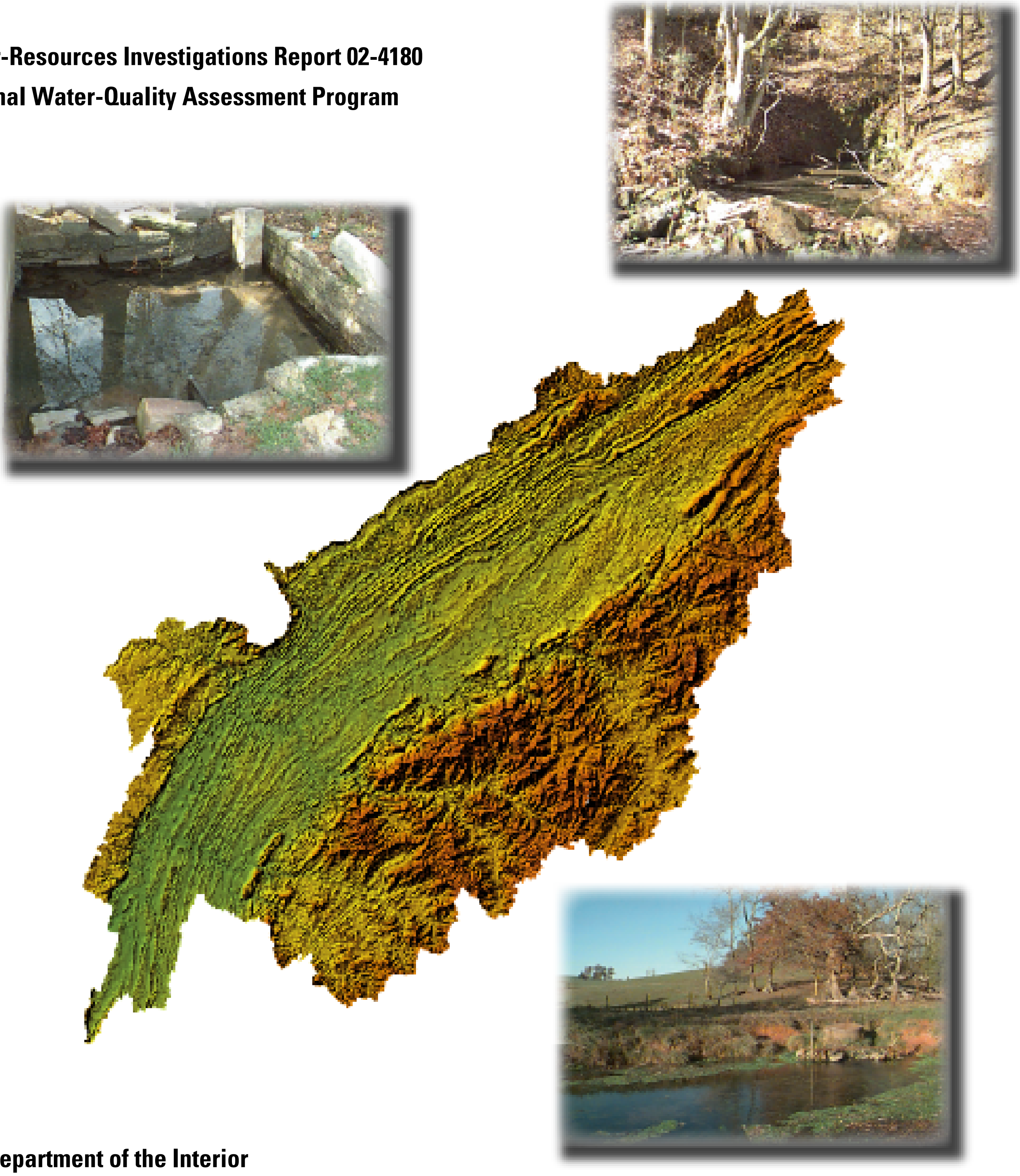
Water Quality of Springs in the Valley and Ridge Physiographic Province in the Upper Tennessee River Basin, 1997

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



U.S. Department of the Interior
U.S. Geological Survey

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.

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

By Gregory C. Johnson

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 02-4180

Nashville, Tennessee
2002

U.S. DEPARTMENT OF THE INTERIOR
Gale A. Norton, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

Any use of trade, product, or firm name in this report is for identification
purposes only and does not constitute endorsement by the
U.S. Geological Survey.

