

Water Quality of Springs in the Valley and Ridge Physiographic Province in the Upper Tennessee River Basin, 1997

Water-Resources Investigations Report 02-4180
National Water-Quality Assessment Program



Cover illustration: Relief map of the upper Tennessee River Basin study area. **Photos:** Top left photo is Nelson Spring at Mill Creek Road at Mill Creek, Tenn. Top right photo is Bailey Spring near Kodak, Tenn. Bottom photo is Malone Spring near Niota, Tenn.

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By Gregory C. Johnson

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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.

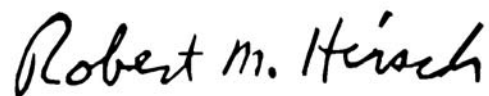
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program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

	Multiply	By	To obtain
	inch (in.)	2.54	centimeter
	foot (ft)	0.3048	meter
	mile (mi)	1.609	kilometer
	acre	0.4047	hectare
	square mile (mi ²)	2.590	square kilometer
	inch per year (in/yr)	2.54	centimeter per year
	foot per hour (ft/hr)	0.00847	centimeter per second
	cubic foot per second (ft ³ /sec)	0.02832	cubic meter per second
	million gallons per day (Mgal/d)	0.04381	cubic meter per second
	pound, avoirdupois (lb)	453.5924	gram

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F), and conversely, by use of the following equations:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32 \qquad ^{\circ}\text{C} = (^{\circ}\text{F} - 32) \times 0.5555$$

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

Horizontal datum: Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Water-Quality Units

µm	micron
mg/L	milligrams per liter
µg/L	micrograms per liter
col/100 mL	colonies per 100 milliliters

Abbreviations and Acronyms

CALC	Canadian aquatic-life criterion
DOC	Dissolved organic carbon
GCMS	Gas chromatography/mass spectrometry
HA-L	Health advisory level
HPLC	High performance liquid chromatography
LRL	Laboratory reporting level
MCL	Maximum contaminant level
MDL	Method detection level
MTBE	Methyl <i>tert</i> -butyl ether
NAWQA	National Water-Quality Assessment Program
NWQL	National Water-Quality Laboratory
RSD	Risk-specific lifetime dose
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UTEN	Upper Tennessee River Basin
VOC	Volatile organic compound

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ABSTRACT

In the fall of 1997, 35 springs in the carbonate rocks of the Valley and Ridge Physiographic Province of the upper Tennessee River Basin were sampled for nutrients, fecal-indicator bacteria, pesticides, and volatile organic compounds (VOCs) as part of the National Water-Quality Assessment (NAWQA) Program. About half of the randomly selected springs were used as untreated domestic drinking-water supplies, either by direct pumpage from the spring or as roadside filling sites. Nutrient concentrations generally were less than 2 milligrams per liter. Nitrate, the most frequently detected nutrient, ranged from 0.091 to 2.17 milligrams per liter, with a median concentration of 1.16 milligrams per liter. Fecal-indicator bacteria were detected at all springs, with total coliform ranging from 10 to 1,900 colonies per 100 milliliters and *Escherichia coli* ranging from less than 1 to 660 colonies per 100 milliliters. Concentrations of bacteria at all springs sampled exceeded bacteriological drinking-water standards for public water supplies.

Eight pesticides or degradation byproducts, all below U.S. Environmental Protection Agency drinking-water maximum contaminant levels, were detected in samples from 24 of the 35 springs. The most frequently detected pesticide was atrazine and its degradation byproduct, deethylatrazine, which were found in water samples from 57 and 54 percent of the springs, respectively. Some pesticides were detected more frequently in water samples from the springs than in ground-water samples from wells in similar NAWQA studies nationwide. Concentrations of

VOCs in the springs also were below maximum contaminant levels. The most frequently detected VOCs were chloroform (20 springs), methyl chloride (18 springs), styrene (12 springs), and tetrachloroethene (11 springs). These detection frequencies of VOCs are consistent with the national NAWQA results when comparing wells and springs in a mixture of urban and rural land uses.

INTRODUCTION

In 1994, the U.S. Geological Survey (USGS) began an investigation to assess the water-quality conditions in the upper Tennessee River Basin (UTEN) as part of the National Water-Quality Assessment (NAWQA) Program. The NAWQA Program is designed to describe, in a nationally consistent manner, the status of, and trends in, the quality of a large representative part of the Nation's surface- and ground-water resources and to relate the assessment of status and trends to the natural and human factors that affect the quality of water (Hirsch and others, 1988). For the NAWQA aquifer studies, wells and springs were sampled in various settings across the United States and offer a baseline comparison of water quality from a national perspective.

In 1997, ground-water quality in springs within the Valley and Ridge Physiographic Province (Valley and Ridge) of the UTEN was assessed as part of the NAWQA Program. The Valley and Ridge was selected because of the prevalence of karst. Karst settings are more vulnerable to contamination than other hydrogeologic settings because of the presence of sinkholes, caves, disappearing streams, and other features that provide pathways for the rapid transport of contaminants to ground water. Despite the vulnerability to

contamination, karst aquifers within carbonate rock units are the primary source of drinking water for about 38 percent of the population in the UTEN Valley and Ridge. Approximately 21 percent of the population in the UTEN Valley and Ridge relies on springs and domestic wells as a source of drinking water, and about 17 percent of the population relies on public-supply wells and springs (Price and Clawges, 1999).

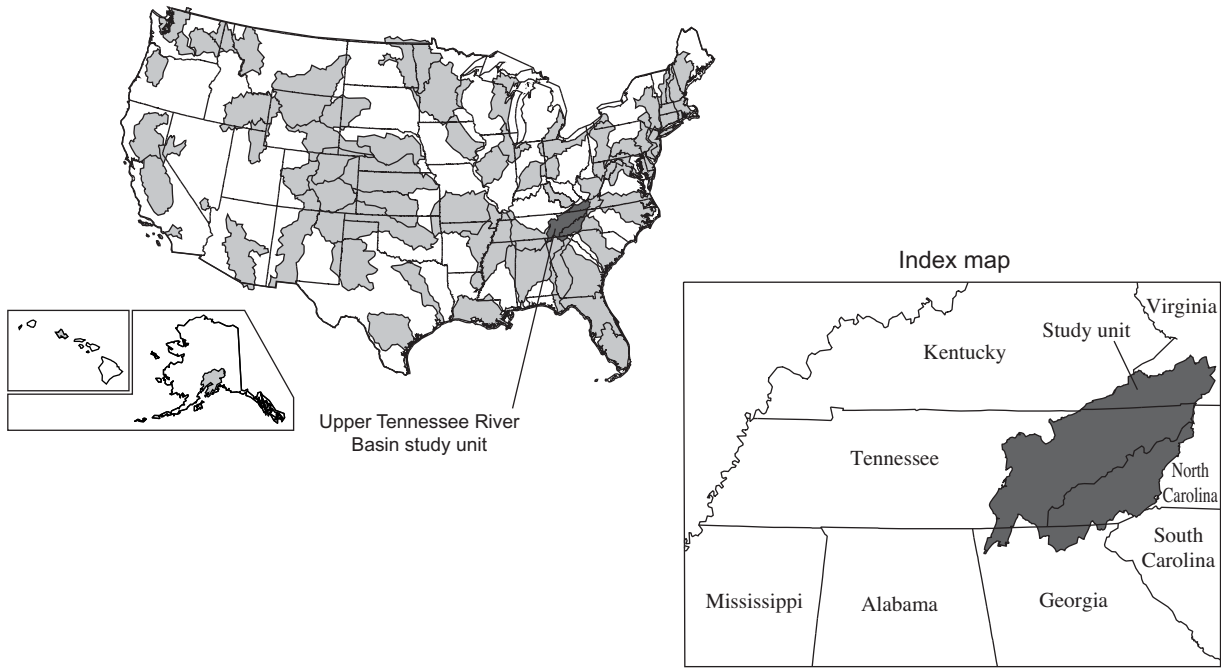
Purpose and Scope

This report describes the water quality of springs in the carbonate rock units of the UTEN Valley and Ridge during fall 1997. Water samples were collected from 35 randomly selected springs for analysis of nutrients, bacteria, pesticides, and volatile organic compounds (VOCs). The purpose of this report is to describe the occurrence and distribution of these constituents that are largely attributed to or affected by anthropogenic sources. Water-quality results are compared with other NAWQA study units nationwide and with other local and regional studies.

Description of the Valley and Ridge Physiographic Province

The UTEN Valley and Ridge extends from southwestern Virginia to northern Georgia (fig. 1). The UTEN Valley and Ridge encompasses an area of about 10,810 mi², with 2,740 mi² in Virginia, 7,690 mi² in Tennessee, and 380 mi² in Georgia. Land-surface elevations range from about 627 feet above sea level in Chattanooga, Tennessee, to 2,340 ft above sea level in

