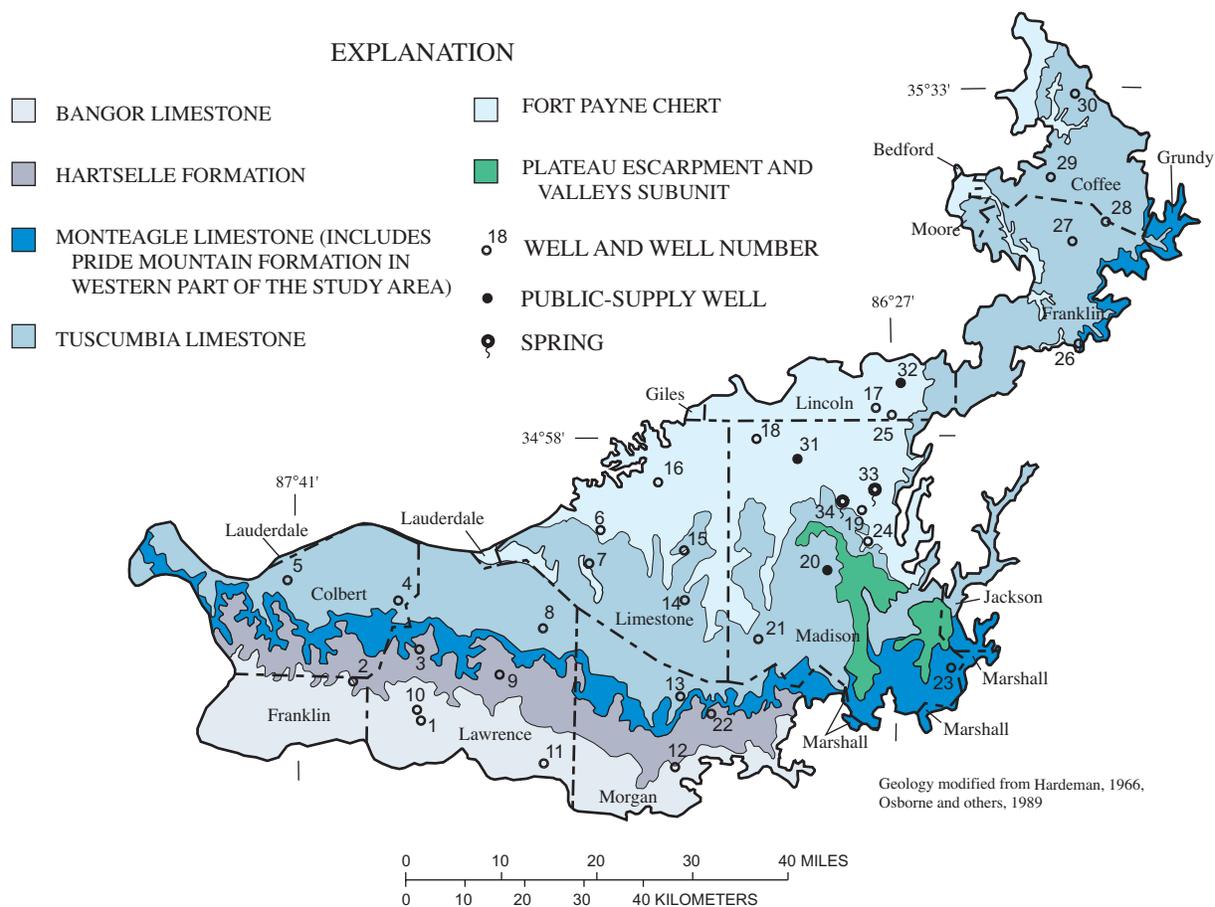


Figure 2. Generalized geology of the Eastern Highland Rim subunit and location of ground-water sites.

Hydrogeology

Mississippian-age rocks underlie most of the Eastern Highland Rim subunit and generally are flat lying to gently dipping. These rocks are predominantly carbonates but include shaly layers as well as some sandstone. Five stratigraphic units are present in Alabama and six in Tennessee (fig. 3). These units include the Bangor Limestone, Hartselle Sandstone, Monteagle Limestone, Tuscumbia Limestone, and the Fort Payne Chert. The Tuscumbia Limestone in Alabama is equivalent to the St. Louis and Warsaw Limestones in Tennessee; however, the Tuscumbia Limestone is used in this report because the majority of wells sampled in these three stratigraphic units are in Alabama. The Monteagle Limestone grades into the Pride Mountain Formation in the western part of the Eastern Highland Rim subunit and the two formations are mapped as undifferentiated in the central part of the subunit (Osborne and others, 1989). In this report, these formations are referred to as the Monteagle Limestone

because no wells were sampled in the central or western part of the subunit where the Pride Mountain Formation is present.

Regolith consisting of residual clay, clay-sized chert, and chert gravel and minor silt and sand overlies bedrock in most areas. Thickness of the regolith varies considerably, and locally it is as much as 100 feet thick. Chert gravels are common at the base of the regolith overlying the Tuscumbia Limestone and Fort Payne Chert. The Fort Payne Chert and Tuscumbia Limestone account for most of the outcrop or subcrop in the area (fig. 2) and are the principal source of ground water in the subunit. The predominantly carbonate geology of the Mississippian-age formations has led to the development of karst landforms such as sinkholes, caves, disappearing streams, and springs throughout much of the subunit.

Aquifers in the Mississippian-age limestones in the Eastern Highland Rim of Middle Tennessee have been referred to as the Highland Rim aquifer system

System	Series	Stratigraphic unit		Lithology and hydrologic significance
		Tennessee	Alabama	
Mississippian	Upper	Bangor Limestone	Bangor Limestone	Limestone, thick-bedded, bioclastic and oolitic. Well yields range from 2 to 5 gallons per minute, but as much as 50.
		Hartselle Formation	Hartselle Sandstone	Sandstone, thick-bedded to massive, some shale interbeds. Well yields range from 2 to 5 gallons per minute, but as much as 50.
		Monteagle Limestone	Monteagle Limestone	Limestone, oolitic, massive-bedded. Well yields generally are less than 10 gallons per minute.
		St. Louis Limestone	Tuscumbia Limestone	Limestone, generally massive-bedded, with abundant chert nodules. Well yields generally range from 2 to 20 gallons per minute. Some locations yield as much as 200 gallons per minute.
	Warsaw Limestone			
Lower	Fort Payne Formation and Maury Formation	Fort Payne Chert and Maury Formation	Limestone, bedded chert locally, some evaporites. Maury Formation, green shale. Well yields range from 2 to 100 gallons per minute. Some locations yield more than 3,000 gallons per minute.	
Devonian		Chattanooga Shale	Chattanooga Shale	Black fissile shale. Confining unit.

Figure 3. Stratigraphic units and their hydrologic significance in the Eastern Highland Rim subunit. (Compiled from Brahana and Bradley, 1986; Bossong and Harris, 1987.)

(Brahana and Bradley, 1986). Generally, in Alabama, these aquifers are designated informally by their formation names, such as the Tuscumbia aquifer. The water-bearing units at or near land surface in the Eastern Highland Rim subunit represent a surficial aquifer and in this report are referred to as the Mississippian carbonate aquifer.

Ground water in the Mississippian carbonate aquifer flows through solution openings along bedding planes, joints, and fractures (fig. 4). Recharge to the aquifer is from precipitation percolating through the regolith to the underlying bedrock aquifer and from surface drainage into karst features. The regolith can store large amounts of water that move slowly downward toward conduits in the bedrock. Much of the area is under water-table conditions; however, clay layers in the regolith provide varying degrees of confinement to the underlying aquifer resulting in locally perched water tables or artesian conditions. The aquifer is underlain by the Chattanooga Shale (fig. 3), a regional confining unit that limits the downward movement of water to a regional flow path. Hence, ground-water flow paths in the Mississippian carbonate aquifer typically are short, and ground water in the aquifer

discharges locally to streams and springs. The Maury Formation (fig. 3) is a thin green shale located at the base of the Fort Payne Chert and serves as part of the lower confining unit together with the Chattanooga Shale.

Soils overlying the Mississippian carbonate aquifer are predominantly silt loams with some cherty silt loams and clay silt loams present locally. The soils generally are slightly to strongly acidic and moderately well to well-drained. The organic matter content of the soils usually is less than 1 percent but locally may be as much as 4 percent (U.S. Department of Agriculture, 1994).

Land Use

Agriculture (pasture and cropland) is the predominant land use in the Eastern Highland Rim subunit (fig. 5) and accounted for about 57 percent of the total land use in 1992. Pasture makes up about three-quarters of the agricultural land, and in 1992, about 193,000 head of cattle were raised in the Eastern Highland Rim subunit. Chicken production in the Eastern Highland Rim is a growing industry, and about

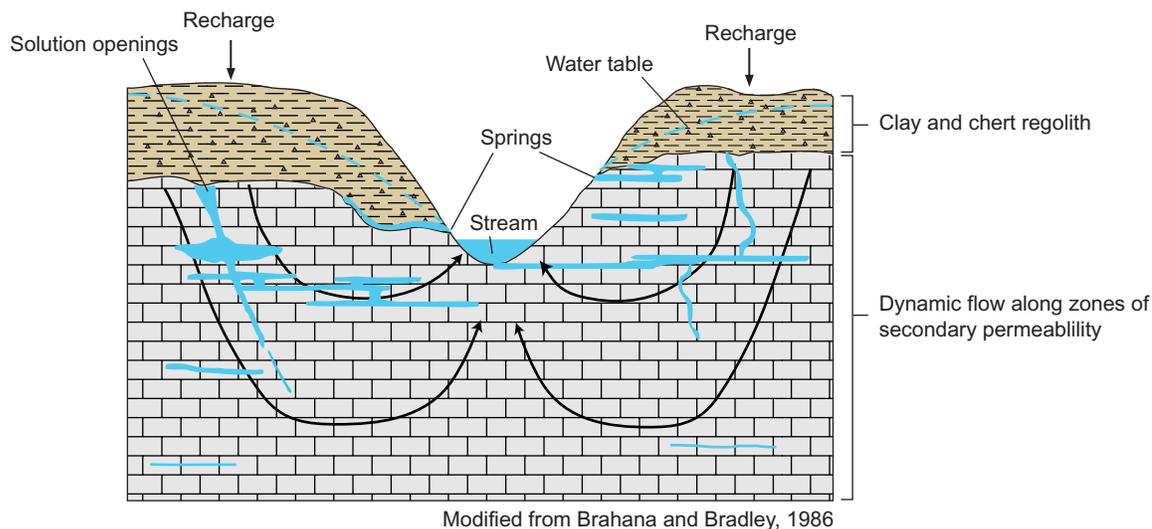


Figure 4. Conceptual model of ground-water flow in the Mississippian carbonate aquifer.

11 million chickens were produced in 1992. The estimated nitrogen and phosphorus inputs from livestock and chickens in the Eastern Highland Rim subunit in 1992 were about 4.7 and 1.4 tons per square mile (tons/mi²), respectively (Kingsbury and others, 1999).

Cropland represents a little more than a quarter of the agricultural land, with much of the cropland concentrated along the Tennessee River in northern Alabama (fig. 5). Cotton, soybeans, and corn are the principal crops grown, with a total of about 334,000 harvested acres of these crops in 1992 (Kingsbury and others, 1999). Cotton accounted for nearly half of this harvested acreage. Nitrogen and phosphorus inputs related to fertilizer use in 1992 were estimated to be about 7 and 1.4 tons/mi², respectively (Kingsbury and others, 1999). An estimated 1.8 million pounds of active ingredients of pesticides were applied to cropland in the Eastern Highland Rim in 1992 (Kingsbury and others, 1999). About 2 percent of the harvested acreage in counties in the Eastern Highland Rim subunit was irrigated in 1997 (U.S. Department of Agriculture, 2000). The sources of irrigation water include both surface and ground water.

Urban land use accounted for only 3 percent of the Eastern Highland Rim subunit in 1992. In 1995, the population was about 584,000 (U.S. Department of Commerce, 2001) with almost half of the population residing in Madison County, Alabama. Madison

County, one of the fastest growing counties in Alabama, is the location of Huntsville, the largest city in the LTEN. Between 1980 and 1995, the population of Madison County increased by about 30 percent. As the population grows, land use is changing from agriculture to suburban development. Nitrogen and phosphorus inputs related to urban land use, such as leaking septic and sewer systems, and residential fertilizer use, were not estimated because reliable data are not available for these potential sources. Data also are not available for pesticide use in urban rights-of-way and residential areas at a local scale.

