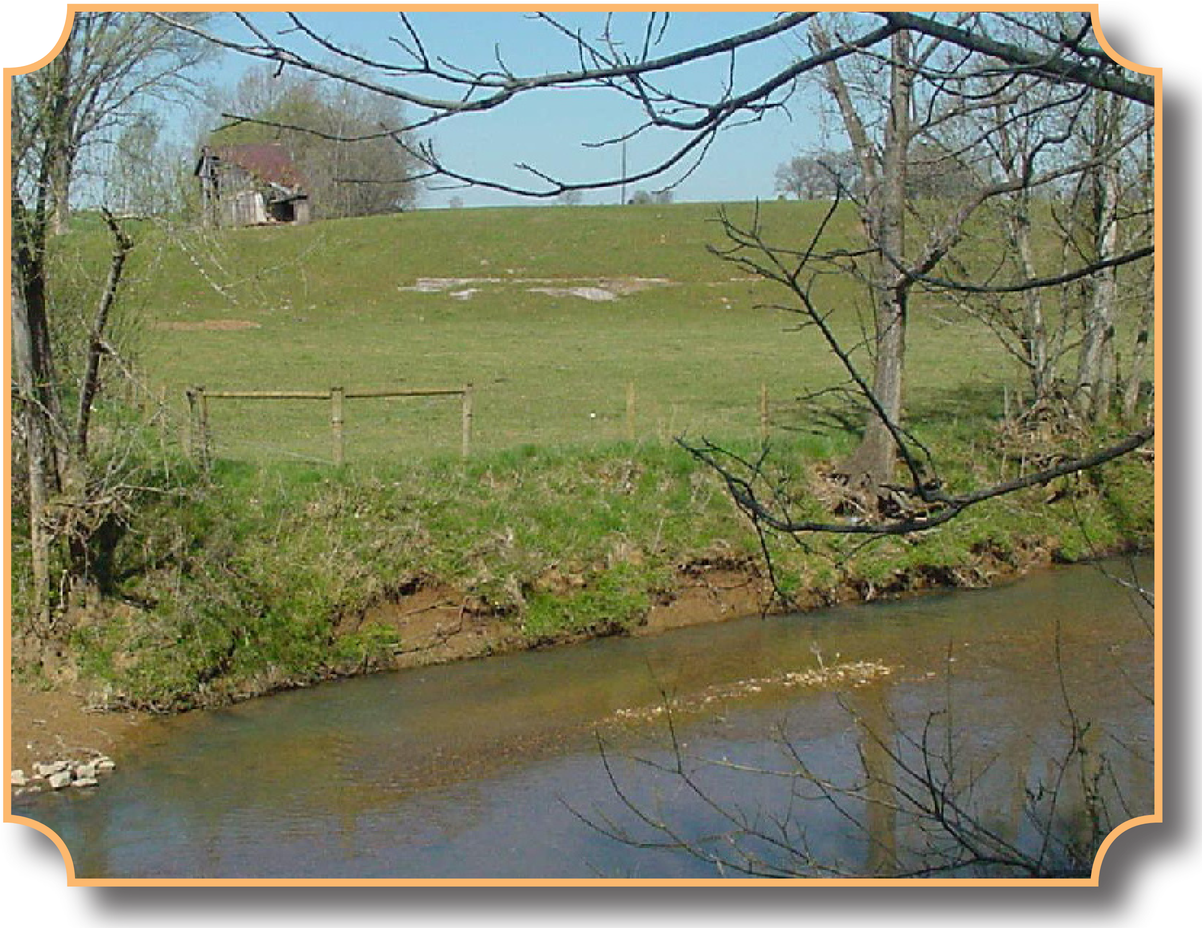
In cooperation with Kentucky Department of Agriculture

Occurrence, Distribution, Loads, and Yields of Selected Pesticides in the Little River Basin, Kentucky, 2003-04



Scientific Investigations Report 2006-5142

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

Cover Photograph. Casey Creek at KY 525 near Cadiz, Kentucky, water-quality site 03437990, April 2003.

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By Angela S. Crain

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Conversion Factors and Abbreviations

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
millimeter (mm)	0.03937	inch (in.)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
mile, nautical (nmi)	1.852	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Application rate	
pound per day (lb/d)	0.4536	kilogram per day (kg/d)
pounds per year (lb/yr)	0.4536	kilograms per year (kg/yr)
pounds per year per square mile ($(lb/yr)/mi^2$)	0.17514	kilograms per year per square kilometer [$(kg/yr)/km^2$]

Temperature in degrees Celsius (˚C) may be converted to degrees Fahrenheit (˚F) as follows:

$$°F=(1.8×°C)+32$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

AIC - Akaike Information Criterion

EDI - equal-discharge increment

EWI - equal-width increment

GC/MS - gas chromatography/mass spectrometry

HAL - health advisory level

KDA – Kentucky Department of Agriculture

MCL - maximum contaminant level

MDL - method detection limit

MRL - method reporting limit

NASS - National Agricultural Statistics Service

NWQL - National Water Quality Laboratory

RPD - relative percent difference

USEPA - U.S. Environmental Protection Agency

USGS - U.S. Geological Survey

Occurrence, Distribution, Loads, and Yields of Selected Pesticides in the Little River Basin, Kentucky, 2003-04

By Angela S. Crain

Abstract

Water resources in the Little River Basin are potentially vulnerable to applications of pesticides associated with both agricultural and nonagricultural activities, because much of the basin is characterized by karst topography. Concerns about water quality resulting from pesticide use in karst areas and lack of data on concentrations of pesticides in surface water led to further investigation of water quality in the Little River Basin, which includes about 600 square miles in Christian and Trigg Counties and a portion of Caldwell County in western Kentucky. Water samples were collected in streams in the Little River Basin, Kentucky during 2003-04 as part of a study conducted in cooperation with the Kentucky Department of Agriculture. The objectives of the study were to assess the occurrence and distribution of pesticides, to evaluate the spatial and seasonal variability of pesticides, and to evaluate loads and yields of selected pesticides in the basin. A total of 91 water samples was collected at 4 fixed-network sites from March through November 2003 and from February through November 2004. An additional 20 samples were collected at 5 synoptic-network sites within the same period.

Twenty-four pesticides were detected of the 127 pesticides analyzed in the stream samples. Of the 24 detected pesticides, 15 were herbicides, 7 were insecticides, and 2 were fungicides. The most commonly detected pesticides—atrazine, simazine, metolachlor, and acetochlor—were those most heavily used on crops during the study. Atrazine and simazine were detected in 100 percent of all surface-water samples, and metolachlor and acetochlor were detected in more than 45 percent. The pesticide degradate, deethylatrazine, was detected in 100 percent of the samples. Only one nonagricultural herbicide, prometon, was detected in more than 50 percent of the samples. Diazinon, the most commonly detected insecticide, was found in 25 percent of all samples and was found at all sites except Casey Creek. Metalaxyl was the most commonly detected fungicide (14 percent); most detections were in samples from the Sinking Fork subbasin.

Concentrations of herbicides were highest following application in the spring (March–May). In contrast, insecticides typically were present during the summer (June-August). The most commonly detected pesticides in the Little River Basin were found at low concentrations in streams year-round. Atrazine and simazine (row-crop herbicides) had the highest measured concentrations (22 and 6.1 micrograms per liter (µg/L), respectively) and were the most heavily applied herbicides in the basin. Metolachlor also was heavily applied in the basin, but measured concentrations did not exceed 0.32 µg/L. The insecticide, Malathion, was only detected in 4 percent of the samples, although it was heavily applied in the basin during 2003-04. Most detections of pesticides were at low concentrations in relation to drinking-water standards and guidelines established for the protection of aquatic life. Only two pesticide compounds—atrazine and simazine—exceeded the U.S. Environmental Protection Agency (USEPA) standards for drinking water. Atrazine exceeded the USEPA's maximum contaminant level (MCL) 19 times in 111 detections; simazine exceeded the established MCL 2 times in 111 detections. These exceedences occurred in the spring. Concentrations of atrazine also exceeded the established aquatic-life criterion (1.8 µg/L) in 32 samples collected from all sites.

Concentrations of deethylatrazine, an herbicide-transformation compound, tended to follow the same monthly concentration pattern as its parent compound (atrazine), but concentrations of deethylatrazine were lower than those of atrazine. Atrazine may have been present in the soil much longer at these sites, which might have allowed microbial populations to transform atrazine into deethylatrazine.

A statistical comparison of concentrations of selected pesticides among four fixed-network sites showed higher differences in median concentrations of atrazine, simazine, and diazinon at the North Fork Little River site than at the other sites. Median concentrations of deethylatrazine were appreciably lower at the North Fork Little River site than at the other sites. Concentrations of metolachlor were higher at Sinking Fork near Cadiz than at the other three sites.

The largest mean annual loads of selected pesticides among the fixed-network sites were at the Little River near Cadiz. Loads were not estimated for the fixed-network site at Sinking Fork near Cadiz. The Little River near Cadiz site had the largest mean annual loads of atrazine (2,337 pounds per year (lb/yr)), metolachlor (19.51 lb/yr), and simazine (330.8 lb/yr) during 2003-04. The North Fork Little River site had the largest mean annual load of diazinon (5.57 lb/yr). The

mean annual load of acetochlor (190 lb/yr) was largest at the South Fork Little River site.

The estimated annual loads of acetochlor, atrazine, diazinon, metolachlor, and simazine for the study period were about 0.01 to 2.2 percent of the amount applied in the basin. Atrazine had the largest estimated use and the largest estimated loads in the basin. The load for diazinon, an insecticide that is primarily used for nonagricultural purposes, was less than agricultural herbicides. The largest load of diazinon, estimated at the North Fork Little River site, was less than 1 percent of the atrazine load.

Total yields of atrazine ranged from 9.07 to 10.88 pounds per year per square mile ((lb/yr)/mi^2). The South Fork Little River site had the largest yields of commonly used row-crop herbicides (acetochlor, atrazine, and metolachlor). The yield of atrazine was 10.88 ((lb/yr)/mi^2); acetochlor and metolachlor yields were 3.27 and 0.18 ((lb/yr)/mi^2), respectively. Simazine, another commonly used row-crop herbicide, had the largest yield at the Little River near Cadiz site (1.36 (lb/yr)/mi^2). The North Fork Little River site, a more urban site, had the largest yield of diazinon (0.08 (lb/yr)/mi^2).

Introduction

Pesticides are chemical or biological substances that are used to control pests such as weeds (herbicides), insects (insecticides), and fungi (fungicides). Nearly 1 billion pounds of pesticides are used annually in the United States (Barbash and Resek, 1997). About 80 percent of pesticides are used for agricultural purposes, but pesticides also are used for industrial, commercial, and household purposes. Although the use of pesticides has resulted in increased crop production and reduced insect-borne diseases, it has raised concerns about potential adverse effects on the environment and human health. Excess pesticides (herbicides, insecticides, and fungicides) in the environment can cause a variety of ecological and human-health effects. Possible human-health effects from overexposure to some pesticides include cancer, reproductive or nervous-system disorders, and acute toxicity. Some pesticides potentially can affect aquatic life by disrupting the endocrine system and by interfering with natural hormones for reproduction (U.S. Geological Survey, 1999).

Water resources in the Little River Basin potentially are vulnerable to applications of pesticides associated with agricultural and nonagricultural activities especially because of karst topography in much of the basin. Karst topography is characterized by internal (sinkhole) drainage and rapid flow through solutional conduits, providing reduced opportunity for natural attenuation of contaminants and enhanced potential for surface- and ground-water contamination (Field, 1990). Previous studies by State water-quality agencies have identified nutrient enrichment and siltation as water-quality issues affecting water resources in the basin; however, one of the largest gaps in Kentucky's water-quality database is a lack of data on concentrations of pesticides in surface water. Thus, concerns about water quality resulting from pesticide use in karst areas and the lack of data on the concentrations of pesticides led to further investigation of the water quality in the basin by the USGS and the Kentucky Department of Agriculture (KDA). The Little River Basin study is intended to provide much-needed information on (1) the presence of pesticides and (2) the spatial and seasonal variability of pesticides in the Little River Basin. The purpose of the study was to determine the presence and distribution of pesticides in streams in the Little River Basin study area, to evaluate the variability in concentrations of pesticides by site and season, and to evaluate the loads and yields of selected pesticides at selected sites in the basin.