National Water-Quality Assessment study units



EXPLANATION

PHYSIOGRAPHIC PROVINCES

- CUMBERLAND PLATEAU
- VALLEY AND RIDGE
- BLUE RIDGE

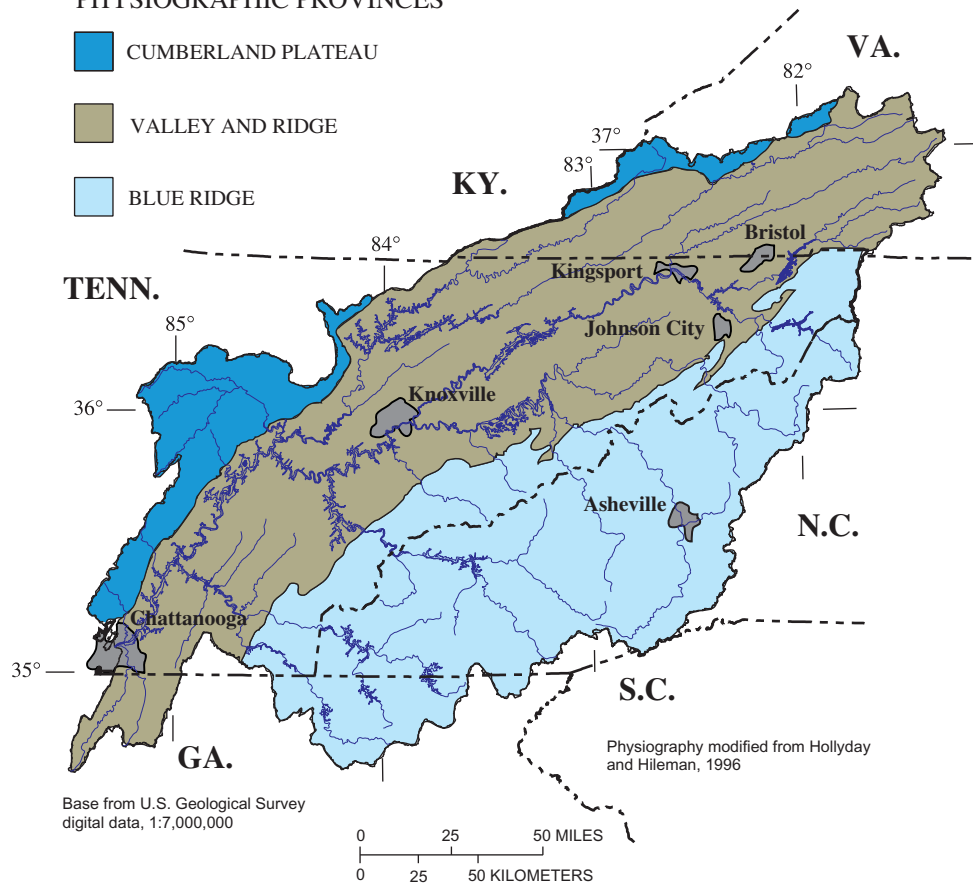
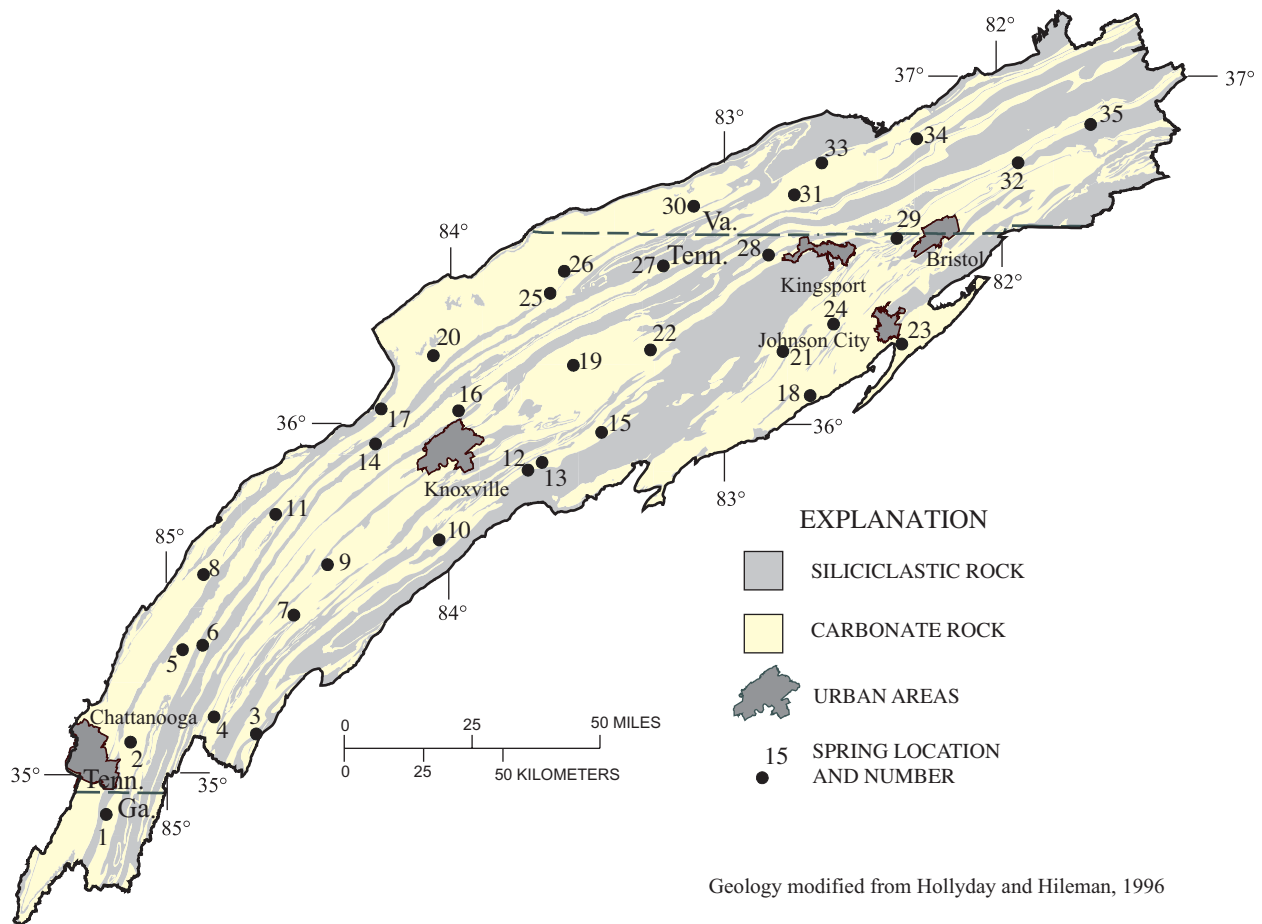


Figure 1. Location and physiographic provinces of the upper Tennessee River Basin.



Base from U.S. Geological Survey digital data, 1:250,000; and U.S. Department of Commerce 1:100,000, 1993

Figure 2. Spring locations and generalized geology of the Valley and Ridge Physiographic Province in the upper Tennessee River Basin.

cropland (4 percent), urban (6 percent), water (3 percent), and barren land (less than 1 percent) (Southern Appalachian Man and the Biosphere Cooperative, 1996). Topography largely dictates land use. In general, forested areas are located on the steeper ridges, cropland in the valley bottoms and benches, and pastures on the less steep parts of ridges and in the valleys. The primary crops produced in 1992 include corn (67,100 acres), soybeans (10,200 acres), and tobacco (40,700 acres) (Gilliom and Thelin, 1999). Pasture is the primary agricultural land use in the UTEN Valley and Ridge covering 3,850 mi². In 1992, about 1.8 million pounds of pesticides were used in the UTEN Valley and Ridge (Majewski, 1997). Livestock production in 1987 was predominantly beef cattle (285,000 head), followed by dairy (76,000 head), chickens

(116,000 layers and 4.58 million broilers), and swine (49,400 head) (Battaglin and Goolsby, 1995).

The urban areas of the UTEN Valley and Ridge account for about 66 percent of the population. In 1990, approximately 1.86 million people lived in the area, with about 23 percent residing in the four major urban areas of Knoxville (173,200), Chattanooga (152,800), Kingsport (42,200), and Johnson City (51,700) (U.S. Census Bureau, 2000). Not all of Chattanooga lies within the UTEN, so a part of the population reported for the city is outside the study area. The population flux from 1990 to 1999 for these urban areas was -3.7 percent in Chattanooga, 1.0 percent in Knoxville, 1.3 percent in Kingsport, and 14.4 percent in Johnson City (U.S. Census Bureau, 2000).

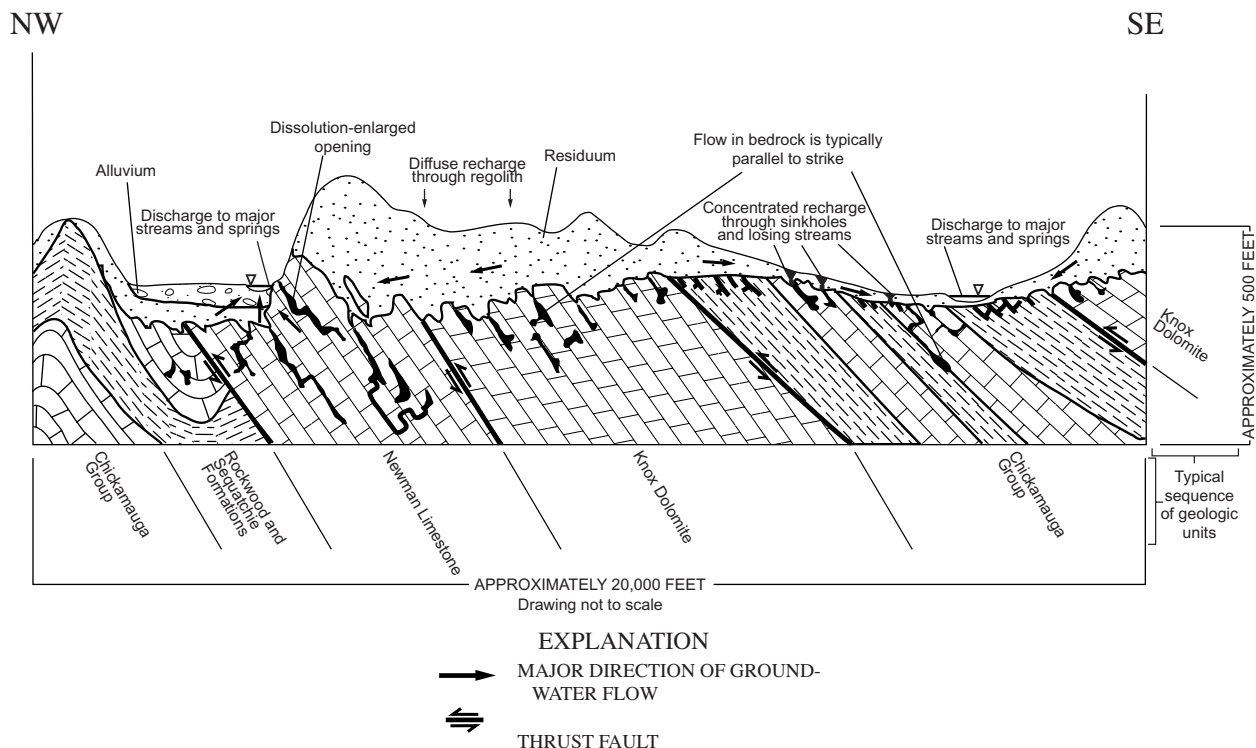


Figure 3. Generalized hydrogeologic section through the Valley and Ridge Physiographic Province in the upper Tennessee River Basin. (Modified from Wolfe and others, 1997.)

As population and urbanization increase, so does the amount of impervious area. Increased impervious area serves to decrease the amount of water that naturally would infiltrate into the soil, thus increasing runoff. The increased runoff alters the magnitude and timing of storm peaks, which increases the likelihood of localized flooding. Urban runoff may increase nonpoint-source loads of sediment and inorganic and organic constituents from paved surfaces, parks, lawns, and golf courses (U.S. Geological Survey, 2001).