APPROACH

A network of randomly located wells was established to characterize the water quality of the Mississippian carbonate aquifer. The Eastern Highland Rim subunit was subdivided into 30 equal areas in which random locations were generated from a grid using a geographic information system (GIS)-based computer program (Scott, 1990). Suitable wells within about a mile radius of these random locations were then located. Criteria used to select wells included availability of construction information, accessibility for measuring water levels, and a sampling point near the wellhead before any water treatment. At a few wells,

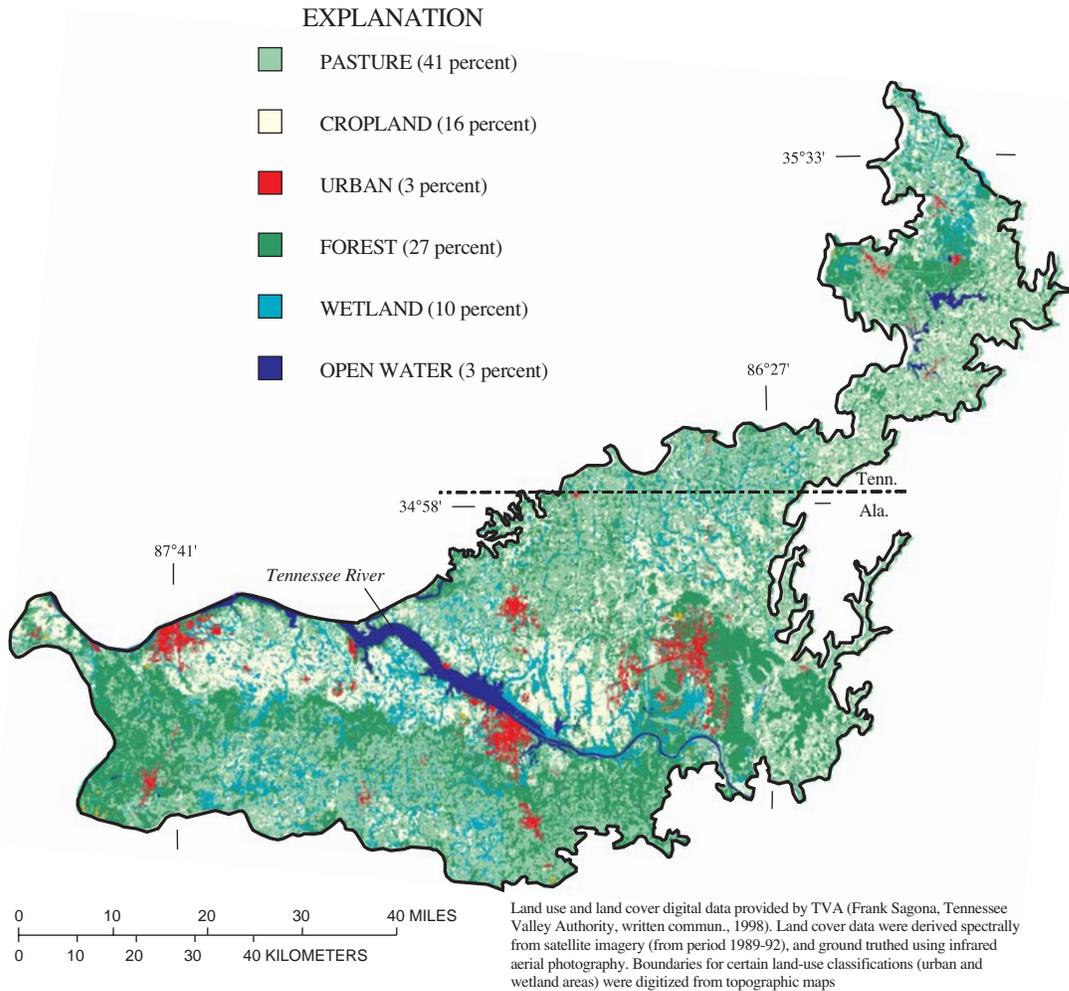


Figure 5. Land use in the Eastern Highland Rim subunit, 1992.

existing plumbing had to be used, and samples were collected from a spigot downstream of the holding tank. In these cases, additional spigots were opened to keep the pump from cycling on and off or to minimize the frequency of pump cycling. Water temperature, specific conductance, pH, and dissolved-oxygen concentrations measured during purging stabilized indicating that holding tanks probably had minimal effects on water quality. Two additional public-supply wells and two springs also were sampled to augment the data set.

Samples were collected and processed according to NAWQA ground-water sampling protocols (Koterba and others, 1995). Wells were purged of three casing volumes, and field water-quality properties were monitored until they stabilized prior to sampling. Wells that could not be pumped continuously without going dry were purged completely, allowed to

recover to within 90 percent of the static water level, and then sampled within 24 hours. Samples for inorganic constituents and nutrients were filtered through a disposable 0.45-micron (μm) capsule filter, and cations were preserved with nitric acid. Samples for dissolved organic carbon (DOC) were filtered through a 0.7- μm silver filter, and pesticide samples were filtered through a 0.7- μm disposable glass-fiber filter. Samples collected for VOC analysis were acidified. Nutrient, DOC, pesticide, and VOC samples were kept chilled and shipped overnight to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado. All sampling equipment was constructed of stainless steel or teflon and was cleaned with three pump-line volumes of soapy wash, a tap-water rinse, and a final rinse with deionized water. The aluminum pesticide filtration unit and tubing were rinsed with pesticide-grade methanol.

Analytical Methods

All samples were analyzed using approved USGS methods at the NWQL with the exception of fecal-indicator bacteria which were enumerated in the field using membrane filtration methods (Myers and Wilde, 1997). Dissolved inorganic constituents were determined using atomic absorption, inductively coupled plasma, ion chromatography, ion-specific electrode, and colorimetric methods (Fishman and Friedman, 1989; Fishman, 1993). Pesticides were extracted from samples by pumping a liter of filtered sample through a C-18 solid-phase extraction column and were analyzed using gas chromatography/mass spectrometer (GC/MS) and high-performance liquid chromatography/mass spectrometer (HPLC/MS). A total of 90 pesticides (appendix 1) and 14 pesticide degradation products (metabolites) were analyzed (Zaugg and others, 1995; Furlong and others, 2001). Reporting levels are as low as 0.001 microgram per liter ($\mu\text{g/L}$) but vary by compound because the levels are based on the method detection limit (MDL) for each compound. 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 compound. Some concentrations are qualified with an "E" indicating an estimated concentration. Estimated concentrations in this data set are generally a result of detections below the lowest calibration standard, or the analyte has had systematically poor recoveries throughout the development and implementation of the analytical method. These estimated concentrations have greater quantification uncertainty than do unqualified concentrations. Pesticides analyzed by the HPLC/MS method were

analyzed prior to final approval of the analytical method by the USGS Office of Water Quality. The analytical method did not change following method approval, but concentrations of pesticides analyzed by this method are considered provisional (appendix 1). A purge and trap capillary-column GC/MS (Connor and others, 1998) was used to analyze 85 VOCs (appendix 2). As with pesticides, some concentrations are reported as estimated if (1) compounds were detected below the concentration of the lowest calibration standard, (2) surrogates indicated the method was not performing adequately, or (3) the sample was diluted.

Quality Assurance and Quality Control

The low levels at which pesticides and VOCs were analyzed during this study necessitated adequate quality-control sampling to identify bias in the methods, and to demonstrate that equipment cleaning, sample collection and processing, and analytical procedures are noncontaminating. Field quality-control samples constituted about 25 percent of all samples analyzed and included blanks, replicates, and pesticide and VOC spikes. Inorganic constituent and pesticide blank data indicate that equipment cleaning procedures were adequate and noncontaminating. Several compounds were detected at low concentrations in VOC blanks. Toluene and styrene were detected in all three field blanks and toluene also was detected in the trip blank analyzed (table 1). As a result of this systematic contamination of toluene and styrene in blanks, at concentrations similar to those measured in environmental samples (table 1), most of these data were omitted from the data set. Two toluene detections in environmental samples that occurred with other

Table 1. Volatile organic compounds detected in field and trip blanks, 1999

[Concentrations in micrograms per liter]

Volatile organic compound	Number of detections in blanks	Maximum concentration in blank	Number of detections in samples	Maximum concentration in samples
Toluene	4	0.019	22	0.11
Styrene	3	.073	32	.097
1,2,4-Trimethylbenzene	2	.01	8	.03
m- and p-Xylene	1	.02	6	.02

hydrocarbons and at concentrations about five times higher than concentrations in the blanks were interpreted as environmental detections. Detections of m- and p-xylene and 1,2,4-trimethylbenzene in samples were omitted from the data set because of random contamination of these compounds in blanks at concentrations similar to concentrations measured in environmental samples (table 1).

Concentrations of compounds in spiked samples generally were within about 75 to 125 percent of the expected concentration, and the median recovery was 98 percent. Recoveries of several spiked compounds showed considerable systematic bias. Deethylatrazine, aldicarb, and hydroxyatrazine recoveries were low, indicating a low bias, and carbaryl and carbofuran, which historically have had poor recoveries with this analytical method (Zaugg and others, 1995), had recoveries greater than 150 percent.

Delineation of Land Use and Soil Properties Near Sites

Land-use data for 1992 and soil data were delineated within a buffer area (3,280 foot radius=1 kilometer) around each of the sampling sites by using a GIS. Digital land-use data were derived spectrally from satellite imagery (from 1989 to 1992) and were verified using infrared aerial photography. Boundaries for wetlands and urban areas were digitized from topographic maps (Frank Sagona, Tennessee Valley Authority, written commun., 1998). Percentages of major land-use categories were calculated within the buffer areas around each site.

Values for soil hydrologic group, slope, percent clay, and organic matter content for each site were derived from the State Soil Geographic (STATSGO) database. The scale of the soil data are 1:250,000 and were developed to support regional, multistate, state, and river basin studies and resource planning (U.S. Department of Agriculture, 1994). The scale of the data is large, but the data are adequate for characterizing differences in soil properties across the Eastern Highland Rim subunit. Procedures used to aggregate the STATSGO data are documented on the web at <http://water.usgs.gov/GIS/metadata/usgswrd/ussoils.html> (accessed May 29, 2002). Properties in STATSGO that are described by character codes such as soil hydrologic group were converted to numeric values. For this study, soil properties for a site were derived by multiplying values for organic matter

content, hydrologic group, slope, and clay content of a given soil map unit by the percentage of the buffer area around a site contained within that unit. Buffers typically consisted of between one and three soil map units. Soil drainage class and soil permeability, soil properties describing the movement of water through soil, were strongly correlated to soil hydrologic group (Spearman's $\rho > 0.7$, $p=0$) and were not included in the analysis. Soil hydrologic group also was strongly correlated to the organic matter content of the soils, but organic matter is included because this property has been shown to affect the movement of pesticides in the subsurface (Barbash and Resek, 1996).

Statistical Methods

Several statistical tests were used in this study to evaluate relations between environmental factors and the presence of constituents in ground water. The Spearman rank correlation test is used to evaluate data that are not normally distributed and heavily censored (Helsel and Hirsch, 1992). Wilcoxon rank sum tests (Helsel and Hirsch, 1992) are used to analyze data for fecal-indicator bacteria, pesticides, and VOCs because of the large number of nondetections for these constituents and the unknown amount of variability associated with estimated concentrations for pesticides and VOCs. Sites with a detection are compared to sites without a detection to determine if environmental factors are significantly different for the two groups of sites. Contingency tables are used with these data when the explanatory variable is categorical rather than continuous. Correlations are considered to be significant if the probability of incorrectly rejecting the null hypothesis is less than 5 percent ($p < 0.05$). Linear regression of log-transformed constituent concentrations with factors related to the presence of these constituents is used to determine the amount of variability in concentrations accounted for by these factors.

WATER QUALITY OF THE MISSISSIPPIAN CARBONATE AQUIFER

Sites sampled in this study are located in five different geologic formations of Mississippian age (fig. 2; table 2). Selected characteristics of the sampled ground-water sites are grouped by geologic unit (fig. 6). Most of the wells are cased to the top of bedrock with the remainder of the borehole open in bedrock; however, five wells are screened in gravels

Table 2. Well depth, water level, and geologic unit of sites sampled in the Mississippian carbonate aquifer, 1999

[B, Bangor Limestone; H, Hartselle Sandstone; M, Monteagle Limestone; T, Tusculumbia Limestone; G, well screened above bedrock; FP, Fort Payne Chert; °, degrees; ', minutes; ", seconds; --, not available; NA, not applicable; well number refers to location on figure 2. Geologic units in this table may not agree with generalized geology shown on figure 2 because of simplifications to geology or because well is completed in an underlying geologic unit]

