USGS
science for a changing world

Seasonal and Spatial Variability of Pesticides in Streams of the Upper Tennessee River Basin, 1996-99

Water-Resources Investigations Report 03-4006
National Water-Quality Assessment Program

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

Cover photo: Streambed in upper Tennessee River Basin study area.

Seasonal and Spatial Variability of Pesticides in Streams of the Upper Tennessee River Basin, 1996-99

By M.W. Treece, Jr.

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 03-4006

Nashville, Tennessee

2003

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

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

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. 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
square mile (mi^2)	2.590	square kilometer
acre-foot (acre-ft)	$1.233x10^{-3}$	cubic meter
cubic foot per second (ft^3/s)	$2.447x10^{-3}$	cubic meter
billion gallons per day (Bgal/d)	$4,381x10^{-2}$	cubic meters per second
inch per year (in/yr)	25.4	millimeter per year

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

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

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD of 1929).

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

Water-quality units

µg/L	micrograms per liter
µm	micrometer
mg/L	milligrams per liter

Abbreviations and Acronyms

DCPA	Dacthal
EWI	Equal width increment
GC/MS	Gas chromatography/mass spectrometry
HAL	Health advisory limit
HCH	Hexachlorocyclohexane
HPLC	High-performance liquid chromatography
MCL	Maximum contaminant level
MRL	Minimum reporting level
NAFAP	National Center for Food and Agricultural Policy
NAWQA	National Water-Quality Assessment Program
SPE	Solid-phase extraction
TVA	Tennessee Valley Authority
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UTEN	Upper Tennessee River Basin

Seasonal and Spatial Variability of Pesticides in Streams of the Upper Tennessee River Basin, 1996-99

By M.W. Treece, Jr.

ABSTRACT

From 1996 to 1999, the U.S. Geological Survey conducted an assessment of pesticides in streams in the upper Tennessee River Basin (UTEN), which includes parts of Tennessee, North Carolina, Virginia, and Georgia. A total of 362 water samples were collected at 13 fixed surface-water sites from March 1996 through June 1999, and an additional 61 samples were collected throughout the UTEN during the spring and summers of 1996, 1997, and 1998. In 1996, 3 of the 13 fixed sites located in agricultural watersheds were sampled intensively (weekly) for about 8 months during the growing season. Water samples were analyzed for 85 herbicides, insecticides, and pesticide metabolites. Based on a threshold concentration of 0.01 microgram per liter, the most frequently detected herbicides were atrazine (59 percent); tebuthiuron (41 percent); the metabolite, deethylatrazine (31 percent); metolachlor (24 percent); simazine (17 percent); and prometon (6.4 percent). The insecticides detected most frequently were carbaryl (6.1 percent), diazinon (1.9 percent), carbofuran (1.7 percent), and chlorpyrifos (1.1 percent). Pesticide concentrations varied seasonally and were closely related to land use. The highest pesticide concentrations occurred in the agricultural watersheds in late spring and early summer (April through July), coinciding with pesticide application and the first substantial storm following pesticide application.

Results of the spatial analysis of pesticides during base-flow conditions indicate that water-quality conditions at the fixed sites were representative of conditions in the upper Tennessee River Basin. Although most of the water samples collected in the upper Tennessee River Basin contained detectable concentrations of one or more pesticides, none of the concentrations exceeded any human health guidelines.

INTRODUCTION

Pesticide use in the United States has greatly increased over the last several decades. Since the 1940s, thousands of chemicals have been synthesized and introduced into the environment. About 1.1 billion pounds of pesticides are used annually in the United States. Agricultural uses of pesticides (herbicides, insecticides, and fungicides) have increased from 190 million pounds of active ingredient in 1964 to an estimated 811 million pounds in 1993 (Larson and others, 1997). Although pesticide use results in increased crop yields by controlling weeds and other nuisance organisms, the occurrence of pesticides in surface waters (especially at elevated concentrations) warrants concern because of their potential toxicity to humans and aquatic life. In addition to agriculture, pesticides also are commonly used in forestry, transportation (weed control along roadsides and railways), urban and suburban areas (control of pests in homes, buildings, gardens, lawns, and golf courses), lakes and streams (control of aquatic flora and fauna), and various commercial and industrial settings (Larson and others, 1997).

The presence of pesticides at low concentrations in the Nation’s surface waters has been recognized for several decades (Larson and others, 1997; U.S. Geological Survey, 1997), and in 1994, the U.S. Geological Survey (USGS) began an assessment of water quality in the upper Tennessee River Basin (UTEN) as part of the National Water-Quality Assessment (NAWQA) Program. One of the objectives of the

NAWQA Program is to describe the presence and distribution of pesticides in the environment. In many streams across the Nation, some pesticides exceed water-quality criteria for seasonal periods, but annual average concentrations seldom exceed regulatory standards for drinking water. Nationwide, the highest levels of pesticides in surface water occur as seasonal pulses lasting from a few weeks to several months, although generally less than 2 percent of the annual amount of pesticides applied to agricultural land is transported to streams (Larson and others, 1997). Herbicides are the most common type of pesticide present in streams within agricultural areas. Insecticides are usually detected at higher concentrations in urban streams than in agricultural streams (U.S. Geological Survey, 1999).

In the UTEN, pesticides are widely used to control insects and nuisance vegetation such as weeds and grasses for agriculture, lawn care, and golf course and right-of-way maintenance. The transport and fate of pesticides in streams strongly depends on the water solubility of the pesticides. Water solubility determines how easily pesticides wash off soil and crop residues and how readily they leach through the soil (Goolsby and Pereira, 1995). Some of the more persistent pesticides have been banned by the U.S. Environmental Protection Agency (U.S. EPA) for use in the United States, but their residues remain in the environment.

Even though pesticides are applied to specific areas, they can be transported to other parts of the environment and pose a threat to nontarget organisms. Most pesticides currently used on crops grown in the UTEN, such as corn and soybeans, are water soluble and enter the aquatic system predominantly in the dissolved state. Despite the widespread application of pesticides in the UTEN, limited information is available on the occurrence and temporal variability of pesticide concentrations in surface waters in the basin.

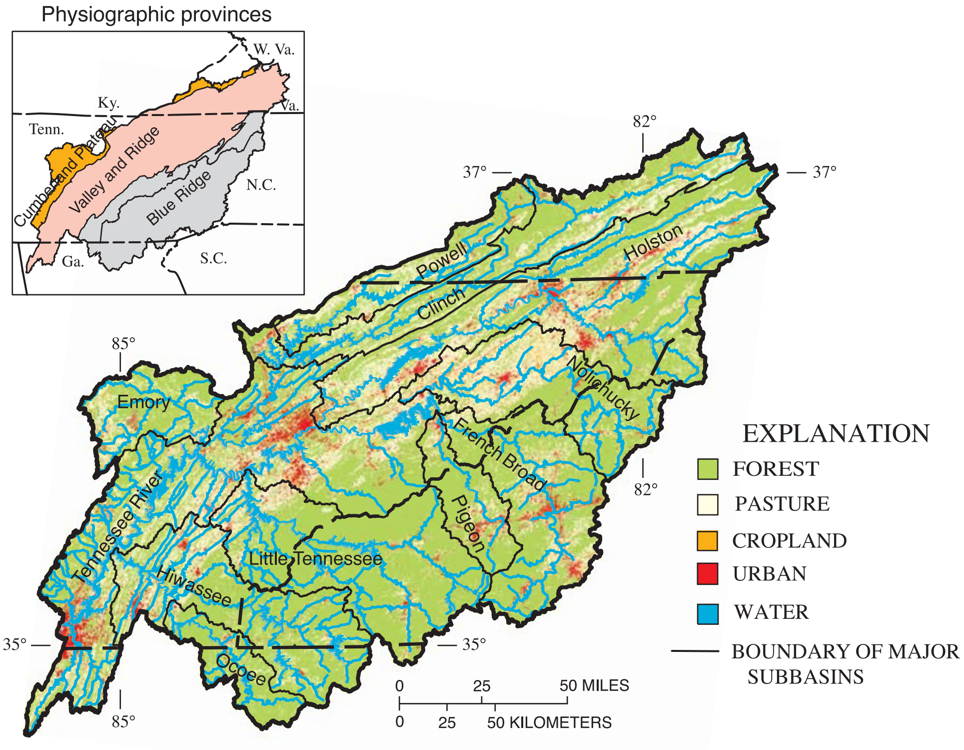
Purpose and Scope

The purpose of this report is to describe the seasonal and spatial variability of pesticides in streams in the UTEN. This report is based on two sets of data: one set of 362 samples collected at 13 fixed surface-water sampling sites in the UTEN from March 1996 through June 1999, and a separate set of 61 samples collected at additional stream sites throughout the UTEN during the springs and summers of 1996, 1997, and 1998. Water samples were analyzed for 77 pesticides and 8 pesticide-degradation byproducts. Evaluation of water-quality conditions in the UTEN included analyses of the presence and spatial distribution of pesticides and analyses of variations of detection frequencies and concentrations of pesticides in surface waters as related to land use, pesticide use, and seasonal changes.

Study Area

The UTEN is located in the Southeastern United States and drains an area of about 21,400 mi^2, which includes the entire drainage of the Tennessee River and its tributaries upstream of the USGS gaging station at Chattanooga, Tenn. The UTEN includes parts of Tennessee (11,500 mi^2), North Carolina (5,480 mi^2), Virginia (3,130 mi^2), and Georgia (1,280 mi^2); and includes parts of the Valley and Ridge, Blue Ridge, and Cumberland Plateau section of the Appalachian Plateaus Physiographic Provinces (fig. 1). The Valley and Ridge Physiographic Province, which composes about 58 percent of the UTEN, is a long narrow belt divided into folded bedrock terrain of low rolling hills and karst formations, and highly faulted terrain characterized by high angle thrust faulting that has resulted in 300- to 500-ft ridges separated by narrow valleys (DeBuchananne and Richardson, 1956). Topography dictates land use in the UTEN; most of the agricultural land is located in the stream valleys, on benches, and on more gently rolling areas of the Valley and Ridge Physiographic Province. The Blue Ridge Physiographic Province accounts for about 35 percent of the UTEN and includes rugged terrain, such as the Great Smoky Mountains. The Blue Ridge Physiographic Province is characterized by dense, massive granitic bedrock containing little water except where extensively faulted and fractured. The Cumberland Plateau section of the Appalachian Plateaus Physiographic Province composes about 7 percent of the UTEN and is characterized by mostly horizontal Pennsylvanian-age sandstones, shales, and coal underlain by Mississippian-age shales and carbonate rocks.

In the UTEN, forests cover about 67 percent of the basin. Much of this forested land lies within five national forests, four of which are located within the Blue Ridge Physiographic Province. Agriculture accounts for about 27 percent of the land use in the UTEN; of this 27 percent, pastureland accounts for about 24 percent and cropland accounts for about



Base from Southern Appalachian Assessment
30-meter land-use GIS database, 1996

Figure 1. Physiographic provinces, major subbasins, and land use of the upper Tennessee River Basin.

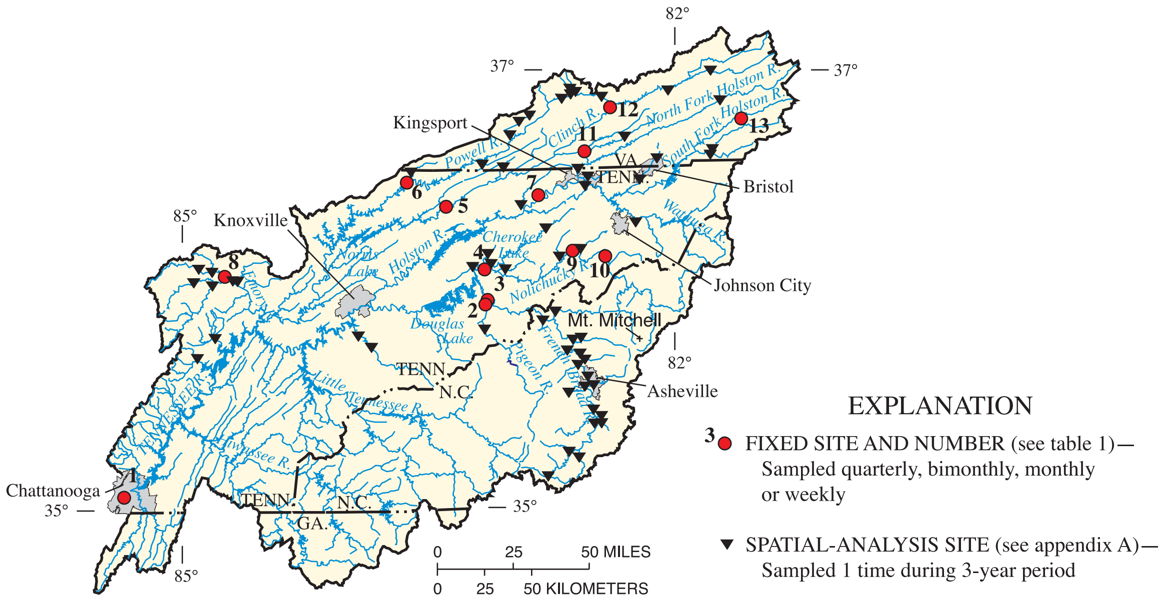
3 percent. Corn, soybeans, winter wheat, tomatoes, burley tobacco, and hay are the main crops (U.S. Department of Agriculture, 1999). Other land uses in the UTEN include urban areas (4 percent) and waterbodies (2 percent).

The climate in the UTEN is characterized by short, wet winters and long, hot summers. The growing season in the UTEN averages about 200 days. In general, precipitation in the UTEN increases as elevation increases (the crest of the Great Smoky Mountains receives more than 100 in/yr). Precipitation decreases from south to north within the study unit. Elevations in the UTEN range from 621 ft above NGVD of 1929 at the Chattanooga, Tenn., gaging station to 6,684 feet at Mount Mitchell, N.C., which is the highest point in the Eastern United States (fig. 2).

