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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.

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By M.W. Treece, Jr.

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 03-4006

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FOREWORD

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

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

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CONVERSION FACTORS, DATUMS, WATER-QUALITY UNITS, AND ABBREVIATIONS

Multiply	By	To obtain
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
acre-foot (acre-ft)	1.233×10^{-3}	cubic meter
cubic foot per second (ft^3/s)	2.447×10^{-3}	cubic meter
billion gallons per day (Bgal/d)	$4{,}381 \times 10^{-2}$	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:

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

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

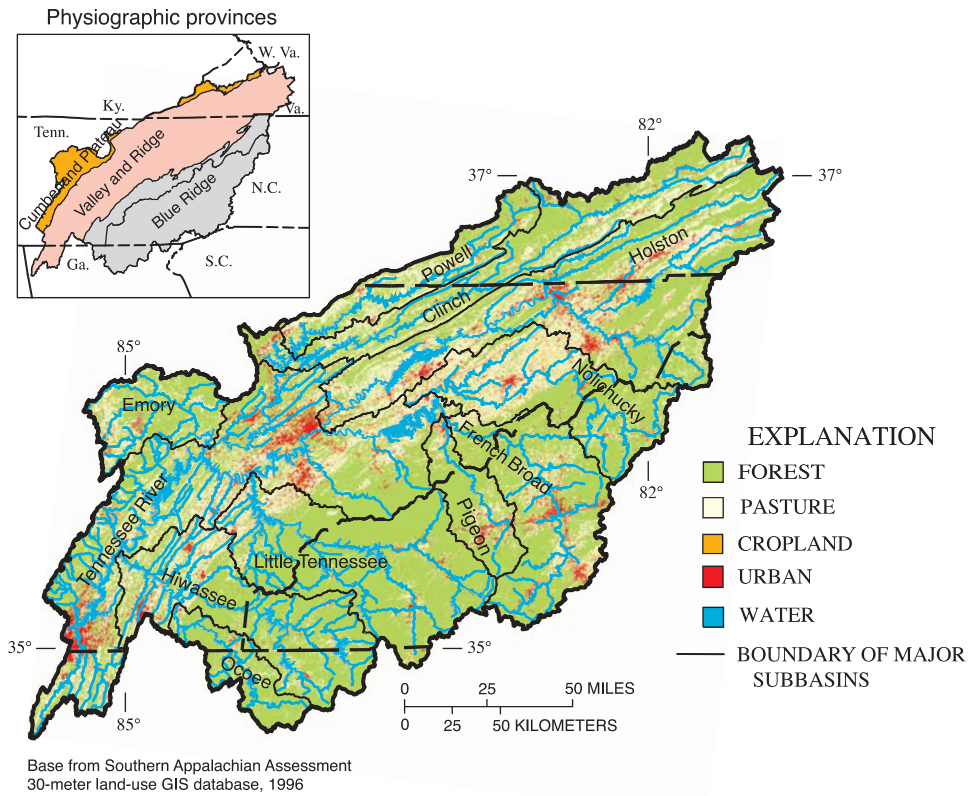

Figure 1. Physiographic provinces, major subbasins, and land use of the upper Tennessee River Basin.

