Prepared in cooperation with the Kentucky Energy and Environment Cabinet

Nutrients, Select Pesticides, and Suspended Sediment in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06

Scientific Investigations Report 2010–5167

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

Cover: Photograph of the headwater of Sinking Creek, Breckinridge County, Kentucky, March 4, 2004. Photograph by Angela S. Crain, U.S. Geological Survey.

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KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

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Contents

Contents—Continued

Figures

Figures—Continued

Tables

Tables—Continued

Conversion Factors and Abbreviations

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
millimeter (mm)	0.03937	inch (in.)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
gallon (gal)	3.785	cubic decimeter (dm^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)
	Application and fixation	
pounds per acre (lb/acre)	1.121	kilograms per hectare (kg/ha)
pounds per square mile per year [lb/mi^2)/yr]	1.7513×10^{-7}	kilograms per square hectare per year [kg/ha^2)/yr]

Conversion Factors and Abbreviations—Continued

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

$$°F = (1.8 \times °C)+32.$$

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

The measurement of the mesh size of sampling devices is measured in micrometers (µm); 1,000 micrometers equals 1 millimeter (mm).

Abbreviations

AIC	Akaike Information Criterion
AMLE	Adjusted Maximum Likely Estimation
CIAT	deethylatrazine
DEA	deethylatrazine
DO	dissolved oxygen
LAD	Least Absolute Deviation
LRL	Laboratory-reporting level
MCL	maximum contaminant level
MDL	method detection level
MOVE.1	Maintenance of Variance-Extension type 1
MRL	method reporting level
NADP	National Atmospheric Deposition Program
NASS	National Agricultural Statistics Service
NPDES	National Pollutant Discharge Elimination System
NWQL	National Water Quality Laboratory
p	probability
R^2	coefficient of determination
RPD	relative percent difference
TMDL	total maximum daily load
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
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Nutrients, Select Pesticides, and Suspended Sediment in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06

By Angela S. Crain

Abstract

This report presents the results of a study by the U.S. Geological Survey, in cooperation with the Kentucky Department of Agriculture, on nutrients, select pesticides, and suspended sediment in the karst terrane of the Sinking Creek Basin.

Streamflow, nutrient, select pesticide, and suspended-sediment data were collected at seven sampling stations from 2004 through 2006. Concentrations of nitrite plus nitrate ranged from 0.21 to 4.9 milligrams per liter (mg/L) at the seven stations. The median concentration of nitrite plus nitrate for all stations sampled was 1.6 mg/L. Total phosphorus concentrations were greater than 0.1 mg/L, the U.S. Environmental Protection Agency's recommended maximum concentration, in 45 percent of the samples. Concentrations of orthophosphates ranged from less than 0.006 to 0.46 mg/L. Concentrations of nutrients generally were larger during spring and summer months, corresponding to periods of increased fertilizer application on agricultural lands. Concentrations of suspended sediment ranged from 1.0 to 1,490 mg/L at the seven stations. Of the 47 pesticides analyzed, 14 were detected above the adjusted method reporting level of 0.01 micrograms per liter (µg/L). Although these pesticides were detected in water-quality samples, they generally were found at less than part-per-billion concentrations. Atrazine was the only pesticide detected at concentrations greater than U.S. Environmental Protection Agency drinking water standard of 3 µg/L, and the maximum detected concentration was 24.6 µg/L.

Loads and yields of nutrients, selected pesticides, and suspended sediment were estimated at two mainstream stations on Sinking Creek, a headwater station (Sinking Creek at Rosetta) and a station at the basin outlet (Sinking Creek near Lodiburg). Mean daily streamflow data were available for the estimation of loads and yields from a stream gage at the basin outlet station; however, only periodic instantaneous flow measurements were available for the headwaters station; mean daily flows at the headwater station were, therefore, estimated using a mathematical record-extension technique known as the Maintenance of Variance-Extension, type 1 (MOVE.1). The estimation of mean daily streamflows introduced a large amount of uncertainty into the loads and yields estimates at the headwater station.

Total estimated loads of select (five most commonly detected) pesticides from the Sinking Creek Basin were about 0.01 to 1.2 percent of the estimated application, indicating pesticides possibly are retained within the watershed. Mean annual loads [(in/lb)/yr] for nutrients and suspended sediment were estimated at the two Sinking Creek mainstem sampling stations. The relation between estimated and measured instantaneous loads of nitrite plus nitrate at the Sinking Creek near Lodiburg station indicate a reasonably tight distribution over the range of loads. The model for loads of nitrite plus nitrate at the Sinking Creek at Rosetta station indicates small loads were overestimated and underestimated. Relations between estimated and measured loads of total phosphorus and orthophosphate at both Sinking Creek mainstem stations showed similar patterns to the loads of nitrite plus nitrate at each respective station. The estimated mean annual load of suspended sediment is about 14 times larger at the Sinking Creek near Lodiburg station than at the Sinking Creek near Rosetta station.

Estimated yields of nutrients and suspended sediment increased from the headwater to downstream monitoring stations on Sinking Creek. This finding suggests that sources of nutrients and suspended sediment are not evenly distributed throughout the karst terrane of the Sinking Creek Basin. Yields of select pesticides generally were similar from the headwater to downstream monitoring stations. However, the estimated yield of atrazine was about five times higher at the downstream station on Sinking Creek than at the headwater station on Sinking Creek. A predominantly cultivated agricultural land area of the karst drainage basin drains into Sinking Creek just downstream of the headwater station. Because the daily mean streamflow was estimated at the headwater monitoring station, the error in the estimated nutrient, select pesticide, and suspended-sediment loads and yields are subject to considerable and unknown biases and imprecision (greater standard error of predictions than reported). Additional streamflow and water-quality data are needed to improve the reliability of the load estimates and the errors associated with them at the upstream and downstream stations on Sinking Creek.

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 residential purposes. Pesticides are present in streams and aquatic ecosystems in many parts of the United States and the world (Larson and others, 1997). Many streams also contain nutrients, including nitrogen and phosphorus compounds, at concentrations exceeding natural conditions. Although pesticide and nutrient applications are useful for many purposes, excessive amounts of these compounds in the environment may cause a variety of adverse ecological or human-health effects. Suspended sediment plays a major role in the transport and fate of contaminants such as pesticides and nutrients, because contaminants may sorb onto the surface of suspended sediment particles and be transported and or deposited, or both, downstream.

About 520 stream miles in Kentucky are considered to have impaired water quality because of nutrients, and about 420 stream miles are considered impaired because of suspended sediment (U.S. Environmental Protection Agency, 2006a). Impaired water quality in Kentucky streams due to pesticides is unknown because of a lack of available data.

Water resources in the Sinking Creek Basin, in north central Kentucky, are particularly vulnerable to applications of pesticides and fertilizers because much of the basin is underlain by karst. Karst topography is characterized by internal or sinkhole drainage and rapid flow through solutional conduits, providing reduced attenuation of contaminants and enhanced potential for surface-water and groundwater contamination relative to nonkarst environments (Field, 1990). Three streams in the Sinking Creek Basin have been listed in the State's 2008 Integrated Report to Congress on the Condition of Water Resources in Kentucky as impaired by nutrients and suspended sediment (Kentucky Energy and Environment Cabinet, 2008a). These streams have been on the State's 303(d) List of Impaired Waters since 2002 (Kentucky Natural Resources and Environmental Cabinet, 2003). Because of these impairments, Sinking Creek Basin has been designated a target priority watershed, and the State must develop plans to restore and maintain the water quality of the streams in the basin. The plans establish a "total maximum daily load," or TMDL, for the impaired streams. A TMDL represents the total amount of contaminant that a water body can assimilate without violating the designated water-quality standard established by the U.S. Environmental Protection Agency.

In 2004, the U.S. Geological Survey (USGS), in cooperation with the Kentucky Department of Agriculture, began a study to determine concentrations and estimate loads and yields of nutrients, pesticides, and suspended sediment in the karst terrane of the Sinking Creek Basin. Information from this study will assist State and local water managers and planners, who are responsible for implementing TMDLs and who are responsible for drinking-water supplies in the Sinking Creek Basin, to make informed management decisions regarding acceptable levels of nutrients, pesticides, and suspended sediment.

Purpose and Scope

This report summarizes data collected at seven sampling stations from 2004 through 2006 to determine the presence and distribution of nutrients, select pesticides (5 of the most commonly detected of 47 analyzed), and suspended sediment in streams, springs, and karst windows in the Sinking Creek Basin in north-central Kentucky. Water samples were collected to make seasonal, spatial, and hydrologic evaluations of constituent concentrations, loads, and yields. Loads and yields of nutrients, select pesticides, and suspended sediment were estimated for two mainstem stations on Sinking Creek by use of S-LOADEST, a U.S. Geological Survey software program used to compute mean constituent loads in rivers by use of regression models.

Description of Study Area

Stratigraphy

The Sinking Creek Basin (fig. 1) is mostly underlain by limestone formations of Mississippian through Pennsylvanian age (fig. 2). The limestone units of significance within the upper Sinking Creek Basin study area are the St. Louis Limestone and Ste. Genevieve Limestone. The St. Louis Limestone is mostly composed of sequences of massively bedded (tabular) limestones and shales, and the Ste. Genevieve Limestone is mostly composed of thin-bedded, cherty limestones. Overlying the Ste. Genevieve Limestone and St. Louis Limestone in parts of the Sinking Creek Basin, is a thick sequence of limestone, sandstone, and shale formations of Chester age (lower part). Rocks of lower Chester age are composed of alternating sandstone and limestone strata that include the Golconda Formation, which is sandstone dominated, and the Girkin Limestone (McDowell, 1986).

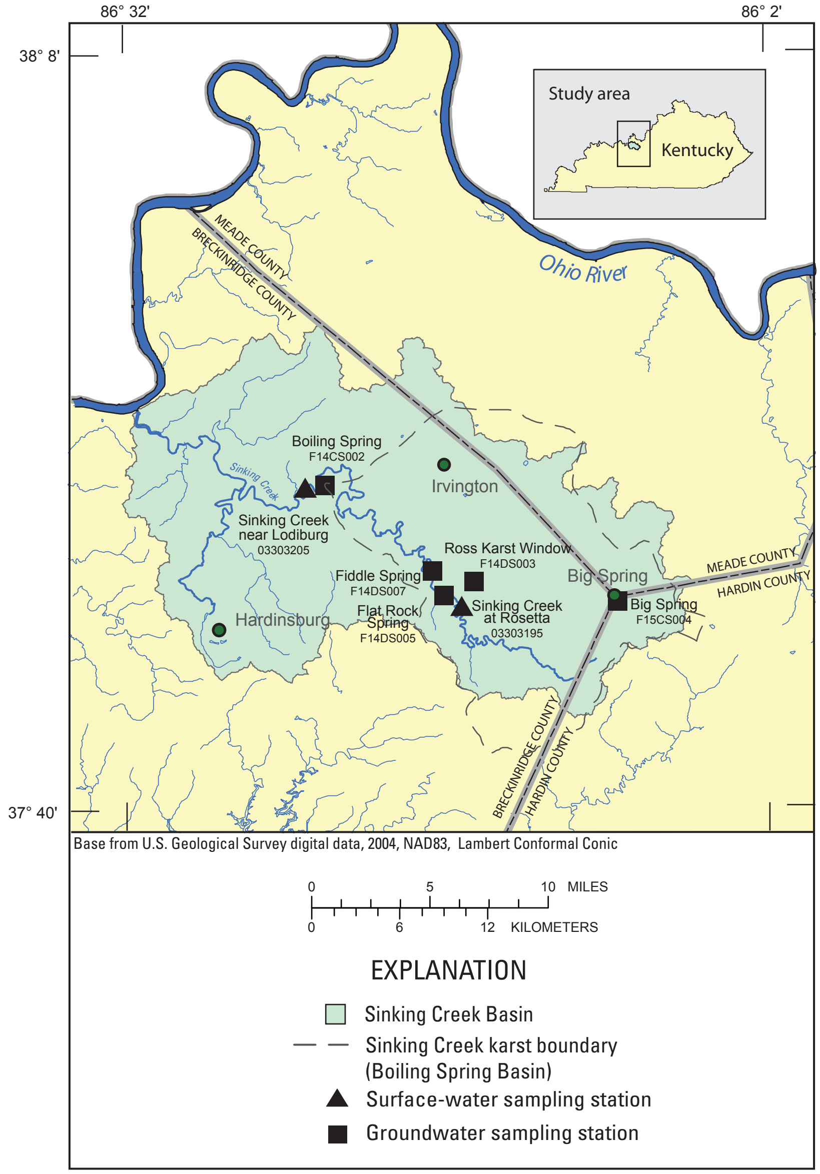

Figure 1. Location of the surface-water- and groundwater-sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, study area.

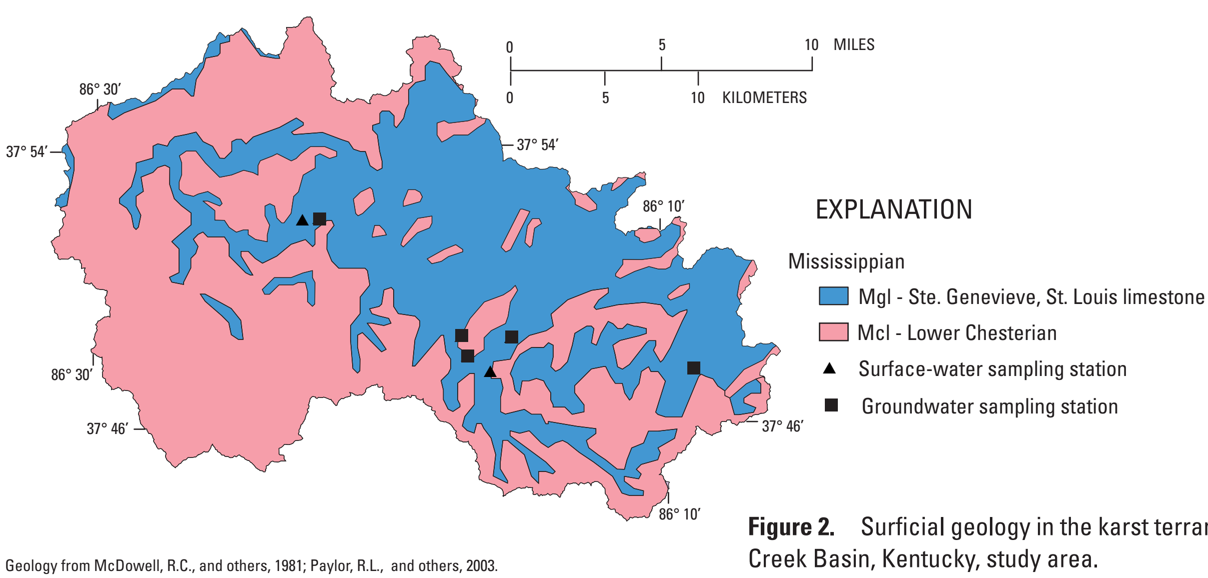

Figure 2. Surficial geology in the karst terrane of the Sinking Creek Basin, Kentucky, study area.

Karst and Groundwater Hydrology

The karst terrane portion of the Sinking Creek Basin, also known as the Boiling Spring Basin, encompasses about 125 square miles (mi^2) (fig. 1 and table 1). Groundwater is contributed to Sinking Creek by numerous karst features including sinkholes (fig. 3), caves, springs, and sinking streams. The exposure of Ste. Genevieve Limestone at the land surface allows 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.

Sinking Creek is one of the largest losing streams in Kentucky (Ray and others, 2005). Blue Fork and Stony Fork are two springs that form the headwaters of Sinking Creek in eastern Breckinridge County. Sinking Creek's main losing reach is about 3 miles (mi) south of Irvington. A dry channel extends about 12 mi from the losing reach to Boiling Spring, where Sinking Creek once again flows on the surface to the Ohio River (George, 1976; Ray, 2001).

Because of its karst terrane, the Sinking Creek Basin is rated as hydrogeologically sensitive, indicating that contaminants in runoff are readily transported to and within a groundwater system (Ray and others, 1994).Water quality throughout the basin is directly affected by natural factors, such as geology, climate, and soils, and human factors, such as population and land use.

Surface-Water Hydrology

Mean annual flow in Sinking Creek does not differ appreciably from year to year, but variations exist within each year based on precipitation conditions. A streamgaging station at Sinking Creek near Lodiburg, Ky. (USGS station 03303205) was installed and operated during the June 2004 through April 2007 study period; however, the time period from July 2006 through April 2007 was not included in this report. Mean annual streamflow at the Sinking Creek near Lodiburg station was 237 cubic feet per second (ft^3/s) in 2005 and 233 ft^3/s in water year 2006 (fig. 4). Mean monthly streamflow from June through September of 2004 was 128 ft^3/s. Mean streamflow was largest in the spring months, defined as March through May, and winter months, defined as December through February, and streamflow typically is lower during the summer and fall months of June through September. The mean daily streamflows for the Sinking Creek near Lodiburg station in water year 2004 ranged from 13 ft^3/s on September 26–30 to 4,140 ft^3/s on May 31; mean daily streamflows in water year 2005 ranged from 9.3 ft^3/s on July 21 to 3,910 ft^3/s on March 28; mean daily streamflows in water year 2006 ranged from 9.1 ft^3/s on November 25 to 5,440 ft^3/s on May 26.

The Kentucky Division of Water has measured Boiling Spring six times in 8 years during low- flow periods. Flow ranged from a low of 6.3 ft^3/s during the 1999 drought to 12.9 ft^3/s. The mean low-flow discharge is 9.8 ft^3/s (Ray and others, 2005). Peak flows at Boiling Spring have been estimated as 2,000 ft^3/s (George, 1976).

Table 1. Surface-water and groundwater stations sampled in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[Percentage of basin area in indicated land use from Kentucky Land Cover Data Set, 2001, Kentucky Commonwealth Office of Technology. **Abbreviations**: USGS, U.S. Geological Survey; GW, groundwater; SW, surface water; KY, Kentucky; mi^2, square mile. **Symbols**: –, data not available; <, less than]

USGS station No.	USGS station name (identifier on figure 1)	Type of station	Latitude	Longitude	Topographic drainage area (mi^2)	Percentage of basin area in indicated land use				
						Agriculture		Forest	Urban	Water
						Cultivated	Pasture			
374755086090401	Big Spring - F15CS004	GW	37°47′55″	86°09′04″	–	–	–	–	–	–
374846086154101	Ross Karst Window - F14DS003	GW	37°48′46″	86°15′41″	–	–	–	–	–	–
374813086171501	Flat Rock Spring - F14DS005	GW	37°48′13″	86°17′15″	–	–	–	–	–	–
374847086172901	Fiddle Spring - F14DS007	GW	37°48′47″	86°17′29″	–	–	–	–	–	–
375209086224001	Boiling Spring - F14CS002	GW	37°52′09″	86°22′40″	–	–	–	–	–	–
03303195	Sinking Creek at Rosetta, KY	SW	37°47′47″	86°16′25″	36	–	–	–	–	–
03303205	Sinking Creek near Lodiburg, KY	SW	37°52′06″	86°23′16″	125	11	37	47	4	<1

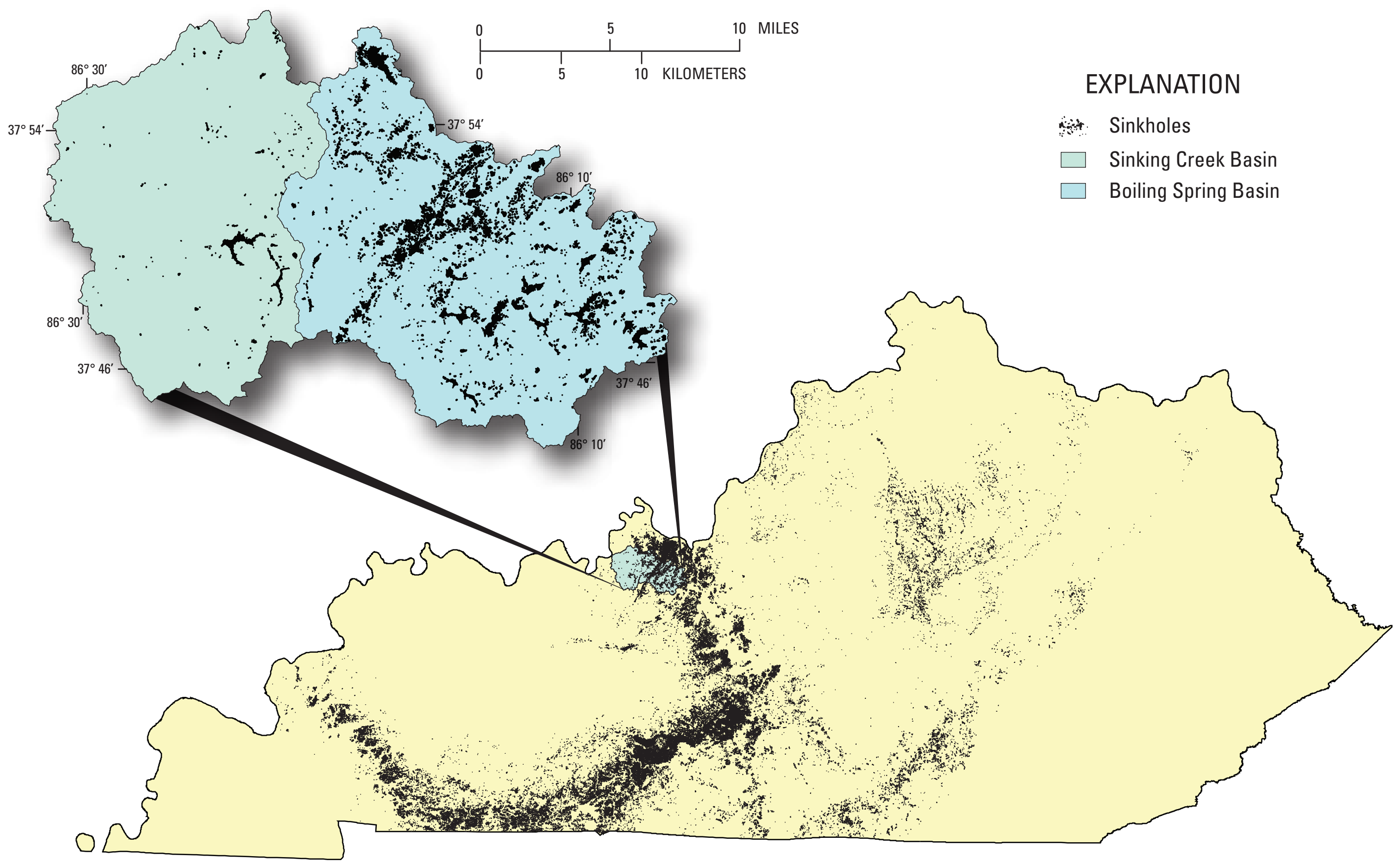

Figure 3. Generalized distribution of sinkholes in the karst terrane of the Sinking Creek Basin, Kentucky, study area.