Site number	Station identification number	Latitude	Longitude	Altitude of land surface, in feet above sea level	Sample date	Well depth, in feet	Water level, in feet below land surface	Geologic unit
1	342948087251301	34°29'48"	87°25'13"	637	07/07/99	105	22.90	B
2	343344087333601	34°33'44"	87°33'36"	601	07/07/99	54	11.30	B
10	343053087254201	34°30'53"	87°25'42"	635	07/06/99	130	5.90	B
11	342528087100401	34°25'28"	87°10'04"	650	06/29/99	38	8.00	B
12	342502086535301	34°25'02"	86°53'53"	620	06/28/99	44	12.34	B
3	343658087252501	34°36'58"	87°25'25"	753	07/01/99	100	35.40	H
9	343425087153001	34°34'25"	87°15'30"	725	06/30/99	75	20.85	H
23	343448086194201	34°34'48"	86°19'42"	588	07/08/99	84	1.10	M
4	344153087280101	34°41'53"	87°28'01"	572	07/06/99	110	49.38	T
5	344355087414401	34°43'55"	87°41'44"	500	07/07/99	110	62.30	T
7	344535087042201	34°45'35"	87°04'22"	680	06/30/99	44	29.55	T (G)
8	343904087100701	34°39'04"	87°10'07"	595	06/30/99	122	11.50	T
13	343128086521101	34°31'28"	86°52'11"	630	06/28/99	77	56.25	T
14	344150086523401	34°41'50"	86°52'34"	600	06/29/99	85	12.10	T
15	344651086523801	34°46'51"	86°52'38"	700	06/24/99	117	50.28	T
21	343752086433001	34°37'52"	86°43'30"	590	06/29/99	82	37.97	T (G)
22	343023086492301	34°30'23"	86°49'23"	780	06/29/99	147	38.90	T
26	350715086032101	35°07'15"	86°03'21"	980	06/22/99	105	60.25	T
27	351733086035701	35°17'33"	86°03'57"	1,020	06/22/99	84	56.00	T
30	353223086032101	35°32'23"	86°03'21"	1,090	06/21/99	87	35.34	T
6	344828087033601	34°48'28"	87°03'36"	730	06/28/99	59	29.82	FP
16	345343086554701	34°53'43"	86°55'47"	795	06/30/99	78	1.00	FP
17	350102086284001	35°01'02"	86°28'40"	840	07/15/99	46	5.55	FP (G)
18	345801086433201	34°58'01"	86°43'32"	882	07/14/99	85	22.15	FP
19	345045086315001	34°50'45"	86°31'50"	688	06/23/99	98	17.10	FP
20	--	34°44'	86°34'	644	06/24/99	104	68.10	FP
24	344655086305601	34°46'55"	86°30'56"	760	06/24/99	157	55.50	FP
25	350019086264201	35°00'19"	86°26'42"	880	06/22/99	74	13.40	FP (G)
28	351928085594501	35°19'28"	85°59'45"	990	06/24/99	85	38.66	FP (G)
29	352402086063201	35°24'02"	86°06'32"	1,040	06/22/99	110	58.54	FP
31	--	34°55'	86°38'	805	07/01/99	87	48.00	FP
32	--	35°03'	86°25'	880	06/28/99	115	16.60	FP
33	03574871	34°50'43"	86°34'06"	710	07/14/99	spring	NA	FP
34	345248086285501	34°52'48"	86°28'55"	680	07/07/99	spring	NA	FP

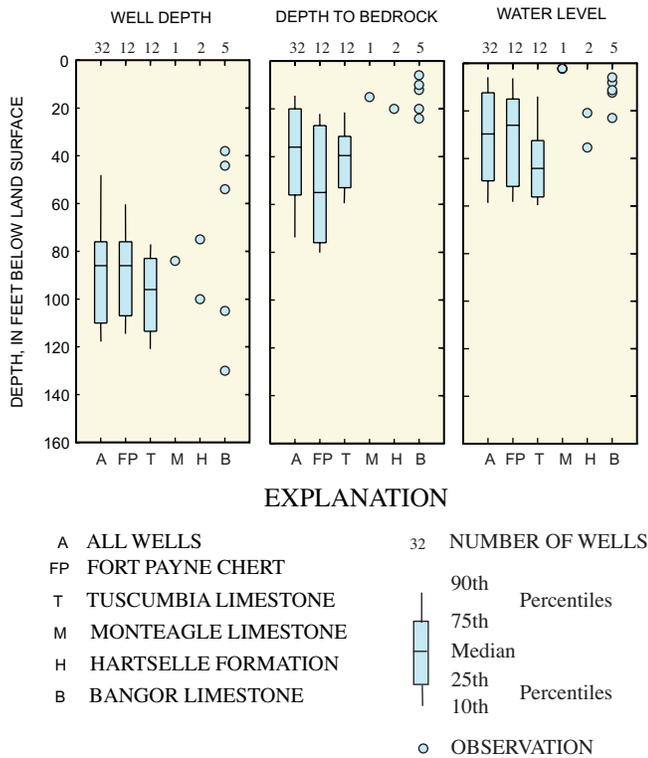


Figure 6. Selected characteristics of ground-water wells sampled in the Mississippian carbonate aquifer by geologic unit.

overlying bedrock in the Tuscumbia Limestone and Fort Payne Chert. The wells screened above bedrock are included with wells completed in bedrock. Median depth of all of the wells was 86 feet below land surface. Depth to bedrock or thickness of the regolith in the wells ranged from about 6 to 87 feet (fig. 6). The median regolith thickness for all sites was 36 feet. Depth to water ranged from 1 to 68 feet below land surface, with a median depth of 26 feet (table 2). Many of the wells sampled had capacities ranging from 5 to 20 gallons per minute (gal/min). Both springs and the three public-supply wells that were sampled yielded between 150 and greater than 3,000 gal/min.

Samples collected from the 34 sites indicate that water in the Mississippian carbonate aquifer is predominantly a calcium bicarbonate type. Specific conductance for all samples ranges from about 30 to 1,500 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) at 25 degrees Celsius (table 3). The variability or range of specific conductance is smaller within geologic units as compared to all of the wells (table 3 and fig. 7), except for samples collected from the Fort Payne Chert, which account for both the highest and lowest values for specific conductance. Specific

conductance generally is low (less than $200 \mu\text{S}/\text{cm}$) for samples collected from wells completed in the Fort Payne Chert because of the large amount of siliceous material (chert) in the formation, which is relatively insoluble in water. The samples with high specific conductances are from two wells completed near the base of the formation. Ground water in these wells likely interacts with evaporites in the Fort Payne Chert or with the underlying Chattanooga Shale, resulting in a calcium sulfate type water. In addition, the residence time for ground water in these wells may be longer than in the remaining wells, allowing for greater interaction of water and rock, and leading to the higher specific conductance observed in these samples.

Differences in specific conductance among wells likely is caused predominantly by lithology rather than significant differences in ground-water residence times. For example, specific conductance of samples collected from wells in the Hartselle Formation and the Fort Payne Chert typically are lower than specific conductance of samples from wells in the other formations because of the lower solubility of sandstone and chert as compared to limestone.

Dissolved-oxygen (DO) concentrations are greater than 1 mg/L at most of the sites in the study area (fig. 7). DO can affect the concentrations of many constituents in ground water. For example nitrogen, iron, and sulfur speciation and concentrations, as well as reactions that affect organic constituent concentrations may be affected by DO concentrations in ground water. In some ground-water systems, decreases in DO concentrations can indicate a long ground-water residence time; however, DO concentrations likely are not good indicators of ground-water residence time in this hydrogeologic setting because the formation with the highest DO concentrations (fig. 7) generally has the thickest regolith (fig. 6). Thick regolith overlying bedrock likely would result in longer average ground-water residence times. Furthermore, DO concentrations are inversely related to dissolved organic carbon (DOC) concentrations (Spearman's $\rho = -0.59$, $p = 0.0007$), suggesting DO concentrations are significantly affected by DOC concentrations in the ground water. DOC concentrations in ground water generally are low (Leenheer and others, 1974), and elevated concentrations in the Mississippian carbonate aquifer (greater than 1 mg/L) may suggest an increase in susceptibility to contamination from surface or near-surface sources. Recharge water with high DOC

Table 3. Water-quality properties and major inorganic constituent concentrations in samples from 32 wells and 2 springs in the Mississippian carbonate aquifer, 1999 [°C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; --, no data]

Map number	Date sampled	Field pH (standard units)	Field specific conductance (µS/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 as Mg)	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)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO ₂)	Iron, dissolved (µg/L as Fe)	Dissolved organic carbon (mg/L as C)
Bangor Limestone																	
1	7/7/1999	7.5	470	0.5	229	278	99	19	12	68	1.5	6.5	12	2.0	10	<10	0.9
2	7/7/1999	6.9	795	.1	291	494	370	52	57	31	2.2	28	95	1.6	14	120	1.2
10	7/6/1999	7.0	444	7.7	201	256	190	72	3.2	14	.75	9.0	6.8	.14	10	<10	1.3
11	6/29/1999	6.6	372	1.4	168	216	190	68	3.5	3.1	.60	5.1	4.5	.10	8.7	<10	1.3
12	6/28/1999	7.3	778	.1	342	490	71	24	3.0	158	1.7	21	39	1.7	8.9	19	3.9
Hartselle Sandstone																	
3	7/1/1999	5.0	57	.8	8	49	18	5	1.2	2.8	.72	3.6	11	.10	10	<10	.5
9	6/30/1999	5.5	70	8.3	14	53	26	9	.92	2.8	.44	3.7	.10	.10	8.4	<10	.2
Monteagle Limestone																	
23	7/8/1999	6.9	316	1.5	119	214	150	56	2.40	3.10	.55	11	2.8	.14	8.6	<10	1.2
Tuscumbia Limestone																	
4	7/6/1999	6.7	642	4.7	231	394	300	110	7.0	2.6	4.7	19	5.9	.11	10	<10	.8
5	7/7/1999	6.8	540	5.4	259	251	260	97	4.5	4.7	1.1	7.6	5.5	.20	10	<10	.8
7	6/30/1999	5.8	53	6.6	23	40	24	7	1.7	1.4	.72	1.9	.31	.10	9.1	<10	.3
8	6/30/1999	6.5	315	5.2	122	194	140	53	2.3	4.2	1.4	7.3	6.0	.10	10	<10	.5
13	6/28/1999	7.4	249	5.2	121	138	110	40	3.4	2.5	.80	5.0	.98	.10	7.1	<10	.4
14	6/29/1999	6.0	232	5.2	35	164	85	28	3.7	3.0	6.3	8.2	5.0	.10	8.5	<10	.4
15	6/24/1999	6.0	130	4.2	10	56	27	6	2.8	2.8	.47	7.1	.13	.10	8.7	30	.2
21	6/29/1999	6.5	172	7.1	80	97	85	30	2.7	1.0	.23	2.6	.46	.10	8.4	<10	.3
22	6/29/1999	6.8	274	1.4	164	201	150	48	6.3	9.1	2.2	1.7	.10	.22	26	700	.6
26	6/22/1999	7.3	343	4.9	175	203	170	51	11	2.4	.62	6.1	6.1	.42	8.7	<10	.4
27	6/22/1999	7.0	380	3.2	208	241	220	66	14	2.8	.72	5.9	5.5	.13	8.3	<10	.5
30	6/21/1999	6.9	325	6.2	156	177	170	42	15	1.7	.22	6.1	4.1	.10	7.9	<10	.5

Table 3. Water-quality properties and major inorganic constituent concentrations in samples from 32 wells and 2 springs in the Mississippian carbonate aquifer, 1999—Continued

Map 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)	Fluoride, dis-solved (mg/L as F)	Silica, dis-solved (mg/L as SiO_2)	Iron, dis-solved ($\mu\text{g}/\text{L}$ as Fe)	Dissolved organic carbon (mg/L as C)
Fort Payne Chert																	
6	6/28/1999	4.5	58	7.6	--	43	16	2	2.5	2.4	0.25	5.7	0.43	0.10	8.6	11	0.2
16	6/30/1999	6.4	174	4.1	76	117	84	29	2.5	1.5	.33	.88	6.9	.10	8.6	<10	.8
17	7/15/1999	5.9	110	5.2	47	75	53	16	2.9	1.2	.20	.95	5.0	.10	8.8	<10	.3
18	7/14/1999	5.6	46	2.2	22	35	18	6	.75	.83	.19	1.1	.57	.10	8.4	2,300	.2
19	6/23/1999	7.0	1,290	1.0	101	818	590	160	48	6.2	1.1	3.5	480	.28	9.0	18	.3
20	6/24/1999	7.1	315	7.1	149	202	160	57	5.5	2.1	.66	4.6	6.3	.10	8.6	<10	.4
24	6/24/1999	6.8	1,500	4.5	202	1,050	800	230	55	7.5	.99	3.1	600	1.70	10	540	.7
25	6/22/1999	5.9	70	8.4	23	72	33	10	2.2	.87	.11	1.5	.19	.10	8.3	<10	.2
28	6/24/1999	6.8	238	4.0	112	144	120	31	9.9	1.0	.30	1.9	5.0	.10	8.9	<10	.3
29	6/22/1999	6.3	138	2.7	63	80	68	19	5.0	.83	.22	1.8	.93	.10	7.4	<10	1.4
31	7/1/1999	5.6	44	8.6	12	40	18	5	1.2	.98	2.2	1.9	1.4	.10	8.1	<10	.1
32	6/28/1999	5.4	31	7.9	9	31	13	4	1.1	.76	.10	1.3	.11	.10	8.1	53	.2
33	7/14/1999	6.7	158	8.0	60	111	73	24	3.3	2.1	.45	3.4	1.0	.10	8.5	<10	.3
34	7/7/1999	6.2	117	6.5	43	77	49	15	3.1	1.1	.49	3.2	1.5	.10	7.4	<10	.3

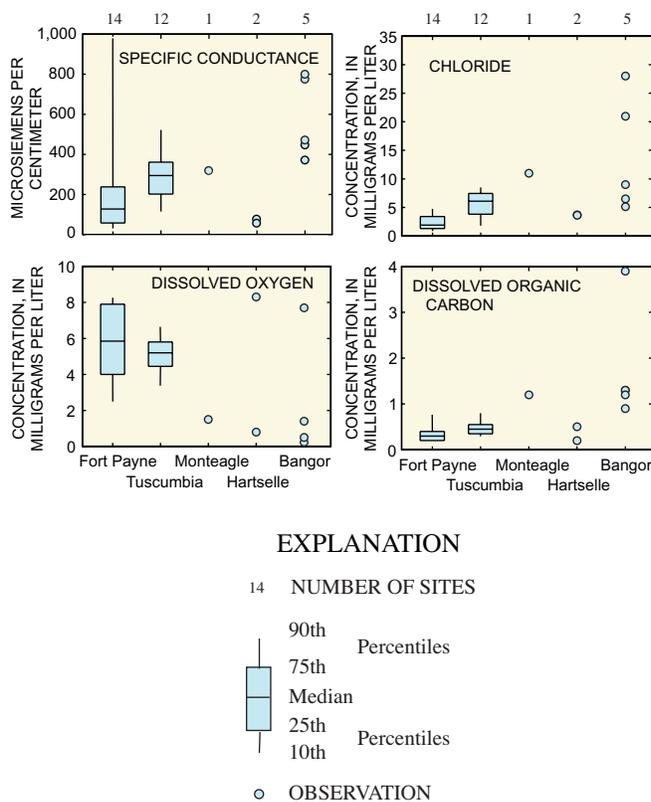


Figure 7. Selected water-quality properties and constituents in water samples from the Mississippian carbonate aquifer by geologic unit.

concentrations, for example runoff into a sinkhole, could rapidly lower DO concentrations in the aquifer.

