WATER-QUALITY ASSESSMENT OF THE OZARK PLATEAUS STUDY UNIT, ARKANSAS, KANSAS, MISSOURI, AND OKLAHOMA--ORGANIC COMPOUNDS IN SURFACE WATER, BED SEDIMENT, AND BIOLOGICAL TISSUE, 1992-95

by Richard W. Bell, Jerri V. Davis, Suzanne R. Femmer, and Robert L. Joseph

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BRUCE BABBITT, ***Secretary***

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, ***Director***

For additional information write to:

District Chief
U.S. Geological Survey, WRD
401 Hardin Road
Little Rock, Arkansas 72211

Copies of this report can be purchased from:

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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ABSTRACT

Organic-compound samples, including pesticides and semi-volatiles, were collected from 1992-95 at 43 surface-water and 27 bed-sediment and biological-tissue sampling sites within the Ozark Plateaus National Water-Quality Assessment Program study unit. Most surface-water, bed-sediment, and biological-tissue sites have drainage basins predominantly in the Springfield and Salem Plateaus. At most surface-water sampling sites, one to three pesticide samples were collected in the spring and early summer of 1994 and 1995; two sites had additional samples collected either weekly, biweekly, or monthly from February 1994 through December 1994. At most bed-sediment and biological-tissue sampling sites, a single organic-compounds sample was collected.

Agricultural pesticide use was approximately 4.9 million pounds of active ingredients per year from 1987-91 in the study unit and was generally greatest in the Springfield and Salem Plateaus pasturelands and in the Osage Plains and Mississippi Alluvial Plain cropland areas. The most frequently applied pesticide in the study unit was 2,4-D. Atrazine was the second most frequently applied pesticide. Corn, pasture, rice, sorghum, and soybeans received approximately 85 percent of the pesticides applied within the study unit. The highest pesticide application rate occurred on these crops in the Mississippi Alluvial and Osage Plains. Pastureland was the crop type that received the greatest amount of pesticides in 53 of the 96 counties in the study unit.

The most commonly detected herbicide (63 samples) in surface water was atrazine. Five other pesticides--desethylatrazine, tebuthiuron, prometon, metolachlor, and simazine--were detected in 15 or more samples. The most commonly detected insecticide (13 samples) was *p,p'*-DDE. Two other insecticides, diazinon and *cis*-permethrin, were detected in seven or more samples. Pesticides were detected at 39 surface-water sites; samples collected at Yocum Creek near Oak Grove, Ark. had the most pesticide detections (13). Seventeen other sites had samples with six or more pesticide detections.

Analysis of pesticide data collected at surface-water sites indicates that the largest variety of different pesticides detected (18) was in small, agricultural drainage basins; the largest percentage of detections of a single pesticide (about 80) was in medium, agricultural basins. Pesticide concentrations were small, and in most cases, at or near the detection limit. Maximum concentrations ranged from 0.001 to 0.007 micrograms per liter (µg/L) at small, forest sites; 0.001 to 0.029 µg/L at medium, forest sites; 0.001 to 0.079 µg/L at small, agricultural sites; and 0.003 to 0.29 µg/L at medium, agricultural sites. Pesticides were detected significantly more often in medium, agricultural basins in the Springfield Plateau.

The most commonly detected (13 samples) organic compound in bed sediment, in concentrations noticeably above background levels, was 2,6-dimethylnaphthalene; the maximum concentration of 2,6-dimethylnaphthalene was 130 micrograms per kilogram. Seventeen or more

compounds were detected in bed-sediment samples collected at three sites.

Four compounds were detected in biological-tissue samples: *p,p'*-DDT in *Corbicula fluminea* (Asiatic clam) tissue collected at the Osage River near St. Thomas, Mo. and *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor in *C. fluminea* tissue collected at the James River near Boaz, Mo.