The water resources in the UTEN Valley and Ridge are abundant and provide water for industrial, municipal, agricultural, and recreational activities. Surface water is the primary source of water used for industrial and municipal water supplies. In 1995, 596 Mgal/d were withdrawn from surface-water sources for industry, 210 Mgal/d for municipal and domestic supplies, and 13.0 Mgal/d for agricultural use (Price and Clawges, 1999). Ground water is used to a lesser extent for water supply in the study area; approximately 9.3 Mgal/d were withdrawn for industrial use. Approximately 41 Mgal/d of ground water were withdrawn by municipal water systems, and about 6.5 Mgal/d were withdrawn for agricultural use.

Much of the area is rural, and about 21 percent of the population in the UTEN Valley and Ridge is not served by municipal water systems. About 27 Mgal/d are withdrawn from shallow wells and springs for domestic use. Roadside springs also are used frequently as a source of drinking water even when public-supply sources are available. Of the 35 springs sampled in the UTEN Valley and Ridge, 16 were used as untreated domestic drinking-water supplies with pumps set directly in the spring, and at least 1 spring was used for roadside filling of drinking-water containers.

Acknowledgments

The author thanks the landowners who graciously allowed USGS personnel access to their land for the collection of water samples. The author also thanks Joseph F. Connell for selecting the springs used for this study and for contacting landowners.

APPROACH

The study of the water quality of springs in the UTEN Valley and Ridge is one of the NAWQA study

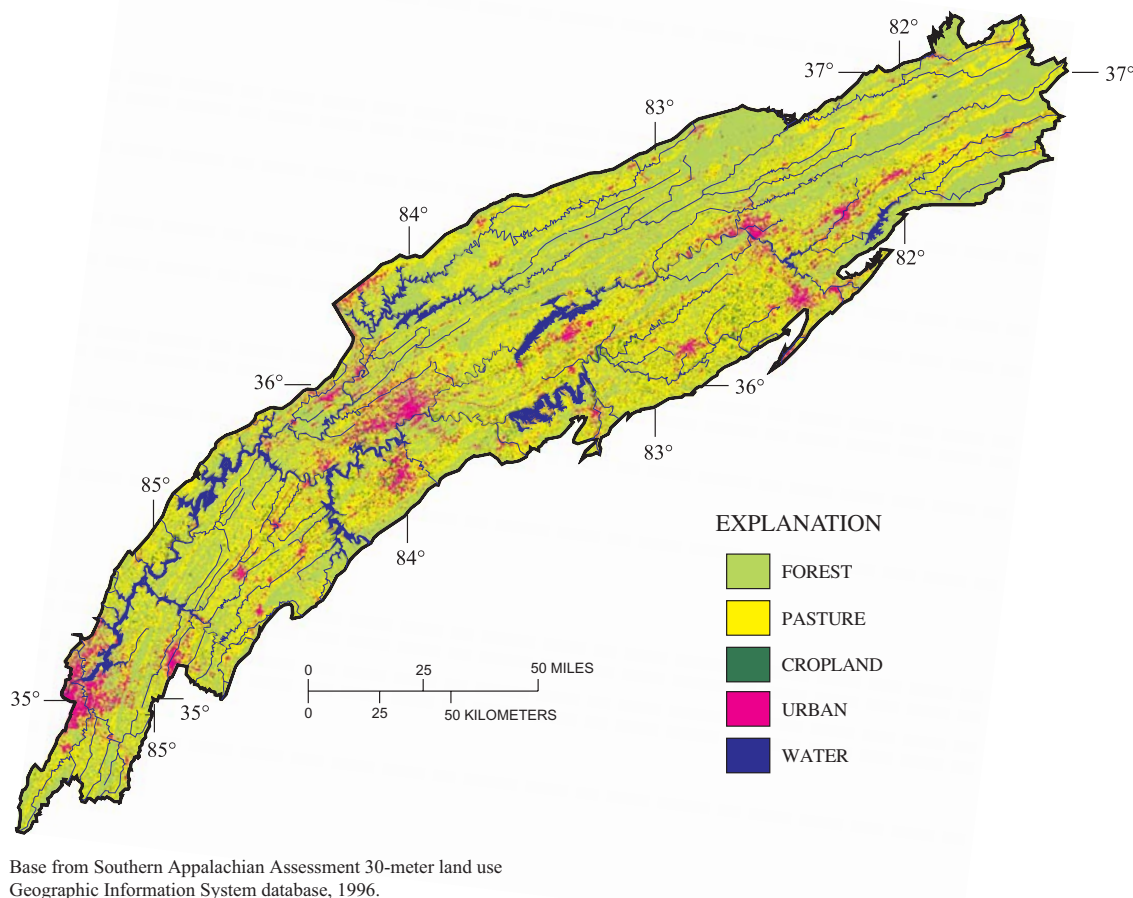


Figure 4. Land use in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin.

unit ground-water surveys designed to provide a spatial characterization of water-quality conditions of major aquifers. The methodology of the study design, site selection, water-quality sampling, and analysis is consistent with the other NAWQA study units nationwide.

Site Selection

Springs were selected randomly by using a geographic information system (GIS) based computer program (Scott, 1990), which divided the UTEN Valley and Ridge into 35 sections of equal area of carbonate rock. Within each of the 35 sections, springs were selected from a list of springs compiled from various sources: a database of springs from previous USGS investigations in Tennessee (Joseph F. Connell, U.S. Geological Survey, written commun., 1997); the Appalachian Valley and Piedmont Regional Aquifer-System Analysis (Hollyday and Smith, 1990); and the

Geographic Names Information System database (U.S. Geological Survey, 1993). For each of the 35 sections, three springs were randomly identified, from which one spring was selected (table 1, fig. 2) on the basis of accessibility and obtaining landowner permission.

Sample Collection

Thirty-five UTEN Valley and Ridge springs were sampled one time each between August and November 1997. Water-quality samples were collected during base-flow conditions, at least 72 hours after a rainfall event to ensure that the water collected was representative of ground water. The water quality of springs can vary with time, and a single sample represents conditions only at the time of collection.

Samples from the UTEN Valley and Ridge springs were analyzed for dissolved inorganic constituents, bacteria, and organic compounds. The dissolved inorganic constituents were composed of nutrients and

Table 1. Location and discharge of selected springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[°, degrees; ', minutes; --, missing data]

Spring number	Station number	Spring name	Latitude	Longitude	Flow rate, in cubic feet per second
1	03566875	Ellis Spring at Ringgold, Ga.	34°55'	85°09'	0.50
2	03566446	Carson Spring near Ooltewah, Tenn.	35°07'	85°04'	--
3	03564900	Maynor Spring near Benton, Tenn.	35°09'	84°37'	0.39
4	03565408	McCaslan Spring near Tasso, Tenn.	35°12'	84°47'	0.32
5	03566265	Big Spring at Big Spring, Tenn.	35°23'	84°54'	0.60
6	03566262	Hawk Spring near Hillsview, Tenn.	35°24'	84°49'	0.02
7	03565425	Malone Spring near Niota, Tenn.	35°30'	84°30'	4.30
8	03543020	Ward Spring near Watts Bar, Tenn.	35°36'	84°50'	--
9	03520060	Reed Spring near Philadelphia, Tenn.	35°38'	84°23'	0.07
10	03498993	Pearson Spring at Maryville, Tenn.	35°43'	83°59'	0.77
11	03520230	Barnard Spring near Bacon Gap, Tenn.	35°47'	84°34'	0.07
12	03470200	Rocky Spring at Boyds Creek, Tenn.	35°55'	83°39'	0.10
13	03470100	Bailey Spring near Kodak, Tenn.	35°56'	83°36'	1.20
14	03535088	Unnamed Spring Number 3 to Scarboro Creek near Oak Ridge, Tenn.	35°59'	84°13'	0.04
15	360153083235900	Riley Spring near Dandridge, Tenn.	36°01'	83°24'	0.17
16	035351825	Hunter Spring near Halls Crossroads, Tenn.	36°05'	83°55'	0.08
17	03538175	Shetterly Spring near Clinton, Tenn.	36°05'	84°12'	0.72
18	03466242	Seaton Spring at Pleasant Hill, Tenn.	36°08'	82°38'	0.83
19	03494520	Mitchell Spring near Talbott, Tenn.	36°13'	83°38'	0.08
20	03528420	Nelson Spring at Mill Creek Road at Mill Creek, Tenn.	36°14'	84°00'	0.32
21	03466820	Morelock Spring near Newmansville, Tenn.	36°15'	82°44'	0.10
22	03491910	Dodson Spring near Russellville, Tenn.	36°15'	83°13'	0.62
23	03486175	Jones Spring near College Park, Tenn.	36°16'	82°18'	0.20
24	03465770	Chalybeate Spring near Sulphur Springs, Tenn.	36°20'	82°33'	0.33
25	362528083353001	Ball Creek Spring near Tazewell, Tenn.	36°25'	83°35'	1.53
26	03531810	Mason Spring near Tazewell, Tenn.	36°29'	83°32'	1.40
27	363019083104101	Fall Branch Spring, Sneedville, Tenn.	36°30'	83°10'	0.22
28	03490361	Henderson Spring above Amis Chapel, Tenn.	36°32'	82°47'	0.06
29	03487530	Bright Spring near Mill Point, Tenn.	36°34'	82°19'	0.63
30	364031083040401	Cheek Spring near Jonesville, Va.	36°40'	83°04'	2.08
31	364228082415901	Johnson Spring near Clinchport, Va.	36°42'	82°41'	0.03
32	364729081531101	Yellow Spring near Lindell, Va.	36°47'	81°52'	0.15
33	364754082355701	Brickly Spring near Fort Blackmore, Va.	36°47'	82°35'	0.22
34	365154082150101	Seven Spring near Banners Corner, Va.	36°51'	82°14'	0.19
35	365402081363901	Cave Spring near Broadford, Va.	36°54'	81°36'	0.43

major ions. The nutrients analyses consisted of nitrate (NO₃), ammonia (NH₃), ammonia plus organic nitrogen, total phosphorus, and orthophosphate (PO₄). All nutrient concentrations in this report are reported as nitrogen or phosphorus. Major ions included calcium, magnesium, potassium, silica, sodium, bromide, chloride, fluoride, sulfate, manganese, and iron. The organic compounds consisted of pesticides and VOCs. The pesticide analysis included 77 pesticides and 8 pesticide degradation byproducts, which account for approximately 75 percent of the total amount (by weight) of pesticides used for agriculture in the United States, as well as selected pesticides used in urban and suburban settings (Gilliom, 1998). VOC analysis included 86 volatile organic compounds. Bacteriological samples were analyzed for two types of fecal-indicator bacteria, *Escherichia coli* (*E. coli*) and total coliform. The compounds analyzed in this study were selected to represent the majority of constituents expected to be present in ground water across the Nation.