Elevated chloride concentrations measured in water samples may indicate increased susceptibility to contamination from surface or near-surface sources at some of the sites. Chloride is not present at high concentrations in most carbonate rocks. Chloride is a conservative constituent in ground water; that is, it does not react appreciably with the aquifer matrix or other dissolved constituents. The median concentration of chloride for all samples was about 4 mg/L (fig. 7). Correlations between chloride and DOC (Spearman's rho=0.49, p=0.005) and chloride and depth to bedrock (Spearman's rho=-0.59, p=0.0016) indicate that chloride concentrations may be affected by anthropogenic activities at land surface.

The quality of water from three wells completed in the Bangor Limestone differs somewhat from the quality of water in samples collected from the other geologic units. In particular, concentrations of sodium, chloride, fluoride, and DOC generally are higher in these samples collected from the Bangor Limestone

than in samples collected from the other geologic units (table 3). Given the small number of sites sampled, determining if these differences represent natural variability between geologic units or anthropogenic inputs at these sites is difficult. However, the regolith overlying bedrock for these sites is thin (fig. 6), and concentrations of these constituents often are influenced by anthropogenic sources.

Nutrients and Bacteria

Nitrate-nitrogen (nitrate) is the nutrient that most commonly has adverse effects on ground-water quality. In samples collected from the Mississippian carbonate aquifer, nitrate was detected more frequently and at higher concentrations than were other nutrients. Nutrients, as referred to in this report, include the various oxidized and reduced forms of nitrogen and phosphorus. Nitrate concentrations ranged from less than 0.05 to about 16 mg/L with a median of about 1.5 mg/L (fig. 8) for all samples. Concentrations were less than 5 mg/L for about 90 percent of the samples; however, samples from two sites exceeded the public drinking-water maximum contaminant level (MCL) of 10 mg/L. Nitrate concentrations are correlated to both DO and chloride concentrations. The correlation between nitrate concentrations and DO concentrations in ground water is well documented (Hem, 1985); denitrification of nitrate often occurs in the subsurface through microbiological reactions when DO concentrations are low. If sites that had low (less than 1 mg/L) DO concentrations (sites where denitrification may be occurring) are not considered, the correlation between chloride and nitrate concentrations is stronger (Spearman's rho=0.53, p=0.02) than if those sites are included (Spearman's rho=0.36, p=0.04). Nitrate and chloride can enter ground water from similar sources, such as cropland and leaking septic systems.

Concentrations of the reduced nitrogen species (ammonia and organic nitrogen) were low in water samples from all sites. These nutrients were detected at concentrations greater than 0.1 mg/L in samples from 12 sites (table 4) and were more common and at higher concentrations in samples collected from wells that also had low DO concentrations. Ammonia and organic nitrogen concentrations correlated with DOC concentrations (Spearman's rho=0.51, p=0.004), which supports the hypothesis that elevated DOC (greater than 1 mg/L) may indicate susceptibility of

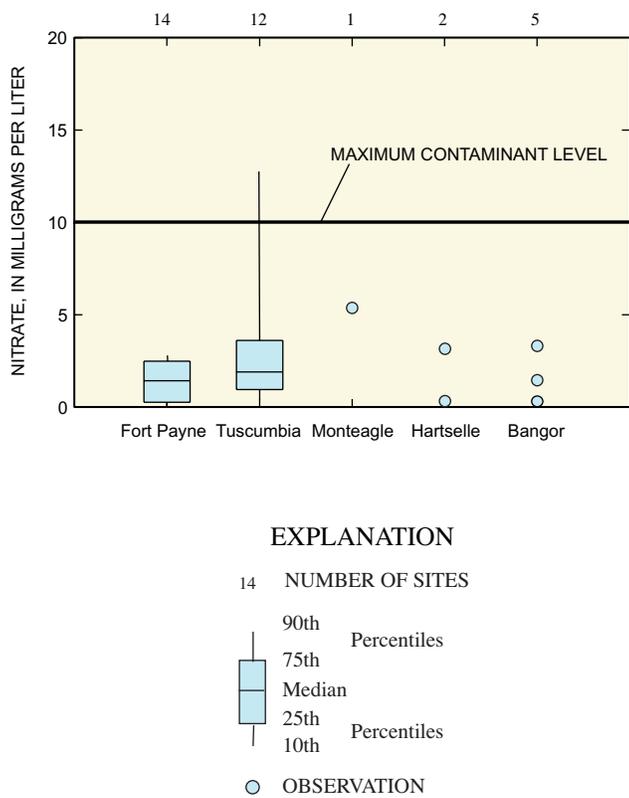


Figure 8. Concentrations of nitrate in water samples from the Mississippian carbonate aquifer by geologic unit.

the aquifer to surface or near-surface contaminant sources. Dissolved phosphorus concentrations also were low (less than 0.04 mg/L) in all of the geologic units. The median concentration for all samples was 0.009 mg/L (table 4). Phosphorus is less mobile than nitrogen in the subsurface and tends to sorb to soil particles and soil organic matter.

Thirty-four sites were sampled for fecal coliform and *Escherichia coli* (*E. coli*) bacteria. These bacteria are indicators of fecal contamination from humans and other warmblooded animals. Consumption of untreated fecal-contaminated ground water can pose a significant health risk. Fecal-indicator bacteria

were present in samples from 14 sites (about 40 percent of the sites) and were detected in each of the geologic units (fig. 9). The maximum *E. coli* concentration of 340 colonies per 100 milliliters was in a sample collected from a site located near a cattle feedlot. Presence of fecal-indicator bacteria was not related to any other constituents.

Pesticides

Pesticides were detected in water samples collected from sites throughout the Mississippian carbonate aquifer (fig. 10), but concentrations generally were low (less than 1 µg/L). Of the 34 sites sampled, a pesticide or pesticide metabolite was detected at 25 sites (74 percent). A total of 28 compounds were detected (table 5), and the maximum concentration measured was 2.62 µg/L for metolachlor. No pesticide concentrations exceeded established MCLs for drinking water, but 23 of the 28 pesticides detected do not have MCLs. The maximum number of pesticides detected in any single sample was 17, and the total pesticide concentration was about 4 µg/L. The greatest number of pesticides were detected in and the highest concentrations generally were measured in samples collected from sites in areas predominated by cropland (fig. 10). The median number of pesticides detected in a single sample was three, and the median total pesticide concentration was 0.11 µg/L.

The frequency of detection generally is related to estimated use of a pesticide (fig. 11). Pesticide use was estimated by using statewide application rates (Gianessi and Anderson, 1995) and crop acreages from the 1992 Census of Agriculture (U.S. Department of Commerce, 1994). Local differences in pesticide usage are not reflected in these estimates nor are changes in pesticide use between 1992 and 1999. Fluometuron, atrazine, and norflurazon, the three most frequently detected pesticides, are among the highest in estimated application rates (table 5). Fluometuron

Table 4. Summary statistics of selected nutrients in the Mississippian carbonate aquifer, 1999
[Concentrations in milligrams per liter; MRL, minimum reporting level; N, nitrogen]

Constituent	MRL	Number of samples with concentrations greater than the MRL		
		Median	Maximum	
Nitrate as N	0.05	30	1.5	16
Ammonia and organic-nitrogen as N	.1	12	.1	1.7
Phosphorus	.004	25	.009	.04

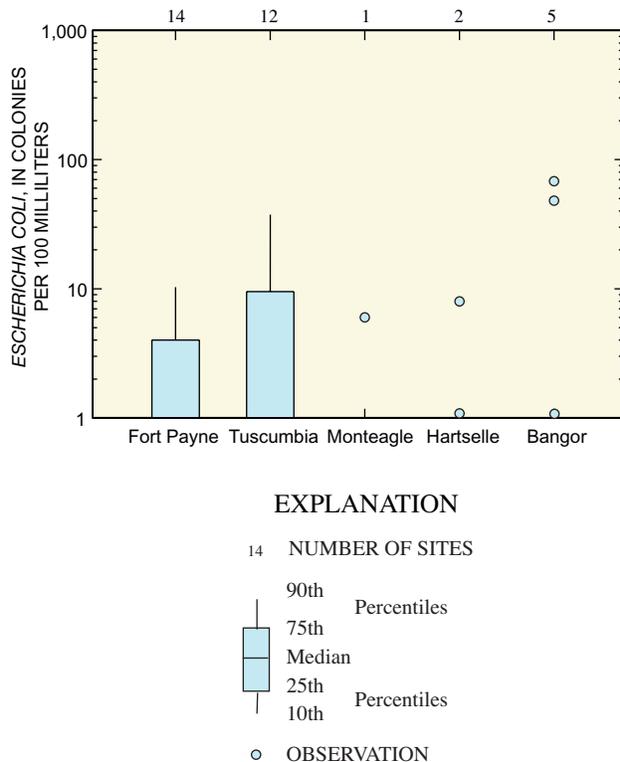


Figure 9. Concentrations of *Escherichia coli* (*E. coli*) bacteria in water samples from the Mississippian carbonate aquifer by geologic unit.

was detected at concentrations greater than 0.01 $\mu\text{g/L}$ in samples collected from 10 sites (29 percent) with a maximum concentration of 2.26 $\mu\text{g/L}$. Atrazine and norflurazon also were detected frequently (26 percent of the samples, each) with maximum concentrations of 0.122 and 0.523 $\mu\text{g/L}$, respectively. The presence of pesticides was not related to other water-quality constituents with the exception of nitrate, which was related to the detection of these three pesticides ($p \leq 0.01$). This relation suggests a common source of nitrate and pesticides to the aquifer.

Pesticide metabolites account for 25 percent of the total number of compounds detected, but represent only 13 percent of the compounds analyzed (appendix 1). The most frequently detected pesticide is deethylatrazine (38 percent of samples), an atrazine metabolite. Metabolites detected in ground water generally are more water soluble than are their parent compounds, and the toxicological effects of metabolites and their parent compounds may be similar (Barbash and Resek, 1996). For the pesticides having greater than 50,000 pounds of estimated use, atrazine and aldicarb are the only pesticides for which metabolites were analyzed (table 5). In samples in which atra-

zine was detected, at least one atrazine metabolite also was detected at concentrations comparable to or greater than atrazine (fig. 12). The maximum concentration of total atrazine residue (atrazine plus metabolites) was about four times the maximum atrazine concentration of 0.122 $\mu\text{g/L}$ (fig. 12). Aldicarb was not detected in any of the samples; however, metabolites of aldicarb were detected in about 20 percent of the samples (table 5).

Several pesticides having high estimated use (greater than 48,000 pounds) were not detected in ground-water samples (table 5). Cyanazine, 2,4-D, and pendimethalin were not detected in ground-water samples during this study; however, detection of these pesticides in more than 10 percent of water samples collected at two surface-water sites in the Eastern Highland Rim subunit during the same timeframe as this study (Hoos and others, 2002) indicates that the pesticides are used locally. Detection of these pesticides in surface water but not in ground water in this setting indicates that movement of these pesticides into ground water in the Mississippian carbonate aquifer is not significant. Few detections of malathion and no detections of methyl parathion and trifluralin in surface-water samples indicate that transport of these compounds to ground or surface water is limited, or that use of these compounds may be overestimated (table 5). Samples were not analyzed for monosodium methane arsonate (MSMA), the pesticide with the highest estimated use.