Each major subbasin in the UTEN has distinct climatic and runoff characteristics with average annual precipitation ranging from about 45 in/yr for the Holston River Basin to about 60 in/yr for the Little Tennessee River Basin, which is the highest average rainfall for any basin of similar size in the continental United States, excluding Puget Sound. The drainage basins of nine major tributaries (fig. 1)—Clinch, Powell, Emory, French Broad, Nolichucky, Pigeon, Hiwassee, Holston, and Little Tennessee—make up about 86 percent of the UTEN. The flows from these tributaries account for about 85 percent of the annual mean discharge of 35,890 ft^3/s at the Tennessee River at the Chattanooga, Tenn., gaging station. These nine tributaries drain into the Tennessee River, which is impounded for almost its entire length through the UTEN.

The most prominent surface-water features of the UTEN are the tributary and main-stem reservoirs constructed and maintained by the Tennessee Valley Authority (TVA). Four main-stem reservoirs (with a combined capacity of 3.1 million acre-feet of storage) are primarily flow-through systems that provide power generation and maintain navigational depths. Seventeen tributary reservoirs provide flood storage and power generation and have a combined storage capacity of 10 million acre-feet. Seventeen privately owned and operated reservoirs also are located in the basin.

In 1990, the population of the UTEN was about 2.4 million people, of which about 1.5 million resided



Base from U.S. Geological Survey
1:2,000,000 digital line graph

Figure 2. Location of sampling sites in the upper Tennessee River Basin.

in the four major urban areas of Chattanooga and Knoxville, Tenn., Asheville, N.C., the Tri-Cities area of Kingsport and Johnson City, Tenn., and Bristol, Tenn./Va. (fig. 2). The major urban centers in the UTEN are adjacent to reservoirs or major rivers.

The UTEN is characterized by an abundance of surface-water resources that usually meet existing guidelines for drinking-water supply, recreation, and protection of aquatic life. In 1995, withdrawals of surface water totaled about 4.9 billion gallons of water per day, of which 3.8 billion gallons per day was used for thermoelectric power generation. Of the nonthermoelectric water use, the greatest surface-water withdrawals were for commercial and industrial uses (59 percent) and public supply (24 percent). Public water-supply systems in the UTEN provide drinking water for an estimated 2 million people; 1.6 million (79 percent) of these people are served by public water-supply systems that receive their water from surface-water sources.

Degradation of surface-water quality is a concern to resource managers and environmental scientists. The UTEN contains greater aquatic biodiversity than most areas of similar size in the continental United States. For example, the upper Clinch and Powell River Basins are home to more than 300 globally rare species including the most diverse freshwater mussel fauna in the world. Water-quality impairment in the UTEN generally stems from point-source industrial activities and nonpoint-source inputs from agricultural, forestry, and mining activities (Denton and others, 2000). In the free-flowing streams of the UTEN, nonpoint sources of nutrients, coliform bacteria, pesticides from agricultural areas, and sedimentation resulting from agricultural, mining, and construction activities are serious concerns. The clearing of riparian zones for cattle access to rivers has adversely affected bank stability and the aquatic biota diversity of the area (Denton and others, 2000). Urban effects of most concern are related to aging or malfunctioning sewerage systems. The increased use of pesticides and other compounds in suburban residential areas also warrants concern as a potential threat to surface-water quality.

Study Design

Surface-water quality in the UTEN was assessed to determine the presence and distribution of pesticides in the water column. Each study-unit investigation complied with guidelines within the framework of the national study design for the NAWQA Program, yet was afforded flexibility to customize efforts to address important local water-quality issues. The sampling strategy in the UTEN study was designed to characterize the spatial and temporal distribution of pesticides in relation to hydrologic conditions, seasonal changes, land use, and contaminant sources.

Selection of Sampling Sites and Sampling Frequency

Stream sampling sites in the UTEN were selected to assess the spatial and seasonal variability of selected pesticides in subbasins consisting of mixed land use and different mixtures of agricultural cropland. The assessment of pesticides in streams focused mainly on seven tributaries—the Clinch, Emory, French Broad, Holston, Nolichucky, Pigeon, and Powell Rivers—to the Tennessee River and mostly upstream of three major reservoirs (Norris, Douglas, and Cherokee Lakes). About 60 percent of the herbicide use in the UTEN occurs in these subbasins. These tributaries drain about 47 percent of the total area and account for about 42 percent of the mean annual discharge of the UTEN.

Thirteen fixed stream sampling sites were selected to assess the effects of physiographic settings and a variety of land uses on surface-water quality (table 1). The sampling strategy at these 13 sites was designed to assess seasonal variation in distribution and presence of pesticides. Water samples were collected monthly at the French Broad River, Clinch River, Clear Creek, Big Limestone Creek, Copper Creek, Guest River, Middle Fork Holston River, and two sites on the Nolichucky River; bimonthly at the Holston and Tennessee Rivers; and quarterly at the Powell and Pigeon Rivers (table 1). In 1996, the sampling frequency at three sites (Big Limestone Creek, Copper Creek, and Nolichucky River near Lowland) was increased to weekly sampling during the growing season (March through October) to increase understanding of the fate of pesticides during the application period. These three sites drain the largest percentage of agricultural land of the 13 sites in the study [Big Limestone Creek (83 percent), Copper Creek (51 percent), Nolichucky River (38 percent)] and are referred to as "agricultural sites" in the remainder of this report.

In addition to the routine sampling at the 13 fixed sampling sites, 61 stream sites (fig. 2) were sampled once to evaluate the spatial distribution of pesticides in various subbasins in the UTEN (full site names and site descriptions are given in appendix A). A different set of sites was sampled each year (1996-98) in the spring or early summer to correspond with the period of peak application of agricultural pesticides and stable, low streamflow conditions. The spatial sampling in 1996 focused on the Clinch, Powell, and Emory River Basins; in 1997, on the French Broad and Nolichucky River Basins; and in 1998, on the Holston River Basin. Five samples were collected from selected streams in other subbasins to address topical issues related to water quality and ecological assessments of these streams.

Field and Laboratory Methods

Water-quality samples were collected using established NAWQA protocols (Shelton, 1994), which require the use of noncontaminating (Teflon and stainless steel) sampling equipment and quality-assurance sampling. Depth-integrated subsamples were collected using the equal-width increment (EWI) sampling method, which specifies sampling at equally spaced verticals across the stream by using either the US DH-81 or US D-77 sampler as described by Edwards and Glysson (1988) and Shelton (1994). Both samplers held Teflon sample bottles, and all other parts that contacted water samples were Teflon. The samples were split into equal aliquots using a Teflon cone splitter (Capel and others, 1995). Water samples were filtered at the sites through 0.7-micrometer-diameter pore-size baked glass-fiber filters to remove suspended particulate matter, and were stored in baked amber glass bottles.

The water samples were processed through a solid-phase extraction (SPE) cartridge either in the field or at the USGS National Water Quality Laboratory (NWQL) within 4 days of collection using techniques described by Sandstrom and others (1992). Samples (bottles or SPE cartridges) to be analyzed at the NWQL were shipped on ice at approximately 4 degrees Celsius. The SPE method uses bonded silica packed into an extraction column, which absorbs specific organic compounds. These compounds subsequently are removed from the extraction column at the NWQL by use of a solvent.

Samples were analyzed for 77 pesticides and 8 pesticide metabolites by using either capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (Zaugg and others, 1995) or high-performance liquid chromatography (HPLC) (Werner and others, 1996) (table 2). The GC/MS method was used for pesticide analyses of 26 herbicides including the triazines and amides, 17 insecticides including the organophosphates, and 4 metabolites. The HPLC method was used to analyze samples for 28 herbicides including the chlorophenoxy acids, 6 insecticides (mostly carbamates), and 4 pesticide metabolites.

Table 1. Fixed sampling sites in the upper Tennessee River Basin study area

[mi^2, square mile; GC/MS, gas chromatography/mass spectrometry (analysis for 47 pesticides); HPLC, high performance liquid chromatography (analysis for 38 pesticides); *, discontinued after February 1997 as a result of low frequency (less than 1 percent) of detections of analytes from this method]

Site number (fig. 2)	USGS station name	USGS station number	Drainage area (mi^2)	Watershed classification	Number of samples collected		Collection period	Land use (in percent)				
					Laboratory method				Agriculture			
					GC/MS	*HPLC		Forest	Pasture	Crop-land	Urban	Other
1	Tennessee River at Chattanooga, Tenn.[1]	03568000	21,400	Mixed	12	6	5/96-2/98	67.4	23.5	2.6	4.3	2.2
2	Pigeon River near Newport, Tenn.[2]	03461500	666	Forest/industrial	6	4	4/96-1/98	80.3	12.9	1.5	5.0	0.3
3	French Broad River near Newport, Tenn.[3]	03455000	1,858	Forest/agriculture/ urban	28	12	4/96-3/98	75.4	16.7	2.3	5.1	0.5
4	Nolichucky River near Lowland, Tenn.[3, 4]	03467609	1,687	Agriculture/forest	66	36	3/96-6/99	57.8	32.6	6.0	3.2	0.4
5	Clinch River above Tazewell, Tenn.[3]	03528000	1,474	Forest/agriculture	27	12	4/96-5/98	69.8	26.5	1.1	2.3	0.3
6	Powell River near Arthur, Tenn.[2]	03532000	685	Forest/agriculture	5	4	5/96-10/97	65.3	30.1	2.0	2.3	0.3
7	Holston River at Surgoinsville, Tenn.[1]	03490500	2,874	Mixed-industrial/ agriculture	13	6	4/96-7/98	63.6	26.9	2.7	5.5	1.3
8	Clear Creek at Lilly Bridge near Lancing, Tenn.[3]	03539778	170	Forest	20	0	3/97-9/98	69.4	24.2	3.7	0.3	2.4
9	Big Limestone Creek near Limestone, Tenn.[3, 4]	03466208	79.0	Intensive-agriculture	62	35	3/96-6/99	15.0	64.3	18.7	1.9	0.1
10	Nolichucky River at Embreeville, Tenn.[3]	03465500	805	Forest/mining	17	10	3/96-1/98	85.1	11.3	0.9	2.5	0.2
11	Copper Creek near Gate City, Va.[3, 4]	03526000	106	Intensive-agriculture	50	34	3/96-2/98	47.1	47.4	3.5	1.8	0.2
12	Guest River near Miller Yard, Va.[3]	03524550	100	Mining/urban	28	13	6/96-5/98	79.2	13.4	0.1	6.7	0.6
13	Middle Fork Holston River at Seven Mile Ford, Va.[3]	03474000	132	Mixed agriculture/ urban/forest	27	12	4/96-7/98	69.2	24.6	1.3	4.7	0.2

[1] Sites sampled bimonthly.
[2] Sites sampled quarterly.
[3] Sites sampled monthly.
[4] Sites sampled weekly during 1996 growing season.

Table 2. Pesticides and pesticide metabolites analyzed in samples collected from streams in the upper Tennessee River Basin, March 1996 through June 1999

[Bold-faced pesticides were detected; Italicized pesticides are metabolites; GC/MS, gas chromatography/mass spectrometry; HPLC, high performance liquid chromatography (discontinued after February 1997)]

Herbicides		Insecticides	
GC/MS	HPLC	GC/MS	HPLC
Acetochlor	Acifluorfen	Azinphos-methyl	Aldicarb
Alachlor	Bentazon	**Carbaryl**	*Aldicarb sulfone*
Atrazine	**Bromacil**	**Carbofuran**	*Aldicarb sulfoxide*
Benfluralin	Bromoxynil	**Chlorpyrifos**	Esfenvalerate
Butylate	Chloramben	***p,p'- DDE***	*3-Hydroxycarbofuran*
Cyanazine	Chlorothalonil (used as a fungicide)	**Diazinon**	Methiocarb
Dacthal	Clopyralid	Dieldrin	Methomyl
Deethylatrazine	2,4-D	Disulfoton	*1-Naphthol*
2,6-Diethylaniline	Dacthal monoacid	**Ethoprop**	Propoxur
EPTC	2,4-DB	Fonofos	
Ethalfluralin	Dicamba	***alpha-HCH***	
Linuron	**Dichlobenil**	**Lindane**	
Metolachlor	**Dichlorprop**	**Malathion**	
Metribuzin	4,6-Dinitro-o-cresol	Parathion	
Molinate	Dinoseb	Parathion methyl	
Napropamide	**Diuron**	cis-Permethrin	
Pebulate	Fenuron	Phorate	
Pendimethalin	Fluometuron	Propargite	
Prometon	MCPA	Terbufos	
Propachlor	MCPB		
Propanil	Neburon		
Propyzamide	Norflurazon		
Simazine	Oryzalin		
Tebuthiuron	Oxamyl		
Terbacil	Picloram		
Thiobencarb	Propham		
Triallate	Silvex		
Trifluralin	**2,4,5-T**		
	Triclopyr		

Pesticide concentrations were reported by the NWQL with appropriate qualifiers to reflect analytical limitations. Laboratory results were reported as “less than” when a pesticide was either not detected or not present at a concentration identifiable or measurable by the NWQL analytical procedures. When the presence of a pesticide in the sample was detected and quantified, but with low analytical confidence, the reported value was labeled as an estimated value. For statistical purposes, estimated concentrations were included in all analyses and considered to be the same as non-estimated concentrations.

Quality Control

The quality of data collected and the validity of any interpretation cannot be evaluated without quality-control data. Quality-control samples are used to quantify data accuracy, precision, and the presence of any field or laboratory contamination and analytical bias (Rinella and Janet, 1998). In addition to the regular water samples, a series of quality-control samples including field blanks, replicates, and field-matrix spike samples were collected and processed throughout the study period to evaluate the reliability and reproducibility of the data. About 15 percent of the water samples collected were quality-control samples.