Precipitation

Total precipitation for the upper Sinking Creek Basin at the streamflow station was 14.7 inches (in.) from June through September 2004, 42.6 in. in 2005, and 51.8 in. in 2006. Total precipitation at the nearest Cooperative (COOP) precipitation station (Hardinsburg, ID 153604) was 54.2 in. in 2004, 35.73 in. in 2005, and 52.5 in. in 2006 (National Oceanic and Atmospheric Administration, 2008) (fig. 4). Precipitation during the growing season from April through October was 32.6 in. or 60 percent of the total precipitation in 2004, 19.8 in. or 55 percent of the total precipitation in 2005, and 33.5 in. or 64 percent of the total precipitation in 2006. The long-term mean annual precipitation for the period 1974–2000 for the Sinking Creek Basin is about 48 in.

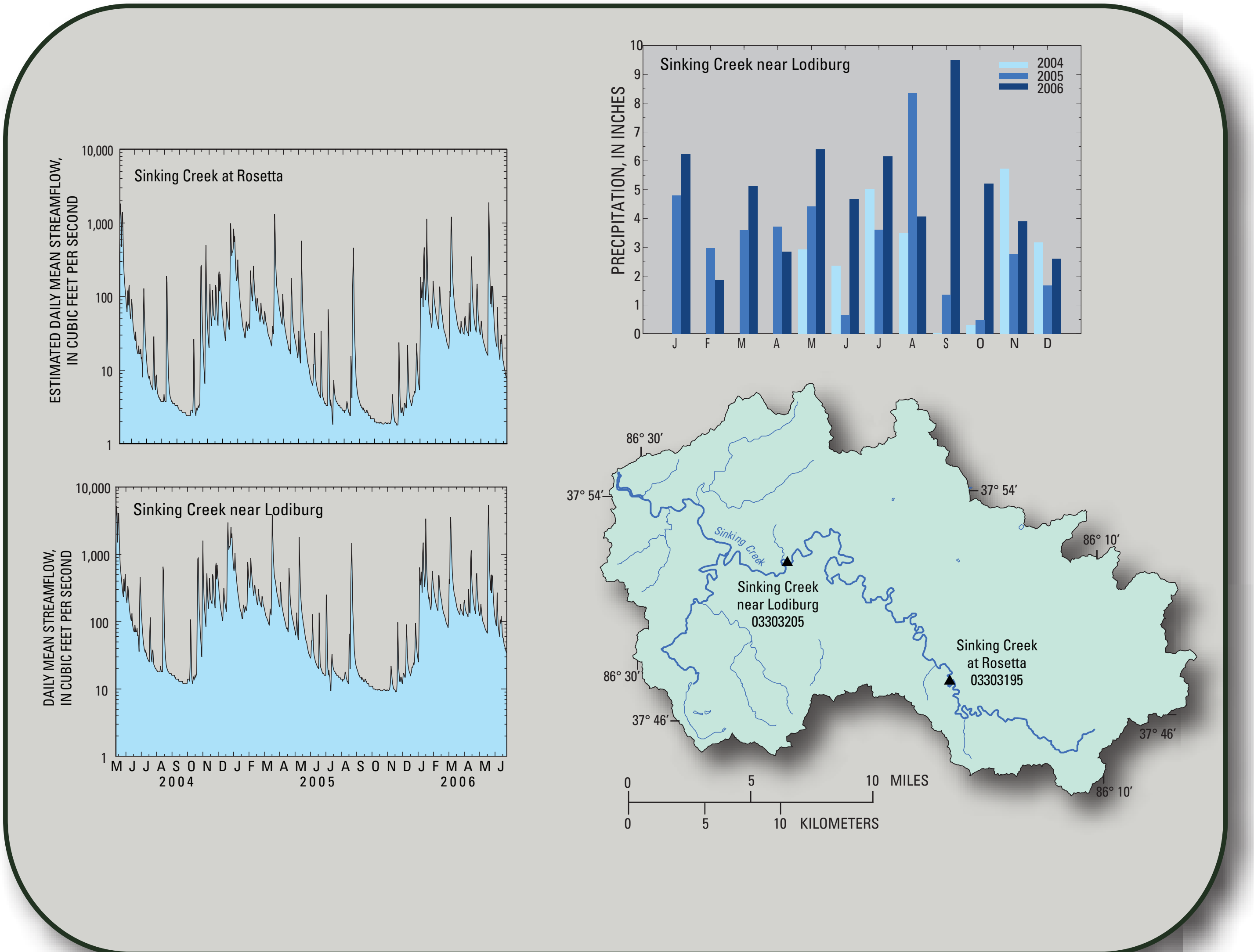

Figure 4. Precipitation and daily and estimated daily mean streamflow at selected surface-water stations in the karst terrane of the Sinking Creek Basin, Kentucky, study area.

Land Use and Land Cover

Streams and springs in the karst terrane of the Sinking Creek Basin drain a diverse landscape of forest, agriculture, and developed areas, such as Irvington, Ky. About 48 percent of the study area is agricultural land (fig. 5). Most of the agricultural land is used for pasture (37 percent); the remaining 11 percent of the agricultural land is used for corn, soybeans, wheat, hay, and tobacco production. Soybeans are the principal row crop harvested in the basin, followed by corn. Table 2 shows the mean land area of soybeans harvested and corn harvested for grain from 2004 to 2006 for Kentucky and for Breckinridge, Hardin, and Meade Counties in Kentucky (U.S. Department of Agriculture, 2008). Forested land comprises about 47 percent of the Sinking Creek Basin, and the most densely forested area is in the headwaters of the basin. Developed areas are about 4 percent of the land use in the basin. The most heavily populated community in the upper Sinking Creek Basin is Irvington, which has a population of about 1,450 people (U.S. Census Bureau, 2002).

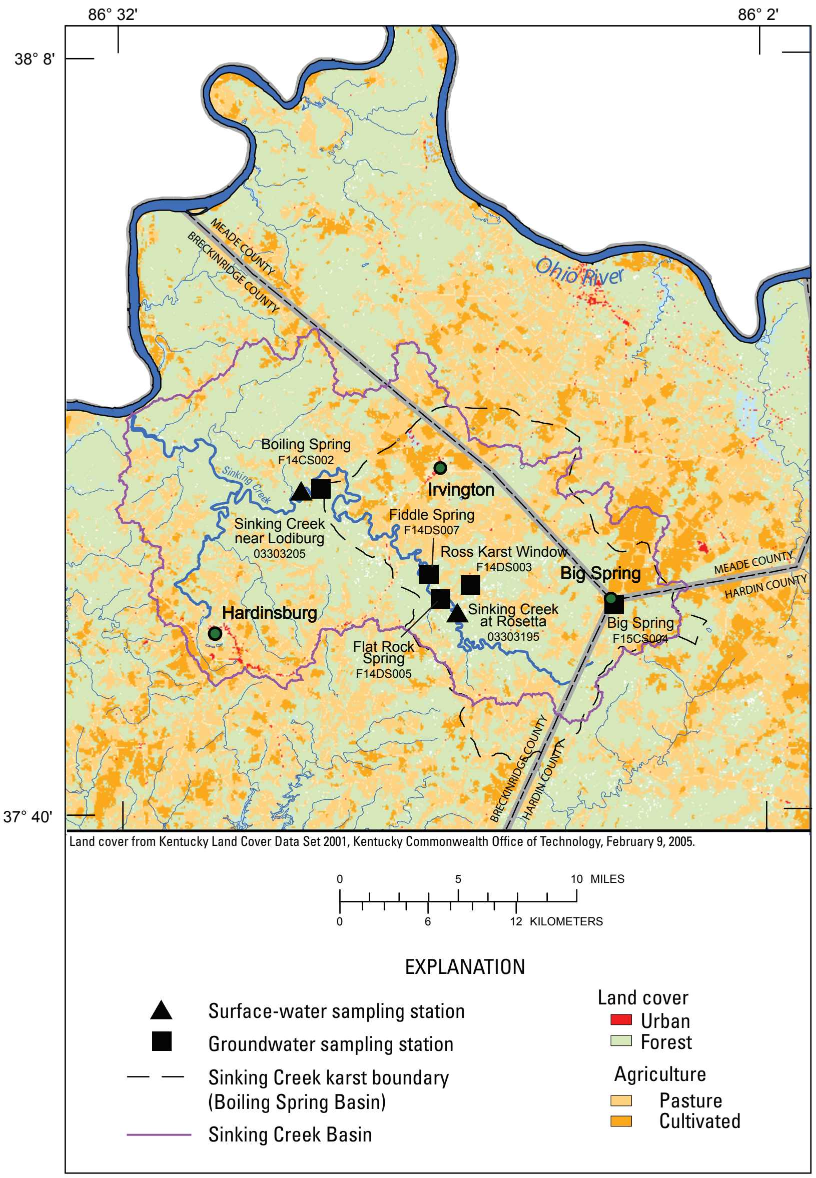

Figure 5. Land cover in the karst terrane of the Sinking Creek Basin, Kentucky, study area.

Pesticide Use, Properties, Application, and Sales

Herbicides commonly are used to control weeds in agricultural areas in the upper Sinking Creek Basin. The three classes of herbicides most commonly used in the upper Sinking Creek Basin are triazines, chloroacetanilides, and organophosphate herbicides, such as glyphosate. The most common triazine herbicides contain atrazine, simazine, and cyanazine and primarily are used on corn. The most common chloroacetanilide herbicides contain acetochlor and metolachlor and are used on both corn and soybeans. The most common organophosphate herbicide, glyphosate, is used on corn and soybeans. Combinations of herbicides applied to row crops are sometimes used for more effective weed control. Multiple applications are common and include some combination of preplanting applications of selective and nonselective herbicides and pre- and post-emergent applications of selective herbicides (Hippe and others, 1994). Both the triazine and chloroacetanilide groups 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 or 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,

Table 2. Mean land area of soybeans harvested and corn harvested for grain statewide, and in Breckinridge, Hardin, and Meade Counties, Kentucky, 2004–06.

[Data from U.S. Department of Agriculture, National Agricultural Statistics Service, 2008. **Abbreviation**: mi^2, square mile]

State and County	Land area (mi^2)	Mean soybean harvest (acres)	Mean land area of soybeans harvested (percent)	Mean harvested corn for grain (acres)	Mean land area of harvested corn for grain (percent)
Kentucky	39,732	1,303,000	5.1	1,120,000	4.4
Breckinridge	572	16,700	4.5	12,300	3.3
Hardin	308	27,300	14	23,870	12
Meade	628	15,200	3.8	10,170	2.5

2001). Pesticide-transformation compounds are generally 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 (Koplin and others, 1998; Scribner and others, 1998). The toxicity of pesticide-transformation compounds is unknown (U.S. Geological Survey, 1999).

The amount of pesticides applied annually to agricultural land within the karst terrane of the Sinking Creek Basin, expressed 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 (U.S. Department of Agriculture, 2008). 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, for weed control along roadways and right-of-ways; aquatic use for algae control; and various commercial and industrial applications.

Atrazine was the top-selling active ingredient of the pesticides studied in Breckinridge, Hardin, and Meade Counties in the Sinking Creek Basin. Other top-selling active ingredients within the counties that were studied included acetochlor, metolachlor, and simazine (table 3). Hardin, Breckinridge, and Meade Counties generally ranked within the top 30 of 98 counties reporting pounds of active ingredient for atrazine from 2004 to 2006. Hardin County consistently ranked higher for pounds of active ingredient for atrazine than Breckinridge and Meade Counties. It is assumed that higher sales equate to higher use of pesticides in the upper Sinking Creek Basin.

Table 3. Pesticide active-ingredient sales from Breckinridge, Hardin, and Meade Counties, Kentucky, 2004–06.

[Amount of active ingredient from Ernest Collins, Kentucky Department of Agriculture, written commun., 2004, 2005, and 2006]

Pesticide active ingredient	Amount of active ingredient, in pounds		
	2004	2005	2006
Acetochlor	18,250	21,500	22,389
Atrazine	85,344	75,836	92,630
Metolachlor	20,777	21,230	24,564
Simazine	23,237	19,642	19,009

Study Design and Methods

Sampling stations in the karst terrane of the Sinking Creek Basin were selected to assess the spatial and seasonal variability of nutrients, pesticides, and suspended sediment in areas of mixed land use and different types of agricultural land (fig. 5). Samples were collected at two Sinking Creek main stem stations, Sinking Creek at Rosetta, which has a 36-square mile drainage area, and Sinking Creek near Lodiburg, which has a 125-square mile drainage area; four springs, Big Spring, Flat Rock Spring, Fiddle Spring, and Boiling Spring; and one karst window, Ross Karst Window (fig. 1 and table 1).

Sample-Station Selection and Sampling Frequency

Water-quality and suspended-sediment samples were collected from April 2004 through November 2004 and March 2005 through December 2005 at all sampling stations and from April 2006 through June 2006 at all stations except Boiling Spring and Ross Karst Window. To help minimize errors in the load estimates, samples were collected during high-flow events in addition to the scheduled monthly sampling. Four instantaneous streamflow measurements were made during high-flow conditions (substantial surface runoff) in addition to the other 18 instantaneous streamflow measurements made during monthly sampling. Water samples were not collected in the winter months so errors in the estimated loads are larger than reported by S-LOADEST. One hundred and thirty-one nutrient samples were collected and 155 suspended-sediment samples were collected at the stations. One hundred and twenty-nine samples were collected for pesticides and transformation compounds. Twenty-two samples composed of blanks, replicates, and pesticide spikes were collected for quality assurance/quality control.

Sampling Methods

Representative water-quality and suspended-sediment samples from the Sinking Creek at Rosetta and Sinking Creek near Lodiburg stations were collected by means of the equal-width-increment method, in which depth-integrated samples were collected at equal distances across the entire stream width and composited (Edwards and Glysson, 1998). Dip samples were collected from the springs for water-quality and suspended-sediment analyses. An automatic suspended-sediment pump sampler was installed at the downstream Sinking Creek near Lodiburg station (station number 03303205). All sampling material was constructed of Teflon® or fluorinated plastic to minimize contamination. Equipment used to collect and process nutrient and pesticide samples was precleaned with a 0.1-percent nonphosphate detergent, triple rinsed with tap water, 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 (Webb and others, 1999).

Water samples for dissolved nutrients were filtered using a 0.45-micrometer (µm) average pore-size capsule filter that was prerinsed with deionized water and filtered native stream water and collected in the appropriate bottle types. Whole-water (unfiltered) nutrient samples were preserved using 1 milliliter (mL) of 4.5N sulfuric acid. Samples for pesticides were pumped through Teflon® tubing and filtered through a 142-millimeter (mm) diameter, 0.7-µm pore size, borosilicate glass-fiber filter placed in a stainless-steel filter unit (Sandstrom, 1995). The filtered water was collected in amber-colored glass bottles and chilled for later analysis of pesticides. Both the glass-fiber filters and the glass bottles had been baked at 450°C in a muffle furnace for a minimum of 2 hours. All nutrient and pesticide samples were chilled and shipped on ice to the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo., for analysis. Suspended-sediment samples were analyzed by the USGS Kentucky Water Science Center Sediment Laboratory in Louisville, Ky.

Field measurements of air temperature, barometric pressure, water temperature, specific conductance, pH, dissolved oxygen (DO), and turbidity were collected at the time of sampling (Wilde, chapter sections variously dated). Alkalinity and bicarbonate were determined by incremental tritration of a filtered water sample with 0.16N sulfuric acid using a digital titrator. Discharge was measured according to standard USGS guidelines as described by Rantz and others (1982).

A continuously recording water-quality monitor with a 15-minute-record interval was installed at the USGS streamflow-gaging station on Sinking Creek near Lodiburg (station number 03303205) on May 25, 2004, and removed on April 30, 2007. Water-quality properties measured with the monitor from May 2004 through April 2007 included water temperature, specific conductance, pH, and DO. Measurements were transmitted every 4 hours via satellite to the USGS Kentucky Water Science Center in Louisville, Ky., and were made available in near-real time on the World Wide Web at URL http//ky.water.usgs.gov/. The water-quality monitor was inspected on-site by USGS personnel approximately every 3 to 4 weeks to maintain calibration. Guidelines and standard operating procedures for maintaining the station and reporting the data are described in Wagner and others (2006). Data are currently available on the USGS public database NWISWeb online at: http://waterdata.usgs.gov/nwis.

Analytical Methods

The USGS NWQL analyzed the water-quality samples for the concentrations of nutrients and pesticides. Water-quality samples for dissolved (filtered) and suspended (unfiltered) species of nitrogen and phosphorus were analyzed by colorimetric methods (Patton and Truitt, 1992; Fishman, 1993; U.S. Environmental Protection Agency, 1993). These analyses quantified sample concentrations of dissolved nitrite plus nitrate, dissolved ammonia (ammonia plus ammonium), dissolved orthophosphate, and total phosphorus (table 4). Concentrations of nutrients discussed in this report represent their concentrations expressed as either nitrogen or phosphorus. For example, a concentration of nitrate expressed as 10 milligrams per liter (mg/L) refers to a concentration of nitrate of 10 mg/L as nitrogen.

Pesticide samples (laboratory schedule 2001) were analyzed using capillary-column gas chromatography/mass spectrometry with selected-ion sampling (Zaugg and others, 1995). Concentrations of 47 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 level (MDL). Table 4 presents the Long-Term MDL of five select pesticides (those that were most commonly detected). 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 and its reported value was less than the reporting level, the concentration was identified as an estimated value and footnoted.

Table 4. Long-term method detection levels, laboratory reporting levels, and method reporting levels for nutrients and select pesticides established by the U.S. Geological Survey National Water-Quality Laboratory, 2004–06.

[In some cases, more than one reporting level is given because these changed over the term of the project. **Abbreviations**: LT-MDL, Long Term-Method Detection Level; LRL, Laboratory Reporting Level; MRL, Method Reporting Level; N, nitrogen; P, phosphorus; mg/L, milligrams per liter; µg/L, micrograms per liter]

Constituent	LT-MDL	LRL/MRL
Nutrients		
Ammonia (as N), dissolved	0.01 mg/L as N	0.04 mg/L as N
Nitrite plus nitrate (as N), dissolved	0.03 mg/L as N	0.06 mg/L as N
Phosphorus (as P), total	0.002 mg/L as P	0.004 mg/L as P
Orthophosphate (as P), dissolved	0.004 mg/L as P	0.006 mg/L as P
Select pesticides		
Acetochlor	0.003 µg/L	0.006 µg/L
Atrazine	0.004 µg/L	0.007 µg/L
Deethylatrazine	0.003 µg/L	0.006 µg/L
Metolachlor	0.003/0.006 µg/L	0.0060/0.013 µg/L
Simazine	0.002 µg/L	0.005 µg/L

The USGS Kentucky Water Science Center analyzed the suspended-sediment samples by filtering samples through a 0.45-µm membrane filter. The filtrate was rinsed with deionized water to remove salts, and the insoluble material and filter were dried at 103°C and weighed (Fishman and Friedman, 1989). The laboratory reporting level for suspended sediment is 1 mg/L.

Quality Control

Quality-control information is needed to estimate potential bias and variability resulting from sample collection, sample processing, and laboratory analysis. About 16 percent of all samples submitted to the laboratory were quality-control samples, which included equipment blanks and field blanks to measure contamination and bias, and replicate samples to measure variability.

A blank is a water sample that consists of water that has undetectable concentrations of an analyte of interest. Blank-water samples are used to test for bias that could result from contamination during any stage of sample collection or the 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 stations; (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, which is a high grade of blank water that also is free of inorganic contaminants, through all sampling and filtration steps as a typical water-quality sample. Field-blank sample concentrations for pesticides or nutrients did not indicate any bias from contamination of the equipment or sample processing methods.

Replicate samples are a set of two or more environmental samples considered to be essentially identical in composition. All replicate samples were collected concurrently by use of one sampler and alternating the collection of samples into two or more compositing containers. Samples were then processed and analyzed independently. Data obtained from the seven sets of replicate samples was used to assess the variability of the overall sampling and analytical process. Replicate samples were compared by use of relative percent differences. Relative percent difference (RPD) for each analyte and replicate sample pair was calculated by the equation:

$$RPD = \left|S1 - S2\right| / (S1 + S2) / 2 * 100 , \qquad (1)$$

where

$S1$ is equal to the concentration in the environmenal sample, in milligrams per liter for nutrients or micrograms per liter for pesticides; and

S2 is equal to the concentration in the replicate sample, in milligrams per liter for nutrients or micrograms per liter for pesticides.

A large RPD can indicate greater variability in those samples. Median concentration differences, as measured by RPD, within replicate sets ranged from 1.7 to 8.2 percent for pesticides, 0 to 3.5 percent for nutrients, and were 5.3 percent for suspended sediment (table 5). The high maximum relative percent differences for some of constituents are likely because both detections in the replicate sample pair were near the reporting level for those constituents. The quality-assurance data indicate that adequate quality-control measures were used in the collection of the synoptic water-quality and sediment samples.

Table 5. Summary of replicate sample data for commonly detected pesticides and pesticide-transformation compounds, nutrients, and suspended sediment.

[The standard deviation is estimated from pairs of duplicate samples where the concentrations were above the reporting limit. The formula for the estimated standard deviation is from Taylor (1987). **Abbreviation**: RPD, relative percent difference]

Constituent	Number of replicate sample sets	Median RPD	Maximum RPD	Estimated Standard Deviation
Pesticides				
Acetochlor	7	2.9	40	0.0020
Atrazine	7	1.9	5.9	0.0166
Deethylatrazine[1]	7	8.2	18	0.0140
Metolachlor	7	1.7	17	0.0013
Simazine	7	4.6	13	0.0077
Nutrients				
Ammonia (as N), dissolved	7	0.0	77	0.0353
Nitrite plus nitrate (as N), dissolved	7	0.4	6.5	0.0251
Phosphorus (as P), total	7	3.5	21	0.0287
Orthophosphate (as P), dissolved	7	2.2	35	0.0045
Sediment				
Suspended sediment	5	5.3	95	6.058

[1]Pesticide-transformation compound.