Water samples were collected and processed using established NAWQA ground-water sampling protocols (Koterba and others, 1995). The sampling lines, the submersible pump, and the plumbing fixtures were made of polytetrafluoroethylene (Teflon) or stainless steel. When collecting the water samples, the pump head was placed as close as possible to the spring orifice. Prior to sample collection, water was pumped until general water-quality constituents (specific conductance, pH, turbidity, and dissolved oxygen) were stable to ensure samples were representative of the ground water issuing from the spring orifice. Samples for inorganic constituents and nutrients were filtered through a disposable 0.45-micron (µm) capsule filter, and cation samples were preserved with nitric acid. Samples for dissolved organic carbon were filtered through a 0.7-µm silver filter, and pesticide samples were filtered through a disposable 0.7-µm glass-fiber filter. Samples collected for VOC analysis were acidified with hydrochloric acid. Nutrient, dissolved organic carbon (DOC), pesticide, and VOC samples were kept chilled and were shipped overnight to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado. Total coliform and *E. coli* fecal-indicator bacteria were cultured in the field using membrane filtration methods (Meyers and Wilde, 1997).

Sample Analysis

Water-quality samples were analyzed at the NWQL, with the exception of fecal-indicator bacteria, which were analyzed in the field. Dissolved inorganic constituents were determined using atomic absorption, inductively coupled plasma, ion chromatography, ion-specific electrodes, and colorimetric methods (Fishman and Friedman, 1989; Fishman, 1993). Pesticides were analyzed by use of two analytical methods for a total of 77 pesticides and 8 degradation byproducts. Compounds were analyzed using gas chromatography/mass spectrometry (GCMS) and high performance liquid chromatography (HPLC). Details of the analytical methods are described by Zaugg and others (1995) and by Werner and others (1996). A purge and trap capillary-column GCMS was used to analyze 86 VOCs (Connor and others, 1998).

Laboratory reporting levels (LRL) for the pesticides and VOCs are as low as 0.001 µg/L, but vary depending 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 and can vary for each compound (Wershaw and others, 1987). Generally, the LRL is twice the MDL, but occasionally the LRL for a sample will be increased because of matrix interference from other compounds in the water sample. Some concentrations are qualified with an "E" indicating an estimated concentration. Concentrations are estimated because they are either above or below the range in concentrations of the calibration standards, and uncertainty is greater in the measurement. Other possible causes for qualifying estimated concentrations include matrix interference, poor surrogate recovery, or required dilution of the sample.

Quality-Control Samples

In addition to the actual samples (referred to as environmental samples), three types of quality-control samples were collected: field blanks, spikes, and replicate samples. About 15 percent of all samples collected were quality-control samples. Blank samples using contaminant-free water were analyzed to test for bias from the introduction of contamination into environmental samples in any stage of the sample collection and analytical process. Spike samples (samples with known amounts of target analytes added to the

environmental sample) were analyzed to test for bias from matrix interference or degradation of analyte concentration during sample processing and analysis. Replicates were used to estimate variability in the collection and analytical processes. These quality-control samples ensured that sampling procedures were non-contaminating and provided information on bias and variability associated with the sampling procedure.

Three field blanks were collected during the study. Field blanks for pesticides and nutrients indicate no contamination from sampling equipment. Major ions detected in field blanks were dissolved iron, silica, calcium, and bromide (table 2). Concentrations of silica and calcium detected in the field blanks were two to three orders of magnitude less than the concentrations in the environmental samples; therefore, the environmental samples are considered to be unaffected by this low level of contamination. Concentrations of iron and bromide were detected in one field blank in the range of detections found in the environmental samples (table 2); therefore, the concentration of these analytes in the environmental samples is questionable. The VOCs detected in field blanks were styrene and toluene (table 2). A source-solution blank (a sample of the VOC-grade water taken directly from the bottle) showed concentrations similar to those in the field blanks, thus the environmental detections for styrene and toluene are considered suspect.

Pesticide and VOC matrix spike samples were collected to analyze for bias resulting from matrix interference or sample degradation. Recovery of compounds in spiked VOC samples generally ranged from 75 to 125 percent, with a median recovery of 92 percent. Two VOCs, vinyl chloride and methyl *tert*-butyl

ether (MTBE), had recoveries of less than 41 percent. Recovery of spiked pesticide compounds ranged from 75 to 125 percent. The median recovery for the pesticides was 87 percent, in which the GCMS method had a median recovery value of 100 percent and the HPLC method had a median recovery of 76 percent. Recoveries of several spiked compounds had considerable and systematic bias. Deethylatrazine, disulfoton, *cis*-permethrin, aldicarb sulfone, chlorothalonil, dichlobenil, 4,6-dinitro-*o*-cresol (DNOC), neburon, oryzalin, and propoxur were all biased low (less of the compound was recovered than expected). Carbaryl and methyl azinphos were biased high on one sample each, whereas *p*'*p*-DDE, phorate, terbufos, methyl azinphos, and clopyralid were biased low on one sample. Deethylatrazine, aldicarb sulfone, chlorothalonil, dichlobenil, DNOC, carbaryl, and methyl azinphos commonly exhibit poor recoveries using these analytical methods (Zaugg and others, 1995).

Three replicate samples were analyzed and indicated good reproducibility of values with little variability associated with sampling methods or sample analysis. A pesticide was detected once in the three replicate samples and demonstrated good replication. The replicate samples also exhibited good reproducibility for major ions, with only minor variations in values for iron, chloride, and manganese. Nutrient results exhibited variations of less than 0.04 mg/L for nitrate and less than 0.01 mg/L for other nutrients. Two VOCs were detected in the replicate samples with a difference between the detections of less than 0.01 µg/L.

Table 2. Dissolved major ions and volatile organic compounds detected in field blanks

[mg/L, milligrams per liter; µg/L, micrograms per liter]

Constituent	Field blanks		Environmental samples		
	Number of detections	Maximum concentration	Number of detections	Minimum concentration	Maximum concentration
Iron	1	5.1 mg/L	6	3.3 mg/L	34 mg/L
Silica	1	0.02 mg/L	30	4.5 mg/L	10 mg/L
Calcium	2	0.034 mg/L	30	21 mg/L	98 mg/L
Bromide	1	0.038 mg/L	29	0.01 mg/L	0.039 mg/L
Styrene	3	0.046 µg/L	12	0.004 µg/L	0.037 µg/L
Toluene	1	0.123 µg/L	7	0.01 µg/L	0.125 µg/L

WATER QUALITY OF SPRINGS IN THE VALLEY AND RIDGE PHYSIOGRAPHIC PROVINCE

Water-quality samples were collected at 35 springs discharging from carbonate-rock units in the UTEN Valley and Ridge. Discharge from the springs (table 1) ranged from 0.02 to 4.30 ft³/s, with a median value of 0.32 ft³/s. Water from the springs has similar ionic characteristics and is predominantly a calcium bicarbonate type. The largest variation in the ionic composition was the amount of magnesium in the samples, which can be attributed to the amount of dolomite in the recharge area for the springs. The pH, specific conductance, and alkalinity measured in the springs (table 3) were all within ranges expected for springs in carbonate units, and were similar to measurements in surface water in the region (Flohr and others, 1998).

Nutrients

Low concentrations of nitrogen and phosphorus are present naturally in surface and ground water, but

elevated concentrations are commonly associated with human activities. Nitrogen and phosphorus are found in fertilizers, animal waste, human waste, and, to some degree, in atmospheric deposition. Leaching of fertilizers from agricultural areas or infiltration of septic-system effluent can result in elevated nitrogen and phosphorus concentrations in ground water (Barrett and Charbeneau, 1996). Total nitrogen and phosphorus concentrations in surface water in the UTEN were high for sites with high percentages of urban or agricultural land uses and low for sites draining predominantly forested watersheds (Treece and Johnson, 1997; Johnson and Treece, 1998).

Nitrate is the nutrient that most commonly has adverse effects on ground-water quality nationwide, and has a U.S. Environmental Protection Agency (U.S. EPA) drinking-water maximum contaminant level (MCL) of 10 mg/L. Nationally, natural concentrations for nitrate in ground water are usually less than 2 mg/L (Mueller and others, 1995); however, natural or background nitrate concentrations are highly variable and are dependent on many local and regional factors, such as geology, interaction with the atmosphere, and biological processes. Nitrate concentrations in the UTEN Valley and Ridge springs ranged from 0.091 to 2.17 mg/L, with a median concentration of 1.16 mg/L. The median nitrate concentration for the springs was greater than the median values for other NAWQA aquifer studies from 1993 to 1999 (Tom Noland, U.S. Geological Survey, written commun., 2001) (table 4), but are below typical background concentrations.

Studies in the southeastern and northeastern regions of the United States have shown that springs in agricultural areas have nitrate levels above background levels, and in general, nitrate levels in springs are higher than in wells in the same land-use settings. In the Ozark Plateaus Physiographic Province, 91 springs and 89 wells were sampled as part of the NAWQA Ozark Plateaus study unit survey and 2 land use surveys. The median nitrate concentration of the springs (2.6 mg/L) was higher than samples collected from the wells (1.0 mg/L). Land use around the springs was not statistically different from the wells, and field measurements indicate

Table 3. Field constituents and concentration of dissolved major ions for springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[CaCO₃, calcium carbonate; μS/cm, microsiemens per centimeter; μg/L, micrograms per liter; mg/L milligrams per liter; *, one quality-assurance blank showed a possibility of contamination for these constituents; <, less than]

Constituent	Minimum	Median	Maximum
Alkalinity (mg/L as CaCO ₃)	60	159	238
Dissolved oxygen (mg/L)	1.5	7.1	9.8
pH	6.7	7.1	7.8
Specific conductance (μS/cm)	132	310	501
Calcium (mg/L)	21	42	98
Magnesium (mg/L)	2.5	16	26
Potassium (mg/L)	0.5	1.2	2.8
Silica (mg/L)	4.5	8.3	10
Sodium (mg/L)	0.4	1.1	5.3
Bromide (mg/L)*	<0.01	0.21	0.04
Chloride (mg/L)	0.7	2.3	8.9
Fluoride (mg/L)	<0.1	<0.1	0.2
Sulfate (mg/L)	1.0	2.4	66
Manganese (μg/L)	<1.0	<1.0	144
Iron (μg/L)*	<3.0	<3.0	34

Table 4. Dissolved nutrient data summary for National Water-Quality Assessment Program wells nationwide and for springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[N, nitrogen; P, phosphorus; units in milligrams per liter; <, indicates values less than the reporting limit]

Parameter	National study-unit survey wells				UTEN springs (35 samples)		
	Minimum	Median	Maximum	Number of samples	Minimum	Median	Maximum
Ammonia, as N	<0.015	0.024	2.70	1,820 ^b	<0.015	<0.015	0.078
Ammonia plus organic nitrogen, as N	<0.200	<0.200	5.50	910 ^a	<0.200	<0.200	1.50
Nitrate, as N	<0.050	0.395	6.60	1,823 ^b	0.091	1.16	2.17
Total phosphorus, as P	<0.010	0.020	2.20	911 ^a	<0.010	<0.010	0.054
Orthophosphate, as P	<0.010	0.0125	0.18	1,819 ^b	<0.010	<0.010	0.027

^a Data from 1993 to 1995 (Hitt, 1999)

^b Data from 1993 to 1999 (Tom Noland, U.S. Geological Survey, written commun., 2001)

that water issuing from springs generally interacts less with the aquifer, following more shallow flowpaths along fractures and solution openings (Adamski, 1997). Twenty-four springs in agricultural areas in Florida had nitrate values ranging from 2.7 to 10.6 mg/L with a median value of 5.4 mg/L (Katz and others, 1999). In Illinois, 10 karst springs in agricultural areas were sampled, and 39 of 40 samples exceeded background nitrate levels of 1.4 mg/L, however, none exceeded the MCL. Seven springs sampled in non-agricultural areas were all below background levels (Webb and others, 1997). In the UTEN Valley and Ridge, ground-water samples from 30 wells had a lower median nitrate concentration (0.59 mg/L) than the springs (1.16 mg/L) where the springs and wells were in a similar land-use setting (Hampson and others, 2000).