Field-blank samples were processed prior to processing the regular water samples. Field blanks were processed by passing a volume of organic contaminant-free deionized water through all sampling equipment. Results of the field-blank samples indicated that no systematic contamination occurred during sample collection and processing. Pesticides were detected in only 4 of 22 field-blank samples. The insecticide *p,p*'-DDE was detected in two of the four samples; the herbicide atrazine was detected in a third sample. The insecticide chlorpyrifos (0.004 µg/L) and the herbicide pendimethalin (0.006 µg/L) were detected in the fourth field blank.

Sample replicates provide information to estimate the precision of concentration values determined from the combined sample-processing and analytical scheme and to evaluate the consistency of target analytes detected and quantified. The regular and replicate samples were collected simultaneously. Each replicate sample was an aliquot of the regular water sample from the cone splitter, and was processed immediately following the primary cone-split sample using the same equipment and identical processing and handling procedures as the regular water samples. Of the 21 sets of replicate samples, 100 of the 112 (89 percent) pesticide detections occurred in the regular and the replicate samples. Of the 100 paired sample detections, concentrations for 30 pesticide detections were identical for the regular and replicate samples—the average difference in concentrations for the other 70 paired detections was 0.001 µg/L. Five detections in the regular samples were not detected in the paired replicate samples; and seven pesticides detected in the replicate samples were not detected in the paired regular samples. All 12 unpaired pesticide detections were low concentrations and were reported as estimated values. Ten of these estimated values were actually below the laboratory minimum reporting level (MRL). One unpaired detection was equal to the MRL, and another unpaired detection was 0.001 µg/L above the MRL.

Field-matrix spikes are used to assess recoveries and assist in evaluating the precision of results for the target analytes in different matrices. Field-matrix spikes were prepared by adding a standard spike solution, provided by the NWQL, to a replicate sample processed in the same way as the regular water samples. A separate matrix-spike sample for each of the two pesticide analytical methods (GC/MS and HPLC) was prepared, stored, and shipped to the NWQL. Thirteen spiked replicate samples were analyzed for the GC/MS pesticides, and 4 spiked replicate samples were analyzed for the HPLC pesticides. The mean percent recoveries for most of the GC/MS pesticides ranged from 97 to 125 percent. The mean percent recoveries for most of the HPLC pesticides detected in this study ranged from 64 to 87 percent. These results indicate that the HPLC analytical method provides a more conservative estimate (biased low) of pesticide concentrations and detection frequencies.

Estimated Pesticide Use in the Study Area

For the UTEN study area, pesticide-use data were derived from county-based crop acreage data obtained from the 1992 Census of Agriculture (U.S. Department of Agriculture, 1999) and from State-level estimates of pesticide-use rates for individual crops compiled by the National Center for Food and Agricultural Policy (NCFAP) from information collected by State and Federal agencies over a 4-year period (1991-93 and 1995) (Thelin and Gianessi, 2000). County crop acreages were combined with the State use coefficients developed by NCFAP to calculate county-level pesticide usage by pesticide and crop. An area-weighting factor was used to determine the estimated acreage treated with pesticides and the amount of pesticide applied in counties that were not entirely contained within the study basin (U.S. Geological Survey, 1998). Significant amounts of pesticides also are applied in forested, urban, and suburban areas (lawns and golf courses), for forestry, transportation (weed control along roadways and rights-of-way), aquatic uses (control of algae and other aquatic fauna and flora in lakes), and various commercial and industrial uses; however, reliable data for these uses were not available.

Agriculture accounts for about 75 percent of total pesticide use in the United States (U.S. Geological Survey, 1997). Of the 15 herbicides with the highest agricultural use in the UTEN, 11 were analyzed as part of the UTEN study. Eight of the 15 insecticides most heavily used in the UTEN were analyzed in the UTEN study. In contrast, chlorothalonil was the only fungicide among the 15 most heavily used fungicides that was analyzed in the UTEN study (table 3).

The largest applications of herbicides to agricultural land in the UTEN are on field crops such as corn, tobacco, soybeans, and tomatoes, and on pasture and hay fields. The herbicide 2,4-D, the most heavily used herbicide by weight in the UTEN, is applied to pasture, hay, and alfalfa, which combined account for 90 percent of the agricultural acreage in the UTEN. Atrazine is the second most heavily applied herbicide by weight, accounting for about 20 percent of the estimated herbicide use. Atrazine is a pre- and post-emergent herbicide used for the control of most annual grasses and broadleaf weeds. Generally used in combination with other herbicides, atrazine is applied to a variety of crops including corn and sorghum, which accounts for about 4 percent of the agricultural acreage in the UTEN. Alachlor and metolachlor, pre-emergent herbicides used on corn, soybeans, and other crops for the control of broadleaf weeds and grasses, were applied at the third and fourth highest rates in the UTEN, respectively (table 3).

Insecticides with the highest agricultural use in the UTEN are oil, acephate, chlorpyrifos, carbaryl,

Table 3. Pesticides most commonly used for agriculture in the monitored part of the upper Tennessee River Basin, 1992

[Bold-faced pesticides were analyzed in the upper Tennessee River Basin study area; listed in order of estimated total pounds of active ingredient applied in 1992; data from Thelin, 1999]

Herbicides		Insecticides		Fungicides	
2,4-D	93,900	Oil	242,000	Methyl bromide	321,000
Atrazine	56,500	Acephate	63,300	1-3-D	317,000
Alachlor	25,500	**Chlorpyrifos**	60,200	Captan	103,000
Metolachlor	24,900	**Carbaryl**	30,200	Ziram	68,100
Pebulate	22,000	Formetanante	15,900	Sulfur	55,400
Pendimethalin	17,000	**Azinphos-methyl**	13,000	Chloropicrin	32,500
Simazine	13,000	Fenamiphos	12,100	Mancozeb	24,600
Butylate	11,800	**Carbofuran**	11,300	Metalaxyl	19,800
Napropamide	8,750	**Aldicarb**	9,620	Thiran	17,800
Glyphosate	8,000	**Methomyl**	9,450	Copper	9,580
Isopropalin	7,410	Dimethoate	8,210	**Chlorothalonil**	8,410
Cyanazine	6,840	**Ethoprop**	7,490	Dodine	8,370
Benfluralin	5,930	**Terbufos**	7,400	Maneb	6,310
Paraquat	5,100	Phosmet	6,400	Metiram	5,160
Diphenamid	4,700	Endosulfan	4,080	Thiophanate methyl	3,360

formetanante, azinphos-methyl, fenamiphos, and carbofuran (table 3). Of these eight insecticides, chlorpyrifos, carbaryl, azinphos-methyl, and carbofuran were analyzed in the UTEN water samples. Oil solutions are oil concentrates, pesticides diluted with oil, or dilute, ready-to-use oil-based preparations. Petroleum or fuel oils are used as household insecticides and as dormant sprays to control a variety of insects, to inhibit egg development, and to control mosquito larvae. In the UTEN, acephate and fenamiphos primarily are used to control a variety of insects that plague tobacco crops; acephate also is used on a variety of vegetables. Chlorpyrifos is used to control pests on agricultural crops such as tobacco, corn, alfalfa, and apples; and for nonagricultural uses on lawns, in homes, and in stables for the control of soil insects and household pests such as ants, cockroaches, and flies. Chlorpyrifos is the active ingredient in Dursban, which is used in the Southeastern United States to control fire ants. Formetanante is used to control pests primarily on fruit crops such as apples and peaches. Carbaryl and carbofuran are carbamates that have a variety of agricultural and domestic uses. Carbaryl, used in suspension with oil, is applied on corn, pasture, and forest. Carbofuran is used to control various soil and foliar pests in field corn and soybeans, and to control nematodes and foliage-feeding insects on tobacco. Estimates of insecticide use (table 3) do not include these nonagricultural uses.

PESTICIDES IN STREAMS OF THE UPPER TENNESSEE RIVER BASIN

The presence and frequency of detection of 77 pesticides and 8 pesticide metabolites at 13 fixed sites in the UTEN were evaluated. Pesticide detection frequencies in streams in the UTEN are compared to detection frequencies in streams throughout the Nation. Pesticide concentrations are evaluated to determine if concentrations are related to land use or seasonal changes. In addition, pesticide data collected at 61 spatial-analysis sites (sampled once) are compared with detection frequencies and pesticide concentrations at the 13 fixed sites that were sampled at regular intervals (usually monthly) to determine whether the fixed sites are representative of conditions throughout the UTEN.

Pesticides Detected in Streams

Of the 85 pesticides monitored during the study, 22 pesticides (15 herbicides and 7 insecticides) and 2 pesticide metabolites were detected at concentrations greater than 0.01 μg/L (table 4). The herbicides detected most frequently at concentrations greater than 0.01 μg/L included atrazine (59 percent), tebuthiuron (41 percent), the metabolite deethylatrazine (31 percent), metolachlor (24 percent), simazine (17 percent), and prometon (6.4 percent) (fig. 3; table 4). The insecticides detected most frequently at concentrations greater than 0.01 μg/L included carbaryl (6.1 percent), diazinon (1.9 percent), carbofuran (1.7 percent), and chlorpyrifos (1.1 percent). A threshold concentration of 0.01 μg/L was used to calculate detection frequencies among the 85 pesticides because of different laboratory MRLs for several of the pesticides. Five additional herbicides (alachlor, DCPA, terbacil, trifluralin, and molinate) were detected but at concentrations less than 0.01 μg/L (table 4). Two insecticides [*p,p*'-DDE (a metabolite of DDT) and *alpha* HCH (a metabolite of lindane)] also were detected only at concentrations less than 0.01 μg/L. Using the detection frequencies based on the MRLs for each pesticide, 27 pesticides (20 herbicides and 7 insecticides) and 4 pesticide metabolites were detected in stream samples.

Most samples from the 13 fixed sites had detectable levels of more than one pesticide and, therefore, represent a mixture of pesticides. At least one pesticide was detected in 99 percent of the 362 stream samples; two or more pesticides were detected in 96 percent of the stream samples; and three or more pesticides were detected in 89 percent of the stream samples. The maximum number of herbicides detected in a single sample was 11; the maximum number of insecticides detected in a single sample was 3.

Pesticides that were detected frequently in streams in the UTEN were generally the pesticides with the highest estimated use in the basin. Herbicides were detected more frequently than insecticides, which is consistent with the greater use of herbicides in the UTEN and the fact that herbicides are generally more water soluble than insecticides. Atrazine, the herbicide with the second highest application rate (56,500 pounds of active ingredient in 1992, table 3), was the most frequently detected pesticide in the UTEN. Other frequently detected herbicides were metolachlor, the third most heavily used, and simazine, (64 and 42 percent detection frequencies, respectively). Carbaryl was the most frequently

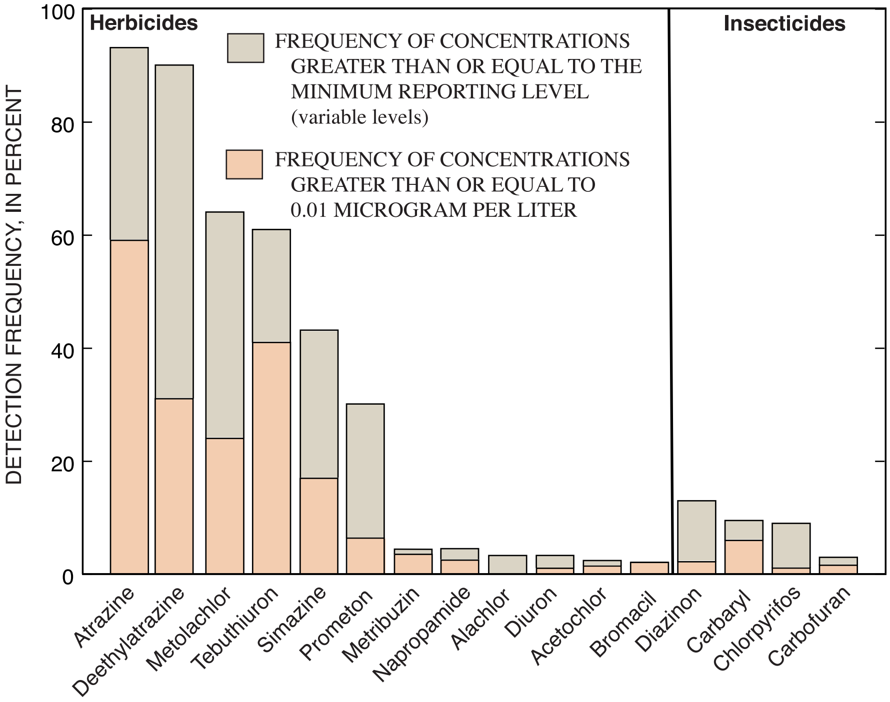


Figure 3. Detection frequency for all pesticides detected in at least 2 percent of samples at fixed sites in the upper Tennessee River Basin, 1996-99.

detected (9.7 percent) insecticide and was among the highest in estimated use. Tebuthiuron and prometon, herbicides commonly used in noncropland areas, also were detected frequently (61 and 30 percent, respectively) in the UTEN study as was the insecticide diazinon (14 percent) (table 4); however, because reliable data were not available to document the magnitude of nonagricultural use of these pesticides, the detection frequencies for these pesticides could not be effectively compared to use.

The presence of pesticides in surface waters can be diminished by many physical and chemical processes that occur after pesticide application (Larson and others, 1997). For example, pesticides that rapidly degrade after application or that quickly sorb to soil particles are transported primarily during runoff. Many pesticides analyzed in the UTEN rarely were detected because of low use; however, some pesticides used extensively in the UTEN were detected in less than 10 percent of the stream samples. Herbicides such as 2-4-D, butylate, and pebulate were not detected, but were among the top eight herbicides used in the UTEN (table 3). Pendimethalin, which is used extensively on corn and tobacco in the UTEN, was detected in only two samples (0.8 percent) during the UTEN study. Alachlor, the third most commonly used herbicide in the UTEN, was detected in 3.3 percent of samples (table 4; fig. 3). Napropamide was among the highest used herbicides in the UTEN, but was only detected in 4.4 percent of samples. Chlorpyrifos, the third most commonly used insecticide in the UTEN, was detected in 9 percent of samples. Chlorpyrifos has a high soil sorption coefficient value indicating low water solubility.