For additional information write to:

District Chief
U.S. Geological Survey
640 Grassmere Park, Suite 100
Nashville, Tennessee 37211

Copies of this report may be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, Colorado 80225-0286

Information regarding the National Water-Quality Assessment (NAWQA) Program is available on the Internet via the World Wide Web. You may connect to the NAWQA home page at:
http://water.usgs.gov/nawqa/naqwa_home.html

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

Robert M. Hirsch
Associate Director for Water

CONTENTS

FIGURES

TABLES

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 (^oC) can be converted to degrees Fahrenheit (^oF), and conversely, by use of the following equations:

$$^oF = (1.8 \times {}^oC) + 32 \qquad {}^oC = ({}^oF - 32) \times 0.5555$$

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 *tert*-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

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

By Gregory C. Johnson

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 mi^2, with 2,740 mi^2 in Virginia, 7,690 mi^2 in Tennessee, and 380 mi^2 in Georgia. Land-surface elevations range from about 627 feet above sea level in Chattanooga, Tennessee, to 2,340 ft above sea level in Virginia. The mean annual precipitation from 1935 to 1997 (Tennessee Valley Authority, written commun., 1999) ranged from 49.2 in/yr in the southern part of the study area to 38.9 in/yr in the northern part of the study area. The wettest part of the year generally is in the spring (March through May) with about 11 in. of precipitation, and the driest part of the year is in late summer and early fall (August through October) with about 7.0 in. of precipitation. Rainfall for the 12-month period prior to sampling was about 2.4 in. below normal.

Hydrogeology

The Valley and Ridge consists of a long, narrow belt of faulted and folded Paleozoic sedimentary rocks. Predominant rock types are, in order of abundance, carbonate rock (dolomite and limestone), shale, and sandstone (Colton, 1970). For this study, the shale and sandstone units were grouped together as siliciclastic rocks (fig. 2).

The Valley and Ridge is characterized by a series of subparallel, northeast-trending ridges. The ridges are made up of less soluble cherty limestone, dolomite, and sandstone, whereas the valleys are developed in more soluble limestone, dolomite, and shale (DeBuchananne and Richardson, 1956). The limestones and dolomites have little or no primary porosity, but large volumes of water are stored in the numerous karst solution-enlarged conduits developed along bedding planes, faults, joints, and fractured zones. The amount of water discharging from springs is dependent on the size and distribution of interconnected openings through which water infiltrates from the land surface. Most of the large springs in the UTEN Valley and Ridge issue from solution openings in limestone and dolomite of the Knox Group, Chickamauga Limestone, and Conasauga Group. Some springs issue from highly fractured and faulted zones, but these are less common and generally have smaller discharges (Sun and others, 1963).

Karst can be defined as a type of terrain underlain by rocks (usually carbonate units) in which chemical dissolution has enlarged joints, fractures, bedding planes, and other openings to create a subsurface system of conduits to transport water. The number of these openings and the degree to which they have been enlarged by dissolution are the major factors determining the hydrologic characteristics of the dense carbonate rock units (Wolfe and others, 1997). Ground-water flow in karst is significantly different from most other types of aquifers because of the conduits. Velocities in karst aquifers can reach hundreds of feet per hour and are often in the turbulent regime (White, 1969). The Valley and Ridge has been deformed by intense folding and faulting that has resulted in a series of long, narrow outcrop belts where the geologic units dip typically to the southeast (fig. 3). Because these units dip steeply, conduits that form parallel to bedding planes may extend to depths of 500 ft or more (Wolfe and others, 1997; Hollyday and Hileman, 1996).

Land Use, Population, and Water Use

One component of the NAWQA Program is to evaluate the effect of various land uses on water quality. In the UTEN Valley and Ridge, land use (fig. 4) includes forest (51 percent), pasture (36 percent),