Statistical Analysis of Nutrients, Pesticides, and Suspended Sediment

The S-Plus software program (Insightful Corporation, 2005) was used to calculate summary statistics such as the mean, median, minimum, and maximum concentrations for nutrients, select pesticides, and suspended sediment. The Kruskall-Wallis nonparametric statistical test (Helsel and Hirsch, 2002) was used to make comparisons in the ranks of concentrations of nutrients, select pesticides, and suspended sediment among the groups of data. This tests for differences in the median ranks of two or more groups. If the Kruskal-Wallis test on the entire group showed significant differences among groups, the Wilcoxon rank-sum test was performed on the ranked data to determine the statistical significance of differences in concentrations between groups of data. Differences between the groups of data with a probability (p) value of 0.05 or less were considered significant in this study.

Estimate of Daily Streamflow at the Sinking Creek at Rosetta Station

A mathematical record-extension technique known as the Maintenance of Variance-Extension, type 1 (MOVE.1) technique (Hirsch, 1982) was used to estimate streamflow for the partial-record station (Sinking Creek at Rosetta) by using same-day streamflows at the nearby gaging station (Sinking Creek near Lodiburg). Only instantaneous streamflow measurements were available at the partial-record station. A total of 22 instantaneous streamflow measurements were made at the partial-record station over a range of flow conditions from April 2004 through November 2004; March 2005 through December 2005; and April 2006 through June 2006 (appendix 1). Of the 22 instantaneous streamflow measurements, 18 were made when the stream appeared to represent moderate-flow and low-flow conditions (no substantial surface runoff). The MOVE.1 method is one of three methods recommended for use by the USGS Office of Surface Water in Technical Memorandum No. 86.02, Low-Flow Frequency Estimation at Partial-Record Stations, issued December 16, 1985. The MOVE.1 technique assumes that a linear relation exists between the logarithms of the same-day streamflows at the partial-record station and a nearby streamgaging station. A graph of the relation between the logarithms of the same-day streamflows at the partial-record station, Sinking Creek at Rosetta, and the nearby gaging station, Sinking Creek near Lodiburg, was linear (fig. 6), and the computed correlation coefficient of 0.95 confirms that a linear relation exists between streamflow at the two stations. The means ($\overline{Y}$ and $\overline{X}$) and standard deviations (Sy and Sx) of the logarithms-base 10 of the same-day flows for the partial-record and streamgaging stations and the logarithms-base 10 of the streamflow statistics ($\hat{X}i$) for the streamgaging station were calculated. Estimates of the streamflow statistics ($\hat{Y}i$) for the partial-record station were obtained by inserting the calculated values into the MOVE.1 equation:

$$\hat{Y}i = \overline{Y} + \frac{Sy}{Sx}(\hat{X}i - \overline{X}). \qquad (2)$$

Estimates of streamflow for the partial-record station are transformed by exponentiating the estimates ($\hat{Y}i$) from logarithms back into their original units of measurement.

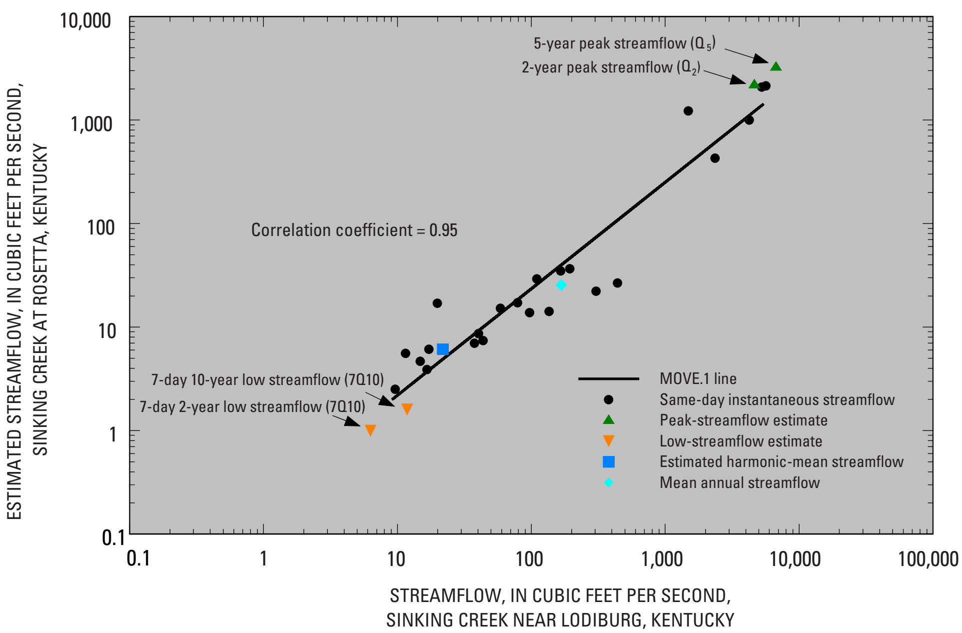

Figure 6. Correlation of same-day instantaneous streamflow between the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station with mean annual streamflow and estimated peak-streamflow, low-streamflow, and harmonic-mean streamflow as supporting data.

There is a large uncertainty in the estimated daily streamflows at the partial-record station, because (1) only instantaneous streamflow measurements were available at the partial-record station; (2) the drainage area at the partial-record station is about 29 percent of the drainage area of the streamgaging station; and (3) the partial-record station is a headwater station indicating streamflow response to precipitation events is usually quicker than at downstream stations. Additional streamflow data were used to support the use of the MOVE.1 technique in extending the streamflow record at the partial-record station. The additional streamflow data used in support included estimates of low-streamflow, peak-streamflow, and mean annual streamflow from the KYGEONET geographic information system datasets, available online at http://kygeonet.ky.gov/kyhydro/main.htm), and the harmonic-mean streamflows (Martin and Ruhl, 1992) (fig. 6). The flow statistics from the KYGEONET, which are calculated using regression-based methods and basin characteristics (Ruhl and Martin, 1991; Martin, 2002; Hodgkins and Martin, 2003) are in good agreement with the line of correlation determined by the MOVE.1 method (fig. 6). The KYGEONET low-flow statistics include the annual minimum 7Q2 and 7Q10 low-flow values. These statistics are based on the minimum average 7-consecutive-day flow from each year of record with a recurrence interval of 2 years and 10 years. For example, a 7Q10 of 1.0 ft^3/s means that the annual minimum average 7-consecutive-day streamflow of less than 1.0 ft^3/s should be expected at the station, on average, once every ten years (Hayes, 1991). The KYGEONET peak-flow statistics include the Q2 and Q5 peak-flow values. These statistics refer to the peak discharges for recurrence intervals of 2 and 5 years. The KYGEONET mean annual streamflow is the arithmetic mean of the individual daily mean discharges for a designate period. This statistic lies within the set of data points on the MOVE.1 correlation line. The harmonic-mean streamflow statistic also lies within the set of data points on the MOVE.1 correlation line, and is determined by summing the inverses of daily mean streamflow data for the entire period of record and dividing the resulting sum by the number of data values. The quotient is reciprocated to yield the harmonic mean.

Load-Estimation Method

Linear-regression models were developed by use of the USGS software S-LOADEST for the estimation of loads for the select pesticides atrazine, acetochlor, simazine, and metolachlor, and the transformation compound, deethylatrazine; loads for the nutrients nitrite plus nitrate, total phosphorus, and orthophosphate; and suspended sediment for the period 2004–2006. This S-LOADEST software is based on LOADEST (Runkel and others, 2004) and 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. The S-LOADEST program is incorporated in the computer program S-Plus (Insightful Corporation, 2005).

S-LOADEST estimates loads using three statistical estimation methods: Adjusted Maximum Likelihood Estimation (AMLE), Maximum Likelihood Estimation (MLE), and Least Absolute Deviation (LAD). The user chooses the most appropriate method for the data being analyzed. The AMLE method was selected for all models, because the input data in this study included censored data (concentrations below the reporting level), and the model calibration residuals were normally distributed within acceptable levels.

The S-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, on the basis of the Akaike Information Criterion (AIC) (Akaike, 1981). The predefined model with the lowest value for the AIC is then selected for use in load estimation. S-LOADEST contains nine predefined rating-curve models that can test the relation between constituent load and streamflow. The seven-parameter regression model has been shown to work well with estimating nutrient loads (Cohn and others, 1992) and was selected for this study. The regression models for the select pesticides in this study did not include all of the terms below, depending on the specific model selected by the software. The “best” model indicated in S-LOADEST was different for each station and select pesticide; however, a consistent model for each select pesticide was chosen to estimate loads for both stations and periods in the basin. Use of the seven-parameter regression model was applicable to estimating pesticide annual loads in this study, because the dataset adequately represents periods when small to negligible concentrations of pesticides are normally found. However, an analysis of the “best” models compared to the general seven-parameter model (equation 3) indicated small improvement in reduction of variance.

The output regression equations take the following general form:

$$\ln(L) = a + b(\ln Q) + c(\ln Q^2) + d[\sin(2pT)] + e[\cos(2pT)] + fT + gT^2, \tag{3}$$

where

L is the constituent load, in pounds per day;
Q is the stream discharge, in cubic feet per second;
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.

Runkel and others (2004) provide a complete discussion of the theory and principles behind the calibration and estimation methods.

The model calibration procedure performed by S-LOADEST uses instantaneous discharge data and concurrent instantaneous concentration data, provided by the user in a calibration file for each station. Data used in the calibration files for this study were collected from April 2004 through November 2004, March 2005 through December 2005, and April 2006 through June 2006. Samples were not collected in the winter months so errors in the estimated loads are larger than reported by S-LOADEST. The total number of concentration measurements in the calibration files for each station varied, depending on the constituent, but ranged from 20 samples for suspended sediment at each station to 24 samples for nutrients and pesticides at each station.

Estimation files containing daily mean streamflow data, in cubic feet per second, were used in S-LOADEST to estimate annual and daily loads at the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station from April 2004 through June 2006. The daily mean streamflow for the Sinking Creek at Rosetta station was estimated by use of the MOVE.1 technique.

Sources of Nutrients

The sources of nutrients in the karst terrane of the Sinking Creek Basin are categorized as being from point or nonpoint sources (table 6). Contaminant sources that are diffuse and do not have a single point of origin into receiving streams are called nonpoint sources. Nonpoint sources of nutrients include atmospheric deposition, fertilizer applications from agricultural and residential areas, feed-lot discharges, septic systems, and urban runoff. Point sources differ from nonpoint sources in that they discharge directly into a receiving stream at a discrete or localized point. Point sources primarily consist of a variety of large and small wastewater-treatment facilities, as well as storm-water runoff and sewer overflows.

Nonpoint-Source Contributions

Nonpoint sources of nutrients estimated in this report for the karst terrane of the Sinking Creek Basin include atmospheric deposition, commercial fertilizer application, livestock waste, and nitrogen fixation from soybeans. Nutrient inputs from urban runoff, combined sewer overflows, and septic systems were not included in the nonpoint source estimates of this report because of minimal or no data. In addition, there is limited urban land use in the basin, so urban runoff and combined sewer overflows are not extensive and are possibly minimal nutrient input sources within the basin.

Table 6. Estimated mean annual loads of total nitrogen and total phosphorus from nonpoint and point sources in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[**Abbreviations**: NA, not applicable. **Symbol**: –, data not available]

Source	Mean annual load, in pounds per year	
	Total nitrogen	Total phosphorus
Inputs to land		
Atmospheric deposition[1]	412,000	NA
Farm fertilizer[2]	1,780,000	377,000
Nonfarm fertilizer[2]	22,600	4,560
Livestock waste[3]	328,000	96,300
Nitrogen fixation[4]	16,600	NA
Septic systems[5]	293,000–846,000	67,700–135,000
Input to streams		
Municipal wastewater discharge[6]	1,500	–

[1]Data from National Atmospheric Deposition Program, 2008. Dry deposition nitrogen not included in atmospheric deposition.

[2]Ruddy and others, 2006. Data from 2001.

[3]U.S. Department of Agriculture, 2004.

[4]Kentucky Agricultural Statistics Service, 2004.

[5]U.S. Census Bureau, 1990 and 2002; U.S. Environmental Protection Agency, 2002.

[6]U.S. Environmental Protection Agency, 2006b.

Atmospheric Deposition

Atmospheric deposition of nitrogen has been measured at a National Atmospheric Deposition Program (NADP) station (KY19) located at Seneca Park, in Jefferson County, since October 2003. The wet deposition data from NADP include nitrate, ammonia nitrogen, and other constituents. No dry deposition data are measured; therefore, total atmospheric deposition of nitrogen cannot be obtained. Atmospheric deposition of phosphorus is not measured by NADP because concentrations are generally not significant and samples are subject to contamination (National Atmospheric Deposition Program, 2008).

Rates of wet deposition of inorganic nitrogen in 2004, 2005, and 2006 were 437,000 pounds per year (lb/yr) (3,500 pounds per square mile (lb/mi^2), 350,000 lb/yr (2,800 lb/mi^2), and 450,000 lb/yr (3,600 lb/mi^2), respectively. The 3-year mean rate (2004–06) of wet deposition of inorganic nitrogen was 412,000 lb/yr (3,300 lb/mi^2) (table 6). The NADP provides annual-summary reports that are available online at http://nadp.sws.uiuc.edu/.

Commercial Fertilizer and Livestock Waste

Commercial fertilizers applied to agricultural lands have become a primary nonpoint source of nitrogen and phosphorus in the United States. Commercial nitrogen fertilizer is applied as either ammonia or nitrate and commercial phosphorus fertilizer is commonly applied as phosphate. Application of nitrogen and phosphorus in commercial fertilizers in the United States from 1945–93 has increased by 20 and 3.6 percent, respectively (Ruddy and others, 2006).

County-level data for nitrogen and phosphorus inputs from farm and nonfarm applications of commercial fertilizer and from livestock waste were compiled in a national data set (Ruddy and others, 2006). The methods for allocating data on state total fertilizer sales to individual counties and for estimating livestock-waste inputs from livestock populations are described in detail by Ruddy and others (2006). The county-level data then were disaggregated by parsing the percentage of the basin within the counties and then summing the values. The use of county-level data has some limitations in its application, because fertilizer and livestock waste sources are not evenly distributed within counties and because typically smaller-sized farms do not have to report usage. The use of county-level data are generally more applicable to large drainage basins that encompass entire counties than smaller drainage basins that encompass only parts of one or more counties.

Farm fertilizer inputs of nutrients in 2001 are estimated to have been 1,780,000 lb of nitrogen and 377,000 lb of phosphorus in the karst terrane of the Sinking Creek Basin, an average of about 14,200 (lb/mi^2)/yr of nitrogen and about 3,020 (lb/mi^2)/yr of phosphorus applied (table 6). The amount of cultivated agricultural land in the karst terrane of the Sinking Creek Basin is about 12 percent, or about 15 mi^2. Nitrogen and phosphorus fertilizers generally are applied to corn fields in spring, just before seeding. Livestock waste also can be applied to fields during this time. Nitrogen fertilizer is reapplied to corn fields 6–10 weeks after planting. Phosphorus fertilizer is applied to corn and soybeans at the time of planting. Nitrogen and phosphorus fertilizers and livestock waste are applied in late summer through early fall for cool-season pasture, hay fields, and wheat fields (University of Kentucky, 2001).

Nonfarm fertilizer contributions of nutrients in 2001 are estimated to have been 22,600 lb of nitrogen and 4,560 lb of phosphorus in karst terrane of the Sinking Creek Basin (table 6). The estimated average annual application per square mile is about 181 (lb/mi^2)/yr for nitrogen and 37 (lb/mi^2)/yr for phosphorus.

Nutrient-input estimates from livestock waste were based on county-level livestock-population data collected by the U.S. Census Bureau during the Census of Agriculture. The method and assumptions used in Ruddy and others (2006) to estimate nitrogen and phosphorus content of livestock waste produced by the various types of livestock are described by Goolsby and others (1999). The livestock groups used to estimate nutrient inputs from livestock waste include beef cattle, dairy cows, hogs, and poultry.

Nitrogen and phosphorus in livestock waste can be a major source of nitrogen and phosphorus loads in streams draining agricultural areas. Animal-feeding operations and concentrated animal-feeding operations, which concentrate animals, feed, and waste on a small land area, have greater potential to contribute nutrients to surface runoff and groundwater than other livestock operations. Wastes produced by these operations may be applied to pasture and crop land and are subsequently taken up by plants or lost to the environment. An animal-feeding operation in Kentucky is defined as a facility where animals are confined and fed for a total of 45 days or more in any 12-month period and where crops, vegetation forage growth, or postharvest residues are not sustained over any portion of the facility in the normal growing season (Kentucky Energy and Environment Cabinet, 2008b). An animal-feeding operation is defined as a confined animal-feeding operation when more than 300 animal units are confined at the facility, and there are contaminants discharged into the waters of the Commonwealth, or more than 1,000 head of beef cattle, 700 head of dairy cattle, 2,500 pigs, 25,000 broilers, or 82,000 laying hens or pullets are present at the facility. There were six animal-feeding operations and no confined animal-feeding operations within the karst terrane of the Sinking Creek Basin as of July 2008 (James Seamy, Kentucky Energy and Environment Cabinet-Division of Water, written commun., 2008).

In Kentucky, the average inputs of nutrients from livestock waste were 1,100,000 lb of nitrogen and 320,000 lb of phosphorus in 1997. In Breckinridge, Hardin, and Meade Counties, mean nutrient inputs were 4,030,000 lb of nitrogen and 1,190,000 lb of phosphorus. Disaggregating the county-level data by parsing the percentage of the basin within the counties and then summing the values, the mean nutrient inputs were 328,000 lb of nitrogen and 96,300 lb of phosphorus for the karst terrane of the Sinking Creek Basin. These nutrient inputs average about 2,620 (lb/mi^2)/yr of nitrogen and 770 (lb/mi^2)/yr of phosphorus throughout the area. Actual nitrogen inputs to the land are probably lower because of volatilization of ammonia from the waste and nitrification and denitrification. The county-level data were disaggregated by parsing the percentage of the basin within the counties and then summing the values.

Nitrogen Fixation by Soybeans

Nitrogen fixation by soybeans is an important source of nitrogen in the karst terrane of the Sinking Creek Basin because of the acreage of soybeans in the study area. The amount of nitrogen produced by fixation from soybeans in the basin is based on the area of soybeans planted and an annual nitrogen fixation rate of 105 pounds per acre (lb/acre), as used by Hoos and others (1999) for soybeans in the Southeast. This rate was multiplied by the mean harvested acres for soybeans in 2004–06 in the basin (U.S. Department of Agriculture, 2008) to estimate the amount of fixed nitrogen. The estimated nitrogen fixation for the karst terrane of the Sinking Creek Basin was 16,600 (lb/mi^2)/yr (table 6).

Point-Source Contributions

The Irvington wastewater treatment facility is the only permitted municipal wastewater treatment facility in the karst terrane of the Sinking Creek Basin. This facility has a mean flow of 0.04 million gallons per day (Mgal/d) based on 2007 and 2008 data.

Nutrient inputs from the wastewater facility are based on monthly average information from the National Pollutant Discharge Elimination System (NPDES) permitting program of the USEPA. The required sampling data for NPDES discharges are stored in the USEPA Permit Compliance System data base (U.S. Environmental Protection Agency, 2008b). The Irvington wastewater-treatment facility monitors effluent for ammonia, but concentrations of total nitrogen and total phosphorus were not available. A regression equation, developed from more than 800 observations of effluent concentrations from municipal wastewater-treatment facilities in Virginia and North Carolina, was used to estimate concentrations of total nitrogen from concentrations of ammonia nitrogen (McMahon and Lloyd, 1995, p. 70–71). The regression equation is:

$$\text{Total nitorgen} = 11.97 + 0.55\ (\text{ammonia}),$$

where concentrations are in milligrams per liter, as nitrogen.

Nitrogen inputs to streams from the municipal wastewater-treatment facility were estimated using 2007 and 2008 data in the following equation:

$$L = (RQ)(C)(f)(T), \tag{4}$$

where

L is nutrient load in lb/yr;
RQ is wastewater effluent flow in cubic feet per second;
C is concentraton of nutrient, in milligrams per liter;
f is a unit conversion factor of 5.3943; and
T is time in days per year.

Monthly load estimated for nitrogen were calculated by multiplying the average daily discharge for the month by the average nitrogen concentration. Monthly load estimates were summed over the year. The estimated input from wastewater discharge was 1,500 lb/yr for nitrogen (table 6). The error in this estimate is unknown, because it is based on a set of data outside the study area and because the variability around this relation is not shown in McMahon and Lloyd (1995). Estimated inputs from wastewater discharge for total phosphorus were not available.

The use of septic systems is common throughout the study area. In 1990, more than 22,000 septic systems were in use within Breckinridge, Hardin, and Meade Counties (U.S. Census Bureau, 1990). Septic systems are mostly used for individual households or small commercial establishments, such as churches, restaurants, convenience stores, that are located in rural areas or that are not served by a domestic wastewater facility. Water from septic systems generally is released to the ground through an absorption field after natural biological treatment.

Based on an average discharge of 69 gallons per day (gal/d) per person (U.S. Environmental Protection Agency, 2002) and 2.47 people per household (U.S. Census Bureau, 2002), estimated water released from each septic tank is about 170 gal/d. Discharge from the nearly 22,000 septic tanks in Breckinridge, Hardin, and Meade Counties is about 3.7 Mgal/d. The average concentration of total nitrogen and the average concentration of total phosphorus in typical residential wastewater range from 26 to 75 mg/L for total nitrogen and 6 to 12 mg/L for total phosphorus based on literature values (U.S. Environmental Protection Agency, 2002). Thus, an estimated mean annual load of total nitrogen of about 293,000 to 846,000 lb/yr, and an estimated mean annual load of total phosphorus of about 67,700 to 135,000 lb/yr is discharged from septic tanks throughout Breckinridge, Hardin, and Meade Counties (table 6).

Concentrations, and Estimated Loads and Yields of Nutrients

Summary statistics for the concentrations of ammonia, nitrite plus nitrate, total phosphorus, and orthophosphate were collected from April 2004 through November 2004, and March 2005 through December 2005 at all sampling stations (Sinking Creek at Rosetta; Sinking Creek near Lodiburg; Big Spring; Flat Rock Spring; Boiling Spring; Ross Karst Window; and Fiddle Spring), and April 2006 through June 2006 at all stations except Boiling Spring and Ross Karst Window. Summary statistics for concentrations of nutrients and suspended sediment in samples from all selected stations are shown in table 7. The results of all the samples collected and analyzed are provided in appendix 1. These data provide the basis for analysis of concentrations at the selected sampling stations and the loads and yields at the Sinking Creek near Lodiburg and Sinking Creek at Rosetta stations.