Detection frequencies of pesticides varied from site to site reflecting differences in land use in the upstream drainages. Atrazine or its metabolite (deethylatrazine) was detected in nearly 100 percent of samples from 10 of the 13 fixed sites. Metolachlor was detected frequently at sites with agriculturally dominated drainages, with the exception of a low detection frequency (18 percent) at Copper Creek near Gate City, Va. Metolachlor was detected in more than 90 percent of the samples at six fixed sites. The lowest detection frequencies for atrazine and deethylatrazine occurred at Guest River, which drains the lowest percentage of cropland and the greatest percentage of urban and mining areas of any of the UTEN fixed sites (table 1).

Table 4. Detection frequencies and maximum concentrations for pesticides detected in the upper Tennessee River Basin, 1996-99

[µg/L, micrograms per liter; ≥, greater than or equal to; MCL, maximum contaminant level; HAL, health advisory level; *, summary statistics computed for the set of 362 samples collected at fixed sites; **, pesticides analyzed in only 184 samples (all other pesticides analyzed in all 362 samples); ***, compound detected at spatial-analysis site only; E, estimated value; --, criteria do not exist; na, not applicable; ( ), number of criteria exceedances; RSD, risk-specific dose at a cancer risk level of 1 in 100,000]

Pesticide (in order of detection frequency)	Common or trade name	Minimum reporting level (µg/L)	*Detection frequency (percent)	*Detection frequency of concentrations ≥0.01 µg/L (percent)	*Maximum concentration (µg/L) (date of sample)	MCL (µg/L)	Lifetime HAL (µg/L)	Aquatic life criterion (µg/L)
Herbicides								
Atrazine	AAtrex, Atred, Criazina, Gesaprim	0.001	93	59	2.0 5/29/96	3	3	[a]1.8
Deethylatrazine	Degradation product of atrazine	0.002	90	31	0.095 7/16/97	--	--	--
Metolachlor	Dual, Pennant	0.002	64	24	1.3 7/31/98	--	70	[a]7.8
Tebuthiuron	Perflan, Spike, Tebusan	0.01	61	41	0.076 6/10/97	--	500	[a]1.6
Simazine	Aquazine, Caliber 91, Gesatop, Princep	0.005	42	17	0.214 7/31/98	4	--	[a]10
Prometon	Pramitol, Princep	0.018	30	6.4	0.10 7/12/96	--	100	--
Metribuzin	Lexone, Sencor	0.004	4.2	3.6	0.252 6/4/97	--	100	[a]1.0
Napropamide	Devrinol, Napro-guard	0.003	4.4	2.5	0.057 6/25/96	--	--	--
Alachlor	Alanox, Bronco, Bullet, Lasso	0.002	3.3	0.0	0.007 6/5/97	2	--	--
Diuron**	DCMU, Diumate, Karmex	0.02	3.3	1.1	0.020 6/10/96 6/18/96	--	10	--
Acetochlor	Harness, Plus, Surpass	0.002	2.2	1.4	0.034 6/5/97	--	--	--
Bromacil**	Bromax, Hyvar, Urox B, Uragan	0.035	2.2	2.2	0.32 7/26/96	--	90	[a]5
2,6-Diethylaniline	Degradation product of alachlor	0.003	1.4	0.3	0.318 4/29/97	--	--	--
DCPA	Dacthal, chlorthal-dimethyl	0.002	1.4	0.0	0.005 8/1/96	--	--	--
Cyanazine	Bladex, Fortrol	0.004	1.1	0.3	0.027 6/5/97	--	1	[a]2
Dichlobenil**	Barrier, Casoron, Norosae	0.02	1.1	0.5	0.08 10/21/96	--	--	--
Dichlorprop**	2,4 DP, Sertux 50, Weedone	0.032	1.6	1.6	0.18 5/29/96	--	--	--

Table 4. Detection frequencies and maximum concentrations for pesticides detected in the upper Tennessee River Basin, 1996-99—Continued

Pesticide (in order of detection frequency)	Common or trade name	Minimum reporting level (μg/L)	*Detection frequency (percent)	*Detection frequency of concentrations ≥0.01 μg/L (percent)	*Maximum concentration (μg/L) (date of sample)	MCL (μg/L)	Lifetime HAL (μg/L)	Aquatic life criterion (μg/L)
Herbicides (cont.)								
Trifluralin	Treflan, Tri-4, Trific, Gowan	0.002	1.1	0.0	0.006 1/29/97	--	5	[a]0.20
Pendimethalin	Prowl, Pre-M, Squaron, Stomp	0.004	0.83	0.83	0.037 6/14/99	--	--	--
2,4,5-T**	Hymexazol	0.035	0.5	0.5	0.05 7/25/96	--	70	--
Molinate	Ordram	0.004	0.3	0.0	0.005 6/18/96	--	--	--
Terbacil***	Counter, Sinbar	0.007	na	na	0.006 4/16/97	--	90	--
Insecticides								
Diazinon	D.Z.O., Basadin, Diazatol, Knox Out, Sarolex	0.002	14	1.9	0.59 7/23/96	--	0.60	[b]0.08 (1)
Carbaryl	Adios, Sevin, Carbamine, Denapor, Drexel	0.003	9.7	6.1	0.921 9/25/97	--	700	[a]0.20 (3)
Chlorpyrifos	Dursban, Brodan, Eradex, Genpest, Lorsban, Profos, Scout	0.004	9.1	1.1	0.033 4/4/96	--	20	[c]0.041
Carbofuran	Carbodan, Curaterr, Furandan, Yaltox	0.003	3.0	1.7	0.22 5/29/96	40	--	[a]1.8
p,p'-DDE	Degradation product of *p,p'* -DDT	0.006	1.7	0.0	0.003E 7/17/97	--	1 RSD	--
Malathion	Cythion, Maltox	0.005	1.4	0.5	0.046 8/14/96	--	200	[c]0.10
Lindane	Acitox, *gamma*-HCH, Lintox	0.004	0.8	0.5	0.026 4/17/96	0.20	--	[b]0.01 (2)
Ethoprop	Ethoprophos, Mocap	0.003	0.3	0.3	0.015 7/11/96	--	--	--
alpha HCH	Degradation product of lindane, *alpha* BHC, *alpha* Lindane, Lindol, Kotol	0.002	0.3	0.0	0.006 11/19/97	--	0.06 RSD	--

[a] Freshwater chronic water-quality criteria (U.S. Environmental Protection Agency, 2000).
[b] Great Lakes water-quality objectives (International Joint Commission United States and Canada, 1989).
[c] Canadian water-quality guidelines (Canadian Council of Ministers of the Environment, 1997; Environment Canada, 2001).

Pesticide concentrations at all fixed sites ranged from 0.001 to 2.0 µg/L (table 4). Ten pesticides—atrazine, bromacil, dichlorprop, 2,6-diethylaniline, metolachlor, metribuzin, simazine, carbaryl, carbofuran, and diazinon—were detected in water samples at concentrations greater than 0.10 µg/L (table 4). In 47 of the 362 water samples collected at the fixed sites, one or more pesticides were detected at a concentration greater than 0.10 µg/L. Concentrations of atrazine exceeded 0.10 µg/L in 37 samples, and concentrations of metolachlor exceeded 0.10 µg/L in 11 samples. Seven water samples had concentrations of one or more pesticides exceeding 0.50 µg/L, and only four samples had concentrations of one or more pesticides that exceeded 1.0 µg/L.

Differences in pesticide occurrence among the three agricultural sites (Big Limestone Creek, Copper Creek, and Nolichucky River) were related to the variety of land uses and pesticide application within each basin. Among the agricultural sites, more pesticides (22) were detected in samples from the Nolichucky River near Lowland than from the other agricultural sites (fig. 4). Similarly, more pesticides also were detected in samples from Big Limestone Creek (17) than at Copper Creek (11) probably because of a greater percentage of agricultural land use and a greater variety of crops grown in the Big Limestone Creek Basin. Tebuthiuron, a noncropland herbicide often applied to powerline and road rights-of-way, was detected at a substantially higher frequency at Copper Creek than at the Nolichucky River or Big Limestone Creek. Detection frequencies for Big Limestone Creek and the Nolichucky River near Lowland were similar for atrazine, deethylatrazine, metolachlor, napropamide, and carbofuran (fig. 4). The most noticeable difference between these two sites was that metribuzin, an herbicide used to control a large number of grasses and broadleaf weeds on a variety of agricultural crops (potatoes, soybeans, and winter wheat), was detected in 17 percent of the samples at the Nolichucky River near Lowland but was not detected at Big Limestone Creek. Big Limestone Creek is a tributary to the Nolichucky River, and both drain the same general agriculturally dominated area; however, the Big Limestone Creek Basin contains a higher percentage of agricultural land use (both pasture and cropland) than the remainder of the Nolichucky River Basin. Agricultural land accounts for only about 39 percent (650 mi^2) of the drainage upstream of the Nolichucky River site; however, most of the area adjacent to or directly upstream from the sampling site is predominantly agricultural.

Detection frequencies of pesticides at the three agricultural sites generally characterize pesticide detection at all fixed sites; however, some noticeable differences were observed (fig. 4). At the agricultural

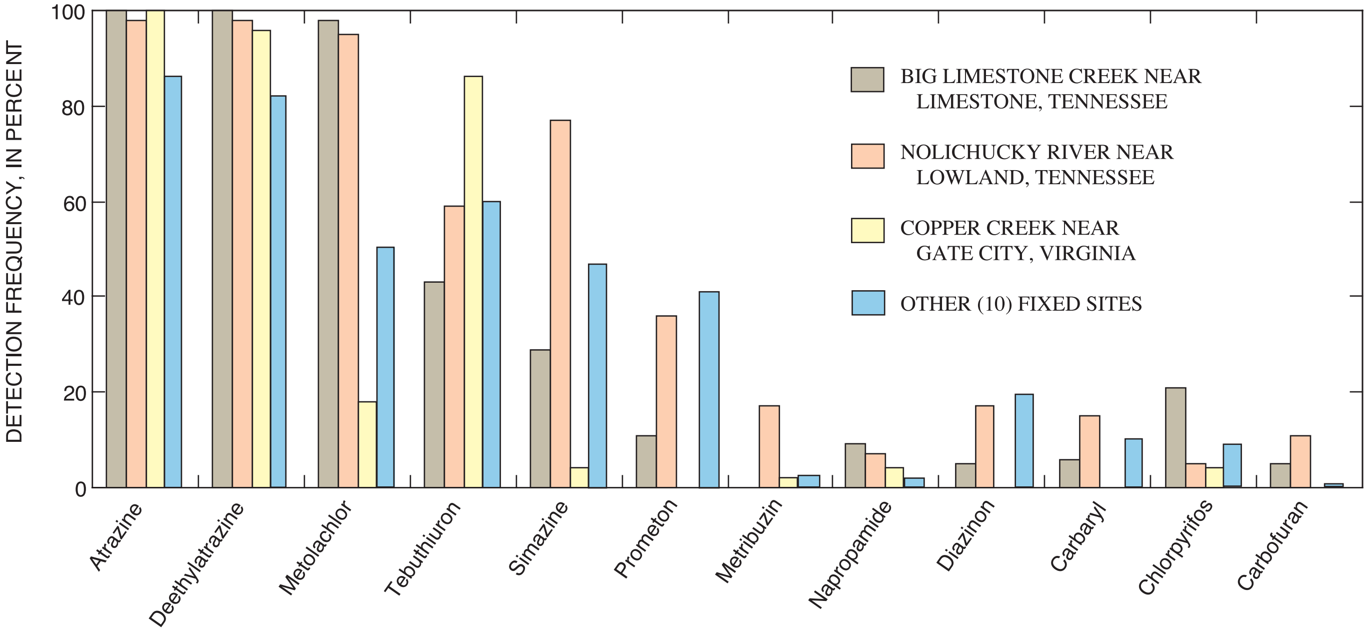


Figure 4. Pesticide detection frequency for the agricultural sites compared with the other fixed sites in the upper Tennessee River Basin.

sites, 27 different pesticides were detected. Detection frequencies at Big Limestone Creek near Limestone and the Nolichucky River near Lowland were particularly high when compared to the detection frequencies at the other fixed sites for the pesticides (atrazine and metolachlor), which are commonly used for agriculture in the UTEN. Detection frequencies of pesticides in water samples at the Nolichucky River site more closely resembled detection frequencies at the other 10 fixed sites probably because of a greater degree of mixed land use in the Nolichucky River Basin. Detection frequencies of pesticides for Copper Creek, however, varied considerably from the other sites, particularly for some of the more commonly detected pesticides such as metolachlor, simazine, and prometon (fig. 4). Tebuthiuron was detected more frequently at Copper Creek than at the other agricultural sites, perhaps as a result of road construction and weed control on roadway rights-of-way upstream of the sampling site. At Copper Creek, 11 pesticides were detected in 51 samples; however, only 4 pesticides were detected in more than 2 samples (less than 4 percent of samples).

Of the 47 pesticides that were analyzed in all samples (using the GC/MS method), 7 pesticides detected at the fixed sites were not detected at any of the sites included in the spatial analysis. Conversely, only one pesticide (terbacil) was detected at a spatial-analysis site that was not detected in samples collected at the fixed sites.

Comparisons of Detection Frequencies in the Upper Tennessee River Basin with Detection Frequencies Across the Nation

Pesticide detection frequencies for the UTEN were compared to a national summary of pesticide detections compiled by the USGS from NAWQA studies that were completed in 36 of the Nation’s major hydrologic basins from 1992 to 1998 and that included analyses of about 2,500 samples collected at 115 fixed sites. Pesticide detection frequencies in the UTEN were compared to the national averages for stream sites with agricultural drainages as well as for sites with drainages of mixed land use.