Purpose and Scope

The purpose of this report is to provide a summary of the occurrence and distribution of selected pesticides and provides estimates of selected pesticide loads and yields from samples collected from streams in the Little River Basin during 2003-04. Pesticide loads are computed using LOADEST, a U.S. Geological Survey (USGS) software program that uses regression models to compute mean constituent loads in rivers. Loads and yields of selected pesticides are presented for three fixed-network sites in the basin.

Description of the Little River Basin, Kentucky

The Little River Basin encompasses about 600 mi^2 (fig. 1). The Little River discharges into Lake Barkley Reservoir on the Cumberland River. Water quality throughout the basin is directly affected by natural (geology, climate, soils) and human (population, land use) factors. The Little River Basin has a high "hydrogeologic sensitivity rating" indicating it is highly vulnerable to effects from runoff, because much of the area is underlain by karst (Ray and others, 1994). The hydrologic sensitivity of an area is defined as the ease and speed with which a contaminant is transported within a ground-water system (Ray and others, 1994). Some streams in the Little River Basin are listed as impaired streams in the State's 303(d) List of Water report (Corrine Wells, Kentucky Environmental and Public Protection Cabinet, oral commun., 2002). The Kentucky Division of Water has listed the causes of impairments to the streams in the basin as siltation, nutrients, pathogens, organic enrichment (low dissolved oxygen), and habitat alterations (Kentucky Environmental and Public Protection Cabinet, 2005, p.134-136).

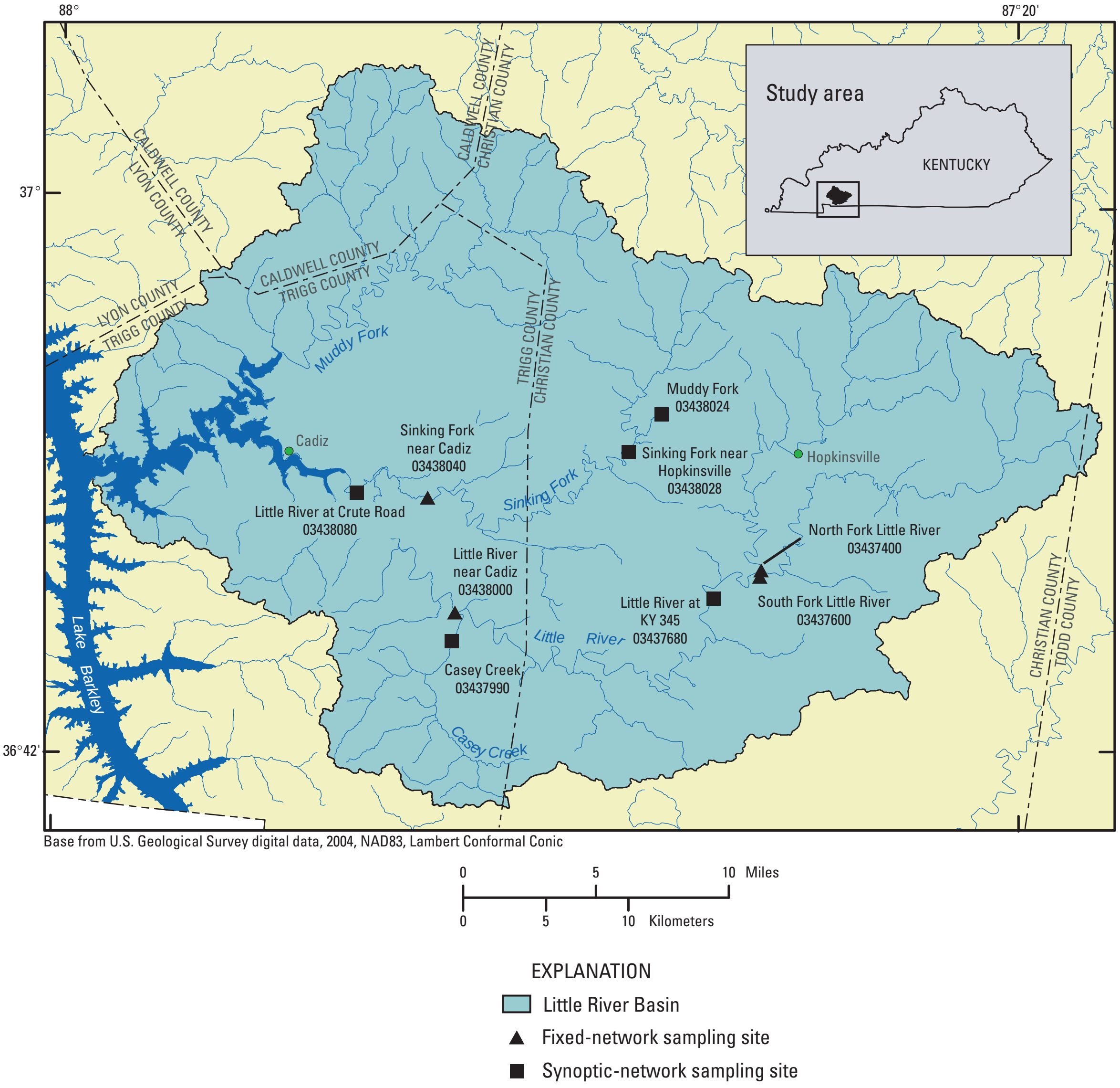


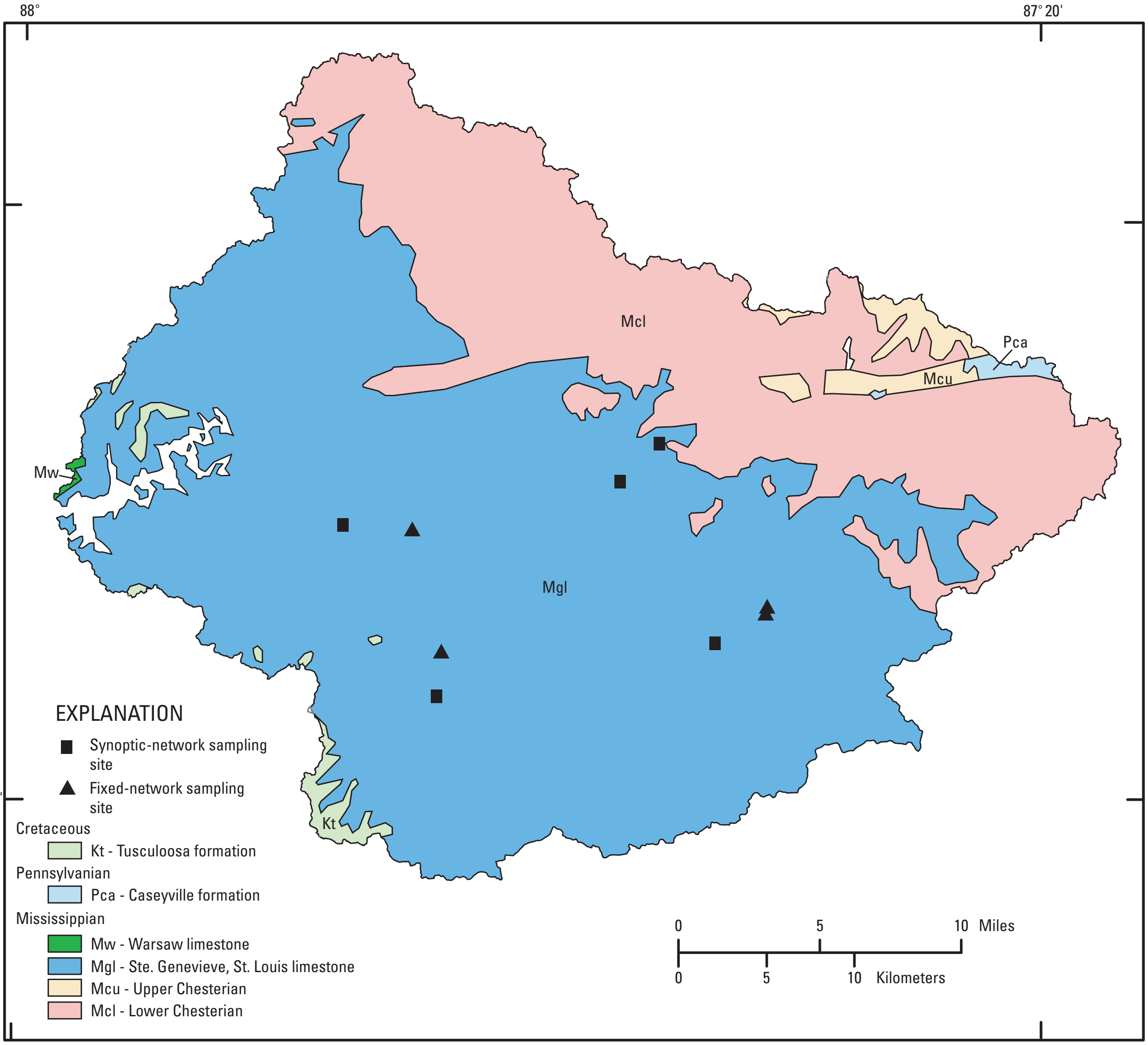
Figure 1. Location of the surface-water-sampling sites in the Little River Basin, Kentucky, study area.

Geology

The Little River Basin mostly is underlain by karstic limestone formations of Mississippian through Pennsylvanian age (fig. 2). The limestone units of significance within the Little River Basin study area are the St. Louis and Ste. Genevieve Limestone Formations. The St. Louis Limestone mostly is composed of sequences of massively bedded (tabular) limestones, and the Ste. Genevieve Limestone mostly is composed of thin-bedded, cherty limestones.

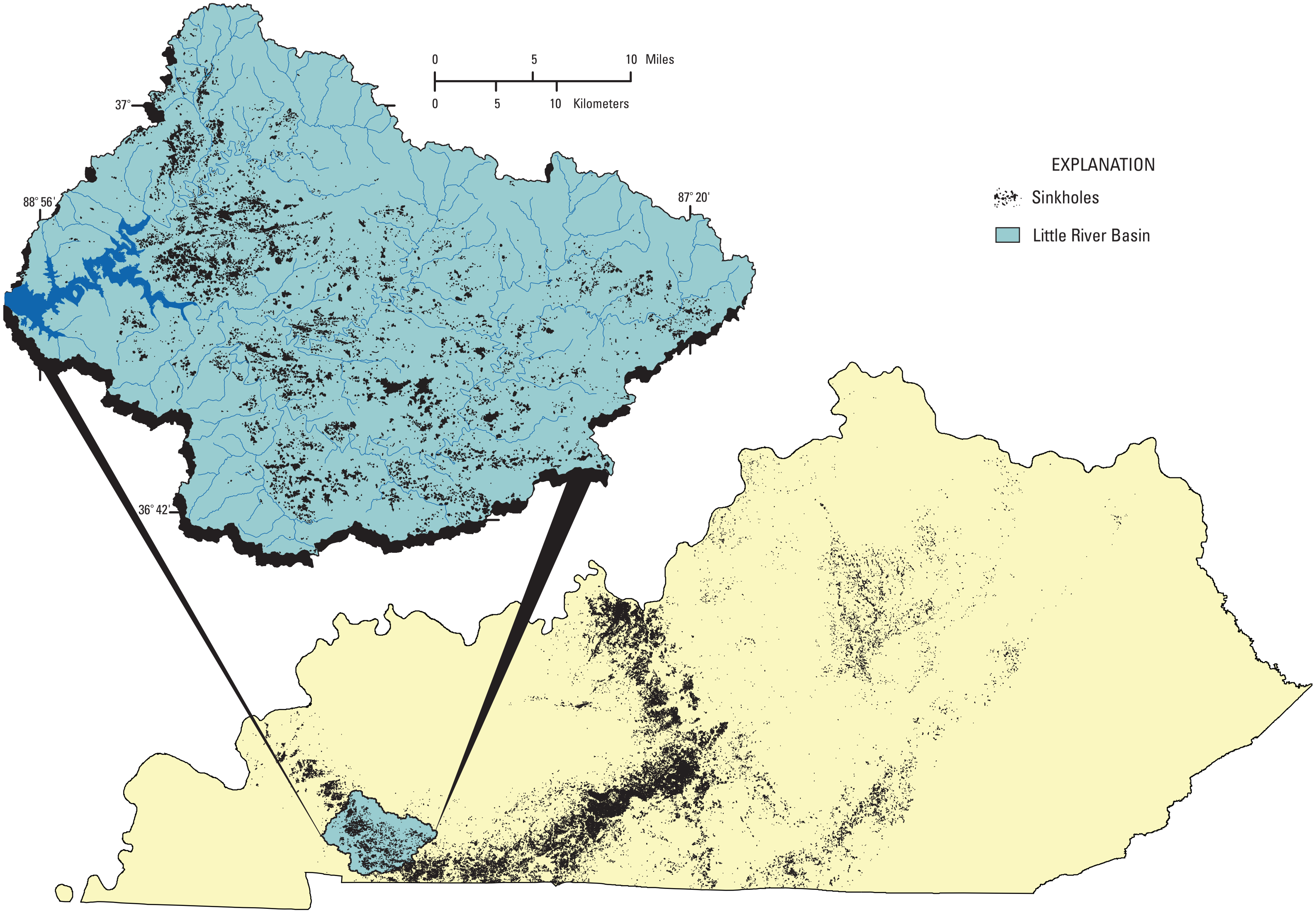
Overlying the Ste. Genevieve and St. Louis Limestone formations on the northeastern side of the study area is a thick sequence of limestone, sandstone, and shale formations of Chesterian age that are divided into upper and lower parts. The Lower Chesterian is composed of alternating sandstone and limestone strata that includes the Golconda Formations (sandstone dominated) and the Girkin Limestone Formation (McDowell, 1986). The Upper rocks of the Chesterian-age formations are mainly composed of siltstone and shale with alternating minor beds of limestone.