Concentrations of Nutrients

Although nutrients such as nitrogen and phosphorus are necessary for plant and animal life, in excessive quantities they can accelerate the growth of aquatic plants and cause algal blooms. Excessive aquatic plant growth may result in unsuitable habitat conditions for aquatic animals and can interfere with recreational activities such as fishing, swimming, and boating. Decomposition of aquatic plant growth can cause odor and taste problems in drinking-water supplies and can consume dissolved oxygen, which can adversely affect aquatic life (Journey and Arrington, 2009).

Spatial Variability of Nutrients

Concentrations of nitrate greater than 10 mg/L in drinking water can have adverse human-health effects (Ward and others, 2005). Concentrations of nitrite plus nitrate ranged from 0.21 to 4.9 mg/L at the seven stations (fig. 7). The highest concentration of nitrite plus nitrate of 4.9 mg/L was observed at the Big Spring station. The lowest concentration of nitrite plus nitrate of 0.21 mg/L was observed at the Sinking Creek at Rosetta station. The median concentration of nitrite plus nitrate for all stations sampled was 1.6 mg/L. The Big Spring station had the highest median nitrite plus nitrate concentration, 2.3 mg/L. The range of median concentrations of nitrite plus nitrate was 0.85 mg/L at the Sinking Creek at Rosetta station to 1.8 mg/L at the Flat Rock Spring station.

The nonparametric statistical tests (Kruskal-Wallis and Wilcoxon rank-sum) were used to examine the nutrient concentrations for significant differences among the sampling stations. The Kruskal-Wallis test does not determine which medians of the nutrient concentrations at the stations are different, so the Wilcoxon rank-sum test was used to determine which stations had significantly different nutrients concentrations. Differences between the groups of data with a probability (p) value of 0.05 or less were considered significant. The number of samples collected at each station during 2004 through 2006 ranged from 12 to 23 samples. Significant differences (Kruskal-Wallis, p-value = <0.001) in concentrations of nitrite plus nitrate occurred among the sampling stations, with pair-wise comparisons (Wilcoxon rank-sum) showing that concentrations of nitrite plus nitrate at the downstream Sinking Creek near Lodiburg station were significantly larger than those at the headwater, Sinking Creek at Rosetta station, and at the Big Spring station.

Table 7. Summary statistics of the nutrients and suspended sediment in samples collected in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[**Abbreviations**: mg/L, milligrams per liter; N, nitrogen; P, phosphorus; LD, less than laboratory reporting level; E, estimated]

Constituent	Number of samples	Laboratory reporting level (mg/L)	Concentrations, in mg/L		
			Minimum	Median	Maximum
Ammonia, as N	131	0.04	LD	LD	0.61
Nitrite plus nitrate, as N	131	0.06	0.21	1.6	4.9
Total phosphorus, as P	130	0.004	LD	0.08	0.89
Orthophosphate, as P	131	0.006	E0.003	0.043	0.46
Suspended sediment[1]	156	1	1	73	1,490

[1]Includes automatic-sampler results.

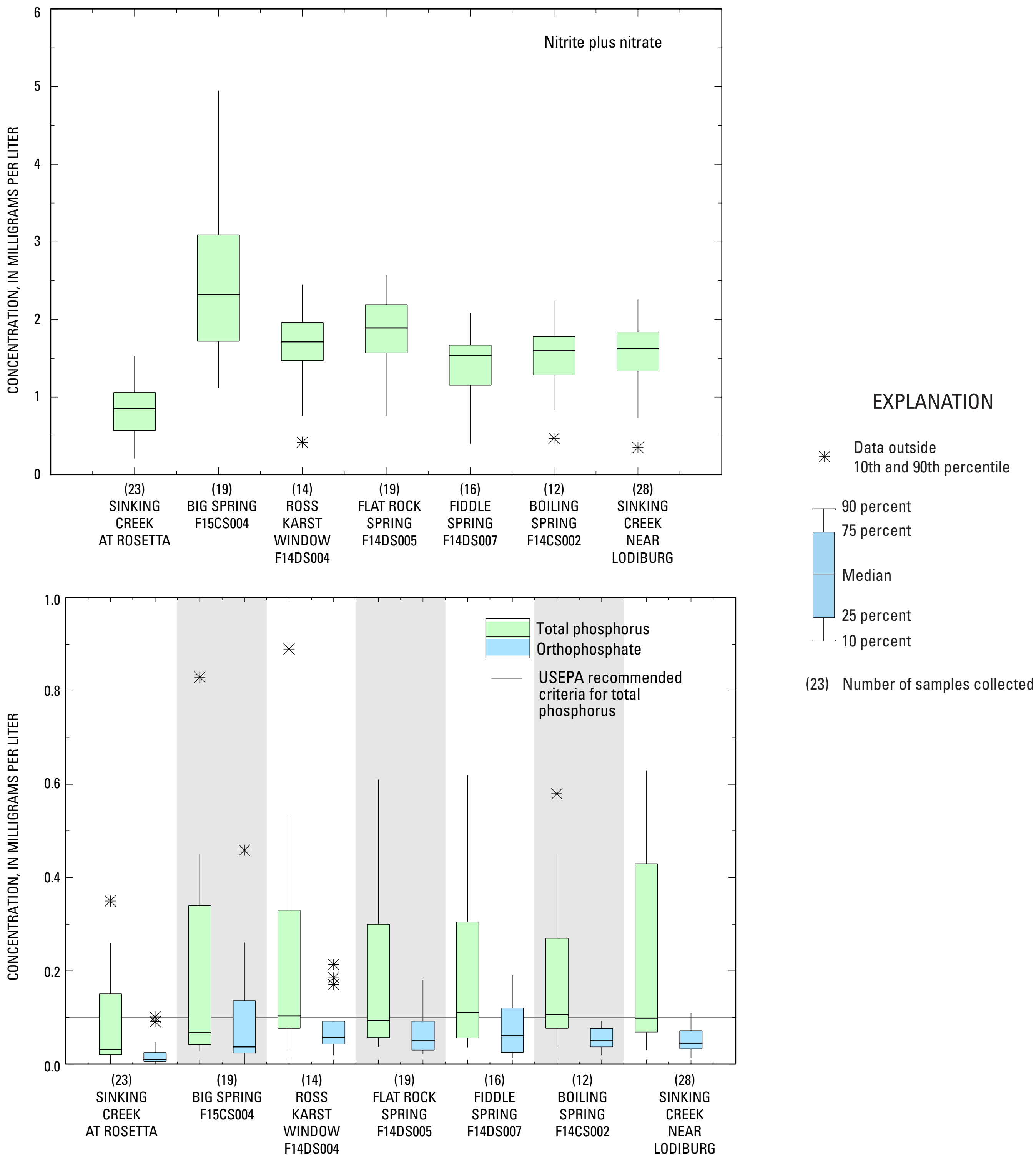

Figure 7. Concentrations of nitrite plus nitrate, total phosphorus, and orthophosphate at seven sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Phosphorus is a common element in the rocks of the Sinking Creek Basin; other sources of phosphorus include sewage effluent, detergents, and leachates from septic tanks. No aquatic-life criterion exists for total phosphorus. However, the USEPA recommends a maximum total phosphorus concentration of 0.1 mg/L in streams that do not directly discharged into lakes and reservoirs to discourage excessive growth of aquatic plants and algae (U.S. Environmental Protection Agency, 1986). Total phosphorus concentrations were greater than 0.1 mg/L in 45 percent of the samples (fig. 7). The median concentration of total phosphorus for all stations sampled was 0.09 mg/L. Concentrations of orthophosphates ranged from <0.006 to 0.46 mg/L. The highest concentration of orthophosphate, 0.46 mg/L, was measured at the Big Spring station (fig. 7).

Significant differences (Kruskal-Wallis, p-value = 0.003) in concentrations of total phosphorus occurred among the sampling stations, with pair-wise comparisons (Wilcoxon rank-sum) showing that concentrations of total phosphorus at the headwater, Sinking Creek at Rosetta station (0.03 mg/L), were statistically significantly smaller than those at the Flat Rock Spring station, the Ross Karst Window station, and the Sinking Creek near Lodiburg station. Results of the Krusal-Wallis test for concentrations of orthophosphate (p-value = <0.001) indicated significant differences among the stations. The Wilcoxon rank-sum test showed that concentrations of orthophosphate at the Sinking Creek at Rosetta station of 0.01 mg/L were significantly smaller than those at all other stations.

Seasonal Variability of Nutrients

Concentrations of nutrients can vary seasonally. Mean concentrations of nitrite plus nitrate measured tended to be higher in the late spring and early summer (June and early July) and early winter (late November and December) and lower in early spring (March) and autumn (September and October) in the karst terrane of the Sinking Creek Basin (fig. 8). An increase in precipitation in the early winter allows for the runoff of nutrients, such as nitrite plus nitrate, into the streams. In addition, increases in the concentrations of nitrite plus nitrate in early winter are possibly because of the release from biota as they become dormant or die off. Precipitation decreases in autumn, allowing plants to uptake much of the available nutrients in the soil; thus, concentrations of nitrite plus nitrate decrease in streams. Concentrations of nitrite plus nitrate, total phosphorus, and orthophosphate in relation to daily mean streamflow at the Sinking Creek near Lodiburg station and Sinking Creek at Rosetta station are shown in figure 9.

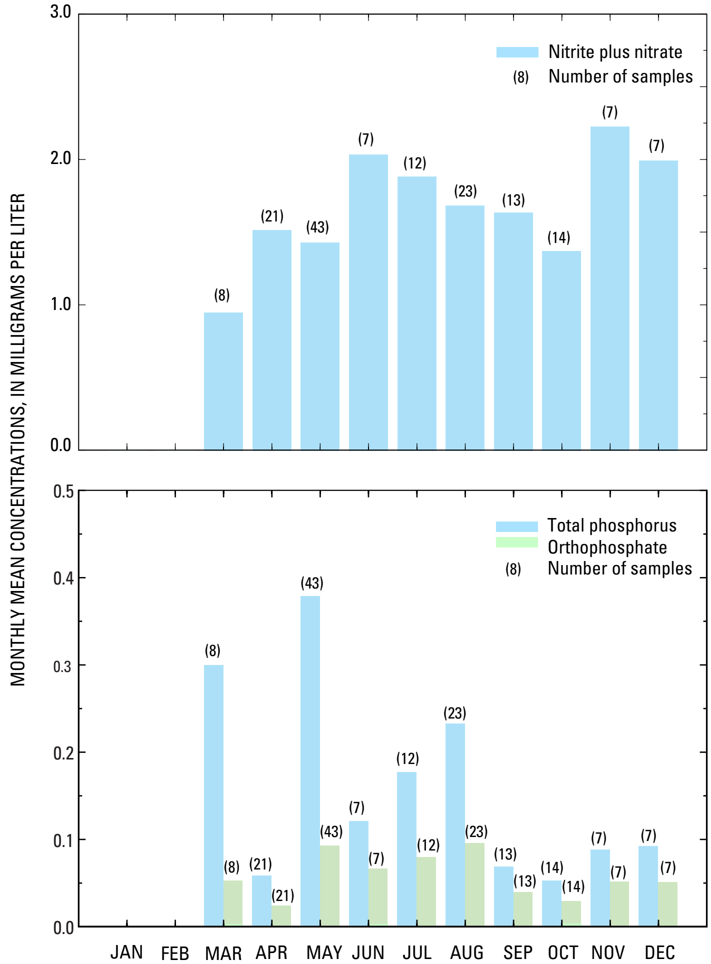

Figure 8. Monthly distribution of nitrite plus nitrate, total phosphorus, and orthophosphate at seven sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Concentrations of nitrite plus nitrate were slightly higher in late spring and early summer and lower in late summer and autumn at the Sinking Creek at Rosetta station. A possible cause of lower concentrations of nitrite plus nitrate in late summer and autumn is increased nutrient uptake resulting from longer days and warmer temperatures. Concentrations of nitrite plus nitrate remained constant throughout the sampling period at the Sinking Creek near Lodiburg station. Significant differences (Kruskal-Wallis, p-value = 0.001) in concentrations of nitrite plus nitrate occurred among the seasons, with pair-wise comparisons (Wilcoxon rank-sum) indicating that concentrations of nitrite plus nitrate were statistically different between spring and summer. No statistical differences were indicated for the other season comparisons.

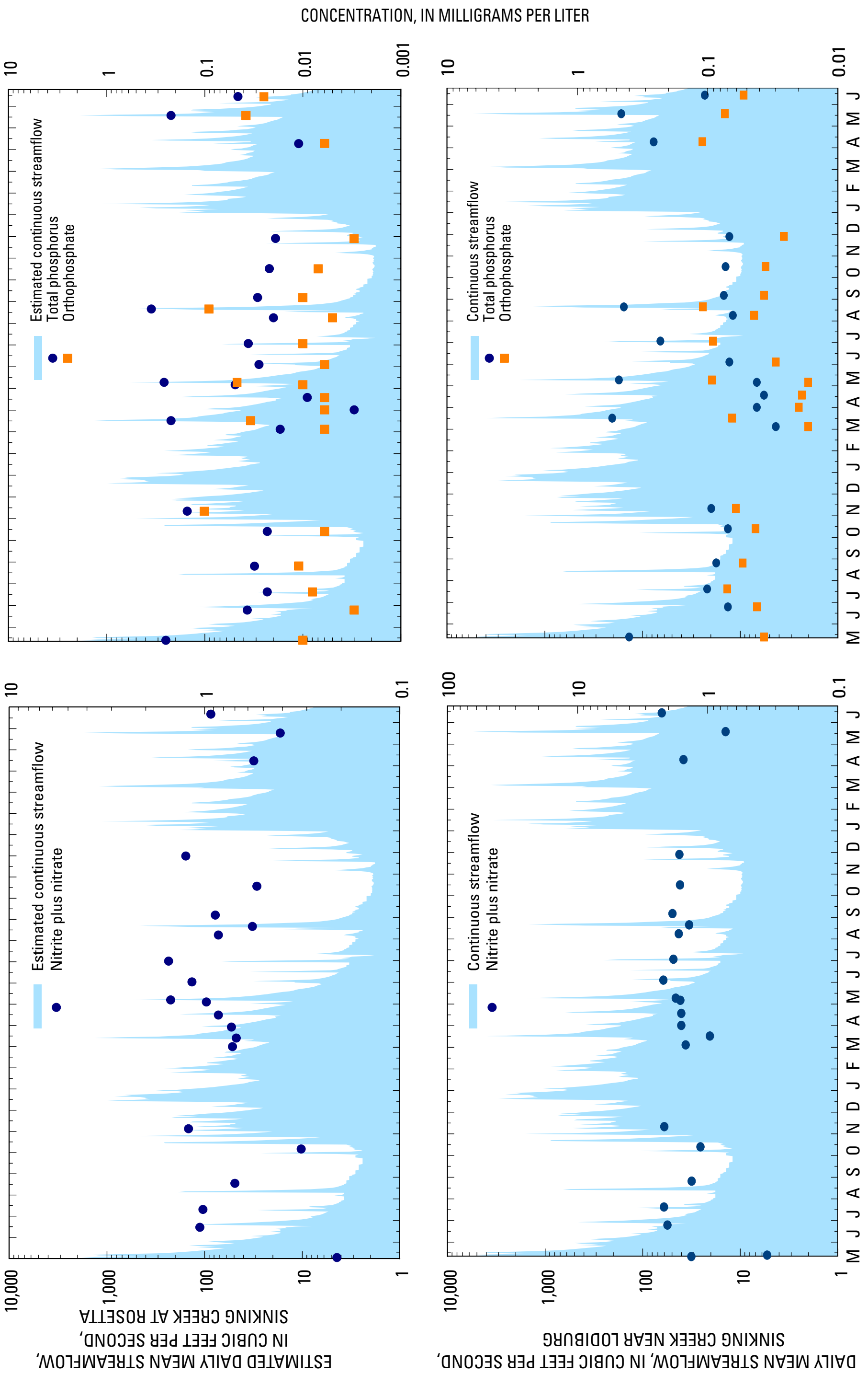

Figure 9. Seasonal variability of nitrite plus nitrate, total phosphorus, and orthophosphate at the Sinking Creek at Rosetta and the Sinking Creek near Lodiburg stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Mean concentrations of total phosphorus and orthophosphate tended to be higher in the spring (March through May) and summer (June through August) and lower in the autumn (September to November) and early winter (December) (fig. 8). Samples were not collected in January and February. Concentrations of total phosphorus and orthophosphate were higher during periods of increased streamflow, mainly in the spring, and lower when streamflow decreased at the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station (fig. 9). This could be because of the relation between phosphorus and sediment, which possibly is mobilized during high-flow events. The seasonal pattern for orthophosphate was similar to that of orthophosphate. The concentration of orthophosphate was slightly higher than total phosphorus in a March 2005 sample at the Sinking Creek at Rosetta station; however, the difference was less than 0.01 mg/L and within the analytical variance of the methods. The Kruskal-Wallis test (p-value = 0.008) performed on the concentrations of total phosphorus indicated significant differences among the seasons. Pair-wise comparisons using the Wilcoxon rank-sum test showed concentrations of total phosphorus were statistically different between summer and autumn with higher concentrations of total phosphorus occurring in the summer.

Estimated Loads and Yields of Nutrients

Load represents the mass, usually expressed in pounds or tons, of a given water-borne constituent moving past a given point per unit of time. Annual loads can vary depending upon drainage basin size, hydrologic conditions, and land uses within a basin. Mean annual loads [(in/lb)/yr] for nutrients were estimated by use of the S-LOADEST program at the two Sinking Creek mainstem sampling stations from samples collected from 2004 through spring 2006 (table 8). The ratio of the standard error of prediction to the mean load standardizes the model error and provides a comparison among the load estimates at the two stations. The prediction error of the mean load of nitrite plus nitrate estimates was 17 percent at the Sinking Creek at Rosetta station, and 10 percent at the Sinking Creek near Lodiburg station (table 8). The prediction error of the mean load of total phosphorus and orthophosphate estimates at the Sinking Creek at Rosetta station were 59 and 69 percent, respectively (table 8). The Sinking Creek near Lodiburg station had prediction errors of the mean of total phosphorus and orthophosphate estimates of 31 and 28 percent, respectively (table 8). These values indicate that the regression models had low error in the estimates of nitrogen and more error in the estimates of phosphorus. Because the daily mean streamflow was estimated at the Sinking Creek at Rosetta station, the error in the estimated nutrient loads at this station is larger than that determined by the S-LOADEST model alone, because it includes considerable and unknown biases and imprecision in the streamflow estimates. Loads were not estimated at the springs or karst window station, because continuous streamflow data were not available.

The coefficients of determination (R^2) for the best-fit regression models for loads of nitrite plus nitrate, total phosphorus, and orthophosphate are listed in table 9. High R^2 values indicate that the models for all four constituents successfully simulated the variability in constituent loads at the two Sinking Creek mainstem stations. Measured instantaneous loads of nitrite plus nitrate, total phosphorus, and orthophosphate for the two Sinking Creek mainstem stations were plotted against estimated loads for the same day to visually assess the fitness of the model (fig. 10). Points above the 1:1 line indicate that the model underestimated the loads; points below the line indicate the model overestimated the loads. The relation between estimated and measured loads of nitrite plus nitrate at the Sinking Creek near Lodiburg station indicate a reasonably tight distribution near the 1:1 line over the range of loads (fig. 10). The model for loads of nitrite plus nitrate at the Sinking Creek at Rosetta station indicates small loads were overestimated and underestimated (fig. 10). Relations between estimated and measured loads of total phosphorus and orthophosphate at both Sinking Creek mainstem stations showed similar patterns to the loads of nitrite plus nitrate at each respective station (fig. 10).

The estimated mean annual loads of nitrite plus nitrate at the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station were 92,900 and 665,000 lb/yr, respectively (table 8). The mean annual total load of nitrogen from the estimate reported by Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006) is similar to the estimate for mean annual load of nitrite plus nitrate in this report. The estimates reported by Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006) are provided by a U.S. Geological Survey internal interactive tool SPARROW-WEB display. Access is provided to reach-level information through a user-navigated hierarchical system of mapped watersheds, based on the Water Resources Council hydrologic drainage basin classification for the United States. This nested drainage basin classification includes 18 water-resources regions, 204 sub-regions, 334 accounting units, and 2,106 hydrologic cataloging units (i.e., 8-digit HUCs). Selection of a river reach displays water-resource statistics for the drainage basin above the reach, including drainage area, mean-annual stream discharge and water velocity, land use, and population, as well as predictions of mean-annual nutrient (total nitrogen and total phosphorus) concentrations and yields and nutrient sources from the SPARROW (SPAtially Referenced Regressions on Watershed attributes) watershed model. The model predictions also include natural background concentrations and yields of nutrients for the river reach (Smith and others, 2003). Estimated mean annual load for total nitrogen was 809,000 lb/yr as reported by

Table 8. Estimated mean annual load and yield of nutrients and suspended sediment at two Sinking Creek mainstem sites in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[**Abbreviations**: N, nitrogen; P, phosphorus; lb/yr, pound per year; (lb/yr)/mi^2, pound per year per square mile; DA, drainage area; mi^2, square mile. **Symbol**: –, not available]

Constituent	Estimated mean annual load (lb/yr)	Standard error of prediction	Prediction error (percent)	Estimated mean annual yield [(lb/yr)/mi^2]	Estimated mean annual load and yield from Ierardi and others (U.S. Geological Survey, unpub. data, 2006)	
					Load (lb/yr)	Yield [(lb/yr)/mi^2]
Sinking Creek at Rosetta, Ky. (DA = 36 mi^2)						
Ammonia (as N), dissolved	–	–	–	–	–	–
Nitrite plus nitrate (as N), dissolved	92,900	15,800	17	2,580	–	–
Phosphorus (as P), total	17,100	10,100	59	475	–	–
Orthophosphate (as P), dissolved	6,700	4,600	69	187	–	–
Suspended sediment	10,300,000	6,360,000	62	280,000	–	–
Sinking Creek near Lodiburg, Ky. (DA = 125 mi^2)						
Ammonia (as N), dissolved	–	–		–	–	–
Nitrite plus nitrate (as N), dissolved	665,000	65,900	10	5,300	809,000	4,600
Phosphorus (as P), total	177,000	54,000	31	1,400	63,900	370
Orthophosphate (as P), dissolved	37,400	10,400	28	300	–	–
Suspended sediment	143,000,000	61,600,000	43	1,140,000	–	–

Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006). Although Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006) reported mean annual loads for total nitrogen but not nitrite plus nitrate, the major form of nitrogen in the karst terrane of the Sinking Creek Basin is nitrite plus nitrate, which is about 84 percent of total nitrogen. This estimate is based on water-quality samples collected by the Kentucky Division of Water mainly under wading conditions. Load estimates from stations that have long periods of record are more reliable than estimates from stations that have short periods of record.