Atrazine, deethylatrazine, tebuthiuron, and napropamide were detected in streams of agricultural drainages in the UTEN more frequently than at agricultural sites included in the national summary of pesticide detections (fig. 5). Atrazine and deethylatrazine were detected in 99 and 98 percent of samples in the UTEN compared to the national average for agricultural sites of 85 and 69 percent, respectively. Tebuthiuron was detected in 62 percent of samples in the UTEN compared to the average of 22 percent for agricultural sites nationwide. The detection frequency for napropamide in the UTEN slightly exceeded the national average for agricultural indicator sites (6.2 and 5.6 percent, respectively). Pesticides that were detected considerably less frequently in the UTEN streams than at the nationwide agricultural sites

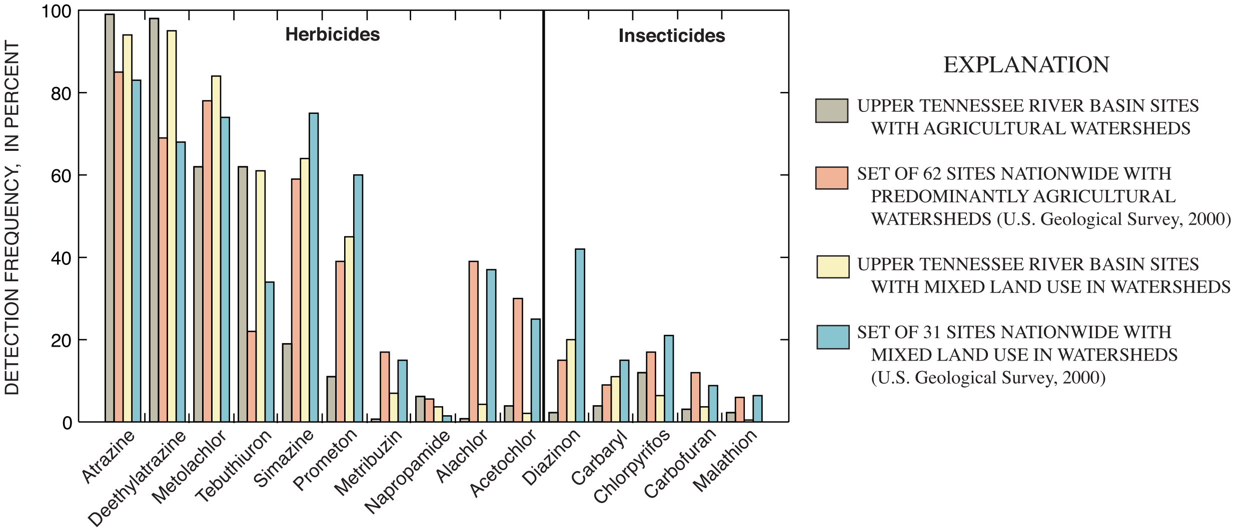


Figure 5. Pesticide detection frequencies in the upper Tennessee River Basin compared with national averages from previous National Water-Quality Assessment Program investigations across the Nation.

included alachlor, acetochlor, carbofuran, diazinon, metolachlor, metribuzin, prometon, and simazine.

Atrazine, deethylatrazine, metolachlor, tebuthiuron, and napropamide were detected more frequently at mixed land-use sites in the UTEN than at mixed land-use sites included in the national summary of pesticide detections (fig. 5). Atrazine and deethylatrazine were detected in 94 and 95 percent of samples from mixed land-use sites in the UTEN compared to the national average for mixed land-use sites of 83 and 68 percent, respectively. For mixed land-use sites, metolachlor was detected in 84 percent of samples in the UTEN compared to 74 percent nationwide; and tebuthiuron was detected in 61 percent of samples in the UTEN compared to the average of 34 percent for mixed land-use sites nationwide. Detection frequency for napropamide in the UTEN slightly exceeded the national average for mixed land-use sites (fig. 5). Comparison of detection frequencies at sites with mixed land-use drainages in the UTEN with national averages reveal results similar to the agricultural sites with the exception of metolachlor, which was detected more frequently in the UTEN.

Water-Quality Standards

The U.S. EPA has established water-quality standards and guidelines that specify thresholds of concentrations of certain chemicals that have adverse effects on human health, aquatic organisms, and wildlife. Although the maximum contaminant levels (MCL) and lifetime health advisory levels (HAL) established by the U.S. EPA (2000) pertain to finished drinking water supplied by a community water system, values are provided with which ambient concentrations can be compared. MCLs or HALs have been established for 21 of the 31 pesticides and metabolites detected at sites in the UTEN study (table 4). Aquatic-life criteria have been established for the protection of aquatic organisms for short-term (acute) and long-term (chronic) exposures. Chronic aquatic-life criteria have been established for 14 of the 31 pesticides and metabolites detected at sites in the UTEN study (table 4).

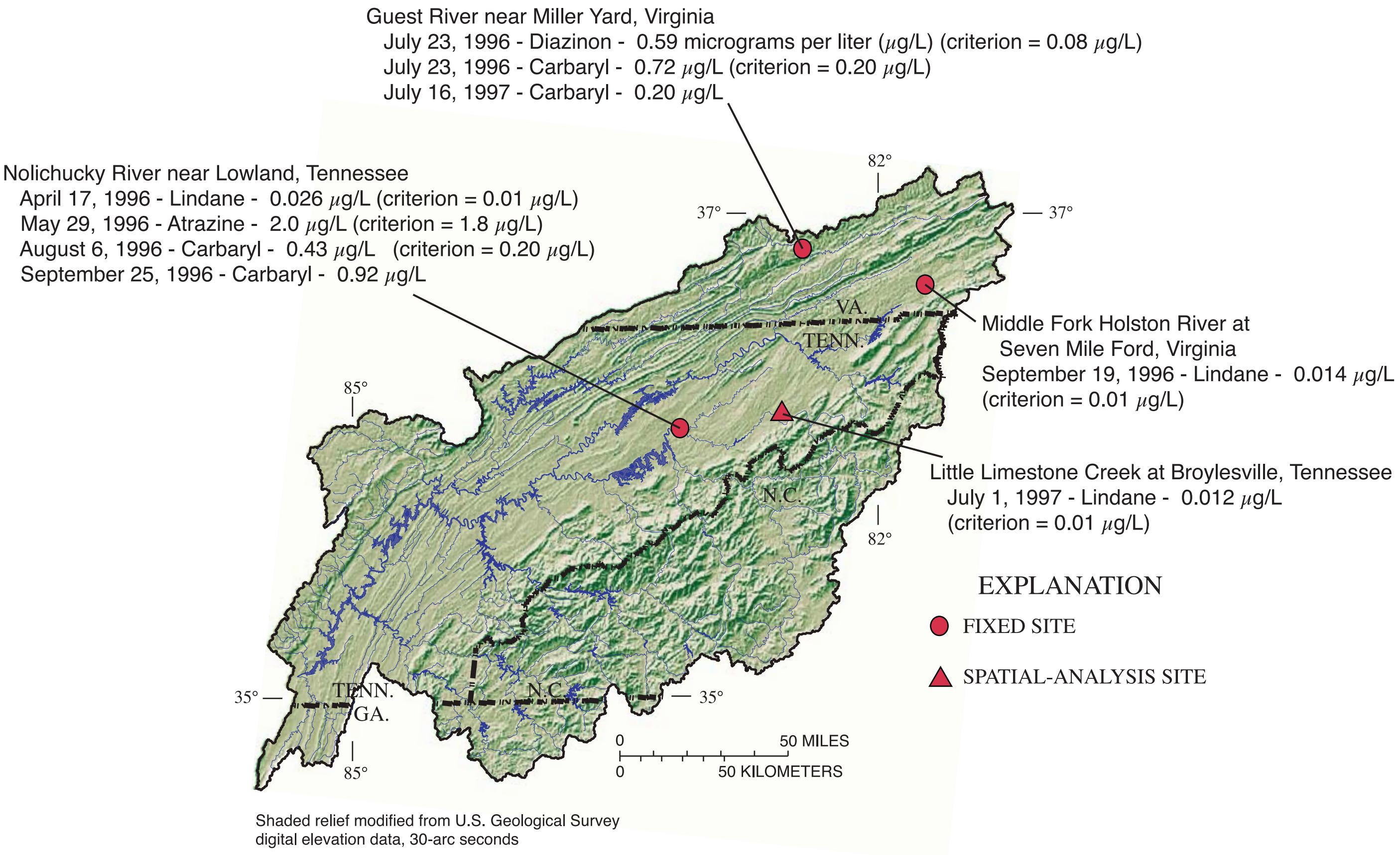
Concentrations of pesticides and metabolites detected in streams in the UTEN generally were below established water-quality standards and guidelines. Although most of the samples collected in the UTEN contained detectable concentrations of one or more pesticides, no concentrations exceeded any human health standards (MCLs or HALs). Only 2 percent of the samples collected at UTEN sites had concentrations of one or more pesticides that exceeded the chronic aquatic-life criteria (fig. 6), and the exceedances were for atrazine, diazinon, carbaryl, and lindane.

Total pesticide concentrations were computed by summing the concentrations of the detectable pesticides (above the MRL) for each sample in order to account for the presence of multiple pesticides. Total pesticide concentrations for samples collected at the fixed sites in the UTEN ranged from less than 0.001 μg/L at Clear Creek at Lilly Bridge near Lancing, Tenn., to 3.15 μg/L for a sample with eight pesticide detections collected at Nolichucky River near Lowland, Tenn. The effects of pesticide mixtures on biota and human health are unknown; however, this is an area of active research, and the U.S. EPA is considering establishing health standards for combinations of pesticides (U.S. Environmental Protection Agency, 1994).

SEASONAL AND SPATIAL VARIABILITY OF PESTICIDES IN STREAMS OF THE UPPER TENNESSEE RIVER BASIN

Pesticide occurrence and concentrations varied seasonally and spatially in the UTEN and were closely associated with land use and time of application. Peak concentrations of pesticides generally were detected during the spring and immediately following pesticide application. However, low levels (concentrations generally less than 0.10 μg/L) of pesticides were detected throughout the year at the fixed sites in the UTEN.

Seasonal variability was evident for several pesticides at the 13 fixed sites. Monthly sampling for pesticides at fixed sites was conducted to characterize the seasonal variation of pesticides in streams in the UTEN. Peak concentrations occurred during the growing season (April through September) for all pesticides except dichlobenil, trifluralin, and *alpha* HCH (table 4). Differences in pesticide concentrations (and detection frequencies) between the growing and nongrowing seasons were pronounced for the French Broad River, Middle Fork Holston River, Clinch River, Clear Creek, Big Limestone Creek, and Nolichucky River. Although comparisons of median concentrations between the growing and nongrowing seasons indicate little change for some sites (Guest River and Copper Creek), maximum concentrations for most pesticides were detected during the growing



Guest River near Miller Yard, Virginia
July 23, 1996 - Diazinon - 0.59 micrograms per liter (μg/L) (criterion = 0.08 μg/L)
July 23, 1996 - Carbaryl - 0.72 μg/L (criterion = 0.20 μg/L)
July 16, 1997 - Carbaryl - 0.20 μg/L

Nolichucky River near Lowland, Tennessee
April 17, 1996 - Lindane - 0.026 μg/L (criterion = 0.01 μg/L)
May 29, 1996 - Atrazine - 2.0 μg/L (criterion = 1.8 μg/L)
August 6, 1996 - Carbaryl - 0.43 μg/L (criterion = 0.20 μg/L)
September 25, 1996 - Carbaryl - 0.92 μg/L

Middle Fork Holston River at
Seven Mile Ford, Virginia
September 19, 1996 - Lindane - 0.014 μg/L
(criterion = 0.01 μg/L)

Little Limestone Creek at Broylesville, Tennessee
July 1, 1997 - Lindane - 0.012 μg/L
(criterion = 0.01 μg/L)

Shaded relief modified from U.S. Geological Survey
digital elevation data, 30-arc seconds

Figure 6. Location of stream sites with samples in which pesticide concentrations were equal to or exceeded aquatic-life criteria in the upper Tennessee River Basin.

season, usually during June and July following the application of agricultural pesticides, at all fixed sites (table 4). Elevated concentrations of several pesticides including atrazine, deethylatrazine, metolachlor, tebuthiuron, simazine, prometon, and chlorpyrifos were detected during the growing season at most fixed sites.

Weekly sampling at the three agricultural sites, where the upstream drainage areas contained large percentages of agricultural land, revealed that the highest pesticide concentrations were detected in late spring and early summer (fig. 7). Peak herbicide concentrations usually coincided with the first substantial storm following agricultural applications in the spring and declined to near-background levels as concentrations were diluted by the increased discharge that accompanied the storm. Maximum concentrations of herbicides were detected during May and June following the application of herbicides to farm fields and residential lawns. Of the 39 samples that contained at least one pesticide with a concentration greater than 0.1 μg/L at the three agricultural sites, 36 samples were collected during the months of May, June, July, and August.