Several pesticides for which estimated-use data are not available were detected frequently. Bromacil and prometon were detected in six samples, and tebuthiuron was detected in three samples at low-level concentrations (table 5). These herbicides have non-cropland uses such as along railroads and utility rights-of-way. Dieldrin, which was last used for termite control in the late 1980s and on cropland in the 1970s, was detected in six samples (18 percent). Four of the six detections exceeded the U.S. Environmental Protection Agency (U.S. EPA) risk specific dose (RSD) of 0.02 $\mu\text{g/L}$ at a 10^{-5} cancer risk level (U.S. Environmental Protection Agency, 2001). The maximum concentration detected (0.809 $\mu\text{g/L}$) was an order of magnitude higher than the other five dieldrin detections. Two samples contained 3(4-chlorophenyl) methyl urea, a breakdown product of monuron, a non-cropland herbicide that has not been registered with the U.S. EPA since 1977 (U.S. Environmental Protection Agency, 1998). Chloramben and dinoseb were

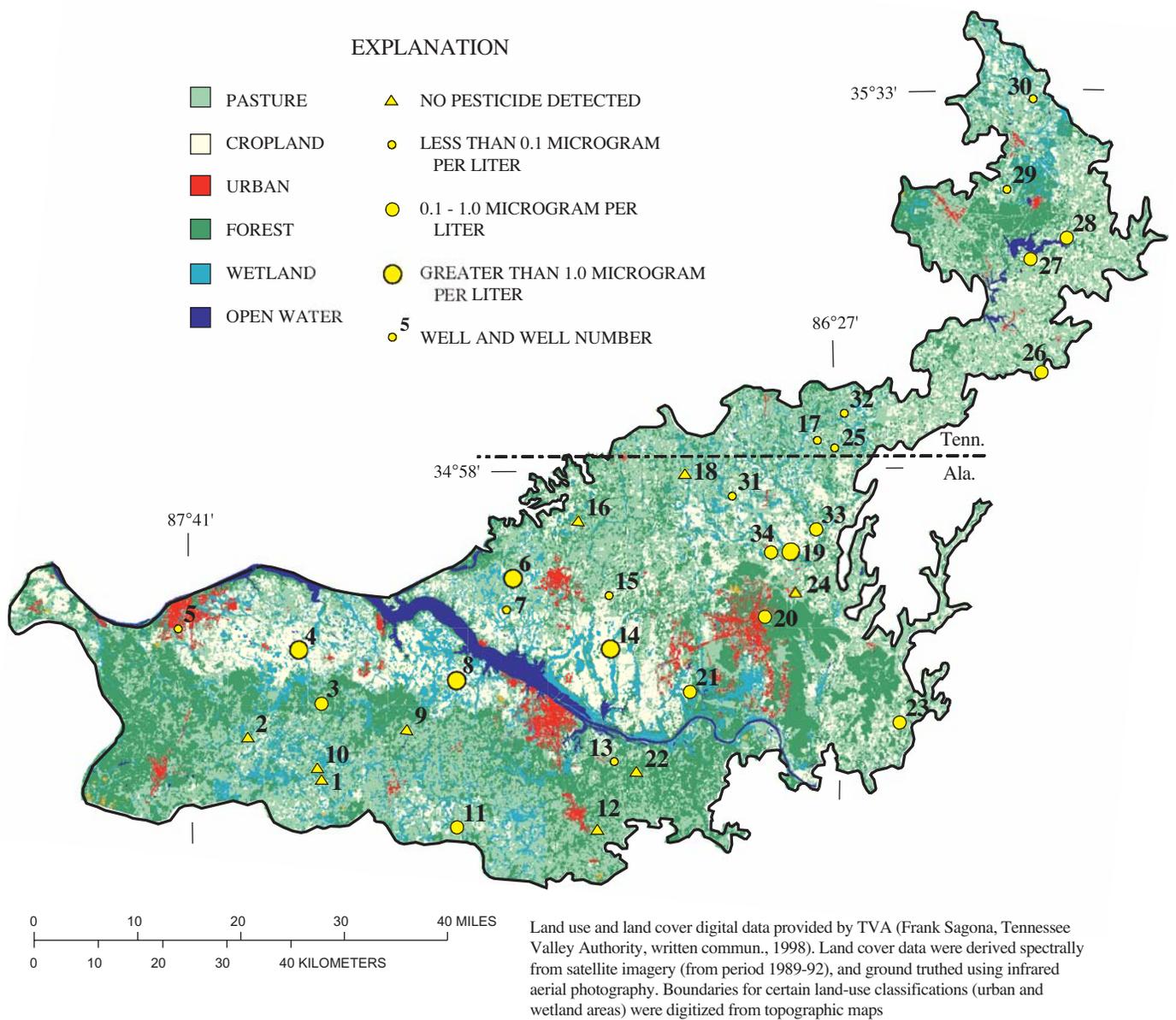


Figure 10. Land use and total pesticide concentrations in water samples from the Mississippian carbonate aquifer in the Eastern Highland Rim subunit.

two other detected pesticides that are no longer registered for use in the United States.

Pesticides detected in the Mississippian carbonate aquifer generally correspond to those detected most frequently in ground water across the Nation. About 1,850 wells have been sampled in subunit surveys as part of the National Water-Quality Assessment Program (Dana Kolpin, U.S. Geological Survey, written commun., 2000). Pesticide detection frequencies were higher in this study (at a common reporting level of 0.05 µg/L) than in nationwide studies; however, the

magnitude of pesticide concentrations generally were comparable to or lower than the maximum concentrations measured in other areas of the country (fig. 13). Fluometuron and norflurazon, cotton-specific herbicides, were detected more frequently in this study than in other areas sampled in the NAWQA program. These high frequencies of detection relative to the national data set reflect the limited use of these pesticides in other areas of the country. Only one other NAWQA study unit had significant estimated use of fluometuron and norflurazon (Thelin and Gianessi, 2000). In

Table 5. Summary statistics for pesticides detected in water samples from the Mississippian carbonate aquifer in 1999 and estimated use of detected and high-use pesticides

[F, fungicide; H, herbicide; I, insecticide; Metab, pesticide metabolite; E, estimated value; --, no data; NA, not applicable; MRL, minimum reporting level; µg/L, micrograms per liter; Total pounds of active ingredient applied values are rounded to the nearest hundred pounds. Estimated use calculated using application rates from Gianessi and Anderson, 1995, and crop acreages from 1992 Agricultural Census, U.S. Department of Commerce, 1994]

Pesticide	Number of detections	MRL (µg/L)	Median (µg/L)	Maximum (µg/L)	Type	Principal use	Total pounds of active ingredient applied
Deethylatrazine	13	0.002	0.027	0.222 E	H-Metab	Corn	NA
Atrazine	12	.001	.038	.122	H	Corn	101,300
Fluometuron	12	.062	.341	2.26 E	H	Cotton	105,600
Norflurazon	11	.077	.034	.523 E	H	Cotton	65,800
Hydroxyatrazine	7	.193	.023	.112 E	H-Metab	Corn	NA
Aldicarb sulfone	7	.160	.015	.084 E	I-Metab	Cotton	NA
Metalaxyl	6	.057	.011	.032 E	F	Cotton	2,400
Bromacil	6	.081	.005	.025 E	H	Noncropland	--
Prometon	6	.018	.022	.036	H	Noncropland	--
Deethyldeisopropylatrazine	6	.060	.025	.05 E	H-Metab	Corn	NA
Dieldrin	6	.001	.055	.809	I	Domestic (cancelled)	NA
Aldicarb sulfoxide	6	.027	.017	.153	I-Metab	Cotton	NA
Diuron	5	.079	.079	1.81 E	H	Cotton	12,700
Metolachlor	5	.002	.006	2.62	H	Corn	37,100
Chloramben methyl ester	3	.110	.010	.02 E	H	Soybeans (cancelled)	NA
Tebuthiuron	3	.010	.034	.068 E	H	Noncropland	--
Deisopropylatrazine	3	.074	.016	.076 E	H-Metab	Corn	--
Bentazon	2	.019	NA	.24 E	H	Soybeans	7,800
Imazaquin	2	.103	NA	.019 E	H	Soybeans	3,600
Simazine	2	.005	NA	.011	H	mixed use	12,000
3(4-Chlorophenyl) methyl urea	2	.092	NA	.004 E	H-Metab	Noncropland (cancelled)	NA
Imidacloprid	2	.106	NA	.054 E	I	Cotton	<100
Acetochlor	1	.002	NA	.046	H	Corn	--
Acifluorofen	1	.062	NA	.004 E	H	Soybeans	8,100
Bromoxynil	1	.057	NA	.008 E	H	Corn	<100
Dinoseb	1	.043	NA	.001 E	H	Soybeans (cancelled)	NA
Sulfometuron methyl	1	.039	NA	.05 E	H	Noncropland	--
Carbaryl	1	.003	NA	.006 E	I	Corn	3,300
2,4-D	0	.077	NA	NA	H	Soybeans and cotton	85,900
Alachlor	0	.002	NA	NA	H	Soybeans	36,800
Cyanazine	0	.004	NA	NA	H	Corn and cotton	58,100
Trifluralin	0	.002	NA	NA	H	Soybeans and cotton	78,100
Aldicarb	0	.082	NA	NA	I	Cotton	58,700
Malathion	0	.005	NA	NA	I	Cotton	48,400
Methyl parathion	0	.006	NA	NA	I	Cotton	134,300
Pendimethalin	0	.004	NA	NA	H	Corn	66,200
MSMA	--	NA	--	--	H	Cotton	242,400

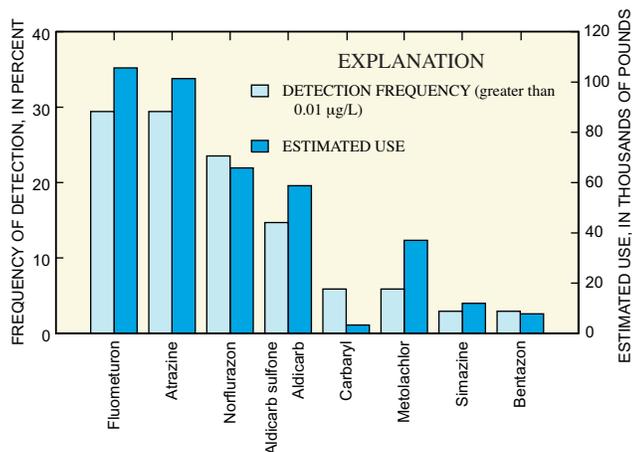


Figure 11. Detection frequency and estimated use of selected pesticides detected in water samples from the Mississippian carbonate aquifer.

contrast, atrazine has widespread use, yet the frequency of detection in the Mississippian carbonate aquifer is twice the national detection frequency (fig. 13).

Volatile Organic Compounds

VOCs were detected frequently in the Mississippian carbonate aquifer; however, concentrations generally were low (less than 1 µg/L). At least one VOC was detected at 26 of the 32 sites sampled (81 percent); of the 86 VOCs analyzed (appendix 2), 19 were detected (table 6). Two sites were not sampled for VOCs. The maximum concentration measured was about 7.5 µg/L for trichloroethylene, one of several chlorinated solvents detected. The maximum concentrations measured for trichloroethylene, tetrachloroethylene, and 1,2-dichloropropane (table 6) equaled or exceeded the drinking-water MCL of 5 µg/L for each compound. The maximum number of VOCs detected in a sample was 14, and the maximum total VOC concentration was about 14 µg/L. The median number of VOCs detected in a sample was two. VOCs were detected in samples from each geologic unit, generally at similar concentrations (fig. 14).

Chloroform was the most frequently detected VOC (fig. 15), present in 21 samples (66 percent). Fifteen of the chloroform detections are estimated concentrations ranging between 0.01 and 0.09 µg/L. In most of these samples, chloroform was either the only VOC detected, or one of only two VOCs detected. These low-level chloroform concentrations were found in samples collected throughout the Eastern

Highland Rim subunit, which suggests widespread sources for chloroform. Possible sources include recharge to the aquifer of treated drinking water from lawn watering, formation of chloroform in the aquifer from domestic well disinfection with bleach, or formation in the subsurface by microbes (Hoekstra and others, 1998; Laturnus and others, 2000). In contrast, the remaining six samples had concentrations ranging from 0.22 to 0.84 µg/L, with other chlorinated solvents also detected in these samples. These detections are likely related to point sources of contamination.

Some of the low-level VOC concentrations detected (less than 0.1 µg/L) may be the result of partitioning of atmospheric concentrations of VOCs into rainfall that recharges the aquifer. For example methyl tert-butyl ether (MTBE), a fuel additive used to increase octane and improve air quality, was detected at low concentrations (less than 0.25 µg/L) in samples from five sites (table 6). Baehr and others (1999) reported that measured atmospheric concentrations of MTBE in New Jersey correspond to aqueous MTBE concentrations of about 0.1 µg/L, and that atmospheric deposition is a possible source for low-level concentrations in ground water. Squillace and others (1996) hypothesized that frequent low-level detections of MTBE in samples without other fuel-related VOC detections may be a result of an atmospheric source. In three of the samples collected from the Mississippian carbonate aquifer, MTBE was detected at low concentrations (less than 0.1 µg/L) and was the only fuel-related VOC present. These low-level detections may indicate an atmospheric source of MTBE.