In the Valley and Ridge springs, concentrations of the reduced nitrogen species (ammonia and ammonia plus organic nitrogen) were less than 0.200 mg/L in samples from all sites except one spring, which had a concentration of 1.50 mg/L (table 4). Concentrations of reduced nitrogen species would be expected to be low in a karst setting because of relatively high levels of dissolved oxygen. The median dissolved oxygen concentration in the UTEN Valley and Ridge springs was 7.1 mg/L (table 3). The presence of ammonia in the ground water may be the result of urea or animal waste applied to agricultural fields, from ammonia used directly as fertilizer, or from other sources. Ammonia was detected at 5 sites with a maximum concentration of 0.078 mg/L, whereas the remaining 30 sites had concentrations less than 0.015 mg/L

(table 4). The median concentrations of ammonia for the UTEN Valley and Ridge springs was less than the median concentration in ground water from wells for other NAWQA aquifer studies (table 4).

Phosphorus is an essential nutrient that can be found in fertilizers, manures, detergents, and atmospheric deposition (Likens and Bormann, 1995). Phosphorus is a common element in igneous rock and sediments, but concentrations present in solution in natural water are normally no more than a few tenths of a milligram per liter (Hem, 1985). Phosphorus is less mobile than nitrogen in the subsurface and tends to sorb to soil particles and soil organic matter. Total phosphorus was detected in only 6 of the 35 samples collected. Concentrations of total phosphorus ranged from less than 0.010 mg/L to 0.054 mg/L with a median of less than 0.010 mg/L. Orthophosphate was detected in 9 of the 35 samples, and concentrations ranged from less than 0.010 to 0.027 mg/L with a median value of less than 0.010 mg/L. Phosphorus concentrations in the UTEN Valley and Ridge springs were less than concentrations in ground water from other NAWQA study units (table 4).

Bacteria

Bacterial, viral, and protozoan pathogens are among the most dangerous contaminants in drinking water. About 50 percent of the waterborne-disease outbreaks in this country since the early 1900s were caused by contaminated ground water that was untreated or inadequately treated. Most of these

outbreaks were caused by pathogenic (disease-causing) microorganisms (Yates and Yates, 1993). A common misconception is that untreated ground water is generally safe for consumptive use, and that most contaminants are removed as the water filters down through the soil. The soil does act as a natural filter for water percolating down through the ground, but this does not guarantee that ground-water supplies cannot become contaminated (Bickford and others, 1996).

Water samples from each spring were analyzed for two types of fecal-indicator bacteria—*E. coli* and total coliform. Fecal-indicator bacteria are used to assess the quality of water because they are associated with the presence of several waterborne pathogens (Dufour, 1977). The concentration of fecal-indicator bacteria is a measure of water safety for body-contact recreation or for consumption. The presence of *E. coli* in water is direct evidence of fecal contamination from warmblooded animals and indicates the possible presence of pathogens (Dufour, 1977). For potable waters, the detection of as few as 4 total coliform col/100 mL, and the detection of 1 col/100 mL of *E. coli* warrant concern for public health (U.S. Environmental Protection Agency, 1986). *E. Coli* is one of the preferred fecal-indicator bacteria as predictors of swimming-associated gastroenteritis in marine and freshwater settings.

All of the springs sampled had fecal-indicator bacteria present, indicating the possibility of fecal contamination. Total coliform values ranged from 10 to 1,900 col/100 mL (table 5), and *E. coli* values in the springs ranged from less than 1 to 660 col/100 mL. Of the 35 springs sampled, 91 percent of the springs had some level of *E. coli*, and all springs had total coliform present. Although private drinking-water supplies are not regulated, the presence of total coliform and *E. coli* in all of the springs sampled exceeded drinking-water standards for public water systems.

In comparison, bacteriological samples were collected at 30 randomly selected wells in similar land use and geological settings in the UTEN Valley and Ridge between September 1998 and February 1999 (Hampson and others, 2000). The samples from these wells had detections of *E. coli* in 9 wells (30 percent) ranging from 1 to 1,200 col/100 mL and total coliform at 11 wells (37 percent) ranging from 5 to 1,600 col/100 mL. These results indicate that these domestic and public water-supply wells are generally less susceptible to bacteriological contamination than are the springs.

Only one water sample was taken at each spring and well, representing water-quality conditions at the time of the sample collection. Bacteria levels can vary over time due to many factors, including rainfall and temperature variations, antecedent soil-moisture conditions, and land-use activities in the recharge area. Of 25 springs sampled in Kentucky, fecal coliform levels indicated seasonal variations of average monthly concentrations from about 70 to 300 col/100 mL. More than 90 percent of the Kentucky springs showed the presence of bacteria from May to June 1995 (O'Dell, 1996). Temporal variation in bacteria concentrations also were noted in ground-water samples in Bedford County in Middle Tennessee (Roman-Mas and others, 1991; Bennett, 1997). Bedford County has thin soils, open fractures, sinkholes, and rapid movement of contaminants in the subsurface. Agricultural activities such as applying manure, the variation of animal populations in feedlots or other livestock operations, as well as failing septic systems, are all potential sources of bacteriological contamination that are subject to temporal variations.

Pesticides

Pesticides were detected frequently at low concentrations (less than 0.01 µg/L) in water samples from springs in the UTEN Valley and Ridge (table 6). Six pesticides and 2 degradation byproducts were detected in samples from 35 springs in the UTEN Valley and Ridge (table 6); however, 71 other pesticides and 6 degradation byproducts were analyzed for but were not detected in any of the springs (table 7). Pesticides were not detected at 11 springs; whereas, 1 to 6 pesticides or degradation byproducts were detected at 24 springs (fig. 5). Of the 8 pesticides and degradation byproducts detected, 7 have at least one of the following established regulations or criteria: the U.S. EPA's MCL; health advisory level (HA-L); risk-specific lifetime dose (RSD) at a cancer risk level of 1 in 100,000; or the Canadian aquatic-life criterion (CALC) (Gilliom, 1999). Concentrations for all of the pesticides detected in the springs were below current drinking-water standards; some detections were below the LRL and were reported as estimated concentrations.

The most frequently detected pesticides in the UTEN Valley and Ridge spring samples (fig. 6, table 6) were atrazine (57 percent of springs), deethyl-atrazine (atrazine-degradation byproduct) (54 percent), tebuthiuron (31 percent), prometon (17 percent),

Table 5. Bacteriological results for springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[<, less than]

Spring no.	Spring name	Total coliform colonies per 100 milliliters	<i>Escherichia coli</i> colonies per 100 milliliters
1	Ellis Spring at Ringgold, Ga.	50	6
2	Carson Spring near Ooltewah, Tenn.	19	2
3	Maynor Spring near Benton, Tenn.	640	23
4	McCaslan Spring near Tasso, Tenn.	260	20
5	Big Spring at Big Spring, Tenn.	21	3
6	Hawk Spring near Hillsview, Tenn.	570	250
7	Malone Spring near Niota, Tenn.	100	4
8	Ward Spring near Watts Bar, Tenn.	57	16
9	Reed Spring near Philadelphia, Tenn.	330	35
10	Pearson Spring at Maryville, Tenn.	130	7
11	Barnard Spring near Bacon Gap, Tenn.	220	4
12	Rocky Spring at Boyds Creek, Tenn.	30	3
13	Bailey Spring near Kodak, Tenn.	63	3
14	Unnamed Spring Number 3 to Scarboro Creek near Oak Ridge, Tenn.	120	19
15	Riley Spring near Dandridge, Tenn.	37	11
16	Hunter Spring near Halls Crossroad, Tenn.	1,900	52
17	Shetterly Spring near Clinton, Tenn.	510	3
18	Seaton Spring at Pleasant Hill, Tenn.	12	<1
19	Mitchell Spring near Talbott, Tenn.	200	110
20	Nelson Spring at Mill Creek Road at Mill Creek, Tenn.	230	13
21	Morelock Spring near Newmansville, Tenn.	63	6
22	Dodson Spring near Russellville, Tenn.	270	16
23	Jones Spring near College Park, Tenn.	1,600	1
24	Chalybeate Spring near Sulphur Springs, Tenn.	1,400	88
25	Ball Creek Spring near Tazewell, Tenn.	800	660
26	Mason Spring near Tazewell, Tenn.	35	3
27	Fall Branch Spring, Sneedville, Tenn.	12	1
28	Henderson Spring above Amis Chapel, Tenn.	220	17
29	Bright Spring near Mill Point, Tenn.	130	13
30	Cheek Spring near Jonesville, Va.	14	<1
31	Johnson Spring near Clinchport, Va.	78	11
32	Yellow Spring near Lindell, Va.	240	<1
33	Brickly Spring near Fort Blackmore, Va.	79	6
34	Seven Spring near Banners Corner, Va.	10	1
35	Cave Spring near Broadford, Va.	300	37

Table 6. Pesticides detected in springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[LRL, laboratory reporting level; MCL, maximum contaminant level; HA-L, health advisory level; RSD, risk-specific lifetime dose at a cancer risk level of 1 in 100,000; CALC, Canadian aquatic-life criterion; µg/L, micrograms per liter; --, not reported; E, estimated value]