Organic compounds collected at surface-water, bed-sediment, or biological-tissue sampling sites were not detected in concentrations that exceeded any health criteria or standards. Based on this information, organic compounds do not pose any widespread or persistent problems in the study unit.

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water-Quality Assessment (NAWQA) Program to provide a nationally consistent description of water-quality conditions for a large part of the Nation's water resources. The long-term goals of the NAWQA Program are to describe the status and trends in the quality of the Nation's surface- and ground-water resources and to provide a better understanding of the natural and human factors that affect the quality of these resources. Investigations will be conducted on a rotational basis in 60 river basins or aquifer systems (referred to as study units) throughout the Nation.

The Ozark Plateaus NAWQA study unit was among the first 20 study units selected in 1991 for assessment under the full implementation plan. The study unit investigation consists of 5 years (1991-95) of intensive assessment, followed by 5 years (1996-2000) of low-level monitoring, and then the cycle will be repeated. Each 5-year assessment period will include about 2 years of retrospective analysis and planning and 3 years of intensive data collection.

The purpose of this report is to summarize organic-compound information for the study unit. In this report, organic compounds refer both to pesticide and semi-volatile compounds. The information summarized includes: pesticide-use data, description of the sampling network, and an assessment of recent (1992-95) conditions. This information will be used as a guide for future data-collection activities. Also, information provided in this report will contribute to national synthesis activities that will compare and contrast water quality in similar and different environments throughout the Nation.

This report includes (1) a brief overview of the environmental setting of the study unit; (2) a summary of pesticide-use data for 1987-91; (3) a description of the surface-water, bed-sediment, and biological-tissue sampling networks; and (4) an assessment of conditions using statistical summaries of organic-compound data collected during water years (October 1 through September 30) 1992-95.

DESCRIPTION OF THE OZARK PLATEAUS STUDY UNIT

This section of the report provides a brief description of the environmental setting of the Ozark Plateaus study unit. For more detail, the reader is referred to the environmental setting report for the study unit (Adamski and others, 1995).

The Ozark Plateaus study unit area encompasses approximately 48,000 square miles (mi^2) and includes parts of northern Arkansas, southeastern Kansas, southern Missouri, and northeastern Oklahoma (fig. 1). The study unit includes most of the Ozark Plateaus Province as well as part of the surrounding Central Lowland Province known as the Osage Plains section, and a small portion of the Mississippi Alluvial Plain section of the Coastal Plain Province (Fenneman, 1938).

The Ozark Plateaus Province consists of a structural dome of sedimentary and igneous rocks. Sedimentary rocks gently dip away from the igneous core of the St. Francois Mountains in southeastern Missouri to form three distinct physiographic sections (Fenneman, 1938)--the Salem Plateau (includes the St. Francois Mountains), the Springfield Plateau, and the Boston Mountains (fig. 1). Topography varies from mostly gently rolling hills in the Springfield Plateau, to rugged with relief up to 500 feet (ft) in the Salem Plateau, to extremely rugged with relief as much as 1,000 ft in the Boston Mountains. The Osage Plains of the Central Lowland Province in the west-northwestern part of the study unit has gently rolling topography with relief rarely exceeding 250 ft. The Mississippi Alluvial Plain of the Coastal Plain Province along the extreme southeastern boundary of the study unit has flat to gently rolling topography with little relief.