The Sinking Creek at Rosetta station contributed an estimated mean annual load of total phosphorus of 17,100 lb/yr during 2004 to 2006, which is about 10 percent of the total estimated mean annual load at the Sinking Creek near Lodiburg station, from about 29 percent of the overall drainage area. The estimated mean annual load of total phosphorus of 63,900 lb/yr, reported by Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006), is much lower than the estimate for mean annual load of total phosphorus in this report for the Sinking Creek near Lodiburg station of 177,000 lb/yr. There is about a 94 percent relative difference between the estimated total phosphorus load in this report and the estimate reported by Michael C. Ierardi and others. As previously stated, the estimates reported by Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006) are provided by a U.S. Geological Survey internal interactive tool SPARROW-WEB display. Access is provided to reach-level information through a user-navigated hierarchical system of mapped watersheds, based on the Water Resources Council hydrologic drainage basin classification for the United States. This nested drainage basin classification includes 18 water-resources regions, 204 sub-regions, 334 accounting units, and 2,106 hydrologic cataloging units (i.e., 8-digit HUCs). Selection of a river reach displays water-resource statistics for the drainage basin above the reach, including drainage area, mean-annual stream discharge and water velocity, land use, and population, as well as predictions of mean-annual nutrient (total nitrogen and total phosphorus) concentrations and yields and nutrient sources from the SPARROW (SPAtially Referenced Regressions on Watershed attributes) watershed model. The model predictions also include natural background concentrations and yields of nutrients for the river reach (Smith and others, 2003).

Table 9. Regression coefficients and coefficients for determination (R^2) for load models used to estimate loads of nitrite plus nitrate, total phosphorus, orthophosphate, and suspended sediment at two stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[The regression equation is $ln(L)=a + b(lnQ) + c(lnQ^2) + d[\sin(2\pi T)] + e[\cos(2\pi T)]+ fT +gT^2$: where L is the constituent load, in pounds per day; Q is stream discharge, in cubic feet per second; T is time in decimal years from the beginning of the calibration period; *a, b ,c, d, e, f, g* are regression coefficients; R^2 represents the amount of variance explained by the model. Estimated residual variance is the maximum likelihood estimation variance corrected for the number of observations, number of censored observations, and number of parameters in the regression model. Station locations are shown in figure 1]

Station name	Number of observations	Regression coefficient *a*	*b*	*c*	*d*	*e*	*f*	*g*	Estimated residual variance	R^2 (percent)
				Nitrite plus nitrate						
Sinking Creek at Rosetta, Ky.	23	6.29	0.942	-0.078	-0.130	-0.204	0.153	-0.341	0.147	97
Sinking Creek near Lodiburg, Ky.	24	7.82	0.910	-0.069	-0.109	-0.061	0.156	-0.136	.060	99
				Total phosphorus						
Sinking Creek at Rosetta, Ky.	23	3.39	1.54	0.003	-0.711	-0.180	-0.037	0.081	.541	96
Sinking Creek near Lodiburg, Ky.	24	5.10	1.49	0.025	-0.601	-0.170	0.152	0.146	.186	98
				Orthophosphate						
Sinking Creek at Rosetta, Ky.	23	2.84	1.51	-0.147	-1.05	0.016	0.485	0.065	.412	97
Sinking Creek near Lodiburg, Ky.	24	4.27	1.27	-0.033	-0.746	-0.180	0.277	0.042	.186	97
				Suspended sediment						
Sinking Creek at Rosetta, Ky.	21	9.10	1.75	0.100	-0.274	-1.30	-0.113	-0.881	.842	96
Sinking Creek near Lodiburg, Ky.	20	11.2	1.97	-0.005	-0.576	-0.773	-0.162	-0.275	.354	99

The estimated mean annual loads for orthophosphate for the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station are 6,700 and 37,400 lb/yr, respectively (table 8). The mean annual load of orthophosphate represented a larger percentage, 33 percent, of the mean annual load of total phosphorus at the Sinking Creek at Rosetta station than at the Sinking Creek near Lodiburg station, where it was 21 percent. A possible reason for the larger percentage of orthophosphate to total phosphorus at the Sinking Creek at Rosetta station may be nutrients contributed by a hog farm located upstream of the sampling station.

Yields are defined as the amount of load per unit area and are useful for comparing basins with varying size, land use, and physiography. Yields for nitrite plus nitrate, total phosphorus, and orthophosphate were computed for each of the three fixed-sampling stations (table 8).

Estimated historical mean-annual yields (Michael C. Ierardi and others, U.S. Geological Survey, unpub. data, 2006) of nitrite plus nitrate and total phosphorus for the Sinking Creek near Lodiburg station were somewhat similar to those computed from samples collected in 2004–06. Estimated mean annual yields of total nitrogen and total phosphorus from Michael C. Ierardi and others (U.S. Geological Survey, unpub. data, 2006) were 4,700 and 370 (lb/yr)/mi^2, respectively; whereas, the mean annual yield of nitrite plus nitrate was 5,300 (lb/yr)/mi^2 and the mean annual yield for total phosphorus was 1,400 (lb/yr)/mi^2 for the years 2004 to 2006 at the Sinking Creek near Lodiburg station. Mean annual streamflow for the Sinking Creek near Lodiburg station was 245 ft^3/s for water years 2004 to 2006, compared to 259 ft^3/s for the 1970–92 period reported by Michael C. Ierardi and others (U.S. Geological Survey, unpub.data, 2006).

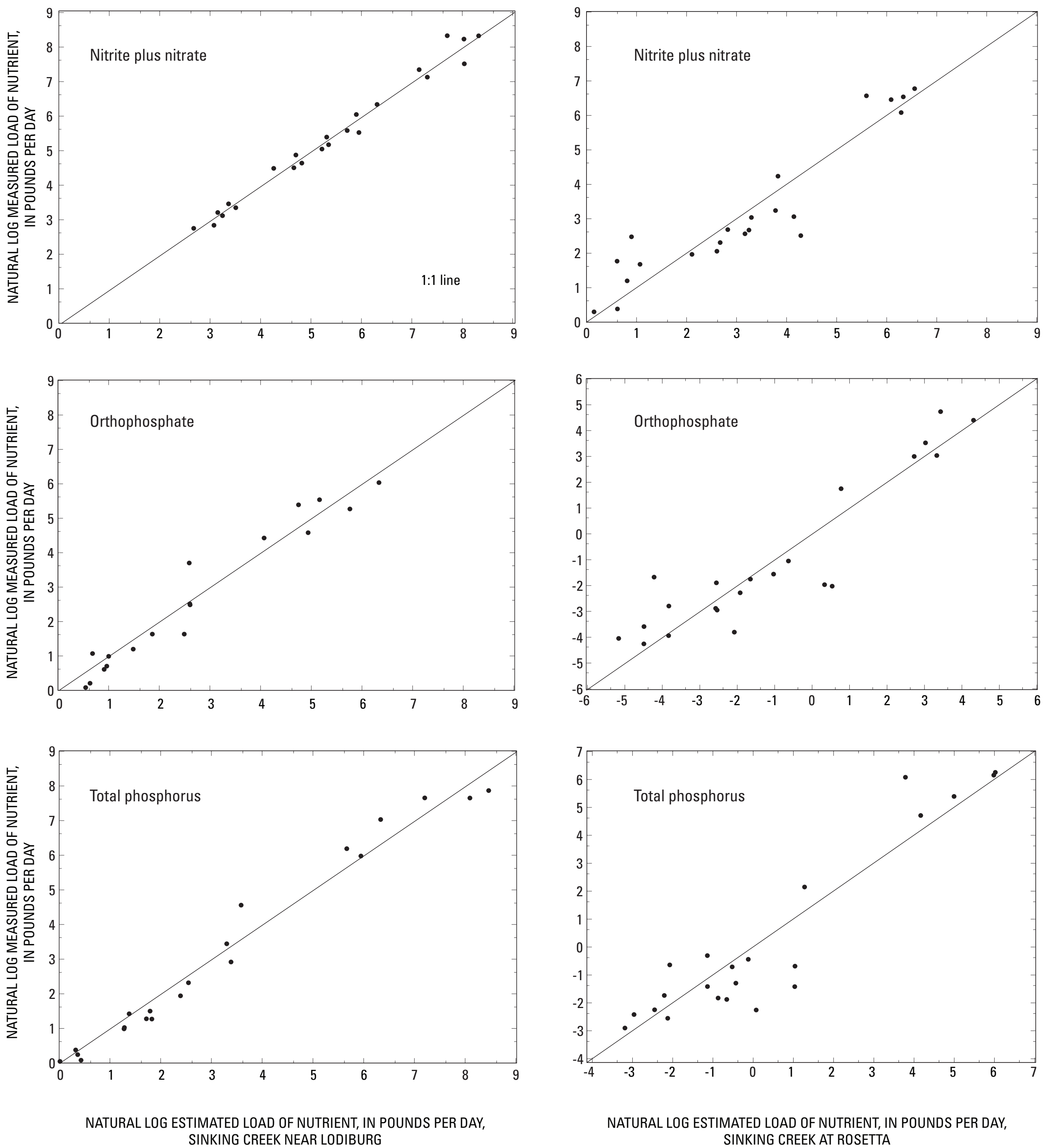

Figure 10. Relation between estimated and measured loads of nitrite plus nitrate, total phosphorus, and orthophosphate at two Sinking Creek mainstem stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Occurrence, Distribution, Concentrations, and Estimated Loads and Yields of Select Pesticides

Summary statistics for the concentrations of pesticides from April 2004 through November 2004, March 2005 through December 2005 at all sampling stations (Sinking Creek at Rosetta; Sinking Creek near Lodiburg; Big Spring; Flat Rock Spring; Boiling Spring; Ross Karst Window; and Fiddle Spring), and April 2006 through June 2006 at all stations except Boiling Spring and Ross Karst Window are presented in table 10. Results for seven compounds in all the samples collected and analyzed are provided in appendix 2. These data provide the basis for the occurrence and distribution and variability by station and season of select pesticides at all sampling stations and estimated loads and yields of select pesticides at the Sinking Creek near Lodiburg and Sinking Creek at Rosetta stations. Water-quality criteria and guidelines were used to evaluate the potential effects of pesticides on human health and aquatic organisms.

Occurrence and Distribution of Select Pesticides

Detections and concentrations of pesticides in streams are influenced by many factors, including the amount of pesticide used, the environmental persistence of the pesticide, the solubility and absorptive properties, and the analytical methods used. The most commonly detected pesticides (5 of the 47 pesticides analyzed) were among the most heavily applied in the karst terrane of the Sinking Creek Basin. Samples from all 7 stations had detectable concentrations of at least 1 pesticide; 1 sample collected at the Ross Karst Window station had 10 pesticides detected. Atrazine (24.6 µg/L), simazine (2.68 µg/L), acetochlor (2.85 µg/L), and metolachlor (1.55 µg/L) had the highest detected concentrations in the basin of the 11 herbicides detected (table 10). These herbicides are row-crop herbicides and are the most heavily applied pesticides in the basin. Median concentrations of the herbicides—acetochlor, atrazine, metolachlor, and simazine—ranged from <0.005 µg/L for simazine to 0.079 µg/L for atrazine for all samples collected during this study (table 10). A common method reporting level (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. Of the 47 pesticides analyzed, 14 were detected above the adjusted MRL of 0.01 µg/L (table 11). The use of the detection threshold allows for comparisons 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, prometon, 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 is greater than or equal to that reported in figure 6.

Herbicides were detected more frequently than insecticides. Eleven of the 14 pesticides detected in water were herbicides. The commonly used herbicides, atrazine, simazine, metolachlor, acetochlor, and prometon, were found throughout the basin. Atrazine was detected in 97 percent of all surface-water samples. Simazine was detected in 60 percent, and metolachlor and acetochlor were detected in more than 30 percent of all surface-water samples (fig. 11). Almost 30 percent of the atrazine and 11 percent of the simazine samples were in the 0.1 to 1.0 µg/L range. The pesticide transformation compound deethylatrazine (DEA) was detected in 93 percent of the samples; however, the method recovery for DEA is poor, so actual concentrations may be higher than reported. Only one nonagricultural herbicide, prometon, was detected in about 17 percent of the samples. Less frequently detected herbicides (less than 10-percent detection frequency) were alachlor, dieldrin, metribuzin, napropamide, pendimethalin, and propachlor. The insecticides carbaryl, a carbamate, and malathion, an organophosphate, were the only insecticides detected at any of the stations. Carbaryl, the most commonly detected insecticide, was found in about 14 percent of the samples and was detected at all stations in the late spring and early summer (May through July) during storm events. Carbaryl was most frequently detected at the Sinking Creek at Lodiburg station and was detected 5 out of 63 samples. Malathion was detected in about 2 percent of the samples. The lower use of insecticides relative to herbicides and their application during periods of reduced runoff probably account for lower detection rates and low concentrations of insecticides in the basin.

Table 10. Summary statistics of the detected herbicides and insecticides in samples collected at the sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06; laboratory reporting levels, drinking-water standards, and aquatic-life criteria.

[Drinking water standards are from U.S. Environmental Protection Agency (2004b), unless otherwise noted. Concentrations in micrograms per liter (μg/L). **Abbreviations**: E, estimated value (for low concentrations, the compound detected, but below the reporting limit; for high concentrations, the compound was detected above the range of the analytical method); MCL, maximum contaminant level; HAL, health advisory level; Ky, Kentucky; CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine. **Symbol**: –, no regulation or guideline]

Compound	Laboratory reporting level (μg/L)	Median concentration detected (μg/L)	95th percentile detected	Maximum concentration detected (μg/L)	Station of maximum concentration	Drinking water standard guideline (MCL or HAL) (μg/L)	Aquatic-Life Benchmark (chronic aquatic community) (μg/L)
Herbicides							
Acetochlor	0.006	0.03	1.07	2.85	Big Spring—F15CS004	–	–
Alachlor	0.005	0.082	0.171	0.186	Big Spring—F15CS004	2	–
Atrazine	0.007	0.079	4.32	[2]24.6	Sinking Creek at Rosetta, KY	3	[1]1.8; [4]17.5
Deethylatrazine (DEA) or (CIAT)	0.006	[2]0.064	[2]0.342	[2]1.11	Big Spring—F15CS004	–	–
Metolachlor	0.006	0.036	0.466	1.55	Big Spring—F15CS004	[3]100	[1]7.8
Metribuzin	0.006	0.021	0.059	0.089	Big Spring—F15CS004	[3]200	[1]1
Napropamide	0.007	0.012	0.013	0.013	Sinking Creek near Lodiburg, KY	–	–
Pendimethalin	0.022	0.026	0.037	0.038	Sinking Creek at Rosetta, KY	–	–
Prometon	0.010	0.010	0.020	0.020	Sinking Creek at Rosetta, KY; Sinking Creek near Lodiburg, KY	[3]100	–
Propachlor	0.025	[2]0.016	0.027	0.029	Fiddle Spring - F14DS007		
Simazine	0.005	0.030	0.708	2.68	Big Spring—F15CS004	4	–
Insecticides							
Carbaryl	.041	<.041	.041	.079	Fiddle Spring—F14DS007	700	[1].20
Malathion	.027	<.027	.027	.211	Ross Karst window—F14DS003	200	0.1

[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).

[4]U.S. Environmental Protection Agency aquatic-life benchmark table for chronic aquatic communities (U.S. Environmental Protection Agency, 2007).

Table 11. Pesticides and pesticide-transformation products analyzed in surface-water and groundwater samples from the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[**Bold-faced** compounds were detected at the method reporting limit of 0.01 µg/L; *italicized* compounds are pesticide-transformation products]

2,6-Diethylaniline	Dieldrin	Pebulate
Deethylatrazine (DEA) or 2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT)	Disulfoton	**Pendimethalin**
Acetochlor	EPTC	Phorate
Alachlor	Ethalfluralin	**Prometon**
alpha-HCH	Ethoprop	Propyzamide
Atrazine	Fonofos	**Propachlor**
Azinphos-methyl	Lindane	Propanil
Benfluralin	Linuron	Propargite
Butylate	**Malathion**	**Simazine**
Carbaryl	Methyl parathion	Tebuthiuron
Carbofuran	**Metolachlor**	Terbacil
Chlorpyrifos	**Metribuzin**	Terbufos
cis-Permethrin	Molinate	Thiobencarb
Cyanazine	**Napropamide**	Triallate
DCPA	pp'-DDE amide	Trifluralin
Diazinon	Parathion	

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

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

Most measured concentrations of pesticides during this study were less than existing drinking-water standards and benchmarks established for the protection of aquatic life (table 10). Only one pesticide compound—atrazine—exceeded the USEPA established MCL of 3 µg/L. Atrazine exceeded the established MCL in 8 percent of the samples. These exceedences occurred in the spring and were observed at four

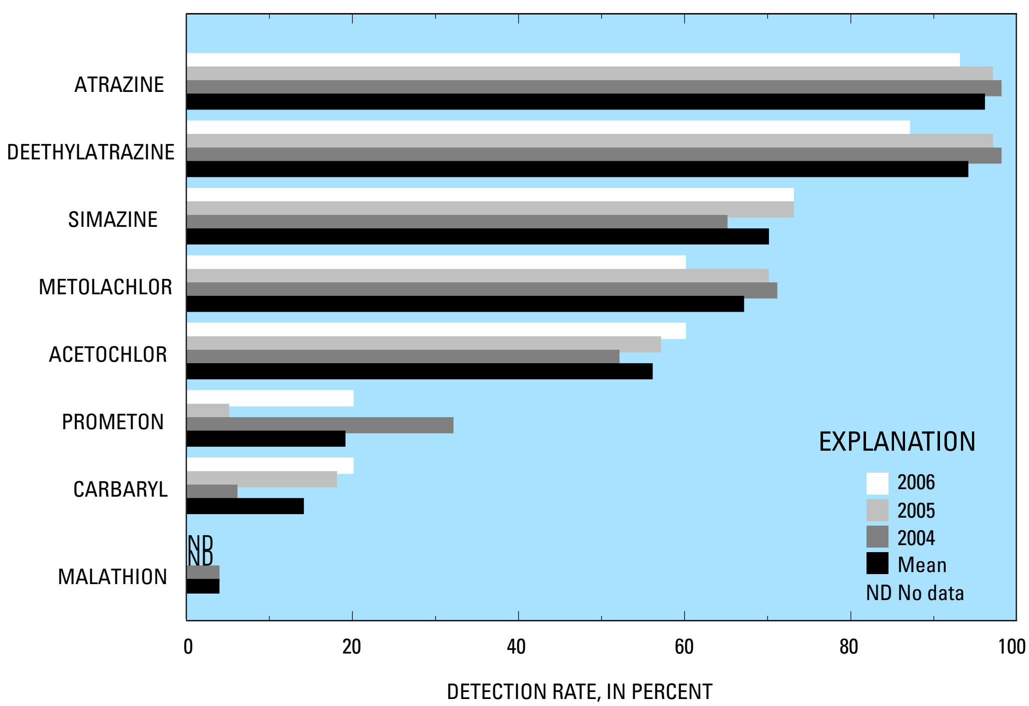

Figure 11. Occurrence of pesticide compounds from all samples at all stations in the karst terrane of the Sinking Creek Basin, Kentucky, study area, 2004–06.

of the seven sampling stations. Atrazine also was detected at concentrations exceeding benchmarks established to protect aquatic life (International Joint Commission Canada and United States, 1977; Canadian Council of Ministers of the Environment, 2003; U.S. Environmental Protection Agency, 2007) (table 10). Concentrations of atrazine exceeded its aquatic-life benchmarks of 1.8 µg/L in 13 samples collected from 4 of the 7 sampling stations. The concentration of atrazine in the storm event sample collected from the Sinking Creek at Rosetta station, 24.6 µg/L, was more than 12 times the Canadian aquatic-life benchmarks and exceeded the USEPA benchmarks for chronic effects on aquatic communities (table 10). Most of the high concentrations of atrazine occurred in storm event samples. Concentrations of the insecticide malathion exceeded its aquatic-life benchmark of 0.1 µg/L in two samples collected from the Ross Karst Window station and Flat Rock Spring station in August 2004.

Spatial Variability of Select Pesticides

Factors such as soil type, pesticide application rates, and the use of pesticides can affect the spatial variability of concentrations of pesticides. A detailed analysis of these factors, among others, is beyond the scope of this report. The nonparametric statistical tests (Kruskal-Wallis and Wilcoxon rank-sum) were used to examine select pesticide concentrations for significant differences among the sampling stations. The Kruskal-Wallis test does not determine which medians of the select pesticide concentrations at the stations are different, so the Wilcoxon rank-sum test was used to determine which stations had significantly different select pesticide concentrations. Differences between the groups of data with a probability (p) value of 0.05 or less were considered significant.

Significant differences (Kruskal-Wallis, p-value = 0.006) in concentrations of atrazine occurred among the sampling stations, with pair-wise comparisons (Wilcoxon rank-sum) showing that concentrations of atrazine were statistically smaller at the Fiddle Spring station than at all stations, except at the Sinking Creek at Rosetta station (fig. 12). A possible explanation is that the Fiddle Spring station has a different recharge area from these stations, and the land use/land cover has minimal cultivated agricultural land. No statistical differences were found among the concentrations of atrazine at the other stations. Results of the Krusal-Wallis test for concentrations of deethylatrazine, the transformation compound of atrazine (p-value = <0.001), indicated significant differences among the stations. The Wilcoxon rank-sum test showed that concentrations of deethylatrazine at the Sinking Creek at Rosetta station and the Fiddle Spring station were statistically less than concentrations of deethylatrazine at the other stations. Lesser concentrations of deethylatrazine at the Sinking Creek at Rosetta station and the Fiddle Spring station are likely related to the small amount of cultivation in their drainage areas.

Significant differences (Kruskal-Wallis, p-value = 0.006) in concentrations of simazine occurred among the sampling stations, with pair-wise comparisons (Wilcoxon rank-sum) showing that concentrations of simazine were statistically less at the Fiddle Spring station than the other stations, except at the Sinking Creek at Rosetta station (fig. 12). Lesser concentrations of simazine at the Fiddle Spring station are likely related to less cultivation in its recharge area. No significant differences between the stations and concentrations of acetochlor or metoachlor were dedected at the 95-percent confidence level.

Seasonal Variability of Select Pesticides

Concentrations of pesticides varied throughout the year in samples collected at all sampling stations, and the highest concentrations generally were found during the spring (fig. 13). The maximum concentrations of select herbicides detected—acetochlor, atrazine, metolachlor, and simazine—occurred in the growing season (April–May) (fig. 13). The pesticides detected above the adjusted MRL of 0.01 µg/L in the karst terrane of the Sinking Creek Basin were found in Sinking Creek and surrounding springs and karst windows year around, but at smaller concentrations (table 10). The most commonly detected insecticide, carbaryl, also was present primarily in the spring. The highest concentrations of carbaryl, 0.09 µg/L, occurred during May 2005. However, most detections of carbaryl were less than the 0.041 µg/L laboratory reporting level. Unlike carbaryl, malathion was detected only in the summer of 2005, and the highest concentration was 0.211 µg/L. Median concentrations of these two most commonly detected insecticides in the karst terrane of the Sinking Creek Basin were less than their reporting levels.