Pesticides and degradation byproducts	Type	LRL (µg/L)	Human and Aquatic Health criterion ^a (µg/L)	Estimated pounds applied in 1992 ^b	Percent (and number) of samples with detections	Percent (and number) of samples above 0.01 µg/L	Maximum concentration (µg/L)
Alachlor	Herbicide	0.0024	2.0 (MCL)	31,100	3 (1)	0	E 0.003
Atrazine	Herbicide	0.007	3.0 (MCL) 1.8 (CALC)	88,160	57 (20)	20 (7)	0.063
Deethylatrazine	Herbicide degradate	0.006	--	--	54 (19)	17 (6)	0.018
Metolachlor	Herbicide	0.013	70 (HA-L)	35,200	11 (4)	3 (1)	0.021
<i>p,p'</i> -DDE	Insecticide degradate	0.0025	1 (RSD)	--	3 (1)	0	E 0.001
Prometon	Herbicide	0.015	100 (HA-L)	--	17 (6)	3 (1)	0.023
Simazine	Herbicide	0.011	4 (MCL) 10 (CALC)	18,100	9 (3)	0	E 0.006
Tebuthiuron	Herbicide	0.016	500 (HA-L) 1.6 (CALC)	--	31 (11)	20 (7)	0.539

^a From Gilliom, 1999, ^b From Majewski, 1997

simazine (9 percent), and metolachlor (11 percent). The remaining pesticide and degradation byproducts (alachlor and *p,p'*-DDE) were detected only once. Five pesticides or degradation byproducts were detected above a common threshold of 0.01 µg/L: atrazine (20 percent of springs), tebuthiuron (20 percent), deethylatrazine (17 percent), prometon (3 percent), and metolachlor (3 percent) (table 6).

Pesticides were detected more frequently in the UTEN Valley and Ridge springs than in 1,848 groundwater samples from wells in similar NAWQA studies across the Nation (fig. 6) (Kolpin, 2000). Atrazine and deethylatrazine were detected at least twice as frequently in the UTEN Valley and Ridge springs than nationwide; however, concentrations were less than 0.1 µg/L in all water samples in the UTEN Valley and Ridge springs, whereas about 4 percent of samples nationwide exceeded 0.1 µg/L. Tebuthiuron was detected in the UTEN Valley and Ridge springs at substantially higher frequencies at all screening levels. Prometon and metolachlor were detected in the UTEN Valley and Ridge springs more frequently than nationwide at levels below 0.01 µg/L, and at similar detec-

tion frequencies above 0.01 µg/L. Alachlor and simazine also were detected more frequently in the UTEN Valley and Ridge springs at levels below 0.01 µg/L, but a greater frequency was detected nationwide at levels above 0.01 µg/L. Concentrations of *p,p'*-DDE were found at similar detection frequencies in the UTEN Valley and Ridge springs and nationwide.

For comparison, pesticide samples also were collected at 30 randomly selected wells in similar land-use and geological settings in the UTEN Valley and Ridge between September 1998 and February 1999 (Hampson and others, 2000). Water samples from these wells contained pesticides similar to those detected in the springs but at lower detection frequencies. Atrazine, deethylatrazine, tebuthiuron, prometon, metolachlor, and simazine were all detected less frequently in the UTEN wells than in the springs, but the detection frequency was higher for wells than the detection frequency for other NAWQA studies.

Results from 20 NAWQA study units, from 1993 to 1995, indicate that the greatest frequency of herbicide detections in major aquifers occurred in

Table 7. Pesticides not detected in springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

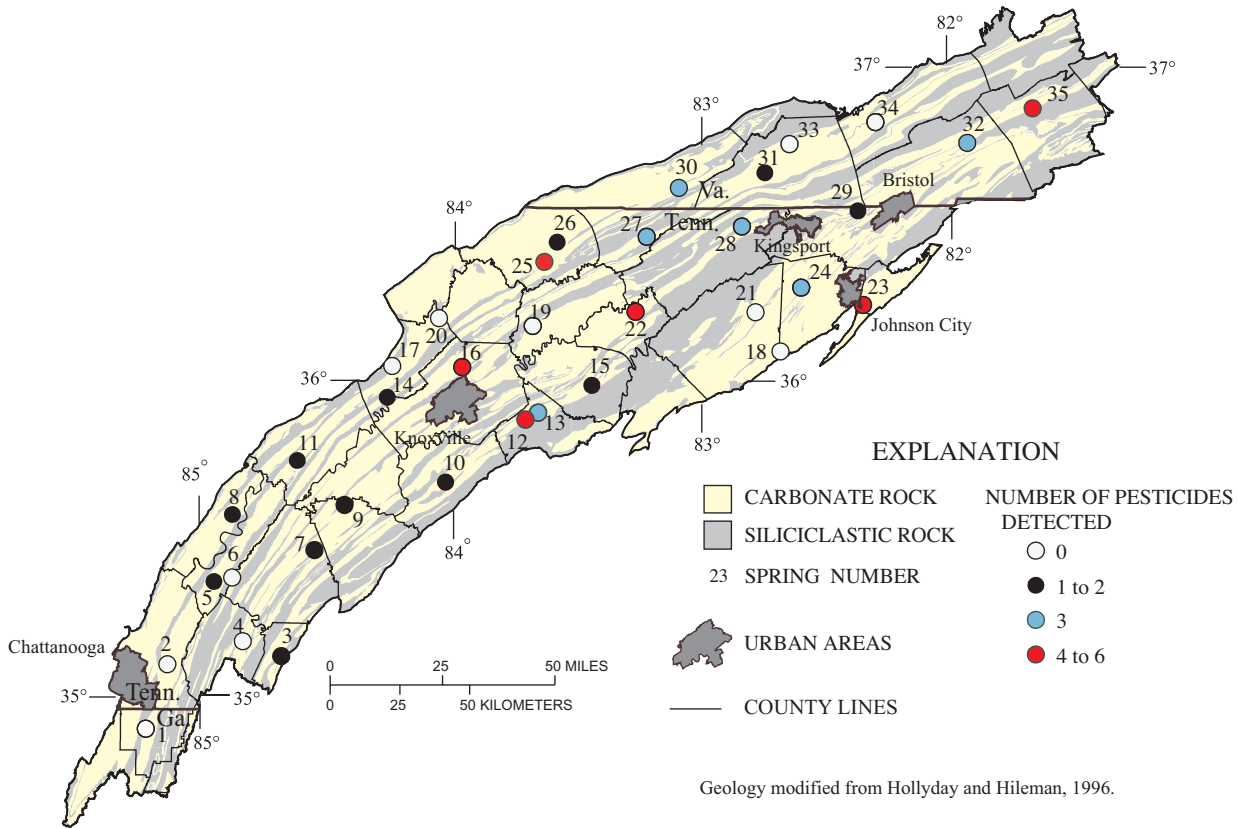
[LRL, laboratory reporting level, in micrograms per liter; <, less than; --, not reported]

Pesticide	Type	LRL	Estimated pounds applied in 1992 ^a
2,4-D	Herbicide	0.110	33,400
Pebulate	Herbicide	0.0016	23,900
Pendimethilin	Herbicide	0.010	20,700
Butylate	Herbicide	0.002	18,800
Cyanazine	Herbicide	0.018	11,200
Napropamide	Herbicide	0.007	9,500
Dicamba	Herbicide	0.043	4,370
2,4-DB	Herbicide	0.100	4,060
Diuron	Herbicide	0.056	2,540
Trifluralin	Herbicide	0.009	2,500
Terbacil	Herbicide	0.034	1,790
Triclopyr	Herbicide	0.070	1,540
Metribuzin	Herbicide	0.006	1,980
Bentazon	Herbicide	0.035	1,310
Linuron	Herbicide	0.021	860
Oryzalin	Herbicide	0.028	710
Ethalfuralin	Herbicide	0.009	370
Norflurazon	Herbicide	0.042	300
Chloramben, methylester	Herbicide	0.140	280
Dichlobenil	Herbicide	0.049	170
Bromoxynil	Herbicide	0.070	<10
MCPA	Herbicide	0.080	<10
2,6-Diethylaniline	Herbicide	0.0017	--
	degradate		
2,4,5-T	Herbicide	0.040	--
2,4,5-TP (silvex)	Herbicide	0.025	--
Acetochlor	Herbicide	0.0041	--
Acifluorfen	Herbicide	0.050	
Benfluralin	Herbicide	0.010	--
Bromacil	Herbicide	0.090	--
Clopyralid	Herbicide	0.420	--
Dacthal (DCPA)	Herbicide	0.003	--
Dacthal, mono acid	Herbicide	0.070	--
Dichlorprop	Herbicide	0.050	--
Dinoseb	Herbicide	0.090	--
DNOC	Herbicide	0.250	--
EPTC	Herbicide	0.002	--
Fenuron	Herbicide	0.070	--
Fluometuron	Herbicide	0.060	
Linuron	Herbicide	0.021	--
MCPB	Herbicide	0.130	--

Table 7. Pesticides not detected in springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin—Continued

Pesticide	Type	LRL	Estimated pounds applied in 1992 ^a
Methiocarb	Herbicide	0.070	--
Molinate	Herbicide	0.0016	--
Neburon	Herbicide	0.017	--
Picloram	Herbicide	0.090	--
Propachlor	Herbicide	0.010	--
Propanil	Herbicide	0.011	--
Propham	Herbicide	0.090	--
Propzamide	Herbicide	0.0041	--
Thiobencarb	Herbicide	0.0048	--
Triallate	Herbicide	0.0023	--
Chlorpyrifos	Insecticide	0.005	54,300
Carbaryl	Insecticide	0.024	20,700
Carbofuran	Insecticide	0.020	12,900
Aldicarb	Insecticide	0.210	7,530
Methomyl	Insecticide	0.020	6,030
Ethoprophos	Insecticide	0.005	5,900
Methyl parathion	Insecticide	0.006	2,260
Diazinon	Insecticide	0.005	1,970
Disulfoton	Insecticide	0.021	1,950
Propargite	Insecticide	0.023	1,820
Terbufos	Insecticide	0.017	1,360
<i>cis</i> -Permethrin	Insecticide	0.006	1,200
Malathion	Insecticide	0.027	930
Oxamyl	Insecticide	0.020	520
Phorate	Insecticide	0.011	440
Fonofos	Insecticide	0.0027	230
Lindane	Insecticide	0.004	10
1-Naphthol	Insecticide	0.007	--
	degradate		
3-Hydroxycarbofuran	Insecticide	0.110	--
	degradate		
Aldicarb sulfone	Insecticide	0.200	--
	degradate		
Aldicarb sulfoxide	Insecticide	0.020	--
	degradate		
Methyl azinphos	Insecticide	0.050	--
Dieldrin	Insecticide	0.0048	--
HCH, alpha	Insecticide	0.0046	--
	degradate		
Parathion	Insecticide	0.007	--
Propoxur	Insecticide	0.120	--
Chlorothalonil	Fungicide	0.130	9,800

^a From Majewski, 1997



Base from U.S. Geological Survey digital data, 1:250,000; and U.S. Department of Commerce 1:100,000, 1993

Figure 5. Pesticides detected in springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin.

vulnerable settings. The three aquifers with the highest frequency of detections were (1) the Platte River Alluvial aquifer, a shallow aquifer overlain by permeable sandy soils, in the Central Nebraska Basins (92.6 percent); (2) the Upper Floridan aquifer, a limestone formation in which flow rates are high, in the Appalachicola-Chattahoochee-Flint River Basin (80 percent); and (3) a shallow limestone aquifer in the Lower Susquehanna River Basin (83 percent) (U.S. Geological Survey, 1999). In comparison, the UTEN Valley and Ridge springs had a 69-percent herbicide detection frequency. The UTEN Valley and Ridge is underlain by weathered limestone and dolomite formations and is equally vulnerable to contamination, but the UTEN area is subject to less intense agricultural production than the three aforementioned aquifers.