VOCs detected in ground-water samples from the predominantly rural sites of the Mississippian carbonate aquifer were detected at higher frequencies than in ground-water samples from other rural areas across the Nation (fig. 15). The frequency of detection and median concentration of VOCs detected in this study were compared to VOC data from 2,542 wells in rural areas sampled by the USGS, local, State, and other Federal agencies as part of the NAWQA Program (Squillace and others, 1999). With the exception of MTBE, all VOCs with detections of 0.2 µg/L and greater (fig. 15) were detected more frequently in samples collected from the Mississippian carbonate aquifer than in samples collected from across the country. Tetrachloroethylene, trichlorofluoromethane, and trichloroethylene had higher median concentrations (median of detections greater than 0.2 µg/L) in samples from the Mississippian carbonate aquifer than

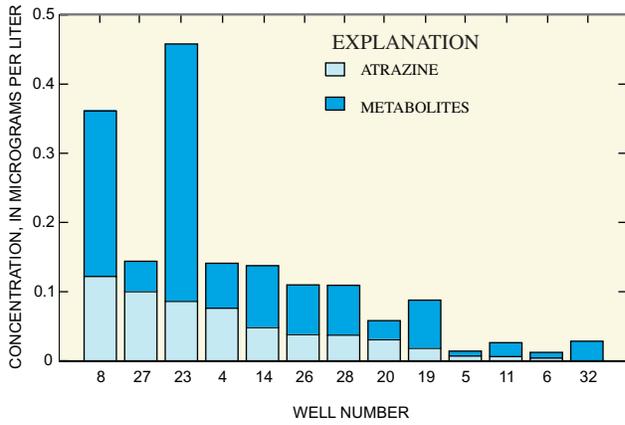


Figure 12. Concentrations of atrazine and its metabolites in water samples from the Mississippian carbonate aquifer.

from the national data set (fig. 15). Many of the compounds detected in Mississippian carbonate aquifer samples were detected at concentrations below the 0.2-µg/L adjusted reporting level, and several compounds were detected only once (no median on figure 15B). Squillace and others (1999) used the VOC data from these rural and also urban areas to model VOC occurrence as a function of population density. They estimated that about 7 percent of the ambient ground water in the United States contains a VOC at greater than 0.2 µg/L. About 22 percent of the sites sampled in the Mississippian carbonate aquifer had a VOC detection greater than 0.2 µg/L.

FACTORS THAT AFFECT WATER QUALITY OF THE MISSISSIPPIAN CARBONATE AQUIFER

Many processes and environmental factors affect the occurrence, movement, and fate of nutrients, bacteria, pesticides, and VOCs in ground water. For this report, univariate analysis of site characteristics, hydrogeology, soil properties, and land-use data (table 7) was used to identify those factors related to the occurrence of these constituents in this hydrogeologic setting. Correlation of water-quality data with an environmental variable does not necessarily imply a cause-and-effect relation. Additional variables or processes not evaluated may be the underlying causal factors. Characterization of the recharge area of these sites is difficult because of the karst hydrology of the Mississippian carbonate aquifer and the limited hydrologic data available for each site. Given the shallow depth to water, the range in well capacities, and the scale of soil properties and land-use data, a buffer area around each site with a 3,280-foot (1-kilometer) radius was selected. This buffer size was considered likely to contain at least part of the recharge area of a site and is comparable to buffers used in similar evaluations (Kolpin, 1997). This analysis served as a starting point for evaluating the relation between water quality and land use or soil properties and whether this type of analysis is appropriate for a karst aquifer.

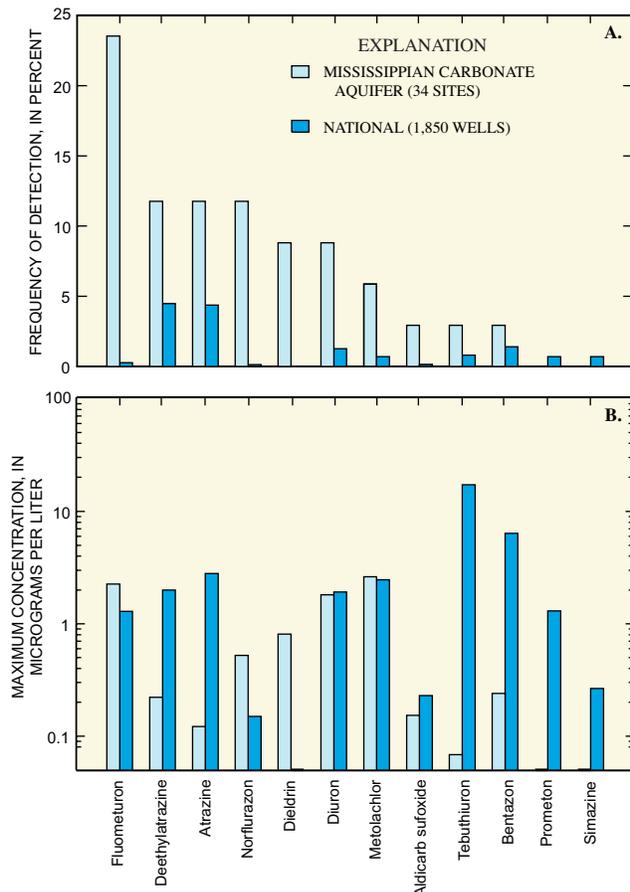


Figure 13. Comparisons of (A) frequencies of detections greater than 0.05 µg/L and (B) maximum concentrations of selected pesticides detected in water samples from the Mississippian carbonate aquifer and other National Water-Quality Assessment Program study units.

Relation of Natural Setting to Water Quality

Site characteristics and hydrogeology generally are not explanatory variables for the occurrence and distribution of bacteria, nutrients, pesticides, and VOCs in the Mississippian carbonate aquifer. The

Table 6. Summary statistics for volatile organic compounds detected in water samples from the Mississippian carbonate aquifer, 1999

[E, estimated value; --, no established maximum contaminant level; NA, not applicable; MRL, minimum reporting level; µg/L, micrograms per liter]

Compound	Detections	MRL (µg/L)	Median (µg/L)	Maximum (µg/L)	Maximum contaminant level	Use
Chloroform	21	0.05	0.02 E	0.84	80 ^a	Disinfection byproduct, solvent
Benzene	7	.10	.01 E	.01 E	5	Gasoline component
Tetrachloroethylene	7	.10	.10	5.0	5	Solvent
1,1,1-Trichloroethane	6	.03	.04 E	.59	200	Solvent
Methyl tert-butyl ether (MTBE)	5	.20	.10 E	.22	--	Oxygenate
Trichloroethylene	5	.04	.95	7.5	5	Solvent
Carbon disulfide	4	.37	.03 E	.11 E	--	Fumigant
Trichlorofluoromethane	4	.09	.78	1.6	--	Refrigerant
Bromodichloromethane	4	.05	.08 E	.12	80 ^a	Disinfection byproduct, organic synthesis
Freon 113	3	.03	.11	.30	--	Refrigerant
1,1-Dichloroethylene	3	.04	.08 E	.85	7	Organic synthesis
cis-1,2-Dichloroethylene	3	.04	.03 E	.12	70	Solvent
Toluene	2	.05	NA	.11	1,000	Gasoline component
Dibromochloromethane	2	.20	NA	.10 E	80 ^a	Disinfection byproduct, organic synthesis
o-Xylene	1	.06	NA	.01 E	10,000	Gasoline component
1,2-Dichloropropane	1	.07	NA	6.4	5	Solvent
1,2-Dichloroethane	1	.10	NA	.20 E	5	Solvent
1,1-Dichloroethane	1	.07	NA	.07 E	--	Solvent
Bromoform	1	.10	NA	.13	80 ^a	Disinfection byproduct, solvent

^a Total concentration for all trihalomethanes combined cannot exceed 80 µg/L.

presence of these constituents did not correlate to well depth, age of the well, thickness of regolith overlying bedrock, nor the presence of sinkholes near a site. The lack of a significant relation between factors such as well depth and thickness of regolith may be, in part, the result of the relatively narrow range in values for some of these variables.

Presence of fecal-indicator bacteria is weakly related to the depth to water in wells. The median depth to ground water in wells with a detection of either *E. coli* or fecal coliform was about 12 feet, in

contrast to a median depth of about 35 feet to ground water in wells where fecal-indicator bacteria were not detected (p=0.09). A higher frequency of detection in shallower ground water may be the result of lower mortality rates and less retention of bacteria in thinner unsaturated zones. Soil moisture is a significant factor for survival of bacteria in the subsurface (Gerba and Bitton, 1984). No other constituents correlated with depth to water in the wells.

Most soil properties evaluated were not related to the presence of bacteria, nitrate, or VOCs in the

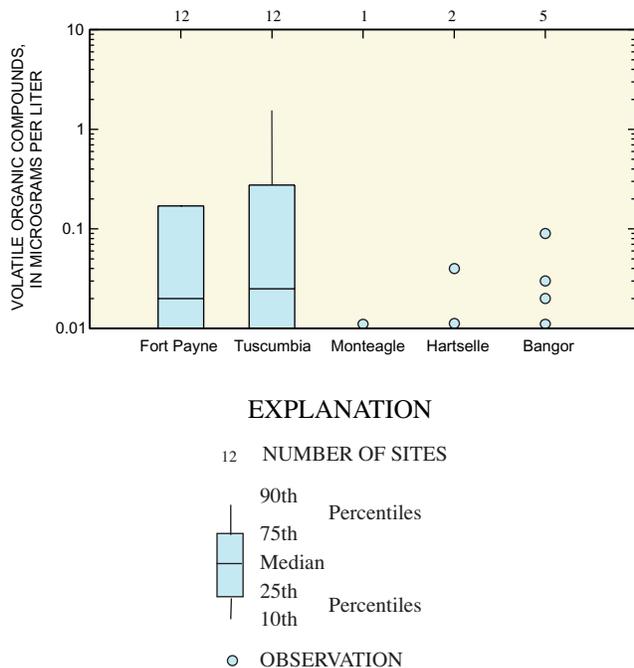


Figure 14. Total volatile organic compound concentrations in water samples from the Mississippian carbonate aquifer by geologic unit.

Mississippian carbonate aquifer. Nitrate concentrations appear to be related to soil organic matter content, but the inverse relation between the two is weak ($p=0.06$). High organic matter content in soils may facilitate denitrification and result in low concentrations of nitrate in ground water in this setting.

Soil properties near sites with pesticide detections were compared (Wilcoxon rank sum test) to sites without detections to determine if soil properties were related to pesticide detections in ground water. Of the soil properties compared, soil hydrologic group and organic matter content of the soils appear to be related to pesticide detections. Hydrologic groups refer to soil groupings based on their runoff-producing characteristics, that is, the infiltration rate of water (and solutes) when the soils are wet (U.S. Department of Agriculture, 1994). Pesticides were detected at sites where soils have high infiltration rates and low organic matter content ($p=0.02$ and $p=0.03$, respectively). Although hydrologic group and organic matter content are not independent of each other, both affect the movement of pesticides in soil in other settings (Burkart and others, 1999). Organic matter in soil can serve as a sink for pesticides and limit movement into ground water. Soil hydrologic group appears to be related to the presence of atrazine and fluometuron

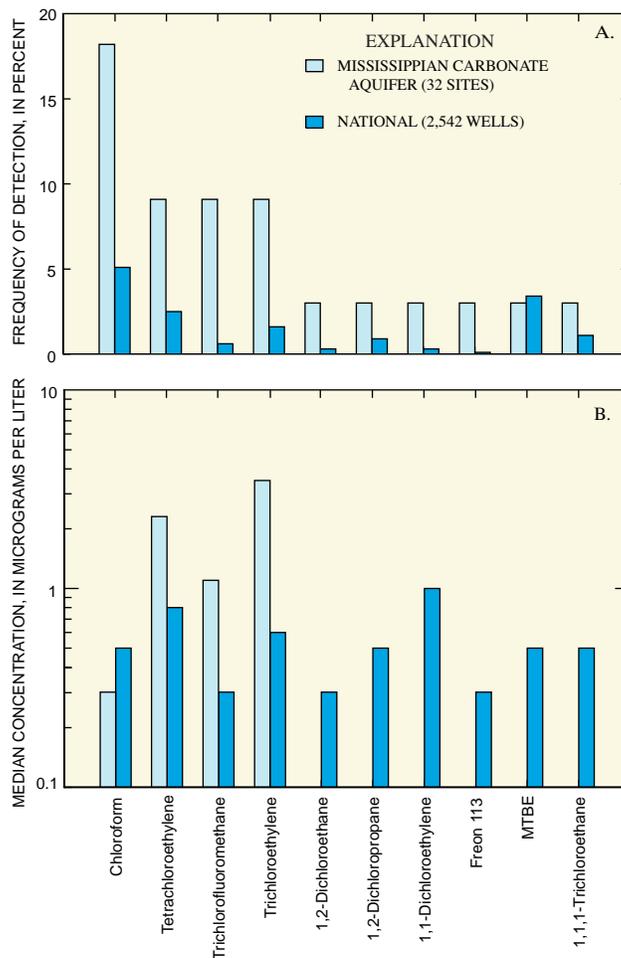


Figure 15. Comparisons of (A) frequencies of detections and (B) median concentrations of volatile organic compounds greater than $0.2 \mu\text{g/L}$ in water samples from the Mississippian carbonate aquifer and in ambient ground water across the United States.

($p < 0.01$), two high-use herbicides. Soil organic matter content also seems to be related to fluometuron detections ($p < 0.001$) as was soil slope, though this relation was weaker ($p=0.04$). Fluometuron was detected in wells overlain by soils with low organic matter content and low slopes. Estimated use (table 5), application rates, solubility, half-lives, and soil sorption coefficients are similar for both pesticides. The stronger relation of fluometuron detections to soil properties may result in part because cotton acreage, and thus fluometuron use, is more prevalent in areas with soils with better drainage and high infiltration rates. Time since application of the two pesticides with respect to when the samples were collected also could be a factor for apparent differences between atrazine and fluometuron detections with respect to soil properties.