Data were collected at 61 stream sites to analyze the spatial variation of pesticides in 7 major subbasins and 3 smaller tributaries to the Tennessee River (fig. 2). Sampling conducted during the late springs and early summers of 1996, 1997, and 1998 was focused on low streamflow conditions in agricultural and mixed land-use settings. A few water samples were collected in urban streams that are influenced by industrial and municipal effluents and urban runoff. In 1996, data collection was focused in the Clinch, Powell, and Emory River Basins; in 1997, in the Nolichucky and French Broad River Basins, and in 1998, in the Holston River Basin. Because of breaks in the sampling schedule as a result of unsuitable hydrologic conditions, these data do not portray nearly instantaneous, concurrent water-quality conditions, as would have been possible if intensive sampling had been performed over a short time period. Instead, greater emphasis was given to sampling under consistent streamflow conditions. Because of the offsets in

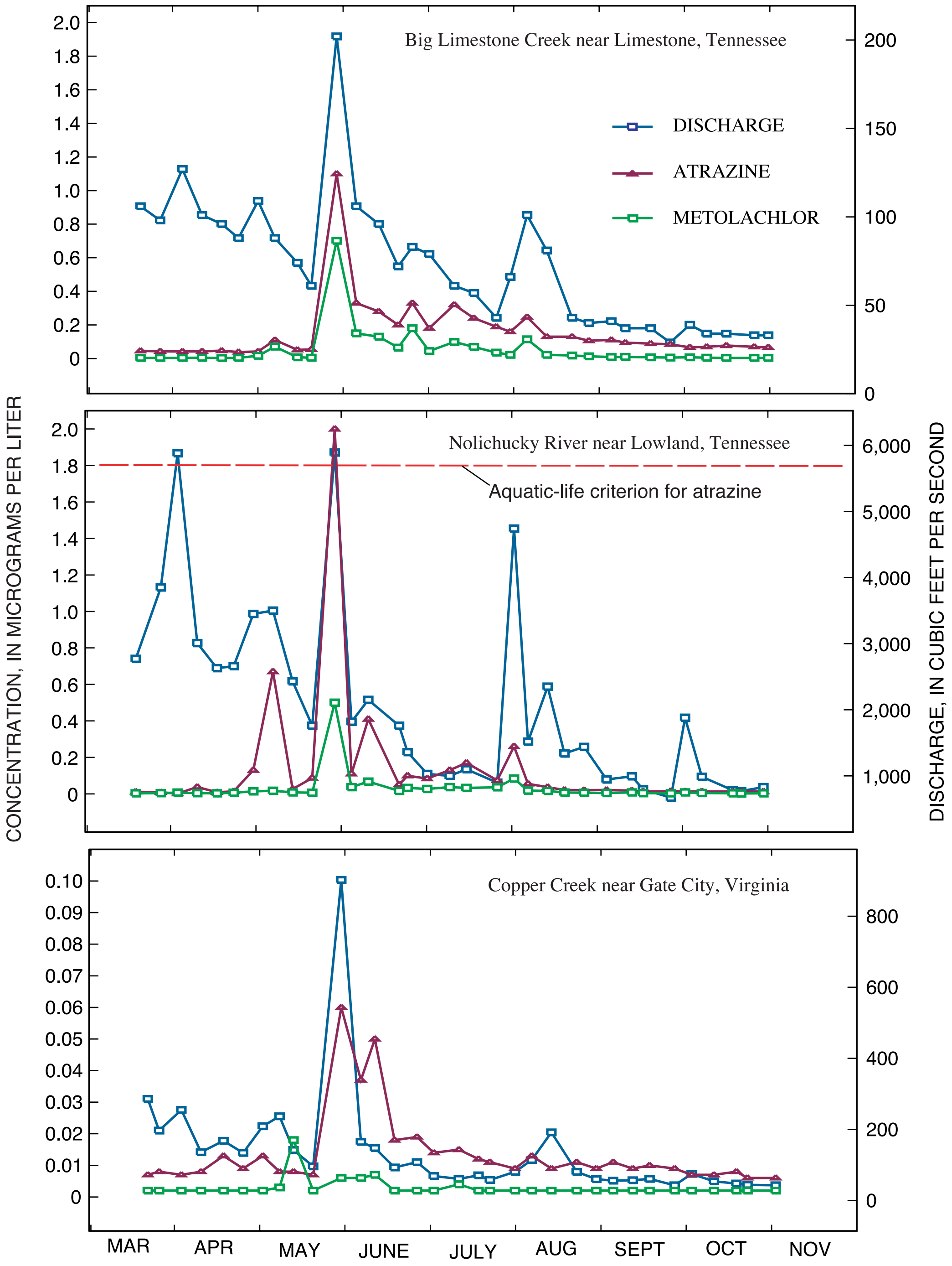


Figure 7. Seasonal variation in pesticide concentrations at agricultural sites in the upper Tennessee River Basin, 1996.

sampling dates, potential for variations of pesticide concentrations exists among sites; therefore, these variations of concentrations can be related to variation in timing of sampling relative to pesticide applications.

In 1996, sampling was conducted at 24 sites primarily in the Clinch, Powell, and Emory River Basins to evaluate spatial distribution of pesticides. Twelve pesticides were detected at sites in the Clinch and Powell River Basins; the number of pesticides detected per sample ranged from one to eight (fig. 8). Atrazine was detected most frequently (100 percent) in samples from the Clinch River Basin sites, and tebuthiuron was detected most frequently (100 percent) in samples from the Powell River Basin sites. Concentrations of all detected pesticides were relatively low (less than 0.10 µg/L), with the exception of two tebuthiuron concentrations (0.21 and 0.26 µg/L) in samples from the Powell River Basin.

The spatial-analysis sites sampled in the Emory River Basin are located within the Obed National Wild and Scenic River system. Two or three pesticides were detected at each of the five sites sampled in the Emory River Basin in 1996 (fig. 9). Six pesticides were detected at one additional site that was sampled in 1998. Atrazine and deethylatrazine were detected in all samples, and prometon was detected in half of the samples. Metolachlor and tebuthiuron were detected in two samples, and diazinon was detected in one sample. Concentrations of the detected pesticides were generally less than 0.10 µg/L.

The French Broad River Basin sites were sampled in the spring and summer of 1997. Sampling began in April but was discontinued for several weeks because of extremely wet weather and high streamflow conditions; sampling resumed in June and was completed in July. Concentrations for 14 different pesticides—8 herbicides, 5 insecticides, and 1 metabolite—were detected at 20 fixed and spatial-analysis

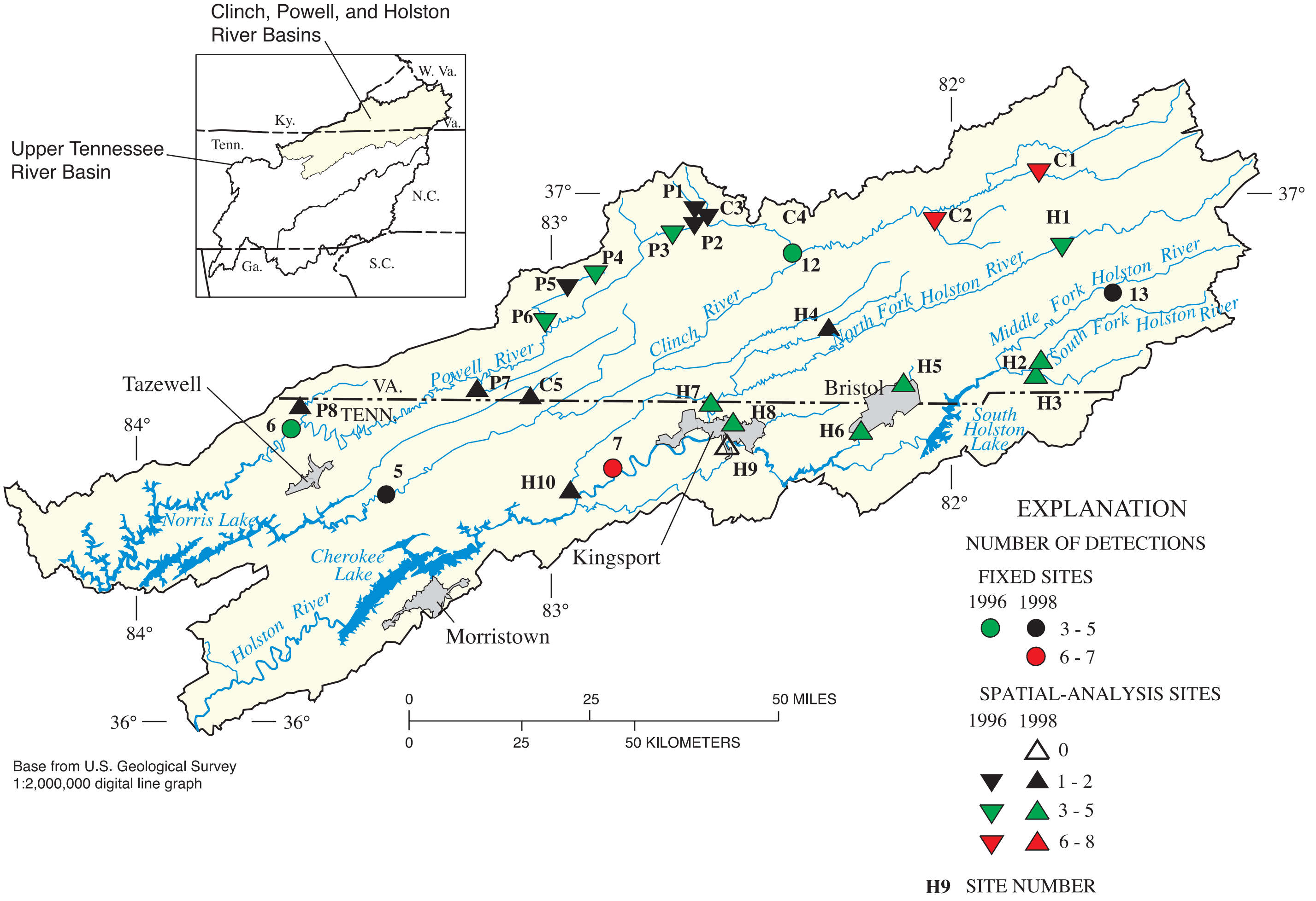


Figure 8. Pesticides detected in samples collected at low flow from 28 stream sites in the Clinch, Powell, and Holston River Basins, 1996 and 1998.

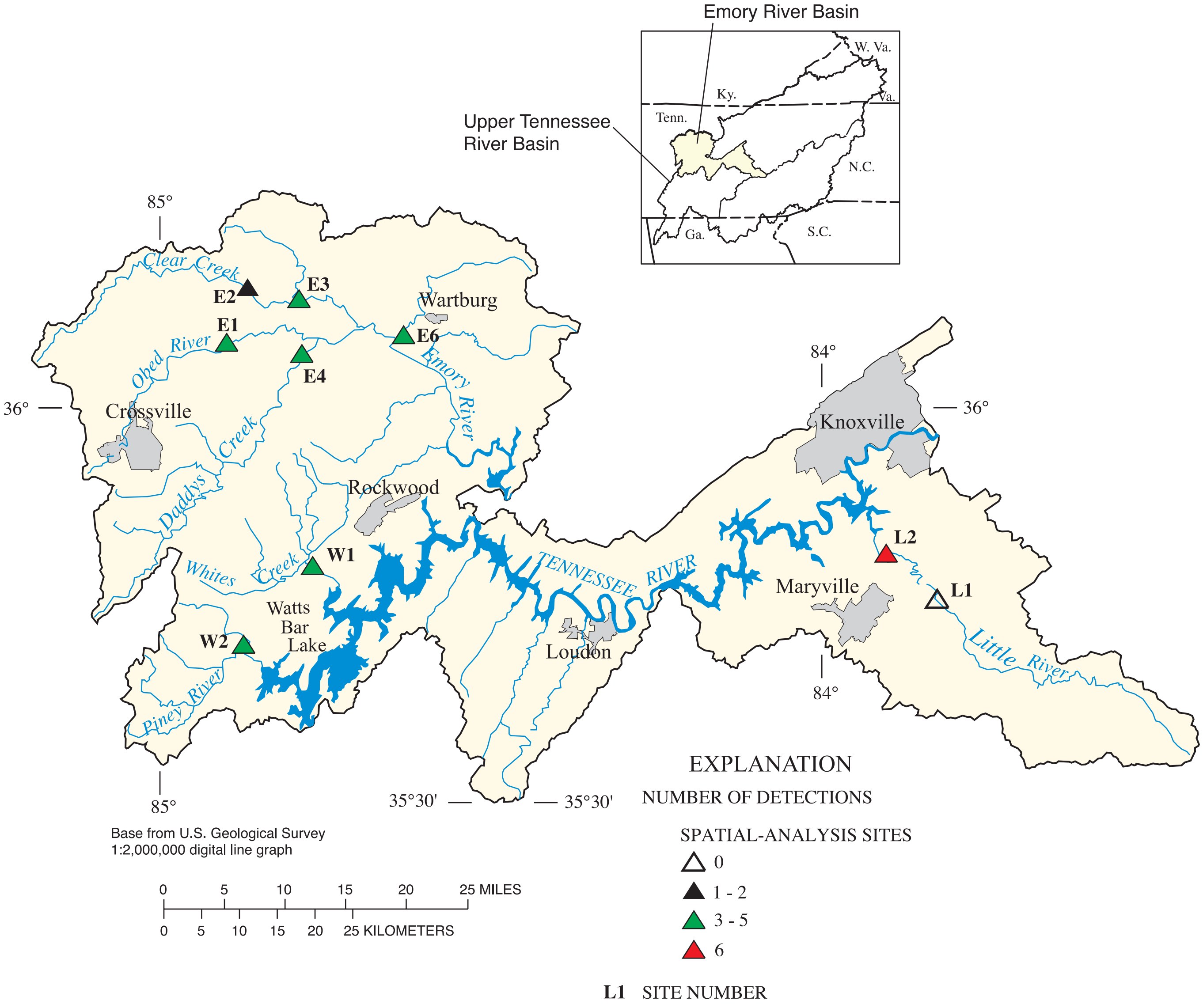
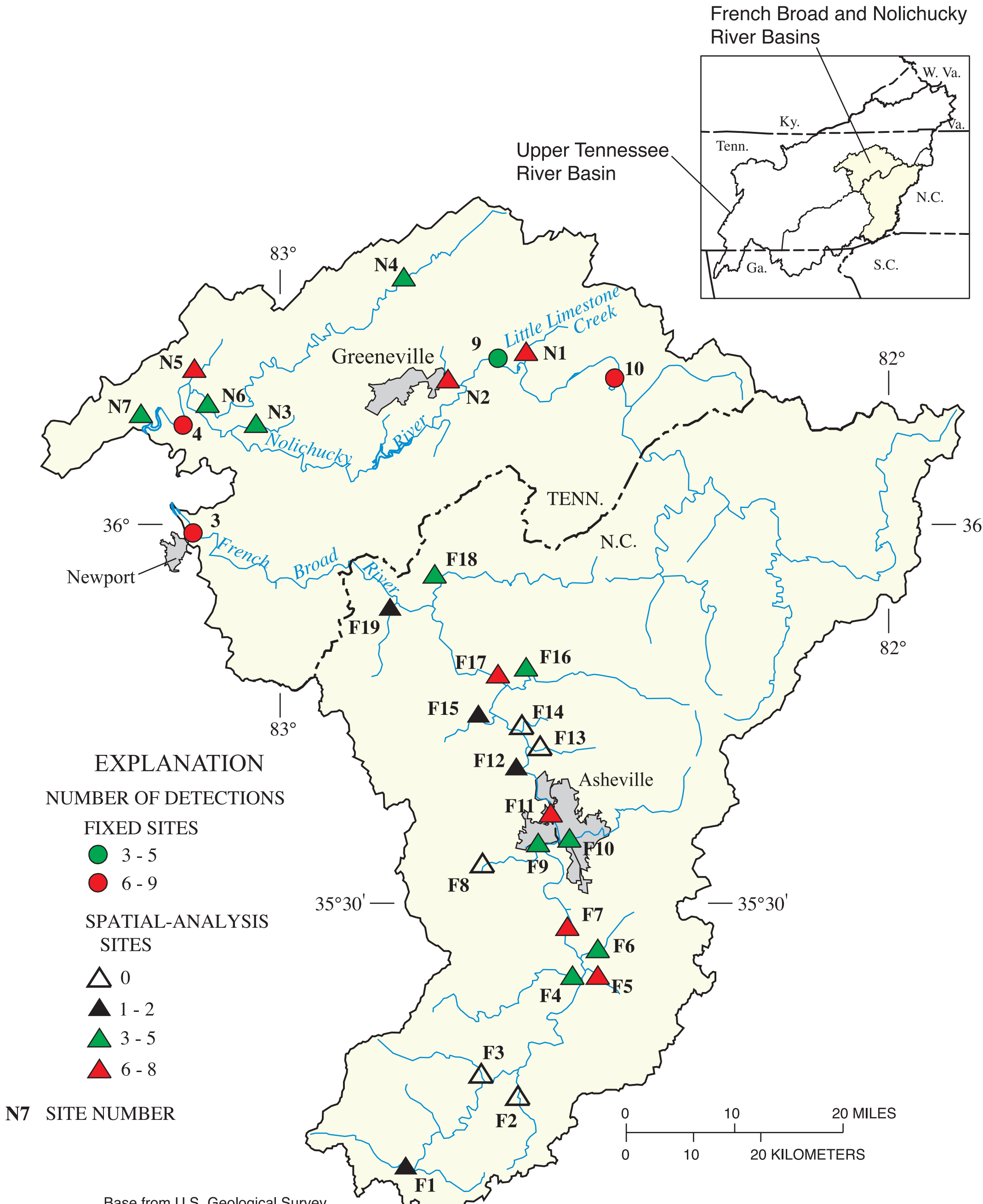