The two most commonly detected pesticides in the UTEN Valley and Ridge springs are atrazine and tebuthiuron. Atrazine is an herbicide used to control broadleaf and grassy weeds on corn, sorghum, Christ-

mas trees, and other crops. Atrazine also is used as a nonselective herbicide on industrial and fallow lands. Atrazine has been the most extensively used pesticide in the United States since the early 1970s and has been the most frequently detected pesticide reported in ground water during many previous state, regional, and national studies (Kolpin and others, 1998). Atrazine and its degradation byproducts also are the most commonly detected pesticide compounds in the surface waters of the UTEN, present at over 90 percent of the surface-water sites (M.W. Treece, U.S. Geological Survey, written commun., 2001).

Tebuthiuron is a broad-spectrum, nonselective, soil-activated herbicide that acts by inhibiting photosynthesis. Tebuthiuron is used to control broadleaf and woody weeds, grasses, and brush on pasture and rangeland and on a variety of nonfood crop sites including industrial areas, rights-of-way, fence lines, hedgerows, and uncultivated areas. Primary uses include rangeland and near railroads and other industrial facilities (U.S. Environmental Protection Agency,

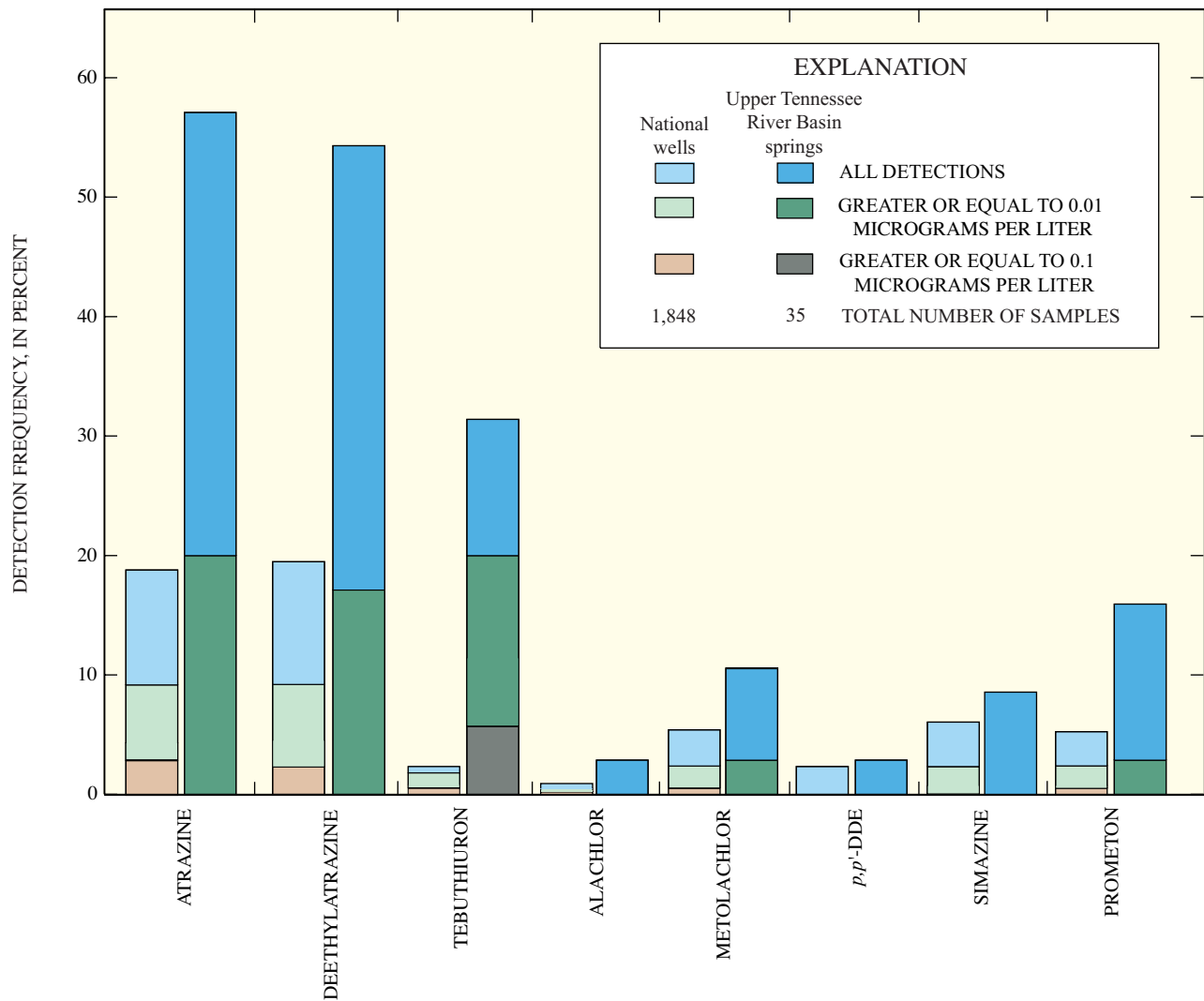


Figure 6. Detection frequency of pesticides for springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin and National Water-Quality Assessment Program wells nationwide from 1993 to 1998.

1994). Tebuthiuron is highly persistent and easily moves with moisture through the soil. Photodecomposition of tebuthiuron is negligible, as is volatilization (or evaporation from the soil surface). Tebuthiuron is readily absorbed through roots and translocated to other plant parts (Extension Toxicology Network, 1996).

Volatile Organic Compounds

Volatile organic compounds include components of petroleum products, metal degreasers, solvents, refrigerants, cleaning compounds, and agricultural fumigants. VOCs also are present in fuels and exhaust from fuel combustion. Direct industrial

and wastewater discharges into surface water and the atmosphere and accidental fuel and oil spills are likely sources of VOCs in ground water. VOCs in rainfall may originate from vehicle and industrial emissions. Storm-water runoff is another possible source of VOC detections in springs. Relating land uses to specific compounds is difficult because of the varied and widespread use of VOCs, as well as the possibility of atmospheric deposition.

Twenty-two VOCs (table 8) were detected in water samples from 30 of the 35 springs (fig. 7), with as many as 9 VOCs detected at 2 springs. Most of the VOC detections were below the LRL (table 8). The most frequently detected VOC was chloroform, which was detected in 20 springs and exceeded the LRL at

Table 8. Summary of volatile organic compound detections for 35 springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin

[Units are in micrograms per liter; --, no applicable standard; MCL, maximum contaminant level; HA-L, health advisory level; LRL, laboratory reporting level; *, quality-assurance blanks showed a possibility of contamination for these constituents]

Constituent	Total number of detections (Number of detections above LRL)	Laboratory reporting level (LRL)	Maximum concentration	Lifetime HA-L ^{a,b}	MCL ^{a,c}
Chloroform	20 (5)	0.052	1.320	--	100 ^d
Methyl chloride	18 (0)	0.254	0.09	3	--
Styrene *	12 (0)	0.042	0.037	100	100
Tetrachloroethene	11 (1)	0.038	0.284	--	5
Toluene *	7 (4)	0.038	0.125	1,000	1,000
1,1,1-Trichloroethane	7 (2)	0.032	0.229	--	200
Trichloroethene	5 (1)	0.038	0.509	--	5
1,1-Dichloroethane	3 (2)	0.066	0.576	--	--
Bromodichloromethane	3 (1)	0.048	0.080	--	100 ^d
<i>cis</i> -1,2-Dichloroethene	2 (1)	0.033	0.08	--	70
Carbon disulfide	2 (0)	0.08	0.020	--	--
Dichlorodifluoromethane	2 (0)	0.096	0.04	1,000	--
1,4-Dichlorobenzene	2 (0)	0.05	0.009	--	4
Freon -113	2 (0)	0.032	0.02	--	--
Metapara xylene	1 (0)	0.064	0.018	10,000 ^e	10,000 ^e
tert-Pentyl methyl ether	1 (1)	0.112	0.17	--	--
Methyl <i>tert</i> -butyl ether (MTBE)	1 (1)	0.112	9.51	20	--
1,1-Dichloroethene	1 (1)	0.044	0.06	--	7
Benzene	1 (0)	0.032	0.010	--	5
Chloroethane	1 (0)	0.12	0.07	--	--
Diisopropyl ether	1 (0)	0.098	0.05	--	--
Ethylether	1 (0)	0.17	0.061	--	--

^a U.S. Environmental Protection Agency (1996) drinking-water regulations and health advisories.

^b Drinking-water lifetime health advisory level (HA-L). The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects over a lifetime of exposure, with a margin of safety.

^c Maximum contaminant level (MCL). Maximum permissible level of a contaminant in water which is deliverable to any user of a public water-supply system (U.S. Environmental Protection Agency, 1996)

^d Total for all trihalomethanes combined cannot exceed 100 micrograms per liter.

^e Guidelines are for total xylene.