Numerous karst features including sinkholes (fig. 3), sinking streams, and springs are present in the study area. The exposure of Ste. Genevieve Limestone at the land surface allows for water from surface-water streams to enter the underground cavities through sinkholes. Water also enters the Ste. Genevieve and Girkin Limestones through sinkholes developed in the sandstone members of the Golconda Formation. Potential contaminants may enter the karstic limestone aquifers with surface runoff drained by sinkholes in the St. Louis and Ste. Genevieve and through sinking streams.



Base from U.S. Geological Survey digital data, 2004, NAD83, Lambert Conformal Conic
Stratigraphic data source: McDowell and others, 1981.

Figure 2. Surficial geology in the Little River Basin, Kentucky, study area.



Source: Kentucky Geological Survey, A GIS Sinkhole Coverage for the Karst Areas of Kentucky, 2003.

Figure 3. Generalized distribution of sinkholes in the Little River Basin and throughout Kentucky.

Streamflow

Direct surface runoff and ground-water discharge are the major sources of streamflow in the Little River Basin. Another source is interflow, which is part of the subsurface flow that moves at shallow depths and potentially can reach the surface channels in a short period of time. During a storm, interflow slowly increases until the end of the storm, then gradually decreases (Viessman and others, 1989, p. 171).

Annual mean flow differs appreciably from year to year, with variations in weather conditions. Mean annual streamflow of the Little River near Cadiz (water years 1940-2004) was about 360 ft^3/s and was 479 ft^3/s in 2003 and 299 ft^3/s in 2004. Mean monthly streamflow peaks in the spring (March–May); however, there is a second peak in the winter (December–February) months. Low streamflow conditions typically occur from late summer (June–August) to early fall (September–November). The mean daily streamflows for Little River near Cadiz in 2003 ranged from 27 ft^3/s (November 7) to 5,170 ft^3/s (May 7); mean daily streamflows in 2004 ranged from 33 ft^3/s (October 11) to 2,670 ft^3/s (April 24).

Mean annual precipitation for the Little River Basin was 55.8 in. in 2003 and 54.0 in. in 2004 (National Oceanic and Atmospheric Administration, 2003 and 2004). About 63 percent of the mean annual precipitation in 2003 (34.9 in.) and about 57 percent of the mean annual precipitation in 2004 (31.0 in.) occurred during the growing season from April through October (fig. 4). The long-term mean annual precipitation for the Little Rive Basin is about 50 in.

Land Use

Streams in the Little River Basin drain a diverse landscape of forest, agricultural areas, and urban areas around Hopkinsville and Cadiz, Kentucky. Agricultural land uses represent about 60 percent of the study area (fig. 5). Most of the agricultural land (34 percent) is used for corn, soybeans, wheat, hay, and tobacco production; the remaining 26 percent of the agricultural land is used for pasture. Corn is the principal row crop harvested in the basin, followed by soybeans. In 2003, about 95,000 acres of corn were harvested for seed, grain, silage, or sweet corn; about 76,500 acres of soybeans were harvested (Kentucky Agricultural Statistics Service, 2004).

Forested land represents about 31 percent of the Little River Basin. The southern and western parts are the most densely forested areas in the basin.

Urban areas represent about 9 percent of the land use in the basin. The most heavily populated communities in the Little River Basin are Hopkinsville and Cadiz. Hopkinsville has a population of about 30,000; Cadiz has a population of about 2,400 (U.S. Census Bureau, 2002).

Pesticide Use, Properties, and Sales

Herbicides commonly are used to control weeds in agricultural areas in the Little River Basin. The most commonly used herbicides are atrazine, simazine, metolachlor, and acetochlor. Glyphosate is another commonly used herbicide, but it was not examined during this study. The largest applications of these herbicides to agricultural land in the Little River Basin are on row crops such as corn, soybeans, tobacco, wheat, and on pasture and hay fields. Combinations of herbicides applied to row crops are sometimes used for more effective weed control. Multiple applications are common and include some combination of pre-plant applications of selective and nonselective herbicides and pre- and post-emergent applications of selective herbicides (Hippe and others, 1994).

The three classes of herbicides most heavily used in the Little River Basin are triazines, chloroacetanilides, and organophosphate herbicides (glyphosate). The most common triazines (atrazine, simazine, and cyanazine) are used primarily on corn. The most common chloroacetanilides (acetochlor, metolachlor, alachlor) are used on both corn and soybeans. The most common organophosphate herbicide, glyphosate, is used on corn and soybeans. Both the triazine and chloroacetanilide groups have moderate to high water solubility and moderately low soil-sorption coefficients and, therefore, can be persistent in soil (Wauchope and others, 1992). As a result, they have moderate to strong potential for transport, primarily in the dissolved phase, from fields through surface runoff (Goss, 1992).

Chemical or biological processes can transform herbicides. Chemical-transformation processes include photolysis (photochemical degradation), hydrolysis, oxidation, and reduction. The transformation of herbicides through microbial metabolic processes is considered the primary mechanism of biological degradation (Ritter and Shirmohammadi, 2001, p. 114).

Pesticide-transformation compounds are more water-soluble than their parent compounds. For example, Mills and Thurman (1994) found that one of the transformation compounds of the parent compound atrazine, deethylatrazine (DEA), sorbs less strongly to soils than does its parent compound. In some studies, pesticide-transformation compounds often have been detected at higher concentrations than their respective parent compound (Kolpin and others, 1998); Scribner and others, 1998). The toxicity of pesticide-transformation compounds is unknown (U.S. Geological Survey, 1999).

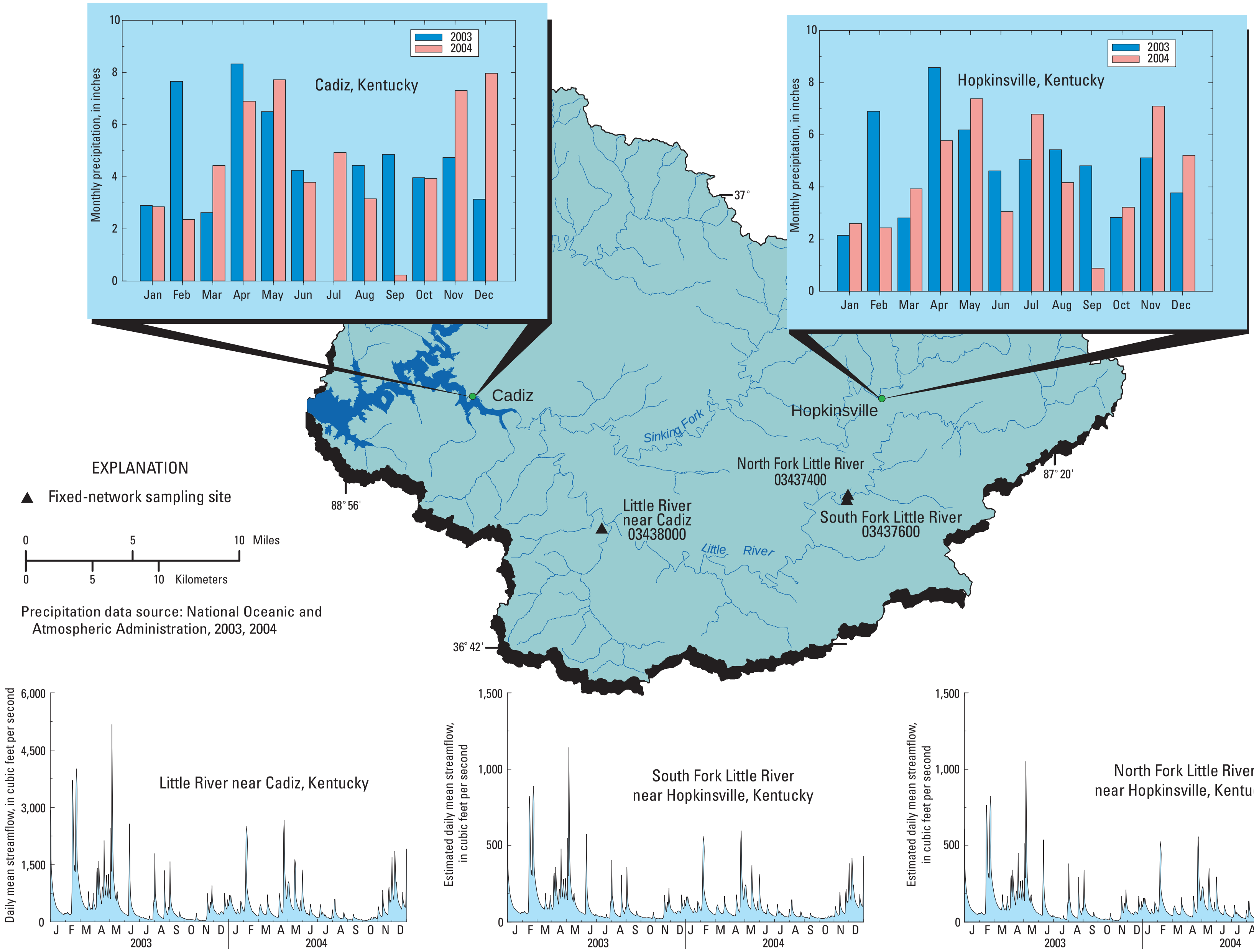
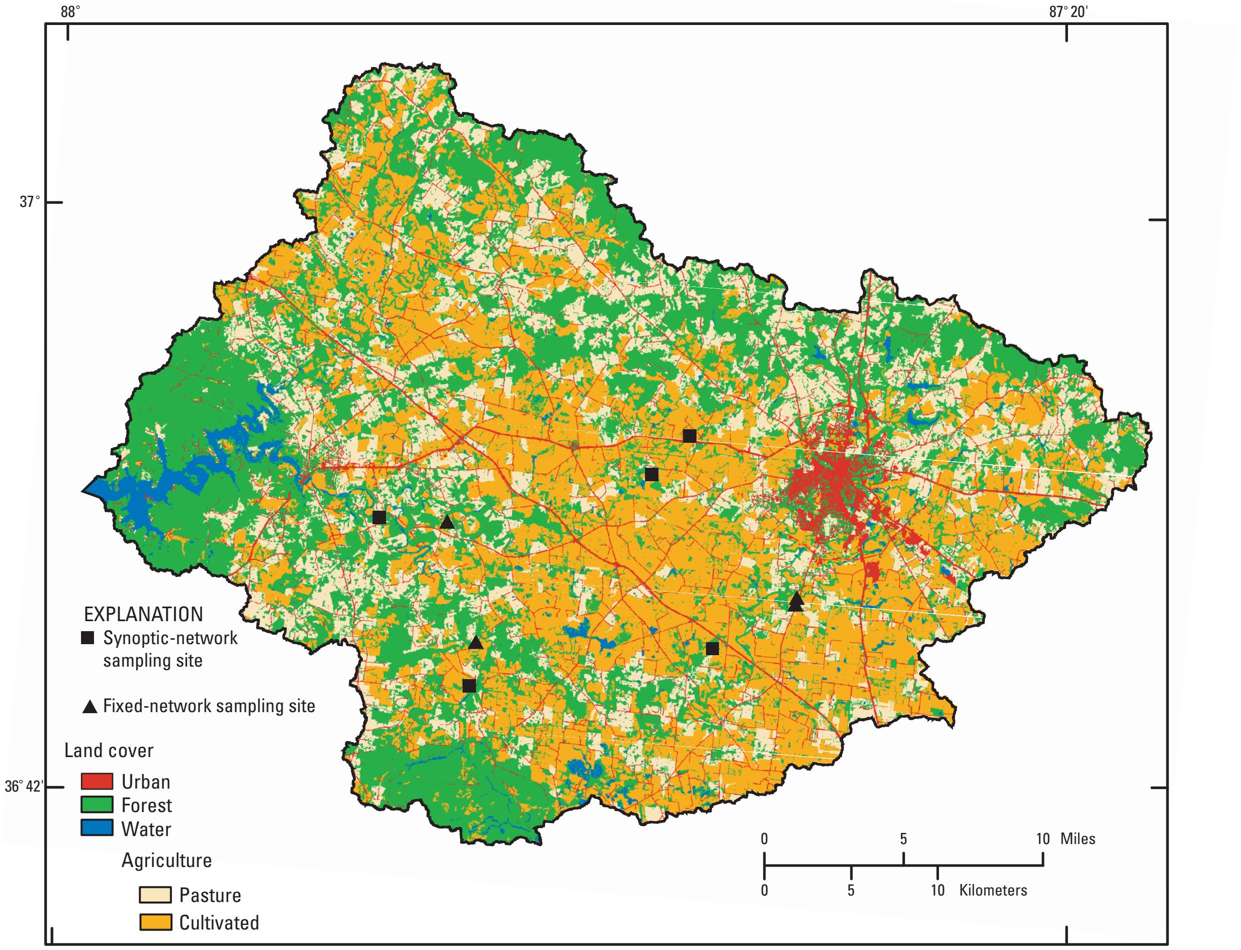