Concentrations of atrazine and its transformation compound, deethylatrazine, in relation to daily mean streamflow at the Sinking Creek near Lodiburg station and Sinking Creek at Rosetta station are shown in figure 14. 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 it is not applied and streamflow is decreased. The seasonal pattern for the pesticide transformation compound, deethylatrazine, mirrored that of its parent compound, atrazine, but generally at lower concentrations. Pesticide transformation compounds generally cooccur with parent pesticide compounds, because most pesticides begin to degrade by chemical or biological processes immediately following application.

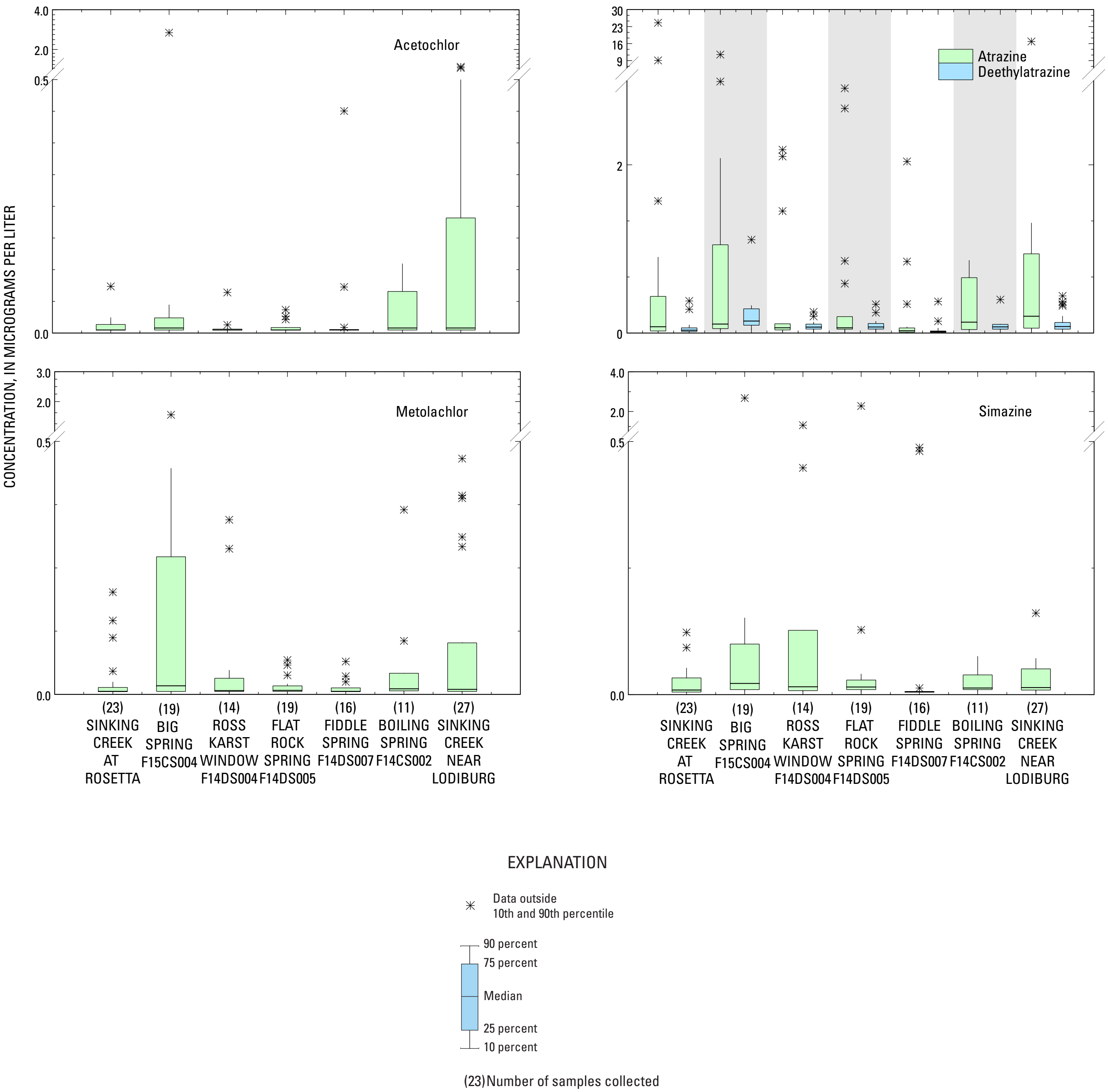

Figure 12. Concentrations of acetochlor, atrazine, deethylatrazine, metolachlor, and simazine at all sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

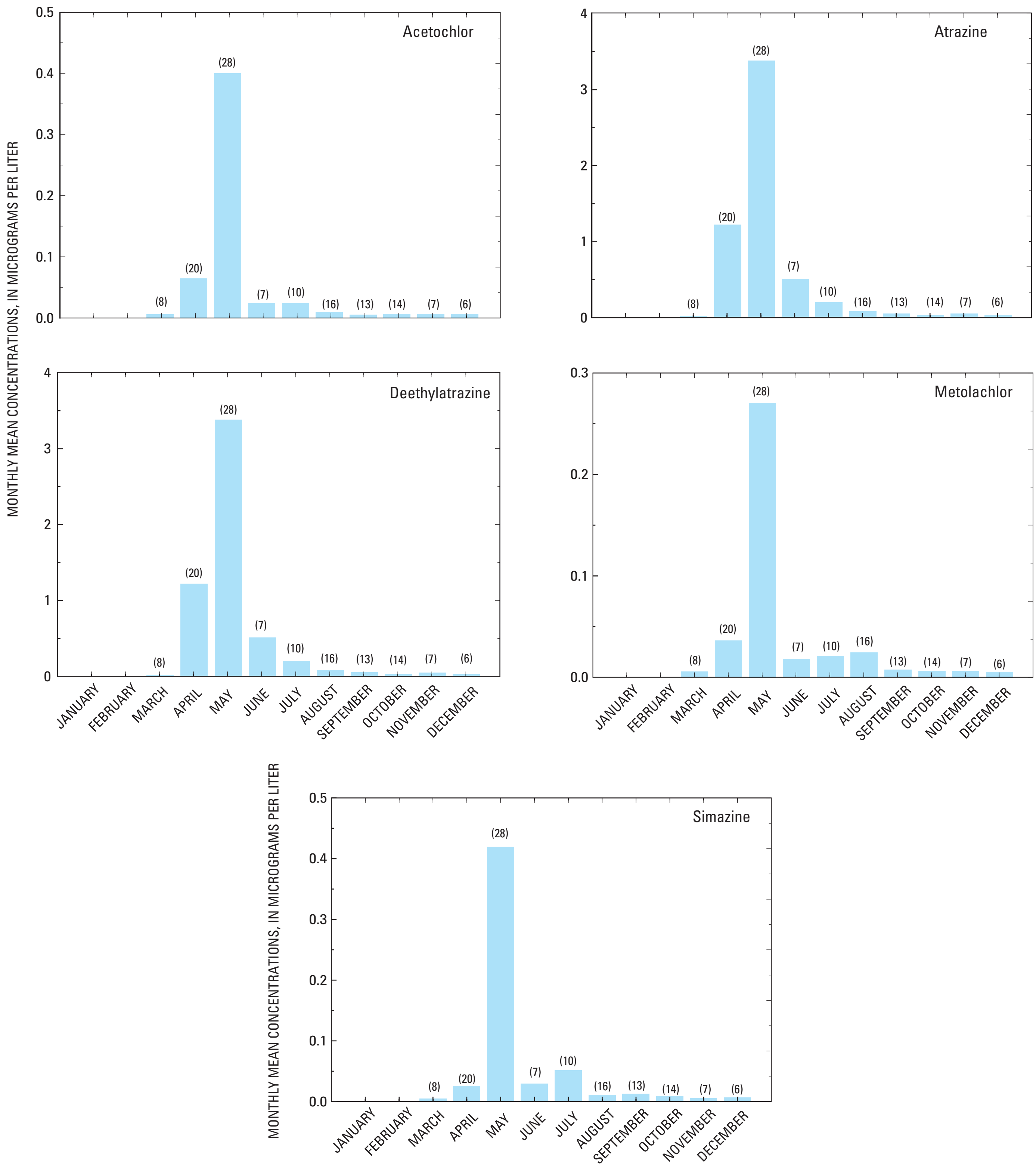

Figure 13. Monthly distribution of select pesticides at seven sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

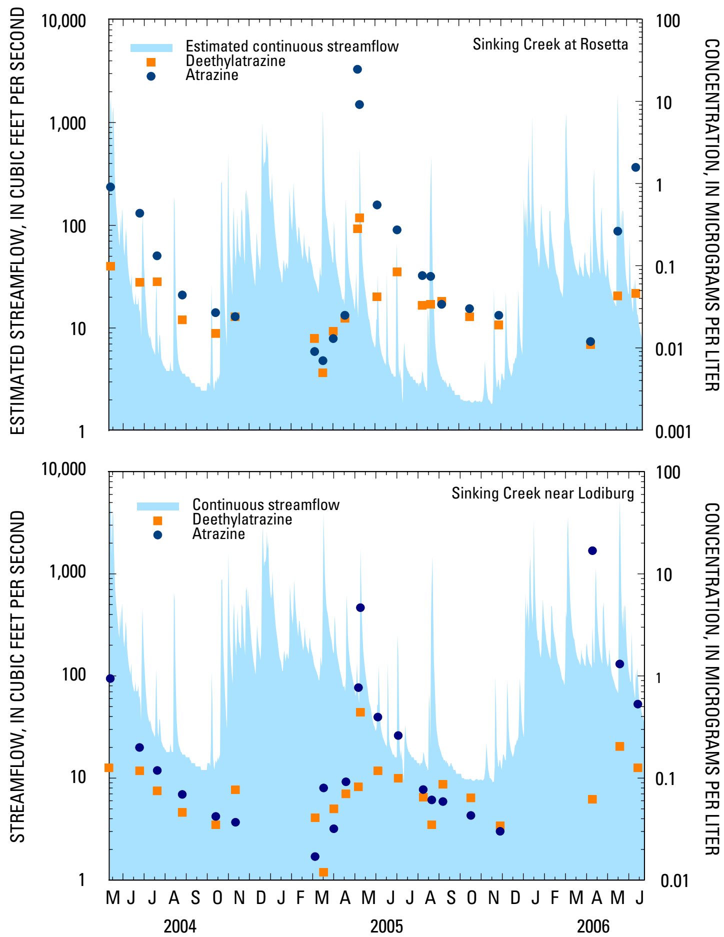

Figure 14. Seasonal variability of atrazine and its transformation product, deethylatrazine, at the Sinking Creek at Rosetta and the Sinking Creek near Lodiburg stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Estimated Loads and Yields of Select 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. Load represents the mass, usually expressed in pounds or tons, of a given constituent moving past a given point per unit time, and yield represents the load for a unit area. Loads and yields were estimated for the four select pesticides and one transformation compound frequently detected in samples for the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station from samples collected in 2004, 2005, and 2006 (table 12). The ratio of the standard error of prediction to the mean load standardizes the model error and provides a comparison among the load estimates at the two stations. In general, the regression model errors for pesticides at the Sinking Creek at Rosetta station were greater than the regression model errors for pesticides at the Sinking Creek near Lodiburg station. Because the daily mean streamflow was estimated at the Sinking Creek at Rosetta station, the error in the estimated nutrient loads at this station is larger than that determined by the S-LOADEST model alone, because it includes considerable and unknown biases and imprecision in the streamflow estimates. Loads were not estimated at the karst window or spring stations, because a streamflow relation between these stations and the Sinking Creek near Lodiburg station could not be established.

Mean annual loads, in pounds per year, for select pesticides were estimated using the S-LOADEST program. Load estimates based on sampling stations with long periods of record are more reliable than estimates from stations with short periods of record. Annual loads vary depending on drainage basin size, discharge conditions, and land uses.

The coefficients of determination (R^2) for the best-fit regression models for loads of the select pesticides are listed in table 13. High R^2 values indicate that the models for the select pesticides reasonably simulated the variability in constituent loads at the two Sinking Creek mainstem stations. Measured instantaneous loads of select pesticides for the two Sinking Creek mainstem stations were plotted against estimated loads for the same day to visually assess the fitness of the model (fig. 15). Points above the 1:1 line indicate that the model underestimated the loads; points below the line indicate the model overestimated the loads. The relation between estimated and measured loads of atrazine at both Sinking Creek mainstem stations suggests that the model overestimated the loads of atrazine at these stations. Relations between estimated and measured loads of deethylatrazine and simazine at the Sinking Creek near Lodiburg station indicate a reasonably tight distribution near the 1:1 line over the range of loads (fig. 15) and suggest that the model had a reasonably good fit; however, the modeled loads of deethylatrazine and simazine at the Sinking Creek at Rosetta station show a much poorer fit of the model. The model for the loads of metolachlor at the Sinking Creek near Lodiburg station indicates a reasonable relation between estimated and measured loads; however, the plot shows the model was not as successful in estimating large loads (fig. 15).

The Sinking Creek near Lodiburg station had the highest mean annual loads of acetochlor (72 lb/yr), atrazine (1,020 lb/yr), metolachlor (35 lb/yr), and simazine (12 lb/yr) from 2004 through spring of 2006 (table 12). The estimated load of atrazine at the Sinking Creek at Rosetta station of 73 lb/yr was about 7 percent of the atrazine load at the Sinking Creek near Lodiburg station of 1,020 lb/yr.

The estimated annual loads of acetochlor, atrazine, metolachlor, and simazine in the karst terrane of the Sinking Creek Basin during the study period were less than 0.01 to 1.2 percent of the amount of assumed applications 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 application practices (Larson and others, 1997).

The Sinking Creek near Lodiburg station had higher yields of the commonly used row-crop herbicides acetochlor, atrazine, deethylatrazine, and metolachlor than the Sinking Creek at Rosetta station. The yield of atrazine upstream from the Sinking Creek at Lodiburg station was 8.2 (lb/yr)/mi^2; acetochlor and metolachlor yields were 0.58 (lb/yr)/mi^2 and 0.28 (lb/yr)/mi^2, respectively (table 12). Simazine, another commonly used row-crop herbicide, had a slightly higher yield at the Sinking Creek at Rosetta station, 0.08 (lb/yr)/mi^2, than at the Lodiburg station, 0.03 (lb/yr)/mi^2.

Table 12. Estimated mean annual load and yield of five select pesticides at two Sinking Creek mainstem stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[**Abbreviations**: lb/yr, pound per year; (lb/yr)/mi^2, pound per year per square mile; DA, drainage area; mi^2, square mile. **Symbol**: <, less than]

Pesticide	Estimated mean annual load (lb/yr)	Standard error of prediction	Prediction of error (percent)	Mean annual yield [(lb/yr)/mi^2]
Sinking Creek at Rosetta, Ky. (DA = 36 mi^2)				
Acetochlor	4.4	4.2	95	0.12
Atrazine	73	110	151	2.0
Deethylatrazine	5.8	1.9	53	0.16
Metolachlor	5.5	7.3	133	0.15
Simazine	2.8	11	393	0.08
Sinking Creek near Lodiburg, Ky. (DA = 125 mi^2)				
Acetochlor	72	137	190	0.58
Atrazine	1,020	370	36	8.2
Deethylatrazine	37	7.6	21	0.29
Metolachlor	35	30	86	0.28
Simazine	12	6.1	51	0.03

Table 13. Regression coefficients and coefficients for determination (R^2) for load models used to estimate the loads of five select pesticides at two stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

[Estimated residual variance is the maximum likelihood estimation variance corrected for the number of observations, number of censored observations, and number of parameters in the regression model. The regression equation is $ln(L)=a + b(lnQ) + c(lnQ^2) + d[\sin(2\pi T)] + e[\cos(2\pi T)] + fT + gT^2$ where L is the constituent load, in pounds per day; Q is stream discharge, in cubic feet per second; T is time in decimal years from the beginning of the calibration period; *a, b, c, d, e, f, g* are regression coefficients; R^2 represents the amount of variance explained by the model. Station locations are shown in figure 1.]

Station name	Number of observations	Regression coefficient *a*	*b*	*c*	*d*	*e*	*f*	*g*	Estimated residual variance	R^2 (percent)
Acetochlor										
Sinking Creek at Rosetta, Ky.	23	-6.46	1.40		0.649	-1.97			1.40	91
Sinking Creek near Lodiburg, Ky.	24	-5.32	1.63		0.646	-2.74			2.63	89
Atrazine										
Sinking Creek at Rosetta, Ky.	23	-3.88	1.01		-0.041	-2.48	-0.022		3.47	73
Sinking Creek near Lodiburg, Ky.	24	-1.81	1.23		.510	-1.36	0.578		1.65	87
Deethylatrazine										
Sinking Creek at Rosetta, Ky.	23	-4.48	1.02		-0.183	-1.06	-0.112		0.736	90
Sinking Creek near Lodiburg, Ky.	24	-2.59	1.04		-.072	-.714	0.149		0.390	94
Metolachlor										
Sinking Creek at Rosetta, Ky.	23	-7.71	1.29		1.00	-3.53	-0.856		1.29	94
Sinking Creek near Lodiburg, Ky.	24	-3.87	1.48		-0.180	-0.874	0.724		1.22	90
Simazine										
Sinking Creek at Rosetta, Ky.	23	-6.20	0.943	0.004	0.416	-1.82	0.798	-0.094	2.78	77
Sinking Creek near Lodiburg, Ky.	24	-5.59	0.901	0.140	0.676	-1.51	0.470	0.741	0.600	94

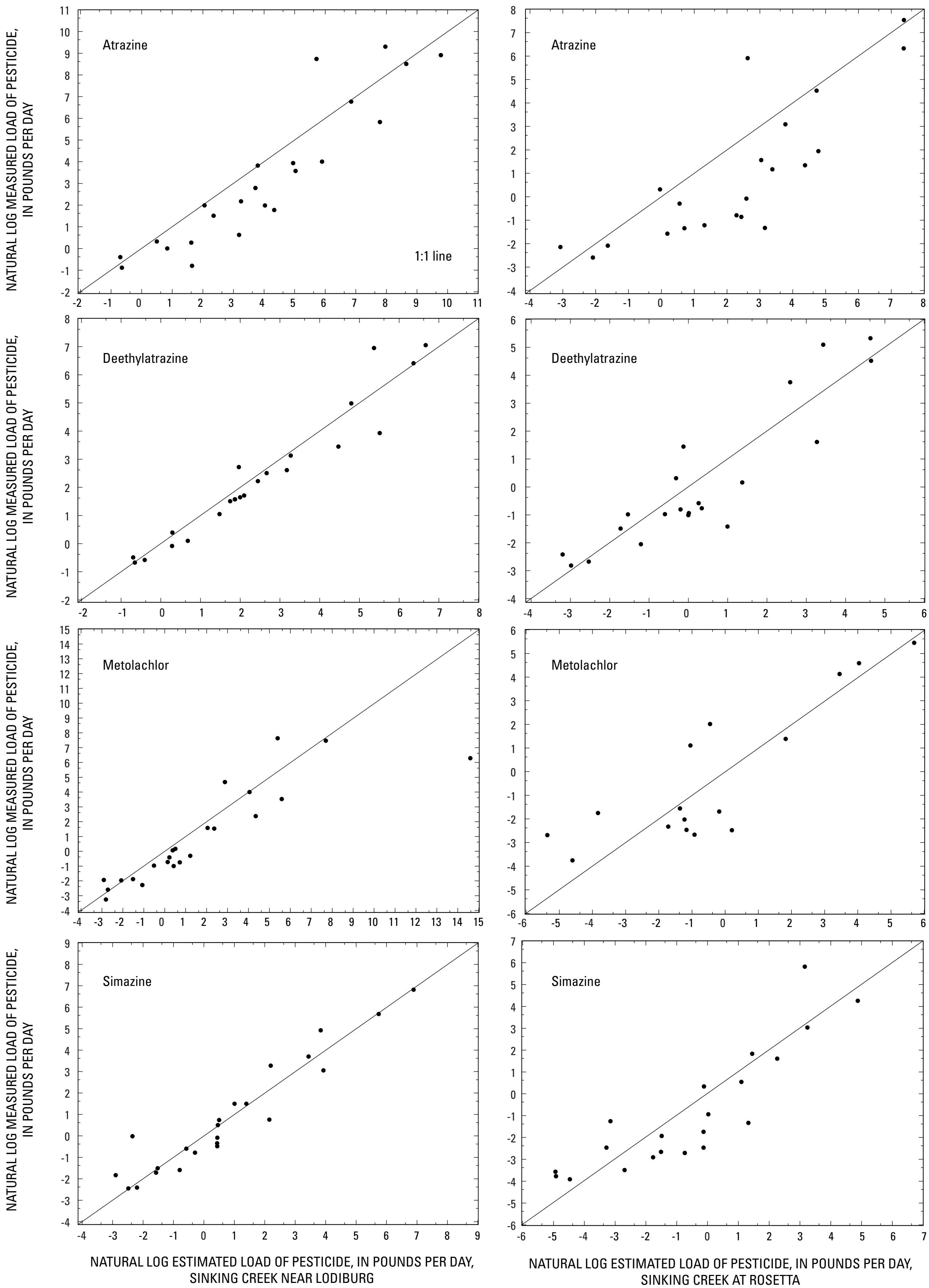

Figure 15. Relation between estimated and measured loads of select pesticides at two Sinking Creek mainstem stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Concentrations and Estimated Loads and Yields of Suspended Sediment

Summary statistics are computed in table 7 for the concentrations of suspended sediment from April 2004 through November 2004, March 2005 through December 2005 at all sampling stations (Sinking Creek at Rosetta; Sinking Creek near Lodiburg; Big Spring; Flat Rock Spring; Boiling Spring; Ross Karst Window; and Fiddle Spring), and April 2006 through June 2006 at all stations except Boiling Spring and Ross Karst Window. Additional high-flow event samples of suspended sediment were collected at the Sinking Creek near Lodiburg station with an automatic sampler. The results of all the samples collected and analyzed are provided in appendix 1. These data provide the basis for analysis of concentrations at the selected sampling stations and the loads and yields at the Sinking Creek near Lodiburg and Sinking Creek at Rosetta stations.