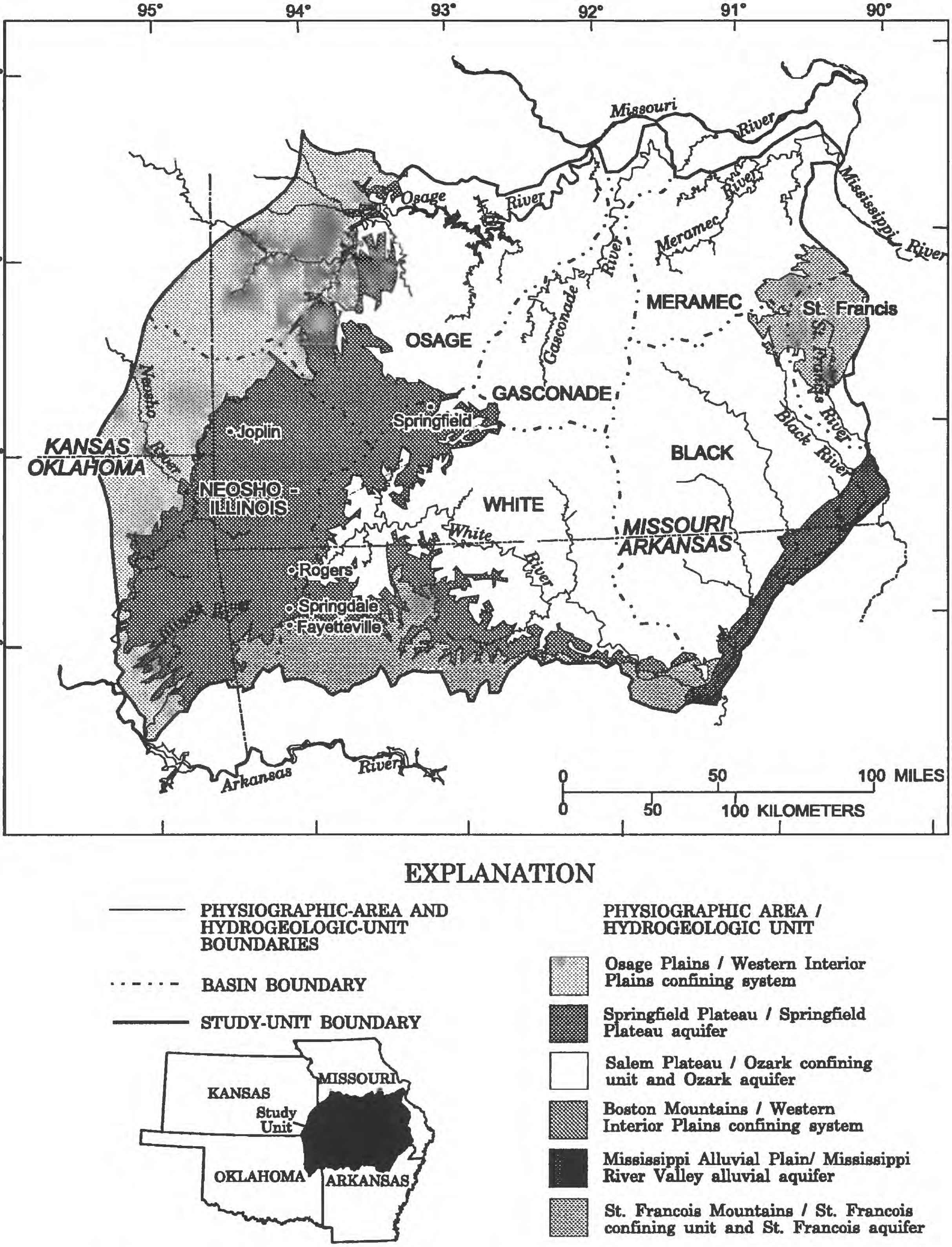


Figure 1. Location of Ozark Plateaus study unit, major river basins, physiographic areas, and surface extent of hydrogeologic units (from Imes and Emmett, 1994).

The St. Francois Mountains area is not a separate physiographic section as defined by Fenneman (1938), but will be discussed in this report separately because of its unique hydrogeologic features. For the purposes of this report, the physiographic sections described above and the St. Francois Mountains will hereinafter be referred to as physiographic areas.

Hydrology

The Ozark Plateaus study unit is divided into seven hydrogeologic units consisting of three major aquifers and four confining units (Imes and Emmett, 1994) (fig. 1). These units, from youngest to oldest, are: the Western Interior Plains confining system, the Springfield Plateau aquifer, the Ozark confining unit, the Ozark aquifer, the St. Francois confining unit, the St. Francois aquifer, and the Basement confining unit. The unconsolidated sediments of the Mississippi River Valley alluvial aquifer form an eighth aquifer, of limited areal extent within the study unit.