Figure 4. Location of fixed-network sampling sites and graphs showing precipitation and daily mean streamflow at selected surface-water sites in the Little River Basin, Kentucky, study area, 2003-04.



Base from U.S. Geological Survey digital data, 2004, NAD83, Lambert Conformal Conic
Land-cover source: Kentucky Land Cover Data Set 2001, Kentucky Commonwealth Office of Technology, November 1, 2005.

Figure 5. Land cover in the Little River Basin, Kentucky, study area, 2001.

The amount of pesticides applied annually to agricultural land within the Little River Basin (in pounds of active ingredient) was derived from county-based crop-acreage data and State-level estimates of pesticide-use rates for individual crops from the National Agricultural Statistics Service (NASS) database. County-crop acreages were combined with the State pesticide-use coefficients to calculate county-level pesticide usage by pesticide and crop. The crops of interest included corn, soybeans, winter wheat, alfalfa hay, pasture, and tobacco. Little information was available for pesticide use in forestry, transportation (weed control along roadways and right-of-ways), aquatic use (algae control), and various commercial and industrial applications.

Every year, the KDA assembles a database of agricultural pesticide sales (reported as amount of active ingredient) to evaluate where pesticides are purchased and potentially applied in each county in Kentucky. The number of active ingredients that were sold statewide in the years 2003 and 2004 were 156 and 183, respectively. The top five active ingredients sold in Kentucky were atrazine, glyphosate, S-metolachlor, 2,4-D, and simazine in 2003, and glyphosate, atrazine, 2,4-D, fatty alcohol, and simazine in 2004.

Atrazine was the top-selling active ingredient in the Little River Basin (Christian and Trigg Counties) of the pesticides studied followed by simazine, acetochlor, metolachlor, Malathion, prometon, and diazinon (table 1). Glyphosate ranked second in pounds of active ingredient in the basin. Christian County ranked fourth out of Kentucky’s 120 counties in pounds of active ingredient for atrazine in 2003-04. It is assumed that high sales equates to high use of pesticides in the Little River Basin, because atrazine and simazine were detected at all of the sampling sites in the basin. Although the insecticide Malathion ranked fifth in sales among the pesticides studied, it was not frequently detected; however, it may not have been widely distributed in the basin and most applications may occur during periods of reduced runoff.

Study Design and Methods

Stream-sampling sites in the Little River Basin were selected to assess the spatial and seasonal variability of selected pesticides in subbasins consisting of mixed land use and different types of agricultural land. Samples were collected on three Little River main-stem sites and five tributaries—North Fork Little River, South Fork Little River, Muddy Fork, Sinking Fork, and Casey Creek (fig. 1 and table 2).

Sample-Site Selection and Sampling Frequency

Pesticide samples were collected monthly (March–November 2003 and February–November 2004) at four fixed-network sites. The sites included North Fork Little River, South Fork Little River, Sinking Fork near Cadiz, and Little River near Cadiz. An additional four samples were collected at each of these sites based on three high-flow events and one low-flow event.

Table 1. Pesticide active-ingredient sales and detections in surface-water samples, Christian and Trigg Counties, Kentucky, 2003-04.

Constituent	Amount of active ingredient for 2003-04 (in pounds)[1]	Detection (in percent)
Acetochlor	36,030	46
Atrazine	353,301	100
Diazinon	433	25
Malathion	1,958	4
Metolachlor	8,137	94
Prometon	798	53
Simazine	88,102	100

[1] Ernest Collins, Kentucky Department of Agriculture, written commun., 2004.

Table 2. Description of surface-water sampling sites in the Little River Basin, Kentucky.

[USGS, U.S. Geological Survey; mi^2, square mile; Ky., Kentucky; N/A, not applicable]

USGS site number	USGS site name	Abbreviated site name	Drainage area (mi^2)	Site type	Percentage of basin area in indicated land use[1]			
					Agriculture	Forest	Urban	Water
03437400	North Fork Little River at Gary Lane Bridge near Hopkinsville, Ky.	North Fork Little River	58	Fixed	50	36	13	1
03437600	South Fork Little River at KY 107 near Hopkinsville, Ky.	South Fork Little River	67	Fixed	63	26	11	0
03438000	Little River near Cadiz, Ky.	Little River near Cadiz	244	Fixed	57	35	6	2
03438040	Sinking Fork at Kings Chapel Road near Cadiz, Ky.	Sinking Fork near Cadiz	107	Fixed	68	26	6	0
03437680	Little River at KY 345 near Hopkinsville, Ky.	Little River at KY 345	134	Synoptic[2]	N/A	N/A	N/A	N/A
03438024	Muddy Fork near Hopkinsville, Ky.	Muddy Fork	7.9	Synoptic[2]	N/A	N/A	N/A	N/A
03438028	Sinking Fork near Hopkinsville, Ky.	Sinking Fork near Hopkinsville	44	Synoptic[2]	N/A	N/A	N/A	N/A
03437990	Casey Creek at KY 525 near Cadiz, Ky.	Casey Creek	35.7	Synoptic[2]	N/A	N/A	N/A	N/A
03438080	Little River at Crute Road near Cadiz, Ky.	Little River at Crute Road	400	Synoptic[2]	N/A	N/A	N/A	N/A

[1] Kentucky Land Cover Data Set, 2001, Kentucky Commonwealth Office of Technology, November 1, 2005.

[2] Site located within the 10-digit hydrologic-unit code of one of the four fixed sites.

In addition to the routine sampling at the four fixed-network sites, five synoptic-network sites were sampled twice each year in 2003 and 2004. Three high-flow events and one low-flow event were collected over the 2-year period to evaluate the spatial distribution of selected pesticides in the various subbasins in the Little River Basin.

A total of 91 samples were collected for pesticide analysis at the fixed-network sites. An additional 20 samples were collected at the synoptic-network sites. Thirty-one samples were collected for quality assurance/quality control (blanks, spikes, and replicates).

Sampling Methods

Representative water samples were collected by use of (1) the equal-width increment (EWI) method, in which depth-integrated samples are collected at equal distances across the entire stream width and composited or (2) the equal-discharge increment (EDI) method, in which equal-volume, depth-integrated samples are collected at the center of each EDI across the stream width and composited (Edwards and Glysson, 1998). All sampling material was constructed of Teflon to minimize contamination of sampling artifacts. Equipment used to collect and process the pesticide samples was precleaned with a 0.1-percent nonphosphate detergent, triple rinsed with tap water, acid rinsed with 5 percent hydrochloric acid for 30 minutes (nonmetal equipment only), triple rinsed with deionized water, rinsed with certified pesticide-free methanol, air dried, and stored in a dust-free environment prior to sample collection (Wilde, 2004).

Water samples for pesticides were pumped through Teflon tubing and filtered through a 142 mm diameter, 0.7-micrometer (µm) pore size, borosilicate glass-fiber filter placed in a stainless-steel filter unit (Sandstrom, 1995). The filtered water was collected in amber-glass colored bottles and chilled for later analysis of pesticides and pesticide-transformation products. Both the glass-fiber filters and the amber-glass bottles had been baked at 450°C in a muffle furnace for a minimum of 2 hours. All pesticide samples were chilled and shipped on ice by overnight air express to the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, for analysis.

Field measurements of stream discharge, air temperature, barometric pressure, water temperature, specific conductance, pH, concentrations of dissolved oxygen, and turbidity were measured at the time of sampling. Alkalinity and bicarbonate were determined by titrating filtered sample water with 0.16N sulfuric acid using a digital titrator. Discharge was measured according to standard USGS guidelines as described by Rantz and others (1982). The field measurement data is available online at *http://ky.water.usgs.gov/* .

Analytical Methods

Pesticide water samples were analyzed using capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (Zaugg and others, 1995; Sandstrom and others, 2001). Concentrations of pesticides were reported by the NWQL with appropriate qualifiers to indicate analytical limitations. Analytical data from the NWQL were reported as “less than” when a pesticide was not detected or not present at the method detection limit (MDL). The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987). When the presence of a pesticide was detected and quantified in the sample, but the reported value was below the MDL, the concentration was identified as an estimated value.

Quality Control

Quality-control information is needed to estimate the bias and variability that results from sample collection, sample processing, and laboratory analysis in order to ensure proper interpretation of water-quality data. About 25 percent of all samples submitted to the laboratory were quality-control samples, which included equipment blanks and field blanks to measure contamination and bias, replicate samples to measure variability, and field-matrix spikes to measure the recovery of analytes.

A blank is a water sample that consists of water that has undetectable concentrations of analytes of interest. Blank-water samples are used to test for bias that could result from contamination during any stage of the sample collection or analysis process. Field-blank samples were collected to demonstrate that (1) equipment has been adequately cleaned to remove contamination introduced by samples obtained at previous sites; (2) sample collection and processing have not resulted in contamination; and (3) sample handling, transport, and laboratory analysis have not introduced contamination (Mueller and others, 1997). The procedure for blank samples was to place pesticide-free water through all of the sampling and filtration steps as a typical water-quality sample. Field-blank sample concentrations for pesticides did not indicate any contamination from the equipment or sample-processing methods.

A spike is an environmental sample that is injected with a known amount (mass) of a specific analyte. Spikes measure bias and variability in the measurements of pesticides. Pesticides added to environmental samples in the field are called field-matrix spikes; a field-matrix spike is a specific type of spiked sample that is injected in the field prior to shipping. Field-matrix spikes not only measure bias and variability of the analytical method, but also measure the potential effects caused by analyte degradation or matrix interference. Matrix interference is the effect that the matrix of the water sample itself has on the measurement of individual analytes within the environmental sample. The amount of pesticide measured (recovered) in a spiked sample is expressed as a percentage (the percent recovery) of the known amount of pesticide added to the sample. The recovery of a spike can be greater or less than 100 percent, so the bias can be either positive or negative. Spike-recovery calculations are described by (Mueller and others, 1997, p. 5).

Table 3 summarizes the percent-recovery data for commonly detected pesticides from the five water samples spiked in the field. Mean spike recoveries ranged from 91 to 106 percent and median spike recoveries ranged from 87 to 107 percent.

Table 3. Summary of percent recovery data for commonly detected pesticides spiked in the field for the Little River Basin, Kentucky, 2003-04.

	Spike recovery, in percent			
Constituent	Minimum	Maximum	Mean	Median
Acetochlor	85	112	98	97
Atrazine	28	147	97	87
Diazinon	87	102	95	94
Metolachlor	96	116	106	107
Prometon	84	113	99	96
Simazine	57	111	91	96

Replicate samples are a set of two or more environmental samples considered to be essentially identical in composition. Concurrent replicates are prepared by using one sampler and alternating collection of the samples into two or more compositing containers. All replicates collected in the Little River Basin were concurrent replicates.