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

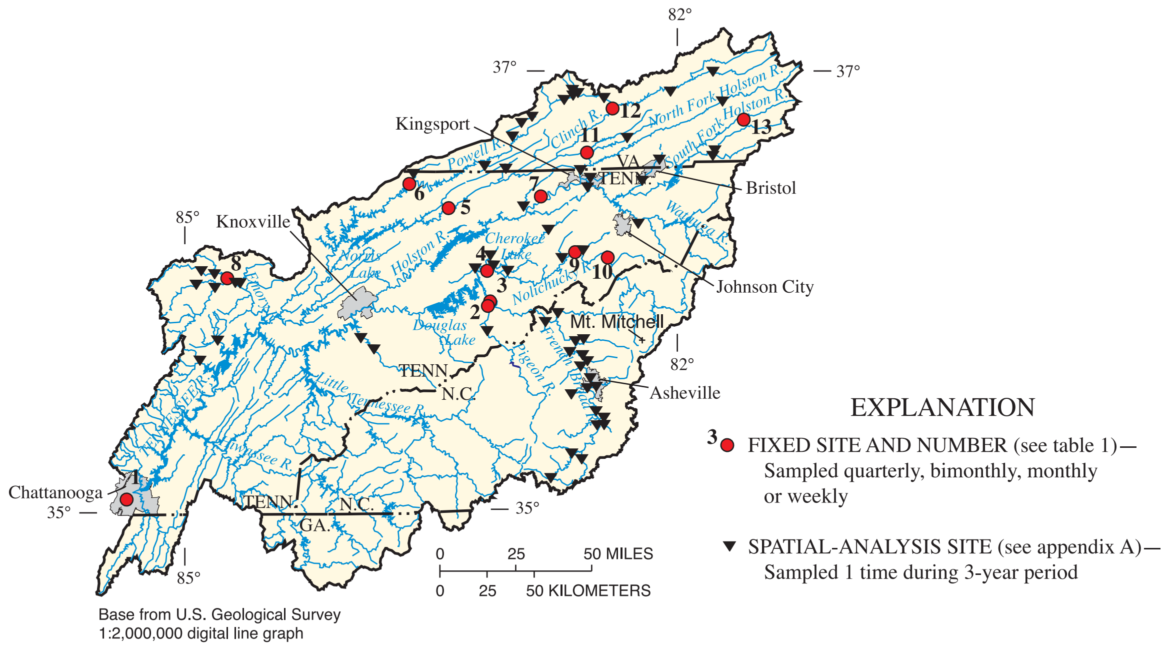

Figure 2. Location of sampling sites in the upper Tennessee River Basin.

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 — Laboratory method		Collection period	Land use (in percent)				
									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

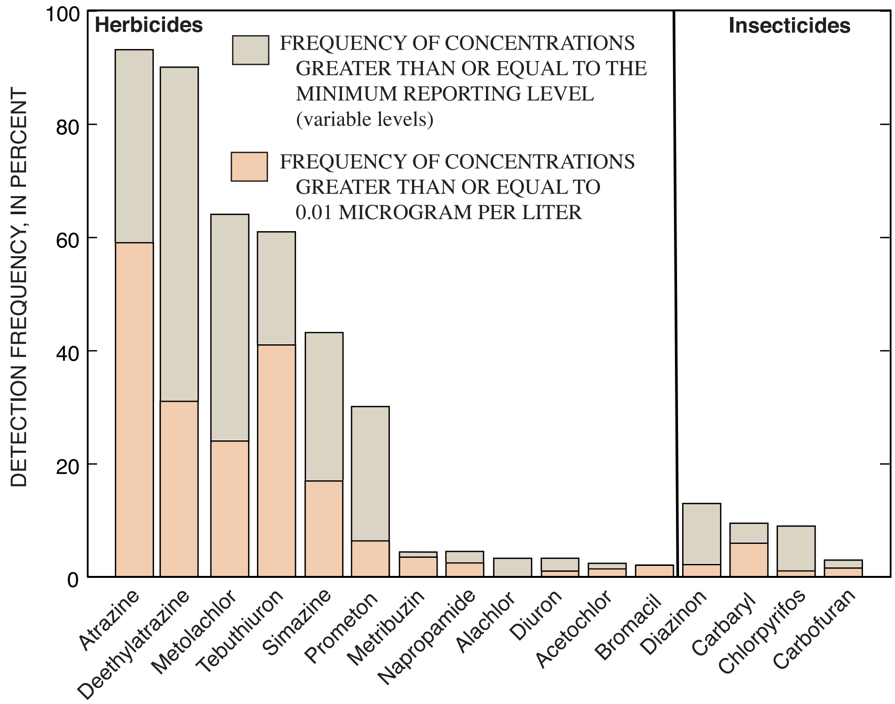

Figure 3. Detection frequency for all pesticides detected in at least 2 percent of samples at fixed sites in the upper Tennessee River Basin, 1996-99.

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).