Table 7. Environmental factors evaluated that may affect water quality of the Mississippian carbonate aquifer

[VOC, volatile organic compound]

Site characteristics and hydrogeology
Well depth
Age of well
Regolith thickness
Depth to water
Sinkhole occurrence
Soil properties
Hydrologic group
Soil slope
Clay content
Organic matter
Land use
Cropland
Urban land
Forest
Wetland
VOC point sources

Relation of Land Use to Water Quality

Land uses that were most likely to affect the presence of fecal-indicator bacteria, nitrate, pesticides, and VOCs in the Mississippian carbonate aquifer included urban, cropland, and pasture land. The scale of the land-use data, or size of the land-use polygons in the GIS coverage, resulted in an underestimation of the amount of urban or suburban land use within the buffer areas around sites. Therefore, in addition to urban land use, the presence of potential point sources of VOCs, such as gas stations, dry cleaners, and automotive repair shops within about a 1,640-foot radius of a site, were evaluated with respect to VOC detections. This distance, rather than a 3,280-foot radius, was used because of the data requirements for the national synthesis of NAWQA ground-water data.

Fecal-indicator bacteria presence was not found to be associated with a specific land use near a site. In this karst aquifer, transport of bacteria over considerable distances is likely and complicates interpretation of the data with respect to land use. Rainfall/recharge events also may affect the presence of bacteria in karst aquifers (for example, Mahler and others, 2000). Lack of a relation between bacteria presence and a specific land use near these sites suggests that bacterial contamination of ground water in this setting is the result

of numerous local or point sources, such as failing septic systems, leaking sewers, or animal feedlots.

Nitrate concentrations appear to be related to land use near each site, and inversely related to the amount of forested land near a site (Spearman's $\rho = -0.47$, $p = 0.007$). Five sites with greater than 50 percent forested land have nitrate concentrations less than 1 mg/L, indicating that background concentrations in this aquifer may be less than 1 mg/L. DO concentrations of these samples ranged between 0.1 and 5.2 mg/L, indicating denitrification is not affecting nitrate concentrations appreciably. Assuming background concentrations of nitrate are less than 1 mg/L, nitrate concentrations seem to reflect anthropogenic activities at about 65 percent of the sites. About 40 percent of the samples had nitrate concentrations greater than 2 mg/L, which is often cited as a threshold concentration indicating anthropogenic effects on ground-water quality (Mueller and Helsel, 1996).

The amount of cropland near a site is correlated to nitrate concentration (Spearman's $\rho = 0.35$, $p = 0.05$) in samples (fig. 16). This relation, however, is dependent on two samples with high nitrate concentrations from two sites with the highest percentage of cropland use (fig. 16). Potential point sources of nitrogen include an animal feedlot and a small cooperative fertilizer storage facility, which are located near these sites. The elevated concentrations (greater than 5 mg/L) in these samples could be the result of both point and nonpoint sources of nitrogen. Linear regression of log-transformed nitrate concentrations with cropland and dissolved oxygen accounts for about

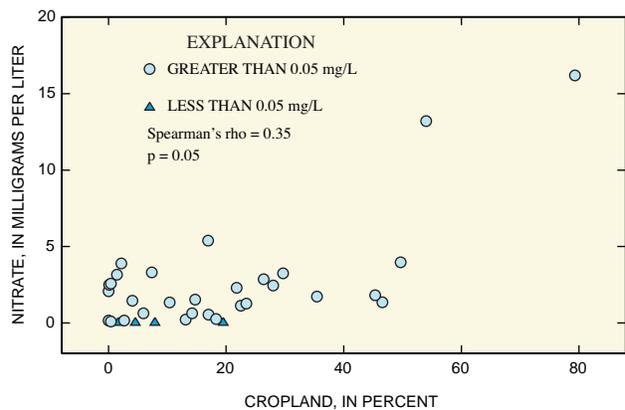


Figure 16. Percentage of cropland near each site in relation to nitrate concentration in water samples from the Mississippian carbonate aquifer, 1999.

48 percent ($r^2=0.48$) of the variability in nitrate concentration.

Pesticide detections also appear to be related to the amount of cropland near a site ($p=0.02$). All sites with more than 20 percent cropland within the buffer area had at least one pesticide detection (fig. 17). A correlation between the amount of cropland and pesticide detection also exists for fluometuron ($p=0.02$); however, the relation is less significant for atrazine ($p=0.06$). Non-agricultural uses of atrazine may account for the weaker relation of atrazine detections with cropland. Pesticides not used on cropland (prometon and tebuthiuron) generally were detected at sites with the greatest amount of urban land use (greater than 50 percent) and at sites located near railroads and highways, which were not accounted for by the land-use data.

The correlation of pesticide detections with both cropland and soil properties raises a question: is pesticide presence determined by both factors, or do soil properties influence land use which, in turn, determines pesticide use and therefore detection? Although the amount of cropland near a site is related to the soil hydrologic group (fig. 17), the highest total pesticide concentrations generally are found at sites with the greatest amount of cropland and soils having higher infiltration rates. Linear regression of log-transformed values of the total pesticide concentration measured at a site, with cropland and hydrologic group accounts for about 45 percent ($r^2=0.45$, $p < 0.001$) of the variability in the total pesticide concentration.

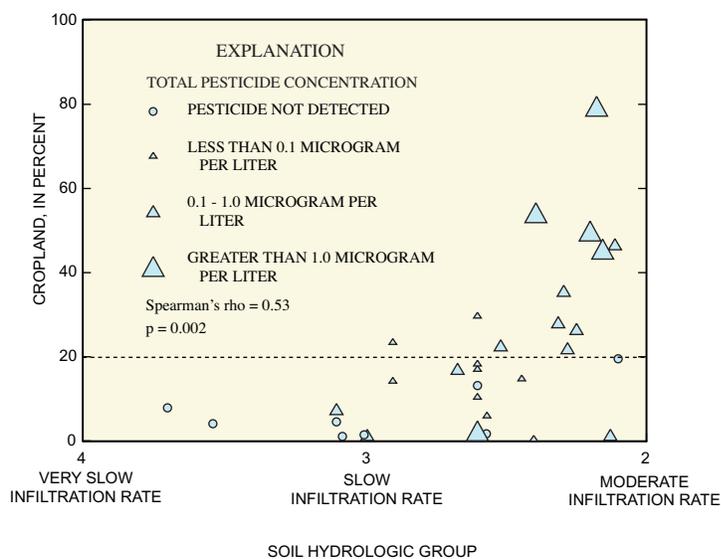


Figure 17. Total pesticide concentration in relation to the percentage of cropland and soil hydrologic group (infiltration rate) near a site.

The presence of VOCs is not significantly related to urban land use near the sites or to potential point sources near a site. A statistically significant relation between land use and VOC detections probably does not exist because VOCs in ground water generally are the result of point releases, though widely distributed, and the land-use data do not adequately account for the distribution of these sources. Although a relation between urban land use and VOC detections is not indicated by the data set, two of the three sites with the highest concentrations (greater than 5 $\mu\text{g/L}$) of VOCs and the largest number of compounds detected (greater than 10) are located in areas with high percentages of urban land use. The third site, where more than 10 VOCs were detected and TCE was detected at 7.48 $\mu\text{g/L}$, is located a little more than a mile from a military base where VOC contamination of ground water has been documented (Haugh, 1996). The compounds detected at the third site are indicative of contamination from the military base (C.J. Haugh, U.S. Geological Survey, oral commun., 2000). The VOC data indicate that the karst hydrogeology of the Mississippian carbonate aquifer allows ground-water contaminants to be transported over distances greater than a mile, at environmentally significant concentrations.

The frequent detection of chloroform at low concentrations throughout the Eastern Highland Rim subunit suggests widespread sources of contamination. Sites with samples having low-level, estimated concentrations were compared to sites without any chloroform detections. Samples with chloroform concentrations greater than 0.1 $\mu\text{g/L}$ and with additional solvents present in the sample were excluded from this evaluation. Samples with low-level detections of chloroform generally were from sites having high percentages of wetlands nearby ($p=0.03$). This relation may indicate that chloroform at low concentrations is the result of biogenic processes in the subsurface near wetland areas. Laternus and others (2000) concluded that chloroform concentrations measured in ground-water samples collected from a spruce forest site were the result of chloroform formation in forest soil. Data describing the distribution of other possible sources of chloroform, such as watering of lawns with treated water and chlorination of domestic wells, were not available; therefore, the effects of these sources could not be evaluated.

SUMMARY AND CONCLUSIONS

Water-quality data for nitrate, fecal-indicator bacteria, pesticides, and VOCs collected from a network of randomly selected sites in the Mississippian carbonate aquifer in parts of northern Alabama and Middle Tennessee in 1999 indicate that this aquifer is susceptible to contamination from point and nonpoint sources. For example, pesticides and VOCs were detected at 74 and 81 percent of the sites sampled, respectively. Most of these compounds were detected more frequently in this study than in other NAWQA well networks in other settings; however, the magnitude of pesticide concentrations generally were similar and most VOC concentrations were lower than in other NAWQA studies. This relatively high frequency of detection is likely the result of a number of factors, including shallow depth to ground water (generally less than 50 feet), low organic content of soils, moderately well to well-drained soils, and the karst ground-water flow system where the potential for rapid contaminant transport is high.

Nitrate concentrations in the Mississippian carbonate aquifer are mostly affected by the geochemistry (for example, dissolved-oxygen concentrations) in the aquifer and nonpoint sources of nitrogen (land use). In general, nitrate concentrations are low. Concentrations exceeding the drinking-water standard are infrequent (less than 6 percent of sites) and more likely in areas with large amounts of cropland (greater than 50 percent) or a nearby point source. About 40 percent of the sites had nitrate concentrations greater than 2 mg/L, which is often cited as a threshold concentration for indicating anthropogenic effects on ground-water nitrate concentrations; however, background nitrate concentrations in this setting may be as low as 1 mg/L. If 1 mg/L is used as an indicator of anthropogenic effects on water quality in this aquifer, then about 65 percent of the sampled sites have increased concentrations of nitrate. The correlation of nitrate concentrations to the amount of cropland near a site and pesticide detections indicate that fertilizer application is the predominant source of nitrate to the aquifer.

Although fecal-indicator bacteria are not the most frequently detected ground-water contaminant, they indicate the most significant short-term health risk from consumption of untreated ground water. The probability of fecal contamination of wells is relatively high in this setting, but predicting where that contamination is likely to occur is difficult. Fecal-

indicator bacteria were present at about 40 percent of the sites, but their occurrence did not correlate with most environmental factors that were evaluated. Wells or springs with a shallow depth to ground water and a potential point source nearby are likely the most susceptible. Additional data are needed to identify the sources and to better understand the processes that affect the occurrence and movement of bacteria in this setting.

Pesticide concentrations generally were low. Only fluometuron, diuron, and metolachlor were detected at concentrations greater than 1 µg/L, and the maximum total pesticide concentration measured in a sample was about 4 µg/L. Frequent detections of metabolites of high-use pesticides, typically at concentrations greater than the parent compounds, indicate that the total concentration of pesticides could be considerably higher if additional metabolites were analyzed. Pesticide use (amounts used and proximity of a site to areas of use) and soil hydrologic group are the primary factors evaluated that affect the detection of pesticides in ground water in this setting.

The presence of VOCs in the Mississippian carbonate aquifer was not related to any of the environmental factors considered. Chlorinated solvents, which are some of the more persistent VOCs, were detected at the highest concentrations (up to 7.5 µg/L) and were the only VOCs that exceeded drinking-water standards. Higher total VOC concentrations and greater numbers of compounds generally were associated with a higher percentage of urban land use near a site. Low-level concentrations of chloroform and MTBE may be related to biogenic and atmospheric sources of these compounds, respectively.

The relation between land use and water quality was stronger for constituents that are contributed to the environment systematically as a result of land use (fertilizer and pesticide application), rather than inadvertently in areas of a given land use (leaking septic tanks or chemical spills or leaks). The use of circular buffer areas to characterize land use and soils near sites sampled in this karst aquifer helped explain some of the variation in nitrate concentration and occurrence of pesticides; however, finer scale land-use and soil data and buffer-area size based on well capacities and withdrawals might help to strengthen this analysis.

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APPENDIXES

Pesticides in italics in appendix 1 were analyzed by a new HPLC/MS method before final approval of the method by the U.S. Geological Survey's Office of Water Quality in 2001. Although the analytical method did not change following approval, data analyzed before method approval are considered provisional. Seventy percent of the samples analyzed with this method in this study exceeded the recommended 4-day holding time prior to sample extraction (Furlong and others, 2001). 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.