Data obtained from the six sets of replicate samples was used to access the variability of the overall sampling and analytical process. Replicate samples were compared by using relative percent differences (RPDs). The RPD for each analyte and replicate sample pair was calculated by the following equation:

$$RPD = |S1 - S2| / (S1 + S2) / 2x100 \qquad (1)$$

where

$S1$ is equal to the concentration in the environmental sample, in milligrams per liter (mg/L) (nutrients) or micrograms per liter (µg/L) (pesticides); and

$S2$ is equal to the concentration in the replicate sample, in mg/L (nutrients) or µg/L (pesticides).

A large RPD can indicate greater variability in those samples. Differences in concentrations, as measured by RPD, within replicate sets ranged from 0 to 6.9 percent for pesticides (table 4).

Table 4. Summary of replicate sample data for commonly detected pesticides and pesticide-transformation compounds.

[RPD, relative percent difference]

Constituent	Number of replicate sample sets	Median RPD	Number of replicate sample sets with greater than 10 percent RPD
Acetochlor	6	1.8	0
Atrazine	6	4.5	1
Deethylatrazine*	6	3.6	2
Diazinon	6	1.5	2
Metolachlor	6	6.9	1
Prometon	6	0	1
Simazine	6	2.8	1

*Pesticide-transformation compound.

Statistical Analysis of Selected Pesticides

The S-Plus software program (Insightful Corporation, 2005) was used to calculate summary statistics such as the mean, median, minimum, and maximum concentrations for selected pesticides. The Wilcoxson rank-sum nonparametric statistical test (Helsel and Hirsch, 1992) was used to compare concentrations of selected pesticides at the four fixed-network sites in the basin. The Wilcoxson rank-sum test ranks the data points to determine the statistical significance of differences in concentrations between groups of data. Differences among the groups of data with a probability (*p*) value of 0.05 or less were considered significant in this study.

Load-Estimation Methods

Selected pesticide (atrazine, acetochlor, simazine, metolachlor, and diazinon) loads were estimated with the USGS software, LOADEST. This software uses time-series streamflow data and constituent concentrations to calibrate a regression model that describes constituent loads in terms of various functions of streamflow and time (Runkel and others, 2004). A complete discussion of the theory and principles behind the calibration and estimation methods can be found in Runkel and others, 2004.

The LOADEST software allows the user to choose between selecting the general form of the regression from several predefined models and letting the software automatically select the best-defined model, based on the Akaike Information Criterion (AIC) (Akaike, 1981). The predefined model with the lowest value for the AIC was then selected for use in load estimation; a user-defined model was used for this study. User-defined results and results defined by the software are listed in table 5. The RPDs between the two methods ranged from about zero to 53 percent (table 5).

Table 5. A comparison of loads for select pesticides at three sites using LOADEST predefined and user-defined models.

[lb/yr, pound per year]

Constituent	Predefined LOADEST model results (lb/yr)	User-defined LOADEST model results (lb/yr)	Relative difference (in percent)
North Fork Little River near Hopkinsville, Ky. (03437400)			
Atrazine	601	613	2.1
Simazine	75	74	.22
Metolachlor	4.3	4.2	3.8
Diazinon	4.3	5.6	27
South Fork Little River near Hopkinsville, Ky. (03437600)			
Atrazine	503	631	23
Simazine	55	55	.58
Metolachlor	10	10	1.6
Diazinon	1.9	1.1	53
Little River near Cadiz, Ky. (03438000)			
Atrazine	2,144	2,337	8.6
Simazine	349	331	5.2
Metolachlor	26	20	28
Diazinon	4.3	3.1	32

The output regression equation has the following general form:

$$\ln(L) = a + b(\ln Q) + c(\ln Q^2) + d[\sin(2\pi T)] + e[\cos(2\pi T)] + fT + gT^2 \qquad (2)$$

where

L is the constituent load, in lb/d;

Q is the stream discharge, in ft^3/s;

T is the time, in decimal years, from the beginning of the calibration period; and

a,b,c,d,e,f,g are regression coefficients.

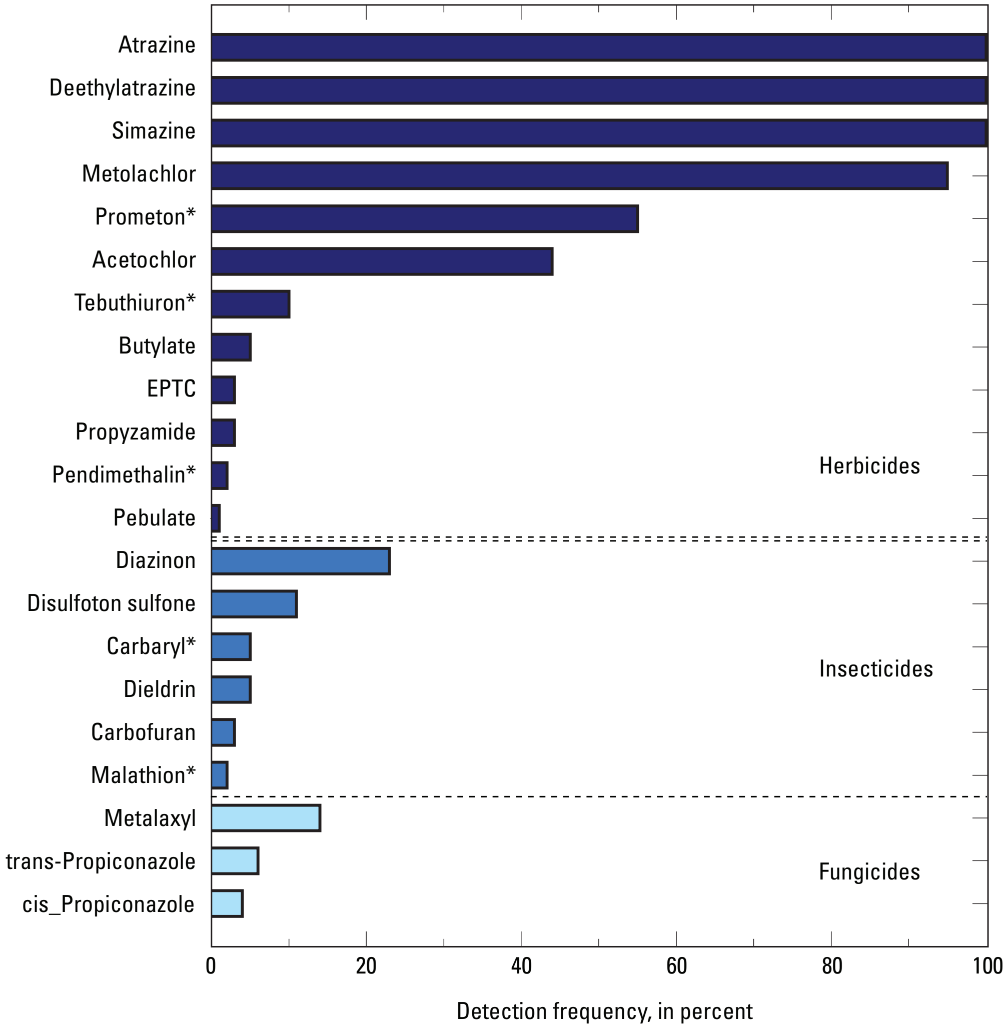
Pesticides in Streams in the Little River Basin, Kentucky

Water samples for pesticides were collected at four fixed-network sites in the Little River Basin during March–November 2003 and February–November 2004. Additional samples were collected at five synoptic-network sites within the same time period. Results of the pesticide samples were evaluated in terms of occurrence, variability by site and season, and loads and yields of selected pesticides at selected sites in the basin. Water-quality criteria and guidelines are used to evaluate the potential effects of pesticides on human health and aquatic organisms.

Occurrence and Distribution

Detections and concentrations of pesticides in streams are affected by many factors, including the amount of pesticide used, the environmental persistence of the pesticide, and the analytical methods used. The most commonly detected pesticides were among the most heavily applied in the Little River Basin. Samples from all nine sites had detectable concentrations of at least one pesticide; 1 sample collected at the North Fork Little River site contained 12 detected pesticides. A common method reporting limit (MRL) of 0.01 µg/L was used to compare the detection frequencies of pesticides, because MRLs vary widely from one pesticide or related compound to another. The use of the detection threshold allows for comparison among pesticides by censoring detections to a common reference concentration. The lowest appropriate MRL for comparing pesticides is 0.01 µg/L for most of the pesticides analyzed in this study; however, several pesticides (prometon, tebuthiuron, pendimethalin, carbaryl, and Malathion) had MRLs that were greater than or equal to 0.01 µg/L. For these pesticides, the detection frequency is preceded by the asterisk (*) symbol to indicate that the true percentage of samples with concentrations greater than the threshold probably are greater than or equal to that reported in figure 6. Of the 127 pesticides analyzed, 24 were detected above the adjusted MRL of 0.01 µg/L (table 6).

Herbicides were detected more frequently than insecticides and fungicides. Fifteen of the 24 pesticides detected in water were herbicides. The commonly used herbicides—atrazine, simazine, metolachlor, acetochlor, and prometon—were found throughout the basin. Atrazine and simazine were detected in 100 percent, and metolachlor and acetochlor were detected in more than 45 percent of all surface-water samples (fig. 6). Almost 60 percent of the atrazine and 93 percent of the simazine samples were in the 0.1 to 1.0 µg/L range. The pesticide-transformation compound, deethylatrazine, was detected in 100 percent of the samples. Only one non-agricultural herbicide, prometon, was detected in more than 50 percent of the samples. Less frequently detected herbicides were butylate, pebulate, propyzamide, EPTC, tebuthiuron, and pendimethalin.



EXPLANATION

* - Indicates that the true percentage of samples with concentrations greater than the threshold probably are greater than or equal to that reported.

Figure 6. Occurrence of pesticide compounds from all samples at all sites in the Little River Basin, Kentucky, study area, 2003-04.

Table 6. Pesticides and pesticide-transformation products analyzed in surface-water samples from the Little River Basin, Kentucky, 2003-04.

[**Bold-faced** compounds were detected; *italicized* compounds are pesticide-transformation products]

Acetochlor
Alachlor
alpha-Endosulfan
alpha-HCH
2-Amino-N-isopropylbenzamide
Atrazine
Azinphos-methyl
Azinphos-methyl
Benfluralin
beta-Endosulfan
Bifenthrin
Butylate
2-(4-tert-Butylphenoxy)-cyclohexanol
Carbaryl
Carbofuran
4-Chloro-2-methylphenol
4-Chlorophenyl
2-Chloro-2',6'-diethylacetanilide
Chlorpyrifos
Chlorpyrifos
cis-Permethrin
Cyanazine
Cycloate
Cyfluthrin
Cypermethrin
DCPA

Desethylatrazine
Desulfinyl
Desulfinylfipronil
Diazinon
Dichlorvos
2,5-Dichloroaniline
3,4-Dichloroaniline sulfate
3,5-Dichloroaniline
4,4'-Dichlorobenzophenone
2,6-Diethylaniline
(E)-Dimethomorph
(Z)-Dimethomorph
Dicrotophos
Dieldrin
Dimethoate
Disulfoton
Disulfoton sulfone
Disulfoton sulfoxide
Endosulfan
Endosulfan
EPTC
Ethalfluralin
Ethion
Ethion
Ethoprop
2-Ethyl-6-methylaniline

2-[(2-Ethyl-6-methyl-phenyl)-amino]-1-propanol
Fenamiphos
Fenamiphos
Fenamiphos
Fenthion
Fenthion
Fipronil alcohol
Fipronil
Fipronil
Flumetralin
Fonofos methyl
Fonofos oxygen analog
***gamma*-HCH (Lindane)**
Hexazinone oxygen analog
4-(Hydroxymethyl)
Iprodione sulfone
Isofenphos sulfoxide
lambda-Cyhalothrin ether
Linuron sulfone
Malaoxon sulfoxide
Malathion
Metalaxyl
Methidathion
Methyl (cis- and trans-)
Methyl paraoxon
Methyl pendimethalin

Metolachlor
Metribuzin
Molinate
Myclobutanil
1-Naphthol
1,4-Naphthoquinone
Napropamide
O-Ethyl-O-methyl-S-propylphosphorothioate sulfide
Oxyfluorfen sulfone
pp'-DDE amide
Paraoxon fipronil
Parathion
Pebulate
Pendimethalin
3-Phenoxybenzyl
Phorate
Phorate
Phosmet
Phosmet
Phostebupirim
Profenofos
Prometon
Prometryn
Propachlor
Propanil
Propargite

Propetamphos parathion
Propiconazole (cis- and trans-)
Propyzamide
Simazine
Sulfotepp
Sulprofos
Tebupirimphos
Tebuthiuron
Tefluthrin
Tefluthrin
Tefluthrin
Temephos
Terbacil
Terbufos
Terbufos
Terbuthylazine
Thiobencarb
Triallate
Tribuphos
Trifluralin
3-(Trifluoromethyl)-aniline

The insecticides carbaryl, carbofuran, diazinon, dieldrin, Malathion, and disulfoton sulfone (transformation compound of disulfoton) were the only insecticides detected at any of the sites. Diazinon, the most commonly detected insecticide, was found in 23 percent of the samples and was detected at all sites, except Casey Creek. Insecticides, such as diazinon, typically are associated with urban areas. Diazinon was most frequently detected (10 out of 26 samples) at the North Fork Little River sampling site, which is 13 percent urban. Although detected in 23 percent of all samples, diazinon was detected in 54 percent of the samples collected in July and August. Disulfoton sulfone was detected in 11 percent of all samples and frequently occurred in the spring. Carbaryl and dieldrin were each detected in 5 percent of all samples. Carbaryl was most frequently detected at the North Fork Little River sampling site (three out of six samples). Carbofuran and Malathion were detected in 3 and 2 percent of the samples, respectively. The lower use, relative to herbicides and the application during periods of reduced runoff, probably accounts for lower detection rates and low concentrations of insecticides in the basin.