The Ozark Plateaus study unit is drained by seven major rivers--the White, Neosho-Illinois, Osage, Gasconade, Meramec, Black, and St. Francis Rivers (fig. 1)--which flow directly or indirectly into the Mississippi River. Many large reservoirs have been constructed on the White, Osage, and Neosho Rivers.

Stream gradients are steepest in the Boston and St. Francois Mountains and flattest in the Osage Plains and Mississippi Alluvial Plain. Channel-bed material ranges from clay and silt in the Osage Plains to sand, gravel, boulders, and bedrock in most of the Ozark Plateaus Province. Streams in the Osage Plains are turbid, with long pools separated by poorly defined riffles. Streams in the Ozark Plateaus Province are mostly clear, with pools separated by riffles, and in places, cascading waterfalls.

Mean annual runoff generally increases from the north to the south (Gebert and others, 1985). Mean annual runoff is least in the northern Osage Plains, ranging from 9 to 10 inches (in.); increases in the Springfield and Salem Plateaus, ranging from 10 to 16 in.; and is greatest in the Boston Mountains, ranging from 14 to 20 in.

Minimum monthly streamflows generally occur in the summer and early fall and maximum monthly streamflows typically occur in the late winter and spring. Maximum monthly streamflows generally coincide with the period of maximum precipitation and minimum evapotranspiration.

Climate, Population, Land Use, and Water Use

The Ozark Plateaus study unit has a temperate climate with average annual precipitation ranging from about 38 inches per year (in/yr) in the north to about 48 in/yr near the southern edge of the study unit (Dugan and Peckenpaugh, 1985). Average monthly precipitation is greatest in the spring, about 3 to 5 inches per month (in/mo), and least in the late fall and winter, about 1 to 3 in/mo. Precipitation was above average for water years 1993-95; the average annual precipitation was exceeded by 16.5 in., 1.3 in., and 7.6 in. for water years 1993-95, respectively. Mean annual air temperature ranges from about 56 degrees Fahrenheit (°F) in the northeastern part of the study unit to about 60°F in the southwestern part of the study unit (Dugan and Peckenpaugh, 1985). Estimated mean annual evapotranspiration in the study unit is 30 to 35 in. (Hanson, 1991).

Population within the study unit in 1990 was approximately 2.3 million people (U.S. Department of Commerce, Bureau of Census, 1990). Population increased by about 28 percent between 1970 and 1990 with the largest increases occurring in northwestern Arkansas and southwestern Missouri. Springfield, Mo., with a population of about 140,000 residents (1990), is the largest city in the study unit. Joplin, Mo., and Fayetteville, Rogers, and Springdale, Ark., are the only other cities within the study unit with populations exceeding 20,000 (1990).

Land use in the study unit (table 1) is predominantly forest and agriculture (includes pasture and cropland) (U.S. Geological Survey, 1990). Deciduous forest is predominant in the Salem Plateau and Boston Mountains, although this is commonly mixed with evergreen forest. Some pasture also occurs in the Salem Plateau where livestock (beef and dairy cattle) are raised, mostly in the southern part. The Springfield Plateau is predominantly pasture, although this is mixed with cropland in the north and forest in the south. Intensive poultry farming occurs in pastures of the Springfield Plateau in northwestern Arkansas, southwestern Missouri, and northeastern Oklahoma. Cropland dominates in the Osage Plains and Mississippi Alluvial Plain. Major crops grown in the Osage Plains are soybeans and sorghum with some corn, wheat, grains, and other field crops. Rice is the dominant crop grown in the Mississippi Alluvial Plain.