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

[MRL, minimum reporting level; CAS, chemical abstracts reference number; H, herbicide; I, insecticide; F, fungicide; Metab., pesticide metabolite; N/A, not applicable; pesticides in italics were analyzed before analytical method approval, and data in this report are provisional]

Compound	Common name	MRL	CAS number	Use
Pesticides detected				
<i>3(4-chlorophenyl) methyl urea</i>	N/A	0.092	1897-46-6	H-Metab.
Acetochlor	Acenit, Guardian, Harness	.002	34256-82-1	H
<i>Acifluorfen</i>	Tackle, Blazer	.062	62476-59-9	H
<i>Aldicarb sulfone</i>	Standak, aldoxycarb	.16	1646-88-4	I-Metab.
<i>Aldicarb sulfoxide</i>	Temik sulfoxide	.0271	1646-87-3	I-Metab.
<i>Bromacil</i>	Bromax, Hyvar, Uragon	.081	314-40-9	H
<i>Bromoxynil</i>	Bromanil, Bucril, Torch	.057	1689-84-5	H
Atrazine	Aatrex	.001	1912-24-9	H
Deethylatrazine	N/A	.087	6190-65-4	H-Metab.
<i>Deisopropylatrazine</i>	N/A	.074	1007-28-9	H-Metab.
<i>Deethyldeisopropylatrazine</i>	N/A	.06	3397-62-4	H-Metab.
<i>Hydroxyatrazine</i>	N/A	.193	2163-68-0	H-Metab.
<i>Bentazon</i>	Basagran, Adagio, Galaxy, Storm	.019	25057-89-0	H
Carbaryl	Sevin	.063	63-25-2	H
<i>Chloramben methyl ester</i>	Amiben, methyl ester	.114	7286-84-2	H
Dieldrin	Dieldrin, Panoram D-31	.001	60-57-1	I
<i>Dinoseb</i>	DNPB, Caldon, Dynamite	.043	88-85-7	H
<i>Diuron</i>	DCMU, Diurex, Aguron, Karmex	.079	330-54-1	H
<i>Fluometuron</i>	Cortoran, Lanex, Cottonex, Flo-met	.062	2164-17-2	H
<i>Imazaquin</i>	Image 1.5LC; Scepter 1.5L	.103	81335-37-7	H
<i>Imidacloprid</i>	Admire, Gaucho, Merit	.106	105827-78-9	I
<i>Metalaxyl</i>	Apron, Subdue, Ridomil	.057	94-81-5	F
Metolachlor	Dual, Pennant	.002	51218-45-2	H
<i>Norflurazon</i>	Solicam, Telok, Evital, Zorial	.077	27314-13-2	H
Prometon	Pramitol, Princep	.018	1610-18-0	H
Tebuthiuron	Graslan, Spike, Perflan	.01	34014-18-1	H
<i>Siduron</i>	Tupersan, Trey	.093	1982-49-6	H
Simazine	Princep	.005	122-34-9	H
<i>Sulfometuron methyl</i>	Oust, DPX-T5648	.039	74222-97-2	H

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

Compound	Common name	MRL	CAS number	Use
Pesticides not detected				
<i>Aldicarb</i>	Temik	0.082	116-06-3	I
<i>2,4-D</i>	Aqua Kleen, Weedone-2,4-DP	.077	94-75-7	H
Alachlor	Lasso, Bronco	.002	15972-60-8	H
2,6-Diethylaniline	N/A	.003	579-66-8	H-Metab.
alpha-BHC	HCH-alpha	.002	319-84-6	I
<i>2,4-D methyl ester</i>	N/A	.087	1928-38-7	H
<i>2,4-DB</i>	Butyrac, Butoxone, Legumex D	.054	94-82-6	H
<i>Bendiocarb</i>	Ficam, Tattoo	.061	22781-23-3	I
Benfluralin	Balan, Benefin	.002	1861-40-1	H
<i>Benomyl</i>	Benlate	.022	17804-35-2	F
<i>Bensulfuron-methyl</i>	Londax	.048	83055-99-6	H
Butylate	Sutan +	.002	2008-41-5	H
<i>3-Hydroxycarbofuran</i>	N/A	.062	16655-82-6	I-Metab.
<i>3-Ketocarbofuran</i>	N/A	.072	16709-30-1	I-Metab.
Carbofuran	Furadan	.003	1563-66-2	I
<i>Chlorimuron-ethyl</i>	Classic	.037	90982-32-4	H
<i>Chlorothalonil</i>	Bravo, Forturf	.048	1897-45-6	H
Chlorpyrifos	Lorsban, Dursban	.004	2921-88-2	I
<i>Clopyralid</i>	Stinger, Lontrel	.041	1702-17-6	H
Cyanazine	Bladex	.004	21725-46-2	H
<i>Cycloate</i>	Ro-Neet, Marathon	.054	1134-23-2	H
<i>Dacthal monoacid</i>	DCPA Monoacid	.072	887-54-7	H-Metab.
DCPA	Dacthal	.002	19719-28-9	H
Diazinon	Spectracide	.002	333-41-5	I
<i>Dicamba</i>	Banvel, Marksman, Clarity	.096	1918-00-9	H
<i>Dichlorprop</i>	Seritox 50, Weedone	.05	120-36-5	H
<i>Diphenamid</i>	Dymid, Enide, Rideon, Dyfen	.058	957-51-7	H
Disulfoton	Di-Syston	.017	298-04-4	I
EPTC	Eradicane, Eptam	.002	759-94-4	H
Ethalfuralin	Sonalan	.004	55283-68-6	H

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

Compound	Common name	MRL	CAS number	Use
Pesticides not detected—Continued				
Ethoprop	Mocap	0.003	13194-48-4	I
<i>Fenuron</i>	Beet-Klean, Fenidim	.074	101-42-8	H
<i>Flumetsulam</i>	DE 498, XRD 498	.087	98967-40-9	H
Fonofos	Dyfonate	.003	944-22-9	I
<i>Imazethapyr</i>	Pursuit, Pursuit DG	.088	81335-77-5	H
Lindane	Isotox	.004	58-89-9	I
Linuron	Lorox	.002	330-55-2	H
Malathion	Cythion	.005	121-75-5	I
<i>MCPA</i>	Bordermaster, Metaxon, Rhomene	.058	86-50-0	H
<i>MCPB</i>	Tropotox, Can-Trol, PDQ	.062	94-74-6	H
<i>Methiocarb</i>	Draza, Mesurol, Slug-geta	.08	57837-19-1	I
<i>Methomyl</i>	Nudrin, Lannate, Lanox	.077	2032-65-7	I
<i>Methomyl oxime</i>	N/A	.01	16752-77-5	I-Metab.
Azinphos-methyl	Guthion	.001	13749-94-5	I
Methyl parathion	Penncap-M	.006	298-00-0	I
Metribuzin	Sencor, Lexone	.004	21087-64-9	H
<i>Metsulfuron-methyl</i>	Escort, Gropper, Ally	.114	74223-64-6	H
Molinate	Ordram	.004	2212-67-1	H
Napropamide	Devrinol	.003	15299-99-7	H
<i>Neburon</i>	Granurex, Herbalt, Kloben	.075	555-37-3	H
<i>Nicosulfuron</i>	Accent, Accent DF	.065	111991-09-4	H
<i>Oryzalin</i>	Ryzelan, Surflan, Dirimal	.071	19044-88-3	H
<i>Oxamyl</i>	Vydate L, Thioxamyl	.016	23135-22-0	I
<i>Oxamyl oxime</i>	N/A	.064	30558-43-1	I-Metab.
p,p'-DDE	N/A	.006	72-55-9	I-Metab.
Pebulate	Tillam	.004	1114-71-2	H
Pendimethalin	Prowl, Stomp	.004	40487-42-1	H
cis-Permethrin	Pounce, Ambush	.005	54774-45-7	I
Phorate	Thimet	.002	298-02-2	I
<i>Picloram</i>	Tordon, Amdon, Grazon	.071	191802-1	H

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

Compound	Common name	MRL	CAS number	Use
Pesticides not detected—Continued				
Pronamide	Kerb	0.003	23950-58-5	H
Propachlor	Ramrod	.007	1918-16-7	H
Propanil	Stam, Stampede	.004	709-98-8	H
Propargite	Comite	.013	2312-35-8	I
<i>Propham</i>	IPC, Chem-Hoe, Premalox	.072	122-42-9	H
<i>Propiconazole</i>	Tilt, Orbit, Banner, Proconazole, Wocosin	.064	60207-90-1	F
<i>Propoxur</i>	Baygon, PHC, Suncide, Unden	.059	114-26-1	I
<i>Terbacil</i>	Sinbar, DPX-D732, Geonter	.007	5902-51-2	H
Terbufos	Counter	.013	13071-79-9	I
Thiobencarb	Bolero	.002	28249-77-6	H
Triallate	Far-Go	.001	2303-17-5	H
<i>Tribenuron-methyl</i>	Express, tribenuron methyl ester, DPX-L5300	.068	101200-48-0	H
<i>Triclopyr</i>	Garlon, Curtail, Redeem, Remedy	.101	55335-06-3	H
Trifluralin	Treflan, Gowan	.002	1582-09-8	H

Appendix 2. Volatile organic compounds analyzed

[MRL, minimum report level in micrograms per liter; CAS, chemical abstracts reference number]

Constituent	CAS number	MRL	Constituent	CAS number	MRL
1,1,1,2-Tetrachloroethane	630-20-6	0.030	Bromochloromethane	74-97-5	0.044
1,1,1-Trichloroethane	71-55-6	.032	Bromodichloromethane	75-27-4	.048
1,1,2,2-Tetrachloroethane	79-34-5	.09	Bromoethene	593-60-2	.10
1,1,2-Trichloroethane	79-00-5	.06	Bromoform	75-25-2	.06
1,1-Dichloroethane	75-34-3	.035	Bromomethane	74-83-9	.26
1,1-Dichloroethylene	75-35-4	.04	Butylbenzene	104-51-8	.19
1,1-Dichloropropene	563-58-6	.026	Carbon disulfide	75-15-0	.07
1,2,3,4-Tetramethylbenzene	488-23-3	.23	Chlorobenzene	108-90-7	.028
1,2,3,5-Tetramethylbenzene	527-53-7	.20	Chloroethane	75-00-3	.12
1,2,3-Trichlorobenzene	87-61-6	.27	Chloroform	67-66-3	.024
1,2,3-Trichloropropane	96-18-4	.16	Chloromethane	74-87-3	.25
1,2,3-Trimethylbenzene	526-73-8	.12	cis-1,2-Dichloroethylene	156-59-2	.038
1,2,4-Trichlorobenzene	120-82-1	.19	cis-1,3-Dichloropropene	10061-01-5	.09
1,2,4-Trimethylbenzene	95-63-6	.056	Dibromochloromethane	124-48-1	.18
1,2-Dibromo-3-chloropropane	96-12-8	.21	Dibromomethane	74-95-3	.050
1,2-Dibromoethane	106-93-4	.036	Dichlorodifluoromethane	75-71-8	.27
1,2-Dichlorobenzene	95-50-1	.048	Dichloromethane	75-09-2	.16
1,2-Dichloroethane	107-06-2	.13	Diethyl ether	60-29-7	.17
1,2-Dichloropropane	78-87-5	.029	Diisopropyl ether	108-20-3	.10
1,3,5-Trimethylbenzene	108-67-8	.044	Ethyl methacrylate	97-63-2	.18
1,3-Dichlorobenzene	541-73-1	.030	Ethyl tert-butyl ether	637-92-3	.054
1,3-Dichloropropane	142-28-9	.12	Ethylbenzene	100-41-4	.030
1,4-Dichlorobenzene	106-46-7	.050	Freon 113	76-13-1	.06
2,2-Dichloropropane	594-20-7	.05	Hexachlorobutadiene	87-68-3	.14
2-Butanone	78-93-3	1.6	Hexachloroethane	67-72-1	.19
2-Chlorotoluene	95-49-8	.026	Isopropylbenzene	98-82-8	.032
2-Hexanone	591-78-6	.7		106-42-3 and	
3-Chloropropene	107-05-1	.07	m- and p-Xylene	108-38-3	.06
4-Chlorotoluene	106-43-4	.06	Methyl acrylate	96-33-3	1.4
4-Isopropyl-1-methylbenzene	99-87-6	.07	Methyl acrylonitrile	126-98-7	.6
4-Methyl-2-pentanone	108-10-1	.37	Methyl iodide	74-88-4	.12
Acetone	67-64-1	7	Methyl methacrylate	80-62-6	.35
Acrylonitrile	107-13-1	1.2	Naphthalene	91-20-3	.25
Benzene	71-43-2	.021	n-Propylbenzene	103-65-1	.042
Bromobenzene	108-86-1	.036	o-Ethyl toluene	611-14-3	.06

Appendix 2. Volatile organic compounds analyzed—Continued

Constituent	CAS number	MRL
o-Xylene	95-47-6	0.038
sec-Butylbenzene	135-98-8	.032
Styrene	100-42-5	.042
tert-Butyl methyl ether	1634-04-4	.17
tert-Butylbenzene	98-06-6	.06
tert-Pentyl methyl ether	994-05-8	.11
Tetrachloroethylene	127-18-4	.10
Tetrachloromethane	56-23-5	.06
Tetrahydrofuran	109-99-9	2.2
Toluene	108-88-3	.05
trans-1,2-Dichloroethylene	156-60-5	.032
trans-1,3-Dichloropropene	10061-02-6	.09
trans-1,4-Dichloro-2-butene	110-57-6	.7
Trichloroethylene	79-01-6	.038
Trichlorofluoromethane	75-69-4	.09
Vinyl chloride	75-01-4	.11