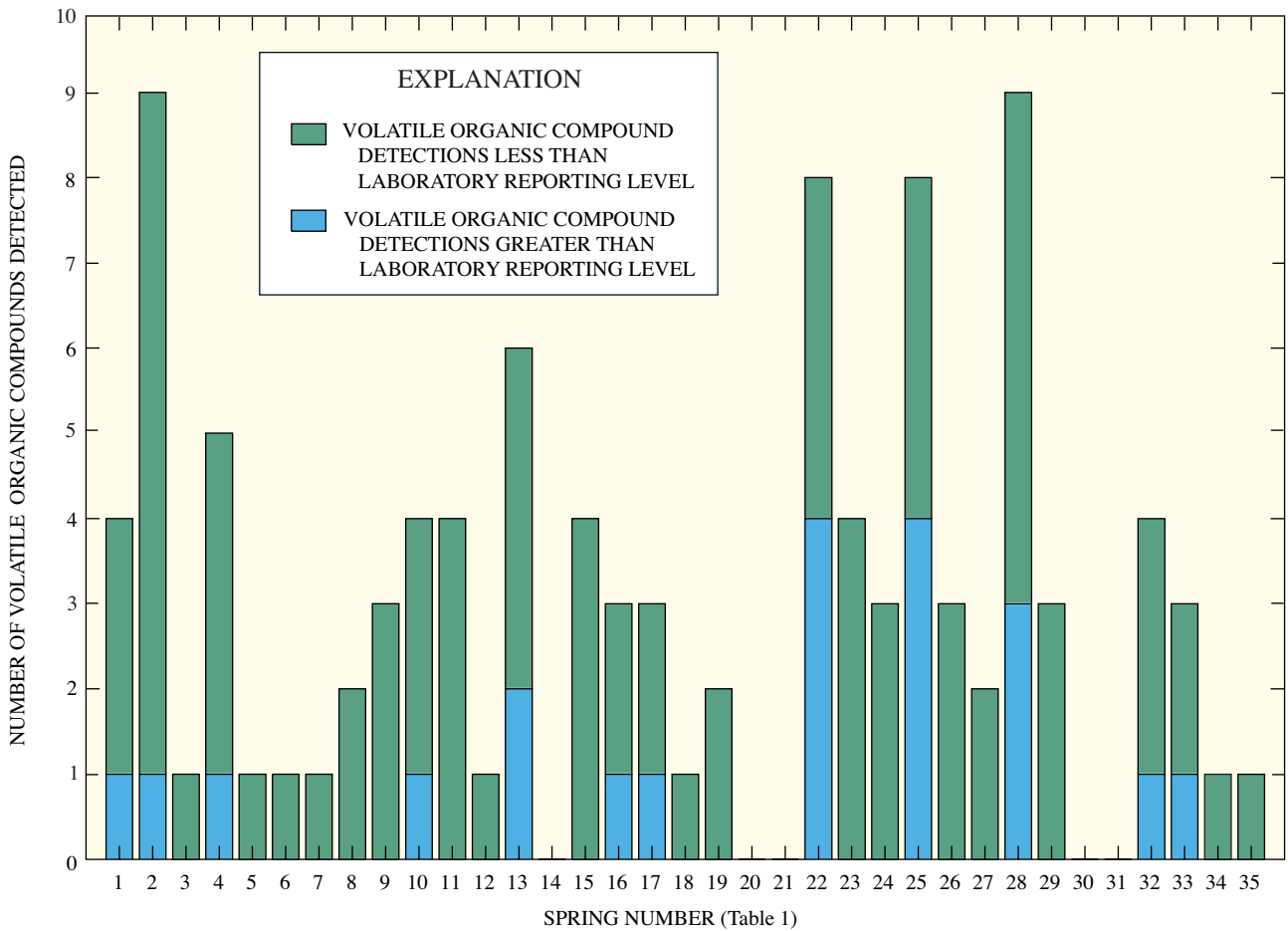


Figure 7. Number of volatile organic compounds detected in springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin.

5 springs (table 8). Other frequently detected VOCs were methyl chloride (18 detections), tetrachloroethene (11 detections), 1,1,1-trichloroethane (7 detections), and trichloroethene, (5 detections) (table 8). Styrene and toluene also were detected frequently, but the validity of those results is suspect because these compounds were detected in blank samples.

None of the VOCs detected in the UTEN Valley and Ridge springs exceeded established drinking-water standards or advisories (table 8). Detection frequencies for VOCs above 0.2 µg/L in the UTEN are similar to the detection frequencies for ground water nationwide (fig. 8) (Squillace and others, 1999; Michael J. Moran, U.S. Geological Survey, written commun., 2001). The detection frequencies for VOCs in the UTEN Valley and Ridge springs generally are between the national detection frequencies for wells in urban settings and wells in rural settings (fig. 8). Land

use in the area surrounding the springs includes a mixture of urban, agricultural, and forest.

SUMMARY

Water-quality data for nutrients, fecal-indicator bacteria, pesticides, and volatile organic compounds (VOCs) were collected at 35 randomly selected springs in the UTEN Valley and Ridge Physiographic Province. The karst hydrology in the carbonate rock units of the UTEN study area can provide rapid pathways for contaminants to enter the ground water by direct runoff through sinkholes and other karst features.

Samples from the springs were analyzed for nutrients including nitrate, ammonia, ammonia plus organic nitrogen, total phosphorus, and orthophosphate. Nutrient concentrations in the springs generally were less than 2 mg/L. Nitrate was the most

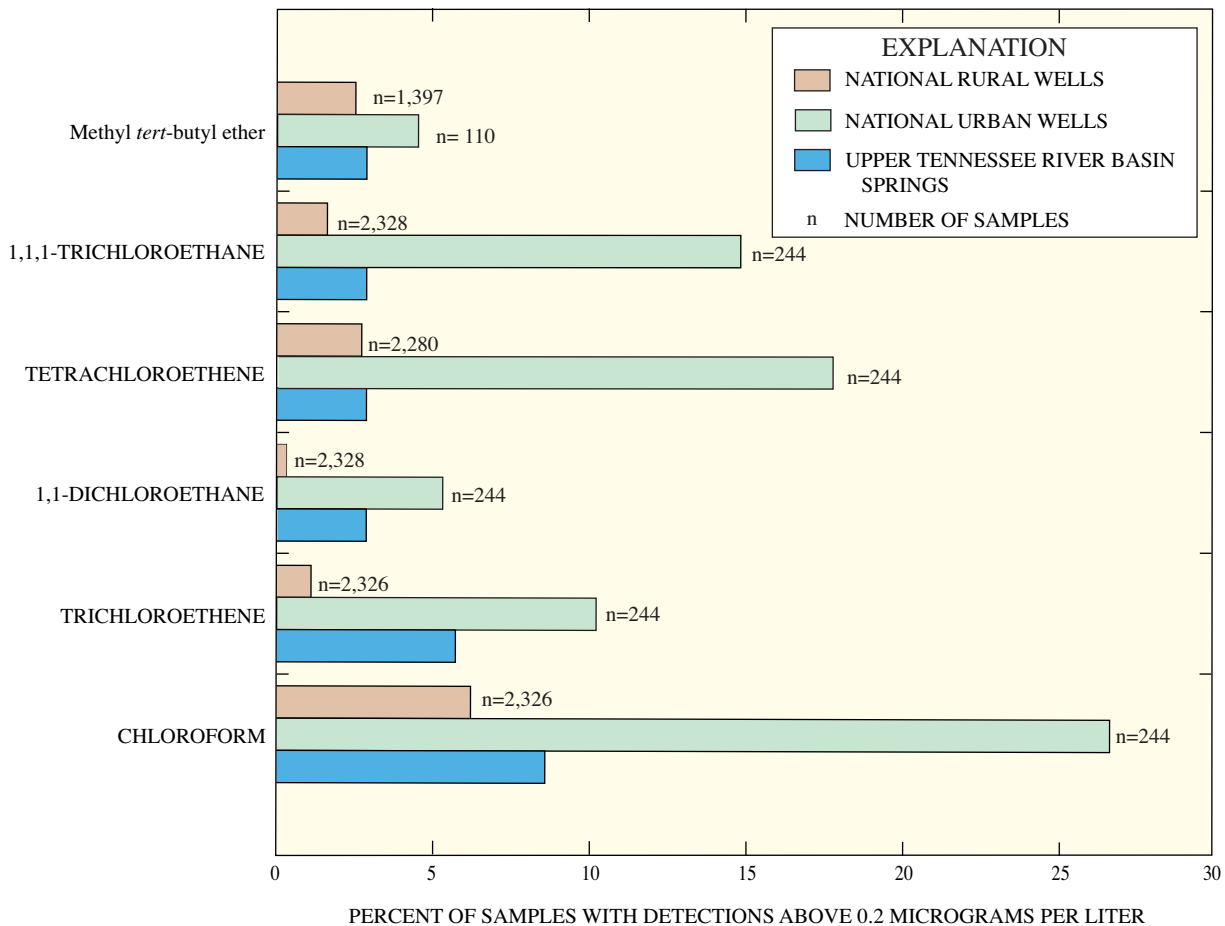


Figure 8. Volatile organic compound detections above 0.2 micrograms per liter for springs in the Valley and Ridge Physiographic Province in the upper Tennessee River Basin and National Water-Quality Assessment Program wells in rural and urban settings nationwide from 1993 to 1998.

commonly detected nutrient species and ranged from 0.091 to 2.17 mg/L, with a median concentration of 1.16 mg/L. The median nitrate concentration for the springs was greater than median values found in ground water for other similar NAWQA aquifer studies. During other studies in the southeastern and northeastern United States, higher nitrate levels have been detected in springs in agricultural areas compared to springs in other land-use settings, and higher nutrient levels have been detected in springs compared to wells in similar land-use settings.

Bacteriological contamination of waters in karst settings is of particular concern. Almost half of the springs in the study area were used as untreated drinking-water supplies, either by directly pumping from the spring or as roadside filling sites. Fecal-indicator bacteria were detected at all springs, with total coliform ranging from 10 to 1,900 col/100 mL

and *E. coli* ranging from less than 1 to 660 col/100 mL. All springs sampled had bacteriological levels that warrant concern. Although private drinking-water supplies are not regulated, the presence of total coliform and *E. coli* in all of the sampled springs exceeded drinking-water standards for public water systems. The high concentrations detected in some springs can be a health risk.

Pesticides were detected frequently at low concentrations in the springs. Eight pesticides or degradation byproducts were detected in samples from springs in the UTEN Valley and Ridge. Eleven springs had no pesticides detected. The remaining 24 springs had 1 to 6 pesticides or degradation byproducts detected. All pesticide concentrations were below their respective MCLs. The detection frequency for a number of pesticides was greater than the detection frequency for

ground-water samples from wells in similar NAWQA studies.

Twenty-two VOCs were detected in water samples from 30 of the 35 springs, with as many as 9 different VOCs detected at 2 springs. Concentrations of VOCs were less than their respective MCLs, and the detection frequency above 0.2 µg/L for the most commonly detected compounds ranged between concentrations for wells in urban settings and wells in rural settings for similar NAWQA ground-water studies. The setting for the springs was a mixture of urban and rural land use; therefore, the VOC results of the UTEN study are consistent with the national results.

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