Metalaxyl was the most commonly detected fungicide (14 percent); most detections of metalaxyl were from the Sinking Fork subbasin. Metalaxyl was detected in about 63 percent of the samples collected during June, July, and August, although it was detected in only 14 percent of all samples. Propiconazole (cis- and trans- forms) was the only other fungicide detected in the samples.

Seasonal Variability in Concentrations of Pesticides

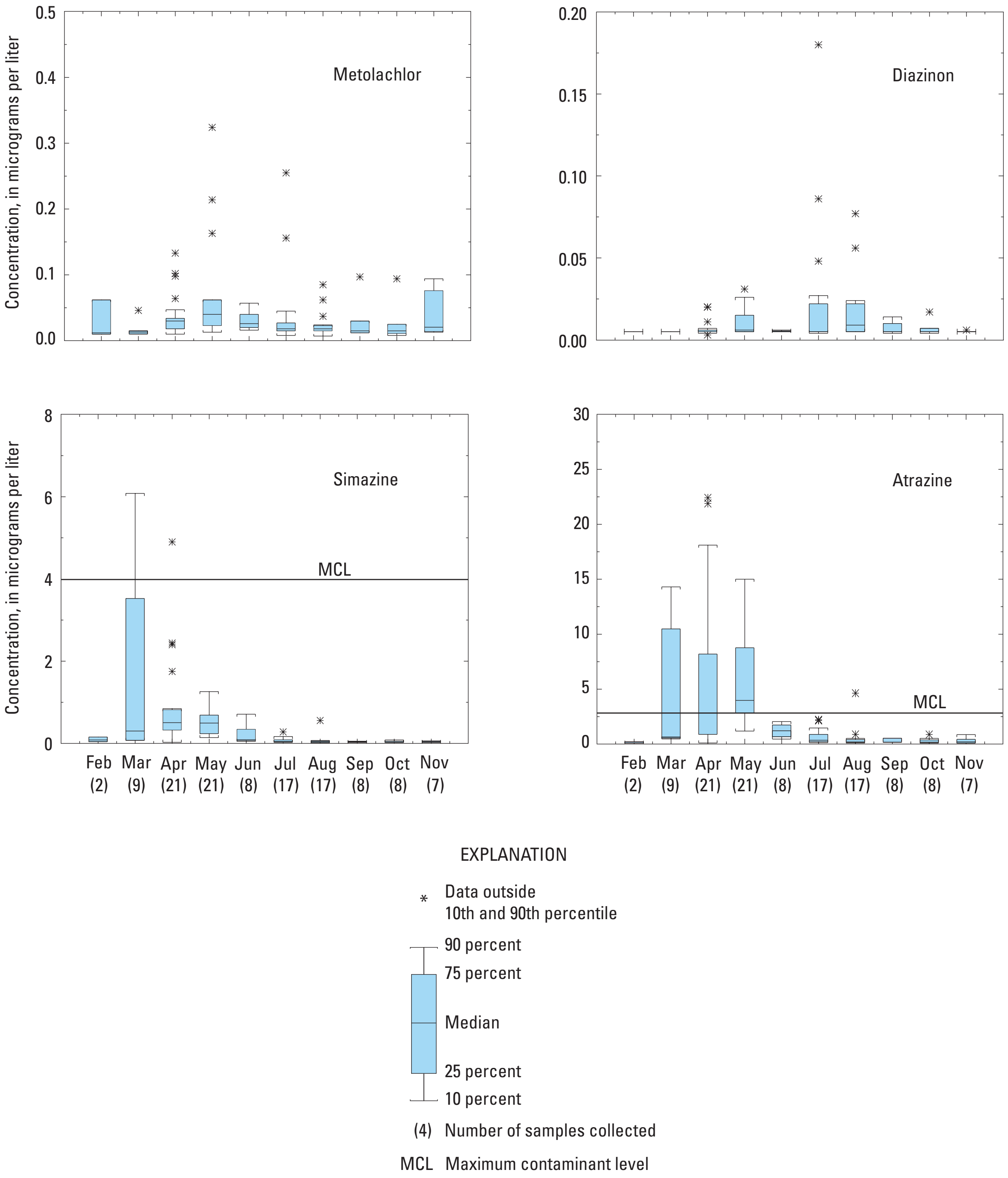
Concentrations of pesticides varied throughout the year in samples collected at all the sampling sites with the highest concentrations occurring during storm runoff in the spring. The maximum concentrations of 11 of the 15 herbicides detected occurred during the growing season (March-May) (fig. 7). The maximum concentrations for the four remaining detected herbicides (EPTC, pebulate, propyzamide, and tebuthiuron) occurred during the non-growing season.

The most commonly detected pesticides in the Little River Basin were found at low concentrations in streams year round (table 7). Atrazine (22 µg/L), simazine (6.1 µg/L), and acetochlor (4.1 µg/L) had the highest detected concentrations in the basin of the 15 herbicides detected. These herbicides are row-crop herbicides and are the most heavily applied pesticides in the basin. Metolachlor also is a heavily applied row-crop herbicide in the basin, but concentrations were never greater than 0.32 µg/L. Median concentrations of the herbicides acetochlor, atrazine, metolachlor, prometon, and simazine ranged from <0.018 µg/L for prometon to 0.58 µg/L for atrazine for all samples collected during this study (table 7). The highest concentrations of herbicides occurred in March, April, and May during storm runoff (fig. 7).

Concentrations of atrazine and its transformation compound (deethylatrazine) in relation to daily mean streamflow at three of the fixed-network sites are shown in figure 8. Daily mean streamflow was estimated for the North Fork Little River and South Fork Little River sites (both ungaged sites) by multiple-regression analysis using the available daily mean streamflow at the Little River near Cadiz site.

Concentrations of the parent-pesticide compound, atrazine, were higher in the spring following application during periods of increased streamflow and lower later in the growing season when there is no application and streamflow is decreased. The seasonal pattern for the pesticide-transformation compound, deethylatrazine, mirrored that of its parent compound, atrazine, but at lower concentrations. Concentrations of deethylatrazine at the South Fork Little River site and at Little River near Cadiz were slightly higher than atrazine during late summer and autumn; however, the difference was <0.1 µg/L (fig. 8). It would be expected for pesticide-transformation compounds to follow a similar seasonal pattern as the parent pesticide compounds, because most pesticides begin to degrade by chemical or biological processes following application.

In contrast to the most commonly detected herbicides, the most commonly detected insecticide, diazinon, was primarily present during the summer. The highest concentrations of diazinon occurred during July and August (fig. 9). When present, concentrations of diazinon were less than 0.18 µg/L. Diazinon typically is applied to lawns later in the season to control fleas, ticks, and white grubs, which would probably explain its high detection rate and concentrations during the summer months. It also is used to control cockroaches. Unlike diazinon, disulfoton sulfone was most frequently detected in the spring; the highest concentrations occurred in April. Disulfoton is a systemic insecticide used to control aphids and various other insects; disulfoton sulfone is a transformation product of disulfoton.



Fgure 7. Monthly concentrations of selected pesticides at all sampling sites in the Little River Basin, Kentucky, study area, 2003-04.

Table 7. Summary statistics of the detected herbicides, insecticides, and fungicides in samples collected in the Little River Basin, Kentucky; laboratory reporting limits; drinking-water standards; and aquatic-life criteria.

[Concentrations in micrograms per liter (µg/L); MCL. maximum contaminant level; HAL, health advisory level; --, no regulation or guideline; Ky, Kentucky; CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine; LD, less than laboratory reporting level; drinking water standards from U.S. Environmental Protection Agency (2004b), unless otherwise noted]

Compound	Trade name(s)	Method detection limit (µg/L)	Median concen-tration of all sam-ples (µg/L)	90th per centile of all samples	Maxi mum concen tration detected (µg/L)	Site of maximum concentration	Drinking water standard or guideline (MCL or HAL) (µg/L)	Aquatic Life Criterion (µg/L)
				Herbicides				
Acetochlor	Harness	0.002	0.008	0.253	4.14	Little River near Cadiz, Ky.	--	--
Alachlor	Lasso	.002	LD	.006	.015	Sinking Fork near Hopkinsville, Ky.	2	--
Atrazine	Aatrex	.001	.58	9.41	22.4	South Fork Little River at Hopkinsville, Ky.	3	[1]1.8
Butylate	Sutan+	.002	LD	.01	[2].02	North Fork Little River at Hopkinsville, Ky.	350	--
CIAT (DEA)	Degradate of atrazine	.002	[2].218	[2].448	[2].997	South Fork Little River at Hopkinsville, Ky.	--	--
EPTC	Eptam	.002	LD	.009	.035	North Fork Little River at Hopkinsville, Ky.	--	--
Metoalchlor	Dual	.002	.02	.09	.32	South Fork Little River at Hopkinsville, Ky.	[3]100	[1]7.8
Metribuzin	Lexone, Sencor	.004	LD	LD	.029	Little River near Cadiz, Ky.	[3]200	[1]1
Napropamide	Devrinol	.003	LD	LD	.022	South Fork Little River at Hopkinsville, Ky.	--	--
Pebulate	Tillam	.004	LD	LD	.012	North Fork Little River at Hopkinsville, Ky.	--	--
Pendimethalin	Prowl, Tillam	.004	LD	LD	.121	Sinking Fork near Hopkinsville, Ky.	--	--
Prometon	Pramitol	.018	LD	.05	.16	Sinking Fork at Kings Chapel Road near Cadiz, Ky.	[3]100	--
Propyzamide	Kerb	.004	LD	.008	.015	North Fork Little River at Hopkinsville, Ky. and South Fork Little River at Hopkinsville, Ky.	--	--
Simazine	Princep, Aquazine	.005	.07	.77	6.1	Sinking Fork at Kings Chapel Road near Cadiz, Ky.	4	--
Tebuthiuron	Spike, Graslan	.010	LD	LD	.11	South Fork Little River at Hopkinsville, Ky.	500	--
				Insecticides				
Carbaryl	Sevin	.003	LD	LD	[2].404	North Fork Little River at Hopkinsville, Ky.	700	[1].20
Carbofuran	Furadan	.003	LD	LD	[2].035	North Fork Little River at Hopkinsville, Ky.	40	[1]1.8
Diazinon	Diazinon and others	.002	LD	.02	.18	North Fork Little River at Hopkinsville, Ky.	[3].6	[1].08
Dieldrin	Panoram D-31	.001	[2].008	[2].009	.021	North Fork Little River at Hopkinsville, Ky. and South Fork Little River at Hopkinsville, Ky.	--	--
Disulfoton	Disyston and others	.017	LD	LD	.10	South Fork Little River at Hopkinsville, Ky.	.3	--
gamma-HCH	Lindane	.011	LD	LD	.016	Muddy Fork near Hopkinsville, Ky.	[3].2	[1].01
Malathion	Malathion and others	.005	LD	LD	.038	North Fork Little River at Hopkinsville, Ky.	200	.1
				Fungicides				
cis-Propiconazole	Banner, Orbit	.001	LD	LD	.027	Muddy Fork near Hopkinsville, Ky.	--	--
trans-Propiconazole	Banner, Orbit	.001	LD	LD	.04	Muddy Fork near Hopkinsville, Ky.	--	--
Metalaxyl	Apron, Subdue	.002	LD	.02	.05	Little River near Cadiz, Ky.	--	--

[1] Canadian water-quality guidelines for the protection of freshwater aquatic life (Canadian Council of Ministers of the Environment, 2003).