Concentrations of Suspended Sediment

Suspended sediment is all particulate matter suspended in the water column resulting from streambed resuspension, rock weathering, and soil erosion. Although streams transport sediments, anthropogenic impacts such as construction, timber harvesting, and certain agricultural practices can increase sediment transport. High concentrations of suspended sediment can cause habitat destruction and limit light penetration throughout the water column (Osterkamp and others, 1998). In addition, suspended sediment plays a major role in the transport and fate of contaminants and pathogens. Contaminants and pathogens may sorb onto the surface of the suspended sediments and be transported and deposited in other areas downstream (Horowitz, 1991; Rasmussen and Ziegler, 2003).

Spatial Variability of Suspended Sediment

Concentrations of suspended sediment for all hydrologic conditions ranged from 1 mg/L at multiple stations to 1,490 mg/L at the Sinking Creek near Lodiburg station in karst terrane of the Sinking Creek Basin (fig. 16). When storm-event samples collected by the automatic sampler were excluded, the median concentration of suspended sediment for all stations sampled was 15 mg/L. When storm-event samples collected by the automatic sampler were included, the median concentration of suspended sediment was 73 mg/L. The highest concentration of suspended sediment, 1,490 mg/L, was measured at the Sinking Creek near Lodiburg station during an early summer runoff event (fig. 16). The Kruskal-Wallis test (p-value = 0.552) performed on concentrations of suspended sediment indicate no significant differences among the stations.

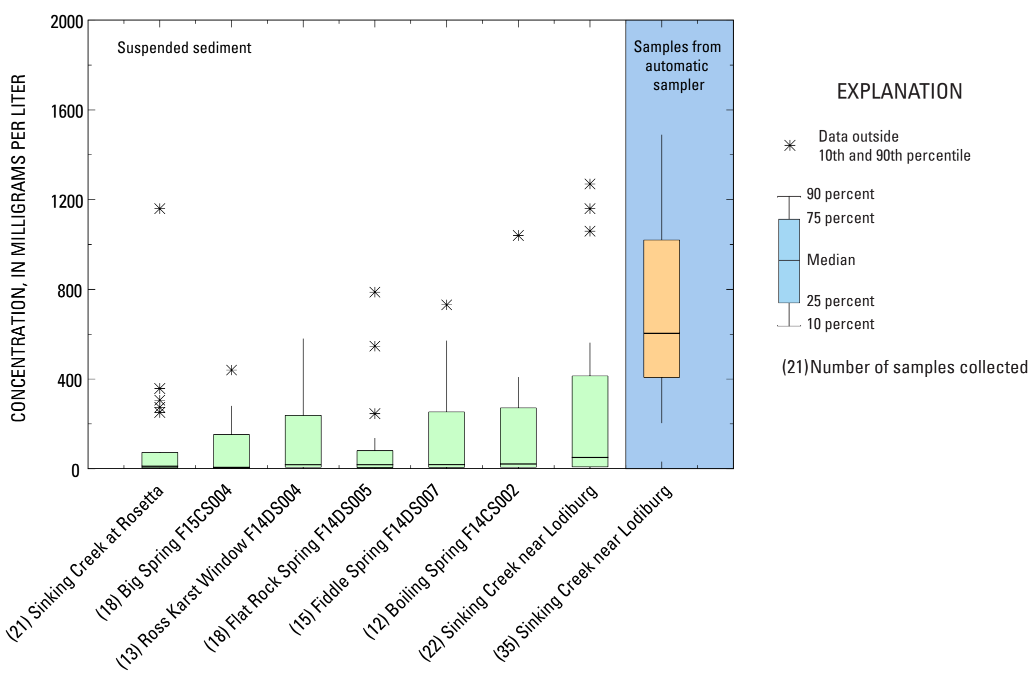

Figure 16. Concentrations of suspended sediment at all sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Hydrologic Variability of Suspended Sediment

Concentrations of suspended sediment were higher in the spring (March through May) and winter (December through February) than in summer (June through August) and autumn (September through November) (fig. 17). Results from the Kruskal-Wallis test (p-value = <0.001) for concentrations of suspended sediment indicate a statistical difference among seasons. The Wilcoxon rank-sum test showed concentrations of suspended sediment were less in autumn compared with the concentrations of suspended sediment in the other seasons. Streamflow is typically lower in autumn than any other time of the year. No statistical differences were found among the concentrations of suspended sediment in spring, summer, and winter. Increases in precipitation in the spring, winter, and during thunderstorms in the summer allow for the runoff of sediment into the streams.

Estimated Loads and Yields of Suspended Sediment

Mean annual loads [(in/lb)/yr] for suspended sediment were estimated using the S-LOADEST program at the two Sinking Creek mainstem sampling stations from samples collected from 2004 through spring 2006 (table 8). Because the daily mean streamflow was estimated at the Sinking Creek at Rosetta station, the error in the estimated nutrient loads at this station is larger than that determined by the S-LOADEST model alone, because it includes considerable and unknown biases and imprecision in the streamflow estimates. Loads were not estimated at the springs or karst window station, because of the absence of continuous streamflow data.

The coefficients of determination (R^2) for the best-fit regression models for loads of suspended sediment are listed in table 9. High R^2 values indicate that the models for suspended sediment reasonably simulated the variability in constituent loads at the two Sinking Creek mainstem stations. Measured instantaneous loads of suspended sediment for the two Sinking Creek mainstem stations were plotted against estimated loads for the same day to visually assess the fitness of the model (fig. 18). Relations between the estimated and measured loads of suspended sediment at the Sinking Creek near Lodiburg station indicate a reasonably tight distribution near the 1:1 line over the range of loads (fig. 18); thus, suggesting that the model had a reasonably good fit. The modeled loads of suspended sediment at the Sinking Creek at Rosetta station indicate overestimations of loads at smaller loads (fig. 18). The estimated mean annual loads of suspended sediment at the Sinking Creek at Rosetta station and the Sinking Creek near Lodiburg station were 10,300,000 and 143,000,000 lb/yr, respectively (table 8). The estimated mean annual load of suspended sediment is about 14 times larger at the Sinking Creek near Lodiburg station than at the Sinking Creek near Rosetta station. The yield of suspended sediment at the Sinking Creek near Lodiburg station is about four times greater than at the Sinking Creek at Rosetta station. The difference indicates a possible increase in yield from a source, such as streambank retreat, and supports the concept that land-cover or land-use changes or both increase streamflows that may result in higher rates of streambank retreat. Other possible sources of sediment include collapse of a swallow hole, or widening of a sinkhole.

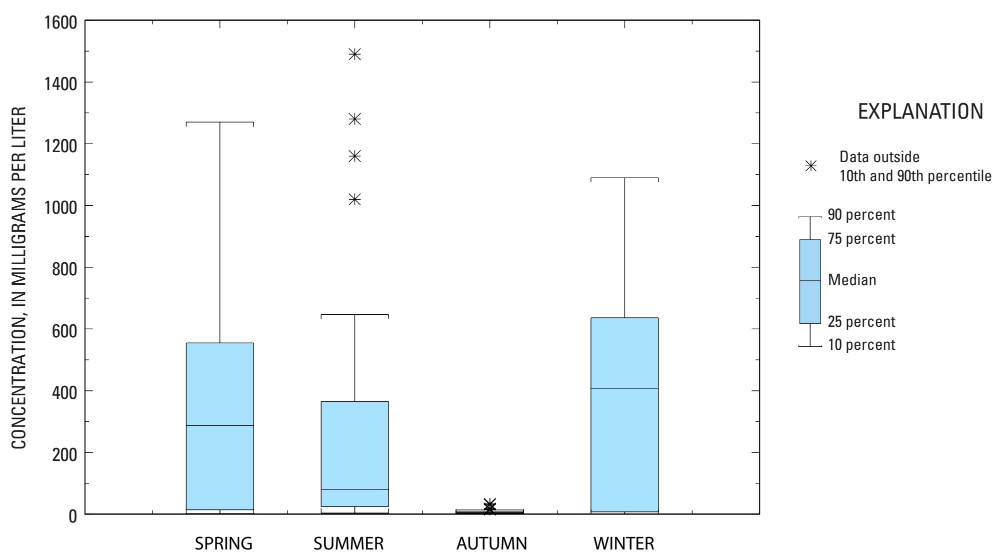

Figure 17. Seasonal distribution of suspended sediment concentrations at seven sampling stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

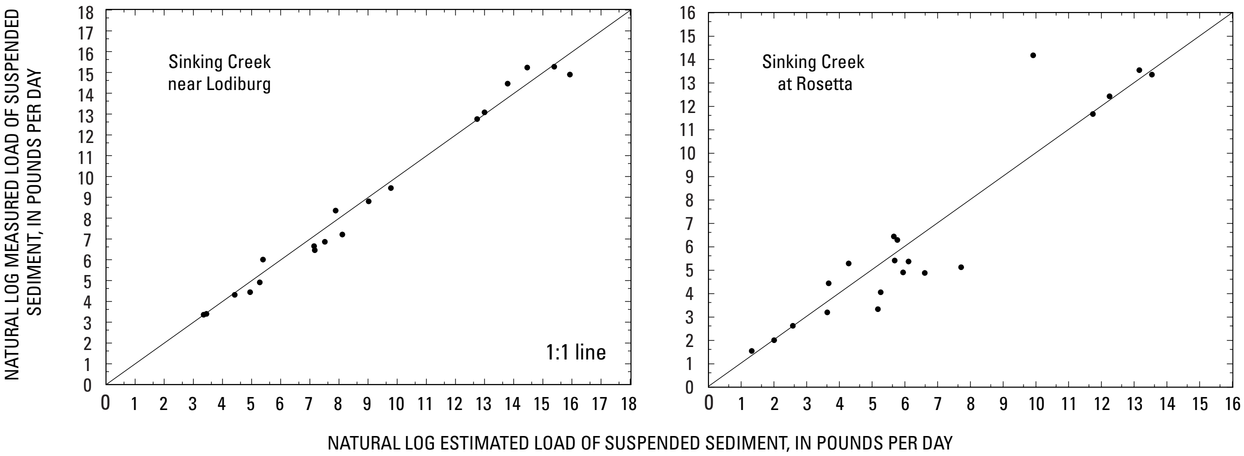

Figure 18. Relation between estimated and measured loads of suspended sediment at two Sinking Creek mainstem stations in the karst terrane of the Sinking Creek Basin, Kentucky, 2004–06.

Summary and Conclusions

A water-quality assessment of springs, karst windows, and streams in the karst terrane of the Sinking Creek Basin, also known as the Boiling Spring Basin, was conducted from April 2004 through November 2004, March 2005 through December 2005, and April 2006 through June 2006, in cooperation with the Kentucky Department of Agriculture. The monitoring network consisted of two stations on the mainstem of Sinking Creek, Sinking Creek at Rosetta, which has a 35-square mile drainage area, and Sinking Creek near Lodiburg, which has a 125-square mile drainage area; four spring stations, Big Spring, Flat Rock Spring, Fiddle Spring, and Boiling Spring; and one karst window station, Ross Karst Window. Water samples were analyzed for nutrients, pesticides, and suspended sediment. Nutrient, select pesticide (5 of the 47 pesticides analyzed), and suspended-sediment data were used to estimate loads and yields from the two mainstem Sinking Creek monitoring stations. A mathematical record-extension technique known as the Maintenance of Variance-Extension, type 1 (MOVE.1) technique was used to estimate streamflow for the partial-record station, Sinking Creek at Rosetta, by use of data from the nearby gaging station Sinking Creek near Lodiburg. Large uncertainty exists in the estimated daily streamflows at the partial-record station, because (1) only instantaneous streamflow measurements were available at the partial-record station; (2) the drainage area at the partial-record station is about 29 percent of the drainage area of the streamgaging station; and (3) the partial-record station is a headwater station indicating streamflow response to precipitation events is usually quicker than at downstream stations. Additional streamflow data were used to support the use of the MOVE.1 technique in extending the streamflow record at the partial-record station. Because the daily mean streamflow was estimated at the Sinking Creek at Rosetta station, the error in the estimated nutrient, select pesticide, and suspended-sediment loads at this station are subject to considerable and unknown biases and imprecision (greater standard error of predictions than reported); thus, the reliability of the results is affected. Additional streamflow and water-quality data are needed to improve the reliability of the load estimates and the errors associated with them at the upstream and downstream stations on Sinking Creek. Loads were not estimated at the karst window or spring stations, because a streamflow relation between these stations and the mainstem stations could not be established.

Concentrations of nitrite plus nitrate ranged from 0.21 to 4.9 milligrams per liter (mg/L) at the seven stations. The highest concentration of nitrite plus nitrate of 4.9 mg/L was observed at the Big Spring station. The lowest concentration of nitrite plus nitrate of 0.21 mg/L was observed at the Sinking Creek at Rosetta station. The median concentration of nitrite plus nitrate for all stations sampled was 1.6 mg/L. Total phosphorus concentrations were greater than 0.1 mg/L, the U.S. Environmental Protection Agency's recommended maximum concentration, in 45 percent of the samples. The median concentration of total phosphorus for all stations sampled was 0.08 mg/L. Concentrations of orthophosphates ranged from <0.006 to 0.46 mg/L. The highest concentration of orthophosphate, 0.46 mg/L, was measured at the Big Spring station.

Concentrations of nutrients were generally larger during spring and summer months, corresponding to periods of increased fertilizer application on agricultural lands. Estimated mean annual yield of nitrite plus nitrate at the downstream monitoring station, Sinking Creek near Lodiburg, were two times larger than yields at the upstream monitoring station, Sinking Creek at Rosetta. The estimated mean annual yields of orthophosphate and total phosphorus at the downstream monitoring station were 1.5 and 3 times larger, respectively, than yields at the upstream monitoring station.

Herbicides were detected more frequently than insecticides at all seven monitoring stations. Eleven of the 14 pesticides detected in water were herbicides. The commonly used herbicides, atrazine, simazine, metolachlor, acetochlor, and prometon were found at all seven monitoring stations. Atrazine was detected in 97 percent of the 129 surface-water samples for pesticides. The atrazine transformation compound, deethylatrazine, was detected in 93 percent of the samples. Prometon was the only nonagricultural herbicide detected. Carbaryl, carbofuran, and malathion were the only insecticides detected.

Most pesticides were present in less than part-per-billion concentrations. Atrazine and simazine, which are row-crop herbicides, had the highest measured concentrations of 24.6 and 2.68 micrograms per liter (μg/L), respectively, and were the most heavily applied herbicides in the basin. Atrazine was the only pesticide compound to exceed the U.S. Environmental Protection Agency standard for drinking water of 3 μg/L. Concentrations of atrazine, deethylatrazine, and simazine at the Fiddle Spring station generally were statistically smaller than those stations draining predominately cultivated agricultural land. Concentrations of pesticides generally were highest in the spring and correspond to the period of heaviest land application.

The estimated annual loads of acetochlor, atrazine, metolachlor, and simazine for the study period were less than 0.01 to 1.2 percent of the amount assumed applied in the basin. Mean annual loads of atrazine of 1,020 pounds per year at the downstream Sinking Creek near Lodiburg station were larger than the 73 pounds per year at the Sinking Creek near Rosetta station.

The concentrations of suspended sediment ranged from 1.0 to 1,490 mg/L at the seven stations. When storm-event samples collected by the automatic sampler were excluded, the median concentration of suspended sediment for the seven stations sampled was 15 mg/L. When storm-event samples collected by the automatic sampler were included, the median concentration of suspended sediment was 73 mg/L. The highest concentration of suspended sediment, 1,490 mg/L, was measured at the Sinking Creek near Lodiburg station during an early summer runoff event. The estimated mean annual yield of suspended sediment at the downstream monitoring station, Sinking Creek near Lodiburg, was about four times greater than the yield at the upstream monitoring station, Sinking Creek at Rosetta. The difference indicates a possible increase in yield from a source, such as streambank retreat, collapse of a swallow hole, or widening of a sinkhole.

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Appendix 1. Station Name, Sample-Collection Date, Nutrient, and Suspended Sediment Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06

[ft^3/s, cubic feet per second; mg-L, milligrams per liter; E, estimated, <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	Ammonia as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Orthophos-phate as P (mg/L)	Total phosphorus (mg/L)	Suspended sediment (mg/L)
Sinking Creek at Rosetta, Ky	03303195	04-22-04	125	<0.04	0.81	0.015	0.066	26
		05-27-04	2,080	<0.04	0.21	0.01	0.250	306
		07-08-04	7.4	<0.04	1.06	E0.003	0.037	73
		08-02-04	7.0	<0.04	1.02	0.008	0.023	4
		09-07-04	17	<0.04	0.7	0.011	0.031	5
		10-25-04	–	<0.04	0.32	<0.006	0.023	3
		11-22-04	–	<0.04	1.21	0.101	0.151	11
		03-16-05	29	<0.04	0.72	<0.006	0.017	2
		03-28-05	1,000	0.05	0.69	0.034	0.220	251
		04-12-05	35	<0.04	0.73	<0.006	E0.003	–
		04-29-05	17	<0.04	0.85	<0.006	0.009	8
		05-17-05	15	E0.03	0.98	0.01	0.049	15
		05-20-05	428	0.08	1.49	0.047	0.260	274
		06-14-05	8.7	E0.03	1.16	<0.006	0.028	–
		07-13-05	14	E0.02	1.53	0.01	0.036	12
		08-18-05	3.9	<0.04	0.85	E0.005	0.020	51
		08-30-05	1,250	0.04	0.57	0.091	0.350	1,160
		09-15-05	6.1	<0.04	0.88	E0.010	0.029	4
		10-25-05	2.5	<0.04	0.54	E0.007	0.022	3
		12-06-05	4.7	<0.04	1.25	E0.003	0.019	1
		04-17-06	22	<0.04	0.56	<0.006	0.011	6
		05-11-06	36	–	–	–	–	6
		05-26-06	2,140	<0.010	0.41	0.038	0.220	358
		06-21-06	14	0.018	0.93	0.025	0.046	9
Sinking Creek near Lodiburg, Ky	03303205	04-22-04	333	<0.04	1.29	0.014	0.096	106
		05-25-04	1,160	<0.04	1.34	0.072	0.420	414
		05-27-04	5,260	<0.04	0.35	0.037	0.400	563
		07-08-04	44	<0.04	2.04	0.042	0.070	67
		07-12-04	–	–	–	–	–	1,490
		07-12-04	–	–	–	–	–	647
		08-02-04	38	<0.04	2.17	0.071	0.101	19
		09-07-04	20	<0.04	1.33	0.054	0.086	8
		10-25-04	16	<0.04	1.14	0.043	0.070	5
		11-22-04	–	<0.04	2.15	0.061	0.094	34
		03-16-05	110	<0.04	1.48	0.017	0.030	8
		03-28-05	4,240	0.11	0.96	0.065	0.540	1,060
		04-12-05	184	<0.04	1.6	0.02	0.042	–
		04-29-05	79	<0.04	1.6	0.019	0.037	14
		05-17-05	59	<0.04	1.62	0.017	0.042	10
		05-19-05	–	–	–	–	–	1,020
		05-20-05	–	0.13	1.84	0.037	0.630	–
		05-20-05	–	–	–	–	–	1,270
		05-20-05	–	0.27	1.79	0.046	0.590	1,070
		05-20-05	–	–	–	–	–	886
		05-20-05	2,360	0.16	1.76	0.093	0.480	811

Appendix 1. Station Name, Sample-Collection Date, Nutrient, and Suspended Sediment Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; mg-L, milligrams per liter; E, estimated, <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	Ammonia as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Orthophos-phate as P (mg/L)	Total phosphorus (mg/L)	Suspended sediment (mg/L)
Sinking Creek near Lodiburg, Ky—Cont.	03303205	05-20-05	–	–	–	–	–	629
		05-20-05	–	–	–	–	–	493
		05-20-05	–	0.09	1.76	0.056	0.420	436
		05-21-05	–	–	–	–	–	364
		05-21-05	–	–	–	–	–	365
		06-14-05	41	<0.04	2.2	0.03	0.068	–
		07-13-05	136	<0.04	1.84	0.091	0.230	93
		08-18-05	17	<0.04	1.67	0.044	0.064	24
		08-30-05	897	0.09	1.39	0.109	0.440	387
		08-30-05	–	–	–	–	–	517
		08-30-05	–	–	–	–	–	1,280
		08-30-05	–	–	–	–	–	1,020
		08-30-05	–	–	–	–	–	580
		08-31-05	–	<0.04	1.03	0.077	0.440	–
		08-31-05	–	–	–	–	–	365
		08-31-05	–	–	–	–	–	293
		09-15-05	17	<0.04	1.87	0.037	0.075	5
		10-25-05	10	<0.04	1.63	0.036	0.073	3
		12-06-05	15	<0.04	1.65	E0.026	0.068	2
		01-11-06	–	–	–	–	–	408
		01-11-06	–	–	–	–	–	203
		01-17-06	–	–	–	–	–	325
		01-17-06	–	–	–	–	–	572
		01-17-06	–	–	–	–	–	877
		01-18-06	–	–	–	–	–	521
		01-23-06	–	–	–	–	–	822
		01-23-06	–	–	–	–	–	1,090
		01-23-06	–	–	–	–	–	1,050
		01-23-06	–	–	–	–	–	636
		01-23-06	–	–	–	–	–	483
		01-23-06	–	–	–	–	–	359
		04-17-06	368	0.11	1.54	0.11	0.260	205
		05-11-06	194	–	–	–	–	294
		05-26-06	–	–	–	–	–	1,160
		05-26-06	–	–	–	–	–	1,140
		05-26-06	–	–	–	–	–	728
		05-26-06	5,660	0.024	0.73	0.074	0.460	761
		05-26-06	–	–	–	–	–	514
		05-26-06	–	–	–	–	–	413
		05-26-06	–	–	–	–	–	331
		06-21-06	97	E0.009	2.26	0.053	0.105	25
Big Spring – F15CS004	374755086090401	04-22-04	46	0.14	2.01	0.052	0.119	62
		05-25-04	–	<0.04	3.09	0.136	0.300	82
		05-27-04	–	<0.04	1.24	0.152	0.340	153
		08-02-04	2.4	<0.04	2.32	0.037	0.052	6
		09-07-04	1.6	<0.04	1.68	0.03	–	2