Table 1. Land-use percentage by physiographic area

[<, less than; 1978-83 land-use data from U.S. Geological Survey (1990)]

Physiographic area	Percent land use				
	Urban	Agriculture[1]	Forest	Water	Barren[2]
Osage Plains	1	82	14	1	2
Springfield Plateau	3	58	38	1	<1
Salem Plateau	1	27	71	1	<1
Boston Mountains	1	29	70	<1	<1
Mississippi Alluvial Plain	1	83	8	[3]8	<1

[1]Includes pasture and cropland.
[2]Includes mining.
[3]Includes approximately 7 percent wetland.

Total water use from both surface- and ground-water sources in the study unit was 1,053 million gallons per day (Mgal/d) in 1990 (Adamski and others, 1995). Of this, 614 Mgal/d was from ground-water sources and 439 Mgal/d was from surface-water sources. About 67 percent of the total ground-water use is for irrigation; most of this use is along the extreme southeastern part of the study unit in the Mississippi Alluvial Plain. Domestic and public supply accounts for about 22 percent of the ground-water use. About 47 percent of the total surface-water use is for public supply and almost 30 percent is for commercial and industrial use. About 6 percent of the total water used in the study unit is for nonirrigation agricultural purposes.

PESTICIDE USE

Pesticide-use data from cropland applications are available for 130 pesticides and 25 crop types for the period 1987-91 (Gianessi and Puffer, 1991; 1992a; 1992b). Only pesticide-use data from cropland applications is considered here; pesticide use in forest areas is minimal in comparison with cropland use (J. Courtenay, U.S. Forest Service, oral commun., 1996) and pesticide use in urban areas is confined to a minor part of the study unit. Pesticide use (table 2) was estimated from county-level totals; for counties located along the study unit boundary, an adjustment was applied based on the percentage of the county within the study unit.

Approximately 4.9 million pounds of active ingredients per year from 130 pesticides were applied on 25 crop types within the study unit from 1987-91. The herbicides 2-4-D, atrazine, propanil, metolachlor, alachlor, and trifluralin were the six pesticides used most extensively throughout the study unit (table 2); use of these herbicides accounts for approximately 56 percent of the total pesticides applied. The estimated application of these six herbicides in the study unit for the period 1987-91 decreased about 27 percent in comparison with a 1982-85 inventory of pesticide-use data (Bell and others, 1996; from data compiled by Gianessi and Puffer, 1988). Pesticide use generally was greatest in areas where the dominant land use was pastureland in the Springfield and Salem Plateaus and in cropland areas in the Osage Plains and Mississippi Alluvial Plain (fig. 2).

The most frequently applied pesticide in the study unit was 2,4-D (table 2, fig. 2). A selective herbicide, 2,4-D was most often applied to control broadleaf weeds in pasture and cropland. Within the study unit, 2,4-D was applied most heavily in areas where pasture was the dominant crop type in the Springfield and Salem Plateaus. An estimated 763,000 pounds per year (lb/yr) of 2,4-D were applied in all 96 counties in the study unit. Usage by county varied from a minimum of 34 lb/yr in Johnson County, Ark. to a maxi-

Table 2. Estimated cropland applications of selected pesticides in the study unit, 1987-91, and description of pesticide type and use

[Source: active ingredient applied from Gianessi and Puffer (1991; 1992a; 1992b); description of use modified from Baldwin and others (1994), Becker and others (1992), Johnson and Jones (1994), Sine (1991), Spradley (1991; 1992)]