[2] Estimated value.

[3] U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult (U.S. Environmental Protection Agency, 2004a).

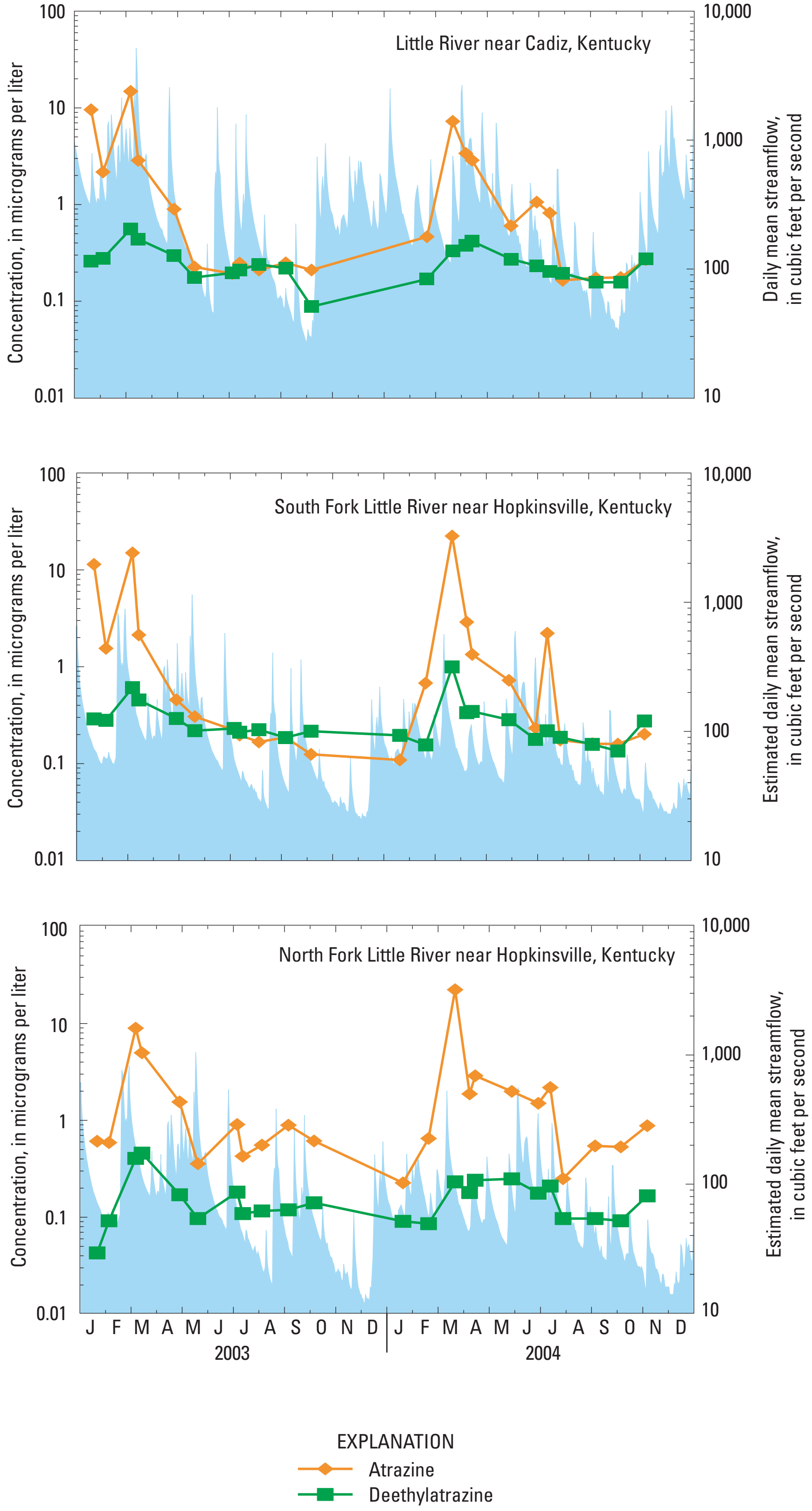


Figure 8. Seasonal variabilty of atrazine and its transformation product, deethylatrazine, at three selected sampling sites in the Little River Basin, Kentucky, study area, 2003-04.

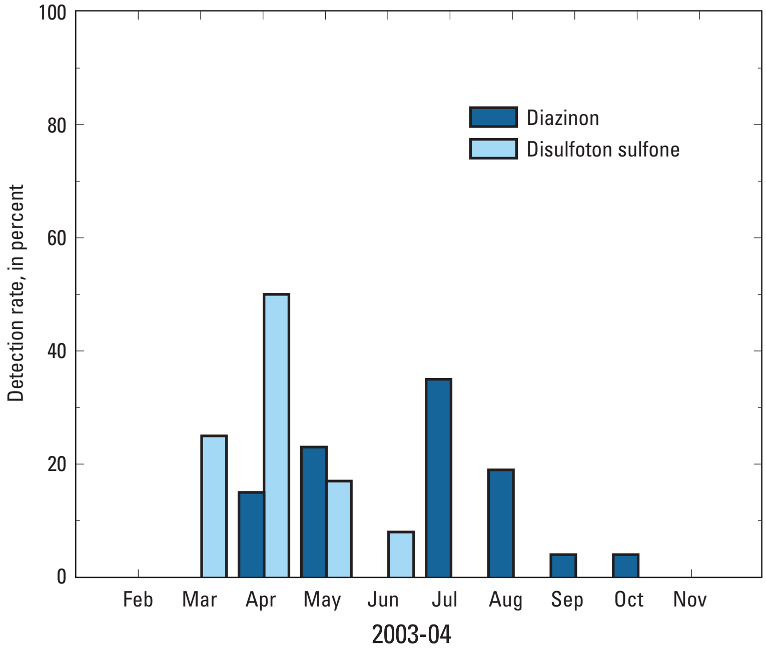


Figure 9. Monthly detection rates of selected insecticides (diazinon and disulfonton sulfone) in the Little River Basin, Kentucky, study area, 2003-04. (Monthly detection rates were combined for 2003 and 2004.)

Median concentrations of the detected insecticides were less than their detection levels with the exception of dieldrin; the median concentration of dieldrin was estimated at 0.008 µg/L. Concentrations of fungicides were highest during summer and late autumn. Concentrations of pesticides can vary seasonally because of differences in the time and frequency that pesticides are applied; hydrologic conditions; types of soil; and the physical, chemical, and biological characteristics of pesticide compounds. Some of the key hydrologic conditions include the timing and amount of runoff from rainfall and the degree of interaction between streams and ground water. Seasonal patterns are important to characterize because they determine the timing and duration of the highest concentrations of pesticides that may affect the quality of water for human aquatic life and wildlife (Gilliom and others, 2006).

Spatial Variability in Concentrations of Pesticides

The Wilcoxson rank-sum nonparametric statistical test (Helsel and Hirsch, 1992) was used to compare concentrations of selected pesticides at the four fixed-network sites in the basin. The Wilcoxson rank-sum test ranks the data points to determine if one data set has higher values than another data set. Differences between the groups with probability (*p*) values of 0.05 or less were considered significant in this study. A total of 23 samples were collected at each of the 4 fixed-network sites during 2003-04. Median concentrations of atrazine and simazine were higher at the North Fork Little River site than at Sinking Fork near Cadiz and at the South Fork Little River site, respectively (fig. 10). There is no clear explanation as to why there are higher concentrations of atrazine and simazine at the North Fork Little River site than at the other sites, since it has the least amount of cultivated land (19 percent). No statistical differences were found among the median concentrations of atrazine or simazine at the other sites. Median concentrations of deethylatrazine (transformation compound of atrazine) were lower at the North Fork Little River site than at the other fixed-network sites. The median concentration of deethylatrazine at the North Fork Little River site was 0.26 µg/L.

Concentrations of metolachlor were higher at Sinking Fork near Cadiz than at the other three sites (fig. 10); the median concentration of metolachlor for this site was about 2.5 times higher (0.05 µg/L) than at the other three sites. Median concentrations of deethylatrazine (transformation compound of atrazine) were lower at the North Fork Little River site than at the other fixed-network sites. The median concentration of deethylatrazine at the North Fork Little River site was 0.26 µg/L.

Differences in median concentrations of diazinon were higher at the North Fork Little River site than at the other three sites (fig. 10). The median concentration for diazinon for the North Fork Little River site was 0.01 µg/L. One explanation for the North Fork Little River site having a higher median concentration of diazinon than the other sites is because the amount of urban land where diazinon (an urban insecticide) might be used is greater in the North Fork Little River subbasin (13 percent).

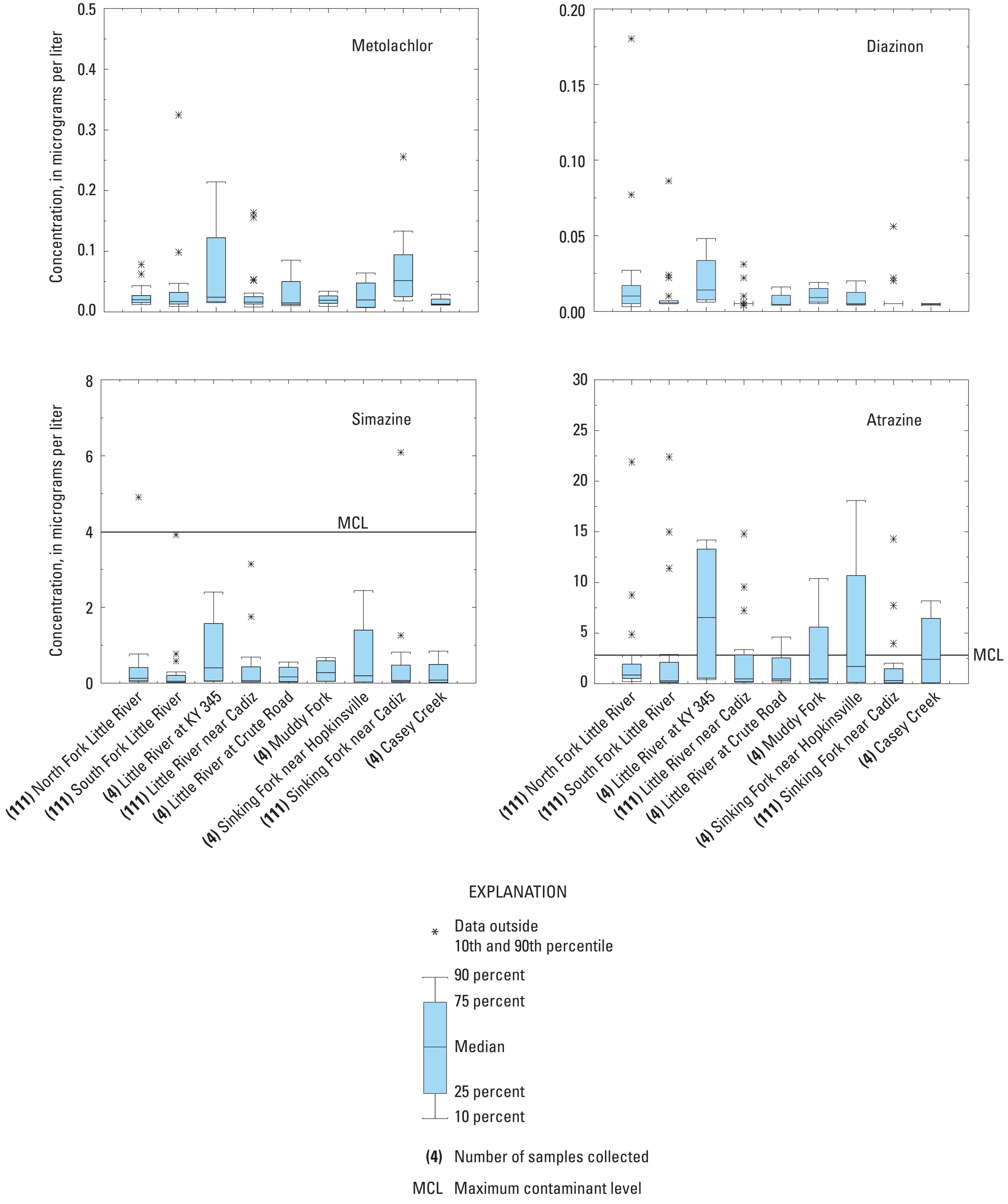


Figure 10. Concentrations of selected pesticides (metolachlor, diazinon, simazine, and atrazine) at all sampling sites in the Little River Basin, Kentucky, study area, 2003-04.