Figure 9. Pesticides detected in samples collected at low flow from 9 stream sites in the Emory River Basin and other tributaries to the upper Tennessee River, 1996.

sampling sites. The number of pesticide detections per sample ranged from none detected at five sites to eight pesticides detected at three sites (fig. 10). The largest number of detections were from samples in the urban drainages of the Asheville, N.C., area. The only detection of the herbicide terbacil was at Mud Creek (F5 on fig. 10 and appendix A), which is an urban stream near Asheville that is influenced by industrial activity. Pesticide concentrations were generally lower in the French Broad River Basin than in the other study-unit basins with the exception of prometon, which was detected at a concentration of 0.16 μg/L in the French Broad River at Glenn Bridge Road near Arden, N.C. (F7 on fig. 10 and appendix A).

Nolichucky River Basin sites also were sampled in the summer of 1997. Concentrations for 15 different pesticides—10 herbicides, 4 insecticides, and 1 metabolite—were detected at 10 fixed and spatial-analysis sampling sites. The number of pesticides detected per site ranged from four to nine. The three fixed sites in the basin, Nolichucky River near Lowland, Tenn. (site 4), Nolichucky River at Embreeville, Tenn. (site 10), and Big Limestone Creek near Limestone, Tenn. (site 9), were sampled during the same time period as the spatial-analysis sites. Nine pesticides were detected at the Nolichucky River near Lowland, six pesticides were detected at the Nolichucky River at Embreeville, and five pesticides were detected at Big



Base from U.S. Geological Survey
1:2,000,000 digital line graph

Figure 10. Pesticides detected in samples from 30 stream sites in the French Broad and Nolichucky River Basins, 1997.

Limestone Creek in samples from this period (fig. 10). Atrazine and deethylatrazine were detected in all samples, and tebuthiuron and metolachlor were detected in 8 of the 10 samples.

Eight detections occurred at the only site (Little Limestone Creek at Broylesville, Tenn.—site N1) that was not sampled during low-flow conditions in 1997. Little Limestone Creek was sampled several hours after a local thunderstorm during a declining stage with high turbidity conditions. Concentrations for several pesticides were elevated for this sample, including atrazine (0.999 µg/L), metolachlor (4.0 µg/L), acetochlor (0.393 µg/L), diuron (0.30 µg/L), and lindane (0.012 µg/L), which was the only exceedance of an aquatic-life criterion detected in stream samples from the spatial-analysis sites in the UTEN. The concentrations for metolachlor, diuron, and acetochlor in this sample were also the highest of all 423 samples (fixed and spatial-analysis sites) collected in the UTEN (1996-99); the atrazine concentration at Little Limestone Creek exceeded 99 percent of measured concentrations. The only detections of alachlor, acetochlor, and lindane at spatial-analysis sites in the French Broad and Nolichucky River Basins occurred at the Little Limestone Creek site. These data indicate that pesticide concentrations can vary significantly in streams during storm flows, particularly during the growing season.

In 1998, samples were collected at spatial-analysis sites and two fixed sites in the Holston River Basin. Seven different pesticides—five herbicides, one insecticide, and one metabolite—were detected in samples from the 12 sites. The number of pesticide detections per sample ranged from zero at Horse Creek near Kingsport, Tenn. (site H9, fig. 8), to four at the North Fork Holston River at Cloud Ford, Tenn. (site H7), and at two sites on Beaver Creek near Bristol, Tenn./Va. (sites H5 and H6) (fig. 8). Atrazine and metolachlor were the two most commonly detected pesticides. Atrazine was detected in 11 samples; metolachlor was detected in 7 samples. Pesticides were measured at relatively low concentrations (less than 0.05 μg/L) with no exceedances of human health or aquatic-life criteria.

At the 61 stream sites, 20 different pesticides were detected, and at least 1 pesticide was detected in 89 percent of the samples collected. Median concentrations of pesticides for all spatial-analysis samples equaled the MRL for all pesticides except atrazine and deethylatrazine. Pesticide concentrations most frequently exceeding the threshold concentration of 0.01 μg/L were atrazine (54 percent), tebuthiuron (41 percent), deethylatrazine (17 percent), metolachlor (16 percent), simazine (14 percent), and prometon (12 percent). Although the detection frequencies were lower for most pesticides at the spatial-analysis sample sites in comparison to the fixed sites, the same group of pesticides were most frequently detected at both sets of sites. Seven pesticides detected at the fixed sites were not detected at any of the spatial-analysis sites.

SUMMARY

The USGS conducted an assessment of pesticides in streams in the UTEN as part of the National Water-Quality Assessment Program. Thirteen stream sites were selected as fixed sampling sites to represent the diverse land uses, physiographic settings, and other drainage-basin characteristics in the UTEN, which includes parts of Tennessee, North Carolina, Virginia, and Georgia and drains about 21,400 mi^2. The fixed sites were sampled for pesticides at fixed intervals and supplemented with storm-flow samples. Samples also were collected at 61 additional sites in the major subbasins of the UTEN during the springs and summers of 1996, 1997, and 1998 to assess the spatial variation of pesticides during low flow in streams.

Pesticides that were detected frequently in streams in the UTEN were generally the pesticides having high estimated use in the basin. A total of 30 pesticides were detected in 362 samples collected at the 13 fixed sites. Herbicides were detected more frequently than insecticides, which is consistent with the greater use of herbicides in the UTEN. Of the 10 most frequently detected pesticides, 8 were herbicides and 1 was a metabolite of atrazine. Atrazine, metolachlor, and simazine, heavily used herbicides in the UTEN, were detected frequently in streams in the UTEN. The herbicides most frequently detected at concentrations at or greater than 0.01 μg/L were atrazine (in 59 percent of samples), tebuthiuron (41 percent), deethylatrazine (31 percent), metolachlor (24 percent), simazine (17 percent), and prometon (6.4 percent). The insecticides most frequently detected at concentrations at or greater than 0.01 μg/L were carbaryl (6.1 percent), diazinon (1.9 percent), carbofuran (1.7 percent), and chlorpyrifos (1.1 percent).

Pesticide detection frequencies also were associated with land use. Generally, the most frequently detected pesticides (atrazine, deethylatrazine, metolachlor, and simazine) were those applied to agricultural land. Detection frequencies of pesticides varied from site to site, reflecting differences in land use in the upstream drainages. Although Copper Creek near Gate City, Va., is an intensively agricultural site, metolachlor was detected in only 18 percent of the samples from the Copper Creek site. Tebuthiuron and prometon, which are most commonly used in noncropland areas and on pastureland, also were among the most frequently detected herbicides in the UTEN study.

Pesticide detection frequencies for the UTEN were compared with the national summary compiled by the USGS from NAWQA studies (1992-98); atrazine, deethylatrazine, tebuthiuron, and napropamide were more frequently detected in the UTEN study than in the national summary of pesticide detections for streams with agricultural drainages and for streams draining areas of mixed land use. Atrazine and deethylatrazine were detected in about 99 and

98 percent of samples, respectively, in the UTEN compared to the national average of about 85 and 69 percent, respectively, for agricultural sites. Tebuthiuron was detected in 62 percent of water samples from agricultural sites in the UTEN as compared to about 22 percent of samples from agricultural sites nationwide. Pesticides that were detected considerably less frequently in the UTEN streams than at the nationwide agricultural sites included alachlor, acetochlor, carbofuran, diazinon, metolachlor, metribuzin, prometon, and simazine. Comparison of detection frequencies at sites with mixed land-use drainages in the UTEN with the national averages reveal results similar to the agricultural sites with the exception of metolachlor, which was detected more frequently in the UTEN.

Low concentrations (generally less than 0.10 µg/L) of pesticides were detected at all 13 fixed sites in the UTEN. Concentrations of individual pesticides ranged from 0.001 to 2.0 µg/L. Atrazine, bromacil, dichlorprop, 2,6-diethylaniline, metolachlor, metribuzin, simazine, carbaryl, carbofuran, and diazinon were detected in samples at concentrations greater than 0.10 µg/L. In 47 of the 362 samples collected, one or more pesticides were detected in samples at concentrations greater than 0.10 µg/L. Concentrations of atrazine exceeded 0.10 µg/L in 37 samples, and concentrations of metolachlor exceeded 0.10 µg/L in 11 samples. Seven samples had concentrations of one or more pesticides exceeding 0.50 µg/L, and only four samples had concentrations of one or more pesticides exceeding 1.0 µg/L.

Peak pesticide concentrations were detected at the agricultural sites in late spring and early summer, generally coinciding with pesticide applications and the first substantial runoff event following pesticide applications. Concentrations of atrazine and metolachlor were elevated more frequently than concentrations of other pesticides, and most of the elevated concentrations were detected at the agricultural sites. The maximum pesticide concentration of 2 µg/L was detected for atrazine at the Nolichucky River near Lowland, Tenn. Agricultural land accounts for only about 39 percent (650 mi^2) of the drainage upstream of this site; however, most of the area adjacent to or directly upstream from the sampling site is predominantly agricultural. The maximum concentration detected for metolachlor was 1.3 µg/L in a sample collected at Big Limestone Creek near Limestone, Tenn., which has a watershed that consists of about 83 percent agricultural land. Elevated concentrations of several pesticides including atrazine, deethylatrazine, metolachlor, tebuthiuron, simazine, prometon, and chlorpyrifos were detected during the growing season at most fixed sites.

Concentrations of pesticides and metabolites in streams in the UTEN generally were well below established water-quality criteria. Although most of the water samples collected in the UTEN study area contained detectable concentrations of one or more pesticides, none of the concentrations exceeded human health standards. Only 21 of the 31 pesticides detected, however, have established MCL or HAL criteria. Of the 14 pesticides detected that have established criteria for the protection of aquatic life, only carbaryl, lindane, diazinon, and atrazine were detected at concentrations exceeding the criteria in 7 of the 362 samples collected at fixed sites.

Spatial analysis of pesticide detections and concentrations in several of the subbasins of the UTEN indicated that the network of fixed sites in the UTEN were generally representative of conditions throughout the basin. The most frequently detected pesticides in water samples from the spatial-analysis sites were atrazine, deethylatrazine, metolachlor, tebuthiuron, simazine, and prometon. Only 1 of the 61 stream samples was collected under hydrologic conditions that did not represent low flow. This site, Little Limestone Creek at Broylesville, Tenn., was sampled several hours after a major storm. High concentrations of several pesticides were measured at this site, including one exceedance of the aquatic-life criterion for lindane. Overall, concentrations of pesticides at spatial-analysis sites were lower than at fixed sites in every subbasin; however, a greater number of detections usually occurred at sites that were influenced by urban or industrial land use. Of the 47 pesticides that were analyzed in all samples, 7 pesticides detected at the fixed sites were not detected at any of the spatial-analysis sites. Conversely, only one of the pesticides (terbacil) detected at a spatial-analysis site was not detected in samples collected at the fixed sites.