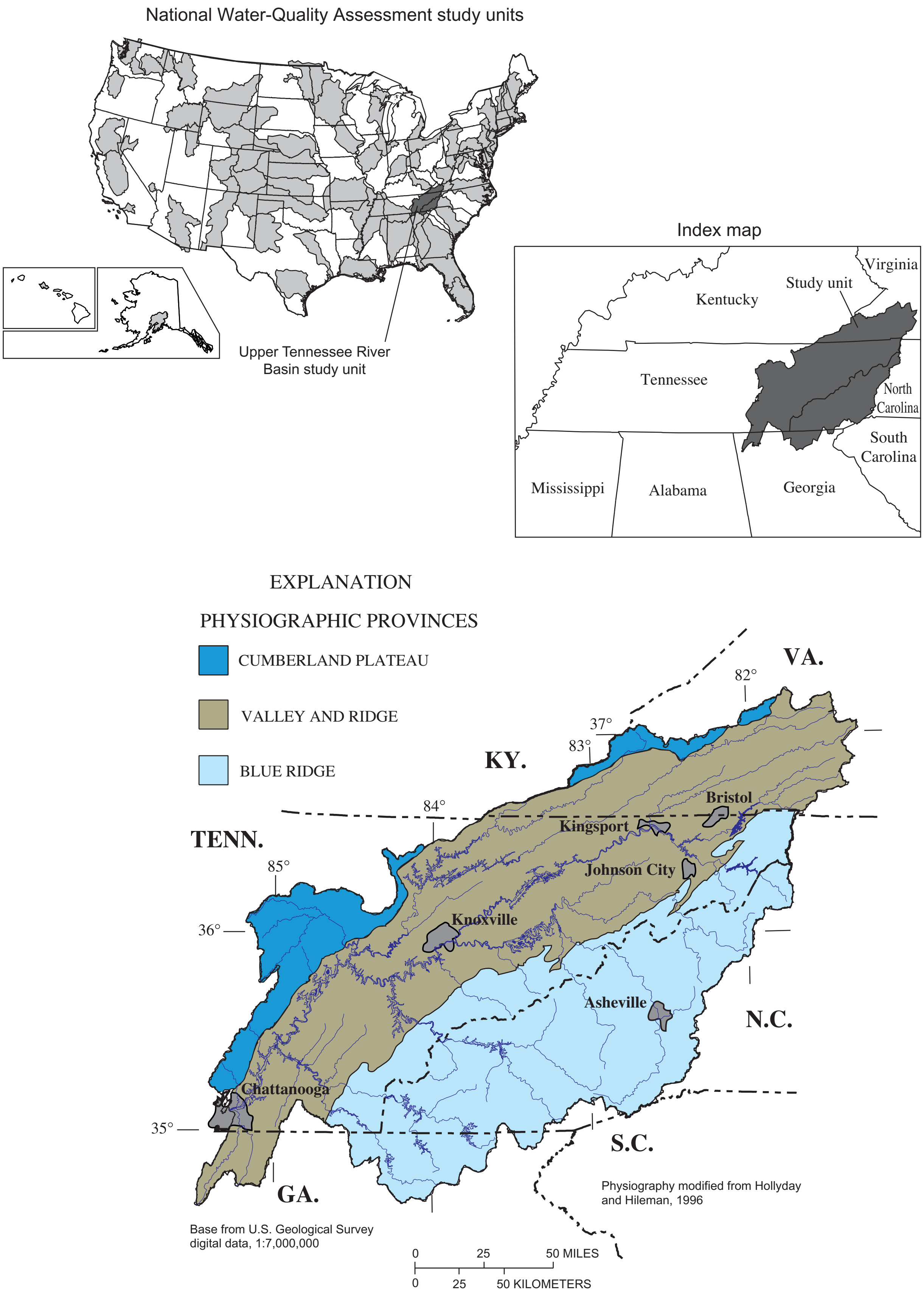