Pesticide	Active ingredient applied (thousand pounds per year)	Type	Use
2,4-D	763	Herbicide	Grains, pasture, selected fruits and vegetables
Atrazine	574	Herbicide	Corn and sorghum
Propanil	447	Herbicide	Rice
Metolachlor	393	Herbicide	Vegetables, nuts, and cotton
Alachlor	323	Herbicide	Vegetables, cotton, and nuts
Trifluralin	253	Herbicide	Grains, vegetables, and nuts
Dicamba	167	Herbicide	Corn and forage
Glyphosate	164	Herbicide	Rice, cotton, soybeans, and sorghum
Propachlor	162	Herbicide	Corn, sorghum, and soybeans
Pendimethalin	159	Herbicide	Corn, sorghum, and soybeans
Molinate	105	Herbicide	Rice
Chlorpyrifos	90	Insecticide	Alfalfa, cotton, fruits
Cyanazine	84	Herbicide	Corn and fallow cropland
Butylate	83	Herbicide	Corn
Carbofuran	82	Insecticide	Fruits, vegetables, grains, and cotton
Bentazon	72	Herbicide	Alfalfa, vegetables, corn
EPTC	70	Herbicide	Vegetables and field crops
Sulfur	62	Fungicide	Fruits and vegetables
Propazine	60	Herbicide	Sorghum
Thiobencarb	45	Herbicide	Rice
Methyl Parathion	42	Insecticide	Vegetables and alfalfa
Carbaryl	41	Insecticide	Fruits, forests, and field crops
Clomazone	38	Herbicide	Vegetables and soybeans
Terbufos	35	Insecticide	Corn and sorghum
Imaziquin	35	Herbicide	Soybeans
Chloramben	33	Herbicide	Corn, vegetables, and soybeans
Metribuzin	33	Herbicide	Wheat
Malathion	32	Insecticide	Fruits and vegetables
Subtotal of 102 pesticides with application rates less than 30,000 pounds per year of active ingredient	453		
Total	4,900		