Appendix 1. Station Name, Sample-Collection Date, Nutrient, and Suspended Sediment Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; mg-L, milligrams per liter; E, estimated, <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	Ammonia as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Orthophos-phate as P (mg/L)	Total phosphorus (mg/L)	Suspended sediment (mg/L)
Big Spring – F15CS004– Cont.	374755086090401	10-25-04	1.1	<0.04	1.87	0.031	0.042	1
		11-22-04	7.5	<0.04	3.95	0.037	0.053	7
		03-28-05	–	0.04	1.25	0.122	0.340	194
		04-29-05	6.8	<0.04	2.3	0.017	0.029	7
		05-20-05	–	0.61	4.95	0.459	0.830	440
		07-13-05	2.5	<0.04	2.87	0.024	0.072	6
		08-30-05	–	E0.03	2.11	0.219	0.360	239
		09-15-05	1.5	<0.04	2.32	0.033	0.053	2
		10-25-05	0.9	<0.04	1.72	0.02	0.038	1
		12-06-05	3.0	<0.04	2.96	0.035	0.062	2
		04-17-06	5.9	<0.04	2.52	0.009	0.028	3
		05-11-06	9.1	<0.04	3.47	0.022	0.040	4
		05-26-06	–	0.057	1.12	0.261	0.450	281
		06-21-06	6	E0.009	3.96	0.079	0.130	18
Flat Rock Spring – F14DS005	374813086171501	04-22-04	50	<0.04	1.61	0.03	0.077	25
		05-25-04	–	<0.04	0.76	0.115	0.300	138
		07-08-04	12	<0.04	2.03	0.043	0.079	28
		08-02-04	8.6	<0.04	1.9	0.092	0.148	20
		09-07-04	4.8	<0.04	1.57	0.066	0.094	5
		10-25-04	3.1	<0.04	1.57	0.045	0.057	3
		11-22-04	23	<0.04	2.54	0.05	0.093	15
		03-28-05	–	0.07	0.84	0.057	0.450	547
		04-29-05	16	<0.04	1.99	0.022	0.040	6
		05-20-05	–	0.11	1.38	0.134	0.610	788
		07-13-05	16	<0.04	2.19	0.181	0.350	81
		08-18-05	3.7	<0.04	2.31	0.043	0.057	25
		08-30-05	–	<0.04	1.73	0.164	0.300	246
		09-15-05	4.5	<0.04	2.35	0.05	0.080	4
		10-25-05	2.1	<0.04	1.97	0.027	0.057	1
		12-06-05	3.5	<0.04	1.89	0.064	0.105	12
		04-17-06	19	<0.04	1.68	0.023	0.037	10
		05-11-06	20	<0.04	2.57	0.028	0.049	5
		06-21-06	21	0.018	1.87	0.091	0.168	38
Ross Karst Window – F14DS003	374846086154101	05-25-04	–	<0.04	0.82	0.092	0.240	106
		05-27-04	–	<0.04	0.42	0.043	0.410	581
		08-02-04	–	<0.04	1.95	0.081	0.140	25
		09-07-04	–	<0.04	1.59	0.06	0.089	6
		10-25-04	–	<0.04	1.47	0.041	0.060	6

Appendix 1. Station Name, Sample-Collection Date, Nutrient, and Suspended Sediment Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; mg-L, milligrams per liter; E, estimated, <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	Ammonia as N (mg/L)	Nitrite plus nitrate as N (mg/L)	Orthophos-phate as P (mg/L)	Total phosphorus (mg/L)	Suspended sediment (mg/L)
Ross Karst Window – F14DS003—Cont.	374846086154101	11-22-04	–	<0.04	2.4	0.045	0.077	14
		03-28-05	–	0.07	0.76	0.054	0.330	489
		04-29-05	–	<0.04	1.96	0.019	0.031	12
		05-20-05	–	0.1	1.54	0.185	0.530	489
		07-13-05	–	<0.04	1.83	0.171	0.320	–
		08-30-05	–	E0.03	1.67	0.214	0.89	238
		09-15-05	–	<0.04	2.45	0.044	0.077	17
		10-25-05	–	<0.04	1.75	0.028	0.055	7
		12-06-05	–	<0.04	2.06	0.06	0.103	5
Fiddle Spring – F14DS007	374847086172901	04-22-04	23	<0.04	1.12	0.025	0.065	11
		05-25-04	–	<0.04	0.4	0.09	0.310	253
		08-02-04	4.4	<0.04	2.08	0.192	0.250	28
		09-07-04	2.7	<0.04	1.44	0.042	0.070	6
		10-25-04	1.4	<0.04	1.13	0.038	0.055	6
		11-22-04	7.4	<0.04	2.08	0.051	0.080	18
		03-28-05	–	0.09	0.91	0.07	0.470	572
		04-29-05	6.6	<0.04	1.69	0.022	0.037	9
		05-20-05	364	0.1	1.32	0.14	0.620	731
		07-13-05	8.7	E0.03	1.64	0.145	0.350	99
		08-30-05	–	E0.02	1.65	0.101	0.210	319
		09-15-05	1.5	<0.04	1.57	0.025	0.057	4
		10-25-05	1.2	<0.04	1.18	0.014	0.036	3
		12-06-05	1.2	<0.04	1.65	0.079	0.141	8
		04-17-06	12.0	<0.04	1.49	0.026	0.047	18
		06-21-06	4.4	0.022	1.88	0.184	0.300	39
Boiling Spring – F14CS002	375209086224001	04-22-04	–	<0.04	1.31	0.019	0.106	135
		05-25-04	–	<0.04	0.83	0.075	0.450	409
		05-27-04	–	<0.04	0.47	0.038	0.310	408
		08-02-04	37	<0.04	2.23	0.078	0.106	11
		09-07-04	3.5	<0.04	1.52	0.057	0.087	7
		10-25-04	16	<0.04	1.26	0.041	0.072	7
		11-22-04	153	<0.04	2.24	0.066	0.139	31
		04-29-05	78	<0.04	1.67	0.022	0.037	8
		05-20-05	–	0.07	1.39	0.093	0.580	1,040
		07-13-05	–	<0.04	1.81	0.086	0.230	81
		10-25-05	10	<0.04	1.67	0.036	0.079	2
		12-06-05	15	<0.04	1.75	0.043	0.075	3

Appendix 2. Station Name, Sample-Collection Date, and Select Pesticide Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; E, estimated; <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	2-Chloro-4-isopropy-lamino-6-amino-s-triazine (DEA) (µg/L)	Acetochlor (µg/L)	Atrazine (µg/L)	Carbaryl (µg/L)	Malathion (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
Sinking Creek at Rosetta, Ky	03303195	04-22-04	125	E0.025	0.027	0.139	<0.041	<0.027	E0.010	0.013
		05-27-04	2,080	E0.099	0.092	0.905	<0.041	<0.027	0.112	0.010
		07-08-04	7.4	E0.063	0.008	0.436	<0.041	<0.027	0.025	0.009
		08-02-04	7.0	E0.064	0.006	0.132	<0.041	<0.027	0.014	<0.010
		09-07-04	17	E0.022	E0.003	0.044	<0.041	<0.027	E0.004	E0.005
		10-25-04	–	E0.015	<0.006	0.027	<0.041	<0.027	<0.006	<0.005
		11-22-04	–	E0.024	<0.010	0.024	<0.041	<0.027	<0.006	<0.005
		03-16-05	29	E0.013	E0.005	0.009	<0.041	<0.027	<0.006	<0.005
		03-28-05	1,000	E0.005	0.007	<0.007	<0.041	<0.027	E0.004	<0.005
		04-12-05	35	E0.016	<0.006	0.013	<0.041	<0.027	<0.006	<0.005
		04-29-05	17	E0.023	E0.004	0.025	<0.041	<0.027	E0.005	<0.005
		05-17-05	15	E0.283	0.031	E24.6	E0.003	<0.027	0.202	0.093
		05-20-05	428	E0.382	0.827	9.12	E0.079	<0.027	0.146	0.789
		06-14-05	8.7	E0.042	0.008	0.550	<0.041	<0.027	0.008	0.045
		07-13-05	14	E0.084	0.017	0.273	<0.041	<0.027	0.006	0.123
		08-18-05	3.9	E0.033	<0.006	0.076	<0.041	<0.027	<0.006	0.014
		08-30-05	1,250	E0.034	0.011	0.074	<0.041	<0.027	<0.006	<0.005
		09-15-05	6.1	E0.037	<0.006	0.034	<0.041	<0.027	<0.006	<0.005
		10-25-05	2.5	E0.024	<0.006	0.030	<0.041	<0.027	<0.006	0.008
		12-06-05	4.7	E0.019	<0.006	0.025	<0.041	<0.027	<0.006	0.006
		04-17-06	22	E0.011	<0.006	0.012	<0.041	<0.027	<0.006	0.012
		05-11-06	36	–	–	–	–	–	–	–
		05-26-06	2,140	E0.043	0.022	0.263	E.025	<0.027	0.046	0.033
		06-21-06	14	E0.046	<0.006	1.57	<.041	<0.027	E0.005	0.053
Sinking Creek near Lodiburg, Ky	03303205	04-22-04	333	E0.047	0.010	0.409	<.041	<0.027	E0.008	0.017
		05-25-04	1,160	E0.126	0.227	0.753	<.041	<0.027	0.047	0.035
		05-27-04	5,260	E0.116	0.091	0.942	<.041	<0.027	0.102	0.056
		07-08-04	44	E0.118	E0.006	0.200	<.041	<0.027	E0.011	0.014
		07-12-04	–	–	–	–	–	–	–	–
		07-12-04	–	–	–	–	–	–	–	–
		08-02-04	38	E0.075	0.008	0.119	<.041	<0.027	E0.010	0.012
		09-07-04	20	E0.046	E0.004	0.069	<.041	<0.027	E0.007	0.009
		10-25-04	16	E0.035	<0.006	0.042	<.041	<0.027	0.009	<0.010
		11-22-04	–	E0.077	<0.006	0.037	<.041	<0.027	0.006	<0.005
		03-16-05	110	E0.041	<0.006	0.017	<.041	<0.027	<0.006	<0.005
		03-28-05	4,240	E0.012	E0.006	0.080	<.041	<0.027	0.008	<0.005
		04-12-05	184	E0.050	<0.006	0.032	<.041	<0.027	E0.004	<0.005
		04-29-05	79	E0.070	0.010	0.092	<.041	<0.027	0.006	0.009
		05-17-05	59	E0.082	0.048	0.772	<.041	<0.027	0.018	0.028
		05-19-05	–	–	–	–	–	–	–	–
		05-20-05	–	E0.372	0.755	3.77	E0.059	<0.027	0.393	0.037
		05-20-05	–	–	–	–	–	–	–	–
		05-20-05	–	E0.442	1.07	4.65	E0.052	<0.027	.875	0.058

Appendix 2. Station Name, Sample-Collection Date, and Select Pesticide Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; E, estimated; <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	2-Chloro-4-isopropylamino-6-amino-s-triazine (DEA) (µg/L)	Acetochlor (µg/L)	Atrazine (µg/L)	Carbaryl (µg/L)	Malathion (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
Sinking Creek near Lodiburg, Ky—Cont.	03303205	05-20-05	–	–	–	–	–	–	–	–
		05-20-05	2,360	E0.324	.807	4.24	E.041	E.008	.466	.051
		05-20-05	–	–	–	–	–	–	–	–
		05-20-05	–	–	–	–	–	–	–	–
		05-20-05	–	E0.342	0.543	30.84	E0.043	<0.027	0.388	0.509
		05-21-05	–	–	–	–	–	–	–	–
		05-21-05	–	–	–	–	–	–	–	–
		06-14-05	41	E0.118	<0.007	0.397	<0.041	<0.027	0.009	0.051
		07-13-05	136	E0.100	0.071	0.262	E0.036	<0.027	0.034	0.033
		08-18-05	17	E0.065	<0.006	0.077	<0.041	<0.027	<0.006	0.012
		08-30-05	897	E0.035	0.017	0.061	<0.041	<0.027	0.012	<0.005
		08-30-05	–	–	–	–	–	–	–	–
		08-30-05	–	–	–	–	–	–	–	–
		08-30-05	–	–	–	–	–	–	–	–
		08-30-05	–	–	–	–	–	–	–	–
		08-31-05	–	–	–	–	–	–	–	–
		08-31-05	–	–	–	–	–	–	–	–
		08-31-05	–	–	–	–	–	–	–	–
		09-15-05	17	E0.087	<0.006	0.059	<0.041	<0.027	0.009	0.013
		10-25-05	10	E0.064	<0.006	0.043	<0.041	<0.027	E0.004	0.009
		12-06-05	15	E0.034	<0.006	0.030	<0.041	<0.027	E0.005	0.006
		01-11-06	–	–	–	–	–	–	–	–
		01-11-06	–	–	–	–	–	–	–	–
		01-17-06	–	–	–	–	–	–	–	–
		01-17-06	–	–	–	–	–	–	–	–
		01-17-06	–	–	–	–	–	–	–	–
		01-18-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		01-23-06	–	–	–	–	–	–	–	–
		04-17-06	368	E0.062	1.13	16.9	<0.041	<0.027	0.292	0.072
		05-11-06	194	–	–	–	–	–	–	–
		05-26-06	–	–	–	–	–	–	–	–
		05-26-06	–	–	–	–	–	–	–	–
		05-26-06	–	–	–	–	–	–	–	–
		05-26-06	5,660	E0.204	0.330	1.31	E0.039	<0.027	0.311	0.161
		05-26-06	–	–	–	–	–	–	–	–
		05-26-06	–	–	–	–	–	–	–	–
		05-26-06	–	–	–	–	–	–	–	–
		06-21-06	97	E0.126	0.043	0.528	<0.041	<0.027	0.05	0.022

Appendix 2. Station Name, Sample-Collection Date, and Select Pesticide Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; E, estimated; <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	2-Chloro-4-isopropy-lamino-6-amino-s-triazine (DEA) (µg/L)	Acetochlor (µg/L)	Atrazine (µg/L)	Carbaryl (µg/L)	Malathion (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
Big Spring – F15CS004	374755086090401	04-22-04	46	E0.172	<0.010	4.92	<0.041	<0.027	0.309	0.152
		05-25-04	–	E0.300	0.014	2.08	<0.041	<0.027	0.447	0.043
		05-27-04	–	E0.330	0.009	2.99	<0.041	<0.027	0.736	0.548
		08-02-04	2.4	E0.133	0.018	0.097	<0.041	<0.027	0.017	0.018
		09-07-04	1.6	E0.093	0.007	0.065	<0.041	<0.027	E0.006	0.010
		10-25-04	1.1	E0.042	0.010	0.034	<0.041	<0.027	<0.006	0.010
		11-22-04	7.5	E0.289	<0.006	0.118	<0.041	<0.027	<0.006	<0.010
		03-28-05	–	E0.038	<0.006	0.030	<0.041	<0.027	E0.003	<0.005
		04-29-05	6.8	E0.121	E0.006	0.212	<0.041	<0.027	0.017	0.100
		05-20-05	–	E1.11	2.85	11.5	<0.041	<0.027	1.55	2.68
		07-13-05	2.5	E0.135	0.044	0.106	<0.041	<0.027	0.035	0.031
		08-30-05	–	E0.082	<0.020	0.090	<0.041	<0.027	0.193	0.013
		09-15-05	1.5	E0.142	E0.003	0.058	<0.041	<0.027	<0.006	0.029
		10-25-05	0.9	E0.058	<0.006	0.027	<0.041	<0.027	<0.006	0.011
		12-06-05	3.0	E0.143	0.008	0.053	<0.041	<0.027	E0.004	0.009
		04-17-06	5.9	E0.096	<0.006	0.035	<0.041	<0.027	<0.006	0.006
		05-11-06	9.1	E0.289	0.030	1.02	<0.041	<0.027	0.026	0.100
		05-26-06	–	E0.250	0.520	1.05	E0.021	<0.027	0.272	0.141
		06-21-06	5.7	E0.293	0.056	0.352	<0.041	<0.027	0.037	0.022
Flat Rock Spring – F14DS005	374813086171501	04-22-04	50	E0.062	0.011	0.588	<0.041	<0.027	E0.009	0.027
		05-25-04	–	E0.342	0.033	2.91	E0.009	<0.027	0.058	2.28
		07-08-04	12	E0.138	E0.004	0.195	<0.041	<0.027	E0.010	0.020
		08-02-04	9	E0.066	0.007	0.103	<0.041	0.181	E0.007	0.014
		09-07-04	4.8	E0.075	<0.006	0.063	<0.041	<0.027	<0.013	0.019
		10-25-04	3.1	E0.044	<0.006	0.046	<0.041	<0.027	<0.006	<0.010
		11-22-04	23	E0.106	<0.006	0.059	<0.041	<0.027	<0.006	<0.005
		03-28-05	–	E0.009	<0.006	0.010	<0.041	<0.027	<0.006	<0.005
		04-29-05	16	E0.072	E0.005	0.069	<0.041	<0.027	E0.002	0.020
		05-20-05	–	E0.244	0.577	2.67	E0.031	<0.027	0.068	0.665
		07-13-05	16	E0.042	<0.006	0.121	<0.041	<0.027	0.021	0.128
		08-18-05	3.7	E0.074	<0.006	0.050	<0.041	<0.027	<0.006	0.015
		08-30-05	–	E0.043	<0.006	0.052	<0.041	<0.027	0.038	0.014
		09-15-05	4.5	E0.107	<0.006	0.056	<0.041	<0.027	<0.008	0.029
		10-25-05	2.1	E0.060	<0.006	0.032	<0.041	<0.027	<0.006	0.012
		12-06-05	3.5	E0.048	<0.006	0.029	<0.041	<0.027	<0.006	0.008
		04-17-06	19	E0.052	<0.006	0.024	<0.041	<0.027	<0.006	E0.004
		05-11-06	20	E0.143	0.027	0.858	<0.041	<0.027	0.017	0.041
		06-21-06	21	E0.114	0.046	0.138	E0.011	<0.027	0.014	0.011

Appendix 2. Station Name, Sample-Collection Date, and Select Pesticide Results for Samples Collected in the Karst Terrane of the Sinking Creek Basin, Kentucky, 2004–06—Continued

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; E, estimated; <, less than; –, no data]

USGS station name	USGS station No.	Sample-collection date	Discharge (ft^3/s)	2-Chloro-4-isopropy-lamino-6-amino-s-triazine (DEA) (µg/L)	Acetochlor (µg/L)	Atrazine (µg/L)	Carbaryl (µg/L)	Malathion (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
Ross Karst Window – F14DS003	374846086154101	05-25-04	–	E0.252	0.080	2.10	E0.018	<0.027	0.048	1.31
		05-27-04	–	E0.133	0.016	1.45	<0.041	<0.027	0.345	0.507
		08-02-04	–	E0.083	0.008	0.109	<0.041	0.211	E0.009	0.019
		09-07-04	–	E0.070	E0.003	0.080	<0.041	<0.027	E0.005	0.012
		10-25-04	–	E0.042	<0.006	0.041	<0.041	<0.027	<0.010	0.015
		11-22-04	–	E0.107	<0.006	0.057	<0.041	<0.027	<0.006	<0.005
		03-28-05	–	E0.008	<0.006	0.011	<0.041	<0.027	<0.006	<0.005
		04-29-05	–	E0.072	E0.005	0.069	<0.041	<0.027	E0.002	0.016
		05-20-05	–	E0.198	0.806	2.18	E0.039	<0.027	0.288	0.448
		07-13-05	–	E0.048	0.007	0.111	<0.041	<0.027	0.032	0.127
		08-30-05	–	E0.033	<0.006	0.030	<0.041	<0.027	0.021	0.008
		09-15-05	–	E0.094	<0.006	0.052	<0.041	<0.027	0.006	0.021
		10-25-05	–	E0.058	<0.006	0.034	<0.041	<0.027	<0.006	0.011
		12-06-05	–	E0.062	<0.006	0.037	<0.041	<0.027	0.006	0.008
Fiddle Spring – F14DS007	374847086172901	04-22-04	23	E0.031	<0.008	0.345	<0.041	<0.027	<0.013	0.013
		05-25-04	–	E0.141	0.091	0.850	E0.012	<0.027	0.036	0.481
		08-02-04	4.4	E0.026	0.011	0.075	E0.018	<0.027	<0.013	<0.005
		09-07-04	2.7	E0.020	<0.006	0.047	<0.041	<0.027	<0.013	<0.005
		10-25-04	1.4	E0.006	<0.006	0.013	<0.041	<0.027	<0.006	<0.005
		11-22-04	7.4	E0.019	<0.006	0.026	<0.041	<0.027	<0.006	<0.005
		03-28-05	–	<0.010	<0.006	<0.010	<0.041	<0.027	<0.006	<0.005
		04-29-05	6.6	E0.014	<0.006	0.009	<0.041	<0.027	<0.006	<0.005
		05-20-05	364	E0.375	0.438	2.04	E0.093	<0.027	0.065	0.488
		07-13-05	8.7	E0.010	<0.006	0.026	E0.022	<0.027	E0.003	<0.005
		08-30-05	–	E0.024	<0.006	0.028	<0.041	<0.027	0.025	<0.008
		09-15-05	1.5	E0.015	<0.006	0.012	<0.041	<0.027	<0.006	<0.005
		10-25-05	1.2	E0.009	<0.006	E0.006	<0.041	<0.027	<0.006	<0.005
		12-06-05	1.2	E0.006	<0.006	0.01	<0.041	<0.027	<0.006	<0.005
		04-17-06	12	E0.008	<0.006	E0.005	<0.041	<0.027	<0.006	<0.005
		06-21-06	4.4	E0.018	<0.006	0.034	<0.041	<0.027	E0.005	<0.005
Boiling Spring – F14CS002	375209086224001	04-22-04	–	E0.047	0.010	0.424	<0.041	<0.027	E0.008	0.018
		05-25-04	–	E0.104	0.137	0.658	<0.041	<0.027	0.042	0.039
		05-27-04	–	E0.109	0.082	0.866	<0.041	<0.027	0.106	0.050
		08-02-04	37	E0.075	0.007	0.129	<0.041	<0.027	E0.011	0.013
		09-07-04	3.5	E0.046	E0.004	0.073	<0.041	<0.027	E0.007	0.010
		10-25-04	16	E0.035	<0.010	0.04	<0.041	<0.027	0.011	<0.010
		11-22-04	153	E0.074	<0.006	0.042	<0.041	<0.027	0.008	<0.005
		04-29-05	78	E0.063	0.014	0.105	<0.041	<0.027	0.007	0.010
		05-20-05	–	E0.398	0.652	40.35	E0.021	<0.027	0.365	0.076
		07-13-05	–	E0.073	0.076	0.269	E0.045	<0.027	0.033	0.030
		10-25-05	10	E0.042	<0.006	0.031	<0.041	<0.027	E0.003	<0.007
		12-06-05	15	–	–	–	–	–	–	–

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For more information concerning the research in this report, contact the
Director, Kentucky Water Science Center
U.S. Geological Survey
9818 Bluegrass Parkway
Louisville, Kentucky 40299-1906
http://ky.water.usgs.gov

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