Concentrations of Stream Pesticides Compared to Drinking-Water Standards and Aquatic-Life Guidelines

The U.S. Environmental Protection Agency (USEPA) has developed water-quality standards and guidelines for some compounds that can have adverse effects on human health and aquatic organisms. The standards and guidelines (also known as maximum contaminant levels (MCLs)) established by the USEPA pertain to finished drinking water; however, the MCL values provide comparison with sampled concentrations (U.S. Environmental Protection Agency, 2004a). Aquatic-life criteria provide for the protection of aquatic organisms for short-term (acute) and long-term (chronic) exposures to chemical compounds. In certain instances, Canadian guidelines were used for comparison when other criteria were unavailable (International Joint Commission Canada and United States, 1977; Canadian Council of Ministers of the Environment, 2003).

Most detections of pesticides during this study were at low concentrations relative to existing drinking-water standards and guidelines established for the protection of aquatic life (table 7). Many of the pesticides detected during this study, including the pesticide-transformation compounds, do not have established standards or criteria. Only two pesticide compounds—atrazine and simazine—exceeded the USEPA's MCL. Atrazine and simazine exceeded the established MCL in 17 and 2 percent of the samples, respectively. These exceedences occurred in the spring, and for atrazine, were observed at all sampling sites.

Although most detections of pesticides were at concentrations less than the U.S. Environmental Protection Agency (2004b) drinking-water MCLs and health-advisory levels (HALs), several pesticides—atrazine, carbaryl, diazinon, and gamma-HCH (lindane)—were detected in stream samples at concentrations exceeding guidelines established to protect aquatic life (Canadian Council of Ministers of the Environment, 2003; International Joint Commission Canada and United States, 1977).

Concentrations of atrazine exceeded its aquatic-life criterion (1.8 µg/L) in 32 samples collected from all sites. The concentration of atrazine in the storm sample collected from the South Fork Little River site (22.4 µg/L) was more than 12 times its aquatic-life criterion; most of the high concentrations of atrazine occurred in storm samples. The highest concentrations of the insecticides—carbaryl, diazinon, and gamma-HCH—also occurred in storm samples. Carbaryl was detected at concentrations that exceeded the aquatic-life criterion (0.2 µg/L) in 12 samples. Concentrations of diazinon exceeded their aquatic-life criterion (0.08 µg/L) in two samples collected in July 2004 at the North Fork Little River and at the South Fork Little River sites. Gamma-HCH was detected in one sample from Muddy Fork near Hopkinsville (0.016 µg/L), exceeding its aquatic-life criterion (0.01 µg/L).

Estimated Loads and Yields of Selected Pesticides

Water-resource managers often need to know the amount of a contaminant transported in a stream to determine the stream's condition and how it changes over time. Loads and yields of the contaminants are common measures for these assessments. Loads and yields were estimated for the five pesticides frequently detected in samples for three of the four fixed-network sites from samples collected during 2003-04 (table 8). Loads were not estimated at Sinking Fork near Cadiz because a streamflow relation between this site and Little River near Cadiz could not be established.

Mean annual loads (in lb/yr) for selected pesticides were estimated using the LOADEST program. Load represents the mass (usually in pounds or tons) of a given water-bourne constituent moving past a given point per unit of time. Annual loads vary depending upon drainage-basin size, discharge conditions, and land uses. Load estimates based on monitoring sites with long periods of record are more reliable than estimates from sites with short periods of record.

The largest mean annual loads of selected pesticides among the three fixed sites were at Little River near Cadiz. This site had the largest mean annual loads of atrazine (2,337 lb/yr), metolachlor (19.51 lb/yr), and simazine (330.8 lb/yr) during 2003-04. The North Fork Little River site had the largest mean annual load of diazinon (5.57 lb/yr). The mean annual load of acetochlor (190 lb/yr) was largest at the South Fork Little River site.

Atrazine had the largest estimated use and the largest estimated loads. The load for diazinon, an insecticide that is primarily used for nonagricultural purposes, was less than agricultural herbicides. For example, the load of diazinon at the North Fork Little River site was only 0.9 percent of the atrazine load.

The estimated annual loads of acetochlor, atrazine, diazinon, metolachlor, and simazine for the study period were about 0.01 to 2.2 percent of the amount applied in the basin. The large variability in the values for load as a percentage of use is to be expected because of the considerable variability in physical properties and in application practices (Larson and others, 1997).

Yield is equal to the load divided by the drainage area. Yields are helpful in comparison between basins of differing size and streamflow characteristics because they minimize the effect of differences in streamflow. The South Fork Little River site had the largest yields of commonly used row-crop herbicides (acetochlor, atrazine, and metolachlor). The yield of atrazine was 10.9 (lb/yr)/mi^2 (table 8); acetochlor and metolachlor yields were 3.3 and 0.19 (lb/yr)/mi^2, respectively. Simazine, another commonly used row-crop herbicide, had the largest yield at Little River near Cadiz (1.4 (lb/yr)/mi^2). The North Fork Little River site, a more urban site, contained the largest yield of diazinon (0.08 (lb/yr)/mi^2); diazinon is a pesticide typically used in urban areas.

Table 8. Mean annual load and yield of selected pesticides at selected fixed-network sites in the Little River Basin, Kentucky, 2003-04.

[lb/d, pound per day; (lb/yr)/mi^2, pound per year per square mile; DA, drainage area; mi^2, square mile; <, less than]

Pesticide	Mean annual load (lb/d)	95 percent confidence interval		Standard error	Mean annual yield (lb/yr)/mi^2
		Lower	Upper		
Little River near Cadiz, Ky. (DA = 244 mi^2)					
Acetochlor	66	7.3	234	40	0.27
Atrazine	2,300	1,100	4,400	780	9.4
Deethylatrazine	266	219	314	24	1.1
Diazinon	<4	<4	7.3	.8	<.02
Metolachlor	18	11	29	4.8	.07
Simazine	330	175	584	96	1.3
North Fork Little River near Hopkinsville, Ky. (DA = 58 mi^2)					
Acetochlor	33	7.3	95	24	.49
Atrazine	620	274	1,170	217	9.2
Deethylatrazine	36	26	48	5.3	.05
Diazinon	<4	<4	11	2.4	<.06
Metolachlor	<4	<4	<4	.41	<.06
Simazine	73	47	113	16	1.1
South Fork Little River near Hopkinsville, Ky. (DA = 67 mi^2)					
Acetochlor	193	7.3	912	241	3.3
Atrazine	620	193	1,570	338	11
Deethylatrazine	80	55	95	8.0	1.4
Diazinon	<4	<4	4	<4	<.07
Metolachlor	11	4	18	4	.19
Simazine	55	26	106	16	.95

Summary

A water-quality assessment of streams in the Little River Basin (about 600 square miles in western Kentucky was conducted during 2003–04, in cooperation with the Kentucky Department of Agriculture. The purpose of the study was to determine the presence and distribution of pesticides in streams in the study area, to evaluate the variability in concentrations of pesticides by site and season, and to evaluate loads and yields of selected pesticides. Four fixed-network sites were sampled monthly from March through November 2003 and from February through November 2004. Additional samples were collected at each of these sites during floods to define concentrations of pesticides during high-flow events. Samples were collected from five synoptic-network sites during three high-flow events and one low-flow event over the 2 year period to better define spatial variability in concentrations of pesticides. Ninety one samples were collected for pesticide analysis at the four fixed-network sites.

Herbicides were detected more frequently than insecticides and fungicides; 15 of the 24 pesticides detected in surface-water samples were herbicides. The most commonly detected herbicides were those used on row crops. Atrazine and simazine were detected in all surface-water samples. Metolachlor and acetochlor were detected in more than 45 percent of the samples. Deethylatrazine, a transformation compound of atrazine, was detected in 100 percent of the samples. Only one nonagricultural herbicide, prometon, was detected in more than 50 percent of the samples. Diazinon, the most commonly detected insecticide, was detected in 25 percent of the samples and was found at all sites, except Casey Creek. It was detected most frequently in July and August. Samples from all 9 sites had detectable concentrations of at least 1 pesticide; 1 sample collected at the North Fork Little River site contained 12 detected pesticides. Pesticide detections most frequently occurred in the spring to early summer months (March-June) when agricultural pesticides are applied.

Most pesticides were present in low concentrations. Atrazine and simazine (row-crop herbicides) had the highest measured concentrations (22 and 6.1 µg/L, respectively) and were the most heavily applied herbicides in the basin. Metolachlor also was heavily applied in the basin, but measured concentrations did not exceed 0.32 µg/L. The insecticide Malathion was only detected in 4 percent of the samples, although it was heavily applied in the basin during 2003-04. The highest concentration of Malathion (0.04 µg/L) was measured at South Fork Little River.

Concentrations of deethylatrazine, an herbicide-transformation compound, tended to follow the same monthly concentration pattern as its parent compound, atrazine, but concentrations of deethylatrazine were lower than those of atrazine. Atrazine may have been present in the soil much longer at these sites, which might have allowed microbial populations to transform atrazine into deethylatrazine.

Most concentrations of pesticides were low in relation to existing drinking-water standards and guidelines established for the protection of aquatic life. Only two pesticide compounds—atrazine and simazine—exceeded the U.S. Environmental Protection Agency (USEPA) standards for drinking water. Atrazine exceeded the USEPA's maximum contaminant level (MCL) in 17 percent of all samples; simazine exceeded its established MCL in 2 percent of all samples. These exceedences occurred in the spring. Concentrations of atrazine also exceeded its established aquatic-life criterion (1.8 µg/L) in 29 percent of all samples.

A statistical comparison of concentrations of selected pesticides among the four fixed-network sites showed higher median concentrations of atrazine, simazine, and diazinon at the North Fork Little River site than at the other sites. Median concentrations of deethylatrazine were higher at the North Fork Little River site than at the other sites. Concentrations of metolachlor were significantly higher at Sinking Fork near Cadiz than at the other three sites.

The largest mean annual loads of selected pesticides among the fixed-network sites were at the Little River near Cadiz. Loads were not estimated for the fixed-network site, Sinking Fork near Cadiz. The Little River near Cadiz site had the largest mean annual loads of atrazine (2,337 pounds per year (lb/yr)), metolachlor (19.51 lb/yr), and simazine (330.8 lb/yr) during 2003-04. The North Fork Little River site had the largest mean annual load of diazinon (5.57 lb/yr). The mean annual load of acetochlor (189.5 lb/yr) was largest at the South Fork Little River site.

The estimated annual loads of acetochlor, atrazine, diazinon, metolachlor, and simazine for the study period were about 0.01 to 2.2 percent of the amount applied in the basin. Atrazine had the largest estimated use and the largest estimated loads in the basin. The largest load of the insecticide diazinon that was estimated at the North Fork Little River site was only 0.9 percent of the atrazine load.

Total yields of atrazine ranged from 9.07 to 10.88 pounds per year per square mile ((lb/yr)/mi^2). The South Fork Little River site had the largest yields of commonly used row-crop herbicides (acetochlor, atrazine, and metolachlor). The yield of atrazine was 11 (lb/yr)/mi^2; acetochlor and metolachlor yields were 3.3 and 0.19 (lb/yr)/mi^2, respectively. Simazine, another commonly used row-crop herbicide, had the largest yield at Little River near Cadiz (1.36 (lb/yr)/mi^2). The North Fork Little River site, a more urban site, had the largest yield of diazinon (0.08 (lb/yr)/mi^2); diazinon is a pesticide typically used in urban areas.

The results presented in this report provide an assessment of the presence of pesticide compounds that commonly were used during and possibly several years prior to the study period 2003-04. The vulnerability of drinking-water supplies and of aquatic life to applications of pesticides in the Little River Basin is enhanced by development of karst features, which provide reduced opportunity for natural attenuation of contaminants and increased opportunity for surface- and ground-water contamination.

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