REFERENCES

Canadian Council of Ministers of the Environment, 1997, Canadian water quality guidelines (rev. ed.): Ottawa, Ontario, Water Quality Guidelines Task Group, Canadian Council of Resource and Environment Ministers, loose-leaf (originally published 1987), 23 appendixes.

Capel, P.D., Nacionales, F.C., and Larson, S.J., 1995, Precision of a splitting device for water samples: U.S. Geological Survey Open-File Report 95-293, 10 p.

DeBuchananne, G.D., and Richardson, R.M., 1956, Ground-water resources of East Tennessee: Tennessee Division of Geology Bulletin 58, pt. 1, 393 p.

Denton, G.M., Vann, A.D., and Wang, S.H., 2000, The status of water quality in Tennessee 2000, 305(b) report: Tennessee Department of Environment and Conservation, Division of Water Pollution Control, 223 p.

Edwards, T.K., and Glysson, G.D., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Environment Canada, 2001, Summary of Canadian water quality guidelines for the protection of aquatic life, accessed June 6, 2001, at http://www.ec.gc.ca/ceqg-rcqe/water.pdf

Fenneman, N.M., and Johnson, D.W., 1946, Physical divisions of the United States: Washington, D.C., U.S. Geological Survey Special Map, scale 1:700,000.

Goolsby, D.A., and Pereira, W.E., 1995, Pesticides in the Mississippi River: U.S. Geological Survey Circular 1133, accessed November 1999, at http://water.usgs.gov/pubs/circ1133/pesticides.html

Hirsch, R.M., Alley, W.M., and Wilbur, W.G., 1988, Concepts for a national water-quality assessment program: U.S. Geological Survey Circular 1021, 42 p.

International Joint Commission United States and Canada, 1989, Great Lakes water quality agreement of 1978 (revised 1987), v. 2, An International Joint Commission report to the governments of the United States and Canada: International Joint Commission, Windsor, Ontario Canada, accessed March 4, 2000, at http://www.ijc.org/agree/quality.html

Larson, S.J., Capel, P.D., and Majewski, M.S., 1997, Pesticides in surface waters: Distribution, trends, and governing factors: Chelsea, Mich., Ann Arbor Press, Inc., 373 p.

Leahy, P.P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 90-174, 10 p.

Rinella, F.A., and Janet, M.L., 1998, Seasonal and spatial variability of nutrients and pesticides in streams of the Willamette Basin, Oregon, 1993-95: U.S. Geological Survey Water-Resources Investigations Report 97-4082-C, 59 p.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foremen, W.T., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 91-519, 26 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 44 p.

Thelin, G.P., 1999, County-level pesticide use estimates (1991-1993, 1995) in the conterminous United States, accessed November 1, 2001, at ftp://ftpdcascr.wr.usgs.gov/nsp/thelin/ncfap.html

Thelin, G.P., and Gianessi, L.P., 2000, Method for estimating pesticide use for county areas of the conterminous United States: U.S. Geological Survey Open-File Report 00-250, 62 p.

U.S. Department of Agriculture, 1999, National Agricultural Statistics Service, Census of Agriculture, Tennessee: accessed June 8, 2000, at http://www.nass.usda.gov/census/census92/atlas92/html/tn.htm

U.S. Environmental Protection Agency, 1994, Atrazine, simazine and cyanazine; notice of initiation of special review: Federal Register, v. 59, p. 60412-60443, accessed spring 2000 at http://www.epa.gov/fedrgstr/EPA-PEST/1994/November/Day-23/pr-54.html

U.S. Environmental Protection Agency, Office of Water, 2000, Drinking water standards and health advisories, accessed October 12, 2000, at http://www.epa.gov/waterscience/drinking/standards/dwstandards.pdf

U.S. Geological Survey, 1997, Pesticides in surface waters—current understanding of distribution and major influences: U.S. Geological Survey Fact Sheet FS-039-97, 4 p.

———1998, Sources and limitations of data used to produce maps of annual pesticide use, accessed June 8, 2001, at http://ca.water.usgs.gov/pnsp/use92/mapex.html

———1999, The quality of our nation's waters—nutrients and pesticides: U.S. Geological Survey Circular 1225, 82 p.

———2000, Pesticides in surface and ground water of the United States: Summary of results of the National Water-Quality Assessment Program, accessed September 20, 2000, at http://ca.water.usgs.gov/pnsp/allsum

Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, 42 p.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

APPENDIX

Appendix A. Sites sampled for spatial analysis of pesticides in the upper Tennessee River Basin, 1996-98

[USGS, U.S. Geological Survey; dates given as month-day-year]

Site number	USGS station name	USGS station number	Sample date	Drainage area (square miles)	Land use (percent)				
					Forest	Pasture	Cropland	Urban	Other
	Clinch River Basin (fig. 8)								
C1	Little River at U.S. Highway 19 near Wardell, Va.	03522000	6-11-96	105	49.8	46.4	0.7	1.1	0.2
C2	Big Cedar Creek below Daugherty's Cave near Lebanon, Va.	03523080	6-10-96	86	50.6	44.6	1.2	2.8	0.0
C3	Guest River at Esserville, Va.	03524330	5-14-96	23	78.5	13.0	0.2	7.3	0.9
C4	Guest River at Coeburn, Va.	03524500	5-14-96	87	78.0	13.7	0.2	7.6	0.4
C5	Blackwater Creek at Newman Ridge near Kyles Ford, Tenn.	0352763950	5-20-98	32	76.9	20.4	2.0	0.6	0.1
	Powell River Basin (fig. 8)								
P1	Powell River near Esserville, Va,	03529050	6-3-96	7	84.3	10.9	0.1	4.6	0.1
P2	Powell River at Norton, Va.	03529075	6-4-96	11	86.1	10.4	0.0	3.4	0.1
P3	Powell River at Blackwood, Va.	03529295	6-4-96	25	87.0	9.0	0.0	3.6	0.2
P4	North Fork Powell River at Keokee, Va.	03530150	5-15-96	9	85.1	9.9	0.2	2.2	2.6
P5	North Fork Powell River near Dryden, Va.	03530225	6-6-96	23	82.6	11.3	0.4	4.1	1.6
P6	North Fork Powell River at Penningham Gap, Va.	03530550	6-12-96	89	81.7	14.0	0.6	3.2	0.5
P7	Wallen Creek below Lone Branch near Jonesville, Va.	03531518	5-20-98	44	63.3	33.1	2.6	0.5	0.0
P8	Indian Creek at Greers Chapel, Tenn.	03531900	5-21-98	52	57.2	39.9	2.0	0.8	0.1
	Holston River Basin (fig. 8)								
H1	North Fork Holston River near Saltville, Va.	03488000	6-13-96	223	72.9	24.7	1.0	0.6	0.1
H2	South Fork Holston River above Damascus, Va.	03472150	7-15-98	136	66.1	30.4	2.1	1.3	0.1
H3	Laurel Creek at Vails Mill at Damascus, Va.	03472700	7-15-98	158	86.7	11.0	1.1	1.2	0.0
H4	Big Moccasin Creek at Collinwood near Hansonville, Va.	03489870	7-14-98	329	74.9	22.4	0.8	0.9	0.2
H5	Beaver Creek at Bristol, Va.	03478400	7-15-98	26	31.5	48.7	8.8	10.6	0.4
H6	Beaver Creek near Avoca below Bristol, Tenn.	03478592	7-16-98	62	35.2	36.9	5.8	21.8	0.3
H7	North Fork Holston River near Cloud Ford, Tenn.	03490090	7-14-98	717	70.8	25.4	1.6	1.6	0.2
H8	Reedy Creek at Gibsontown near Kingsport, Tenn.	03487595	7-13-98	53	49.9	33.0	3.3	13.6	0.1

Appendix A. Sites sampled for spatial analysis of pesticides in the upper Tennessee River Basin, 1996-98—Continued

Site number	USGS station name	USGS station number	Sample date	Drainage area (square miles)	Land use (percent)				
					Forest	Pasture	Cropland	Urban	Other
	Holston River Basin (fig. 8)—Continued								
H9	Horse Creek at Smoky Valley near Kingsport, Tenn.	03487521	7-13-98	44	52.0	36.4	3.6	7.8	0.2
H10	Big Creek near Rogersville, Tenn.	03491000	7-17-98	48	61.4	33.2	4.3	1.0	0.1
--	Watauga River near Watauga Point, Tenn. (not shown on fig. 8)	03483960	7-16-98	750	78.2	16.0	1.4	2.9	1.5
	Emory River Basin and other tributaries to the Tennessee River (fig. 9)								
L1	Little River at Coulter Bridge near Maryville, Tenn.	03497450	7-9-96	192	94.3	4.6	0.2	0.7	0.2
L2	Little River at Rockford, Tenn.	03498863	6-24-96	300	76.7	18.5	1.9	2.7	0.2
W1	Whites Creek near Roddy, Tenn.	03541498	6-25-96	118	80.5	15.9	2.9	0.4	0.3
W2	Piney River above mouth of Sock Creek near Spring City, Tenn.	03542495	6-27-96	61	71.0	21.5	3.1	4.1	0.3
E1	Obed River at Potters Ford near Crossville, Tenn.	03538860	7-25-96	107	49.0	39.5	7.0	2.7	1.8
E2	Clear Creek at Norris Ford near Jones Knob, Tenn.	03539717	7-23-96	81	60.3	29.4	5.4	0.4	0.2
E3	Clear Creek at Waltham Ford Bridge near Frankfort, Tenn.	03539735	7-22-96	146	68.2	24.9	3.9	0.3	0.2
E4	Daddys Creek at Devil's Breakfast Table, Tenn.	03539690	7-24-96	174	60.5	29.8	4.4	4.2	1.1
E5	Obed River near Lancing, Tenn.	03539800	6-30-98	518	64.2	27.6	4.3	2.4	0.9
E6	Emory River near Lancing, Tenn.	03538580	6-26-96	92	89.3	9.8	0.7	0.2	0.0
	French Broad River Basin (fig. 10)								
F1	French Broad River at Rosman, N.C.	03439000	7-9-97	69	92.8	4.9	1.4	0.8	0.1
F2	Little River at Cascade Lake Road near Little River, N.C.	0344150700	7-9-97	43	91.7	4.9	1.0	1.2	1.2
F3	Davidson River at Old Henderson Highway at Brevard, N.C.	0344114090	7-8-97 7-30-97	47	95.4	2.0	0.8	1.5	0.3
F4	Mills River at Hopper Lane near Mills River, N.C.	0344602100	4-17-97	73	90.3	7.7	1.2	0.4	0.4
F5	Mud Creek at Naples, N.C.	0344700000	4-16-97	110	48.0	32.4	6.3	13.0	0.3
F6	Cane Creek at U.S. 25 at Fletcher, N.C.	0344766600	4-17-97	82	68.0	28.0	1.9	1.9	0.2
F7	French Broad River at Glenn Bridge Road near Arden, N.C.	0344776625	7-29-97	651	73.9	17.9	3.4	4.4	0.4
F8	South Hominy Creek at Candler, N.C.	0344834200	4-9-97	38	80.1	15.3	0.3	4.1	0.2

Appendix A. Sites sampled for spatial analysis of pesticides in the upper Tennessee River Basin, 1996-98—Continued

Site number	USGS station name	USGS station number	Sample date	Drainage area (square miles)	Land use (percent)				
					Forest	Pasture	Cropland	Urban	Other
French Broad River Basin (fig. 10)—Continued									
F9	Hominy Creek near West Asheville, N.C.	0344878100	4-16-97	103	67.8	18.6	1.1	12.3	0.2
F10	Swannanoa River at Biltmore, N.C.	03451000	4-15-97	130	79.3	8.5	0.6	10.9	0.7
F11	French Broad River at Asheville, N.C.	03451500	7-30-97	944	73.2	16.6	2.6	7.0	0.6
F12	Newfound Creek near Alexander, N.C.	0345169000	4-8-97	33	48.0	37.6	6.6	7.7	0.0
F13	Reems Creek at New Stock Road near Weaverville, N.C.	0345182580	4-9-97	34	77.9	14.9	1.1	6.0	0.1
F14	Flat Creek near Weaverville, N.C.	0345195390	4-10-97	25	57.4	32.2	3.7	6.7	0.1
F15	Sandymush Creek near Volga, N.C.	0345199400	4-8-97	45	72.1	23.5	3.5	0.9	0.0
F16	Ivy River at Marshall, N.C.	0345292005	7-8-97	154	75.1	20.1	2.2	2.6	0.0
F17	French Broad River at Marshall, N.C.	03453500	7-31-97	1331	71.3	18.8	2.8	6.6	0.5
F18	Big Laurel Creek near Stackhouse, N.C.	03454000	4-22-97	58	91.6	6.8	0.9	0.7	0.0
F19	Spring Creek at NC 209 near Hot Springs, N.C.	0345458780	4-21-97	70	91.4	7.8	0.5	0.3	0.0
Nolichucky River Basin (fig. 10)									
N1	Little Limestone Creek at Broylesville, Tenn.	03465650	7-1-97	27	15.1	64.8	10.9	9.1	0.1
N2	Sinking Creek at WWTP near Afton, Tenn.	03466233	7-16-97	14	11.9	68.7	16.7	2.5	0.2
N3	Little Chucky Creek near Warrensburg, Tenn.	03466698	6-25-97	39	28.3	55.7	9.4	6.5	0.1
N4	Lick Creek near Lick Creek Mill near Baileyton, Tenn.	03466835	7-17-97	78	38.5	51.4	7.9	2.1	0.1
N5	Bent Creek near Silver City, Tenn.	03467485	6-24-97	39	21.8	63.4	9.7	4.9	0.1
N6	Lick Creek at Scoot Mill, Tenn.	03467300	6-25-97	262	31.1	55.6	9.7	3.6	0.1
N7	Long Creek near Lowland, Tenn.	03468065	6-24-97	39	23.0	58.7	11.5	6.7	0.2
Pigeon River Basin									
PI1	Pigeon River near Denton, Tenn.	03461080	7-10-96	568	82.1	11.2	1.2	5.2	0.3