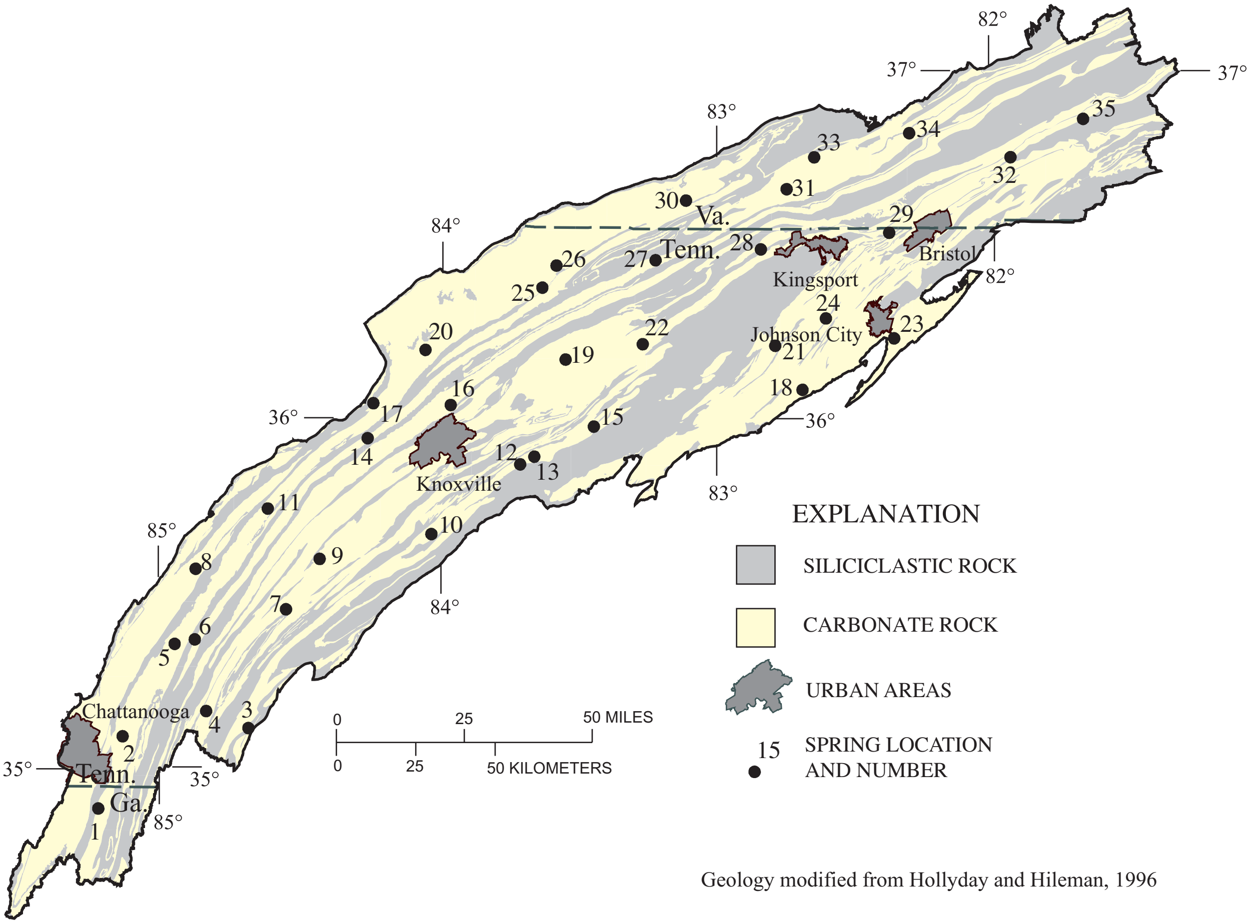


Figure 1. Location and physiographic provinces of the upper Tennessee River Basin.



Geology modified from Hollyday and Hileman, 1996

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 mi^2. 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).

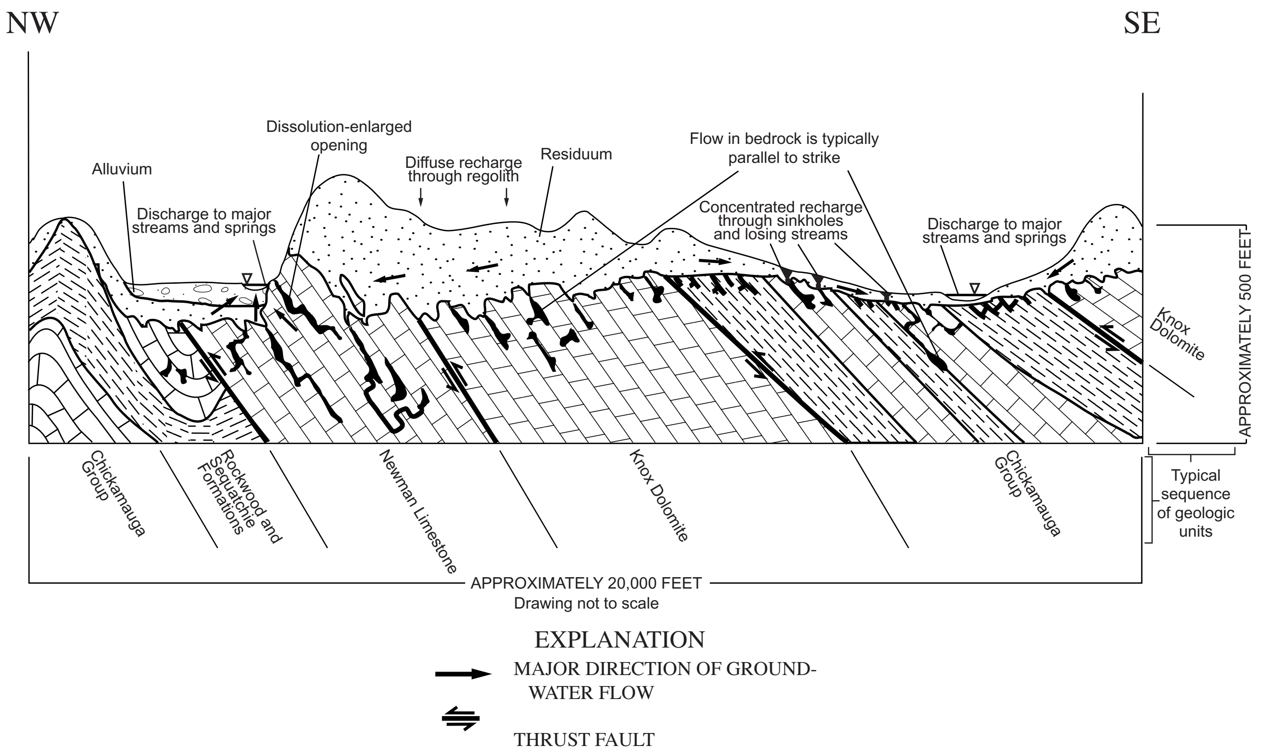


Figure 3. Generalized hydrogeologic section through the Valley and Ridge Physiographic Province in the upper Tennessee River Basin. (Modified from Wolfe and others, 1997.)

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).

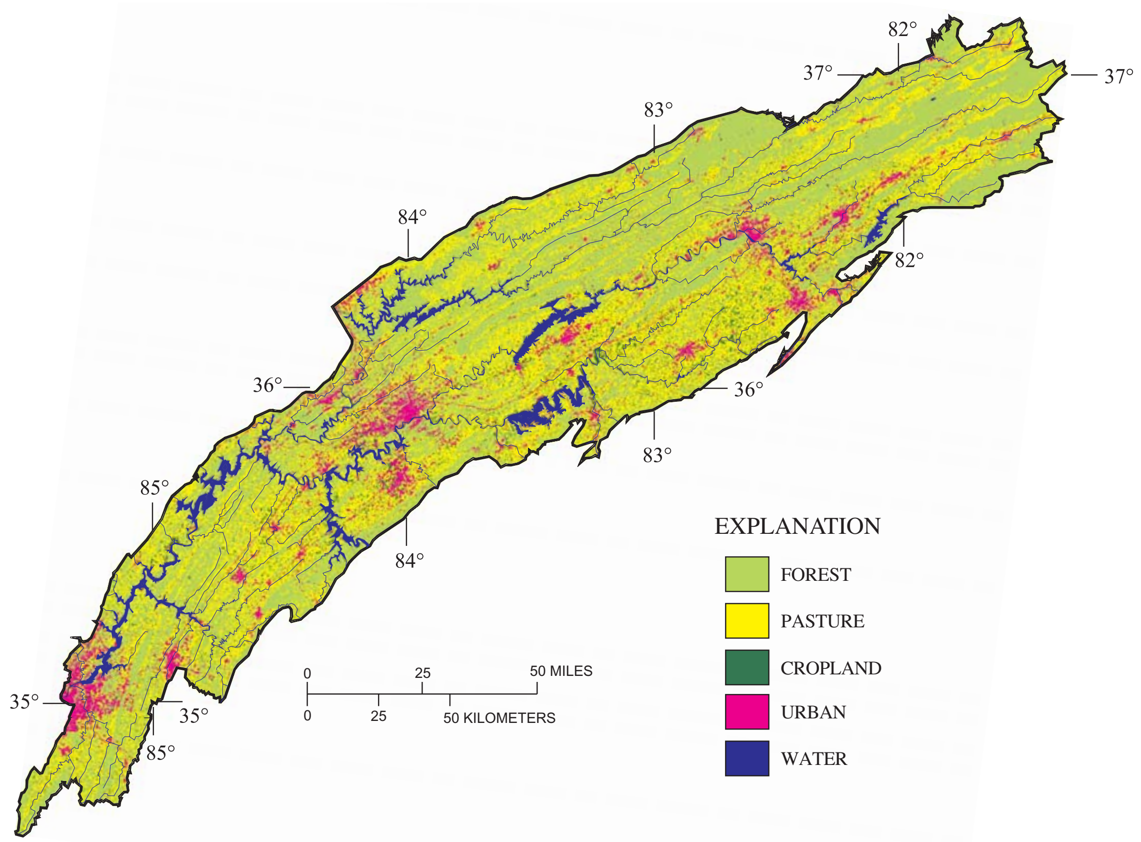
The water resources in the UTEN Valley and Ridge are abundant and provide water for industrial, municipal, agricultural, and recreational activities. Surface water is the primary source of water used for industrial and municipal water supplies. In 1995, 596 Mgal/d were withdrawn from surface-water sources 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



Base from Southern Appalachian Assessment 30-meter land use
Geographic Information System database, 1996.

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 (NO_3), ammonia (NH_3), ammonia plus organic nitrogen, total phosphorus, and orthophosphate (PO_4). 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 noncontaminating 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 ft^3/s, with a median value of 0.32 ft^3/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.

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

[$CaCO_3$, 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

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