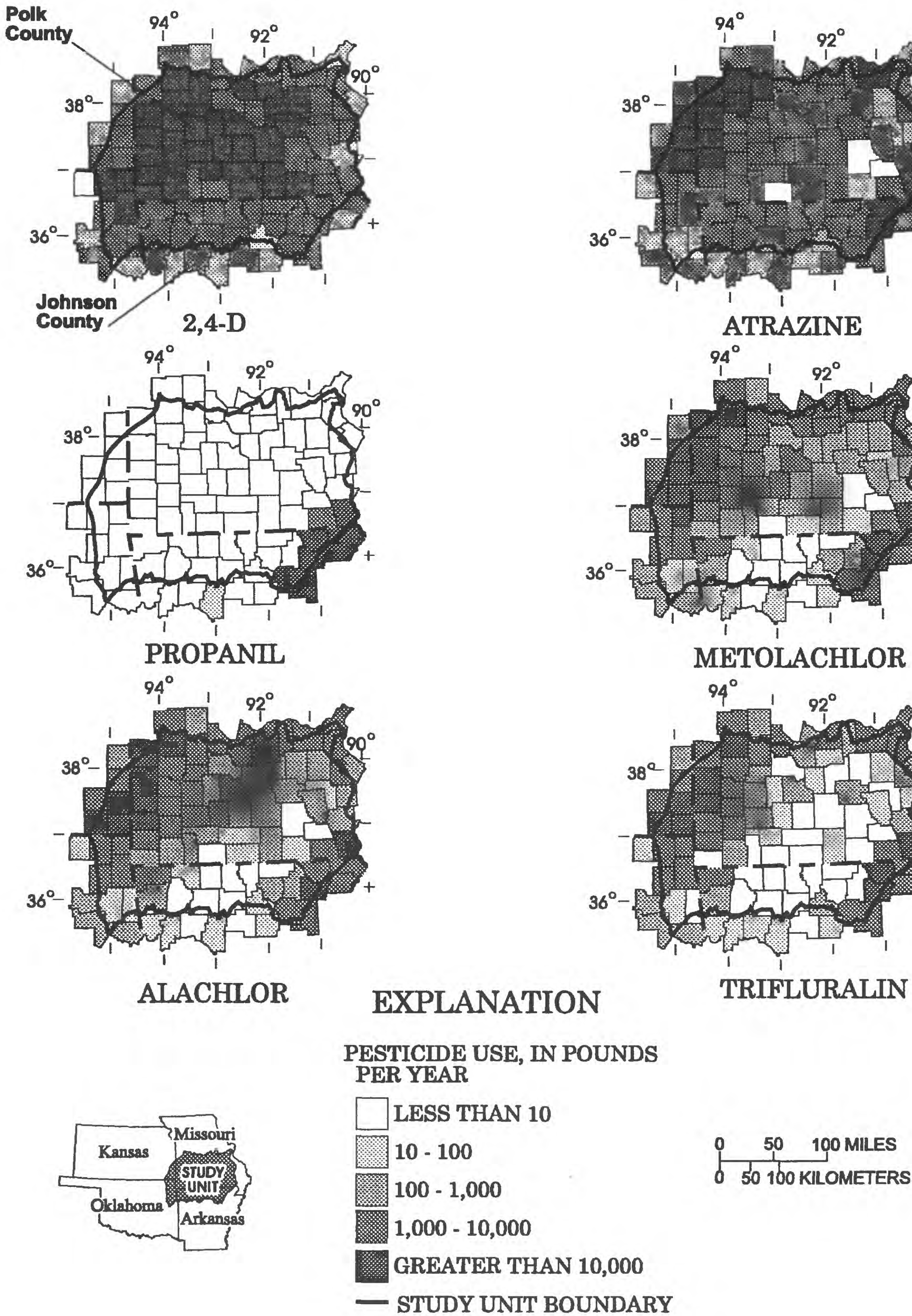


Figure 2. Major pesticide use in the study unit by county, 1987-91 (calculated from data in Gianessi and Puffer, 1991; 1992a; 1992b).

mum of 23,000 lb/yr in Polk County, Mo.; the median usage by county was 7,000 lb/yr.

Atrazine, propanil, metolachlor, alachlor, and trifluralin were the other most frequently used pesticides in the study unit (table 2, fig. 2). All of these pesticides are herbicides used to control various weeds and grasses primarily in cropland areas. Usage for each of these pesticides ranges from 1 lb/yr to about 130,000 lb/yr in individual counties, with median county application rates ranging from about 800 lb/yr to 48,000 lb/yr. Based on the amount of active ingredient applied and the number of counties in which the pesticide was used, propanil had the highest application rate per county in the study unit. Propanil was used on rice in a few counties in the extreme southeastern part of the study unit in the Mississippi Alluvial Plain.

To gain another perspective on pesticide use in the study unit, the total pesticide application rates by county (pounds per year) were converted to pounds per acre (within the entire county) per year. For counties located along the study unit boundary, an adjustment was applied based on the percentage of the county within the study unit. The Mississippi Alluvial Plain, located in the southeastern part of the study unit, had the highest application rate per acre (fig. 3). Application rates ranged from 0.75 to greater than 0.9 pounds per acre per year (lb/acre/yr) in counties in this part of the study unit. The Osage Plains, in the northwestern part of the study unit, also had relatively high application rates, ranging from less than 0.45 to greater than 0.9 lb/acre/yr. The application rates in the Springfield and Salem Plateaus ranged from less than 0.45 to greater than 0.9 lb/acre/yr. The application rates in the Boston and St. Francois Mountains ranged from less than 0.45 to greater than 0.6 lb/acre/yr.

Five crop types (soybeans, sorghum, pasture, rice, and corn) received approximately 85 percent of the pesticides applied within the study unit. Corn, sorghum, and soybeans were grown primarily in the Osage Plains; rice was grown primarily in the Mississippi Alluvial Plain. Pastureland located in the Springfield and Salem Plateaus received moderate amounts of pesticides. Forestland and pastureland in the Boston and St. Francois Mountains received the least amounts of pesticides.

Pastureland was the crop type that received the greatest amount of pesticides in 53 of the 96 counties in the study unit (fig.4). Pastureland received the greatest amount of pesticides in the Boston Mountains, St. Francois Mountains, and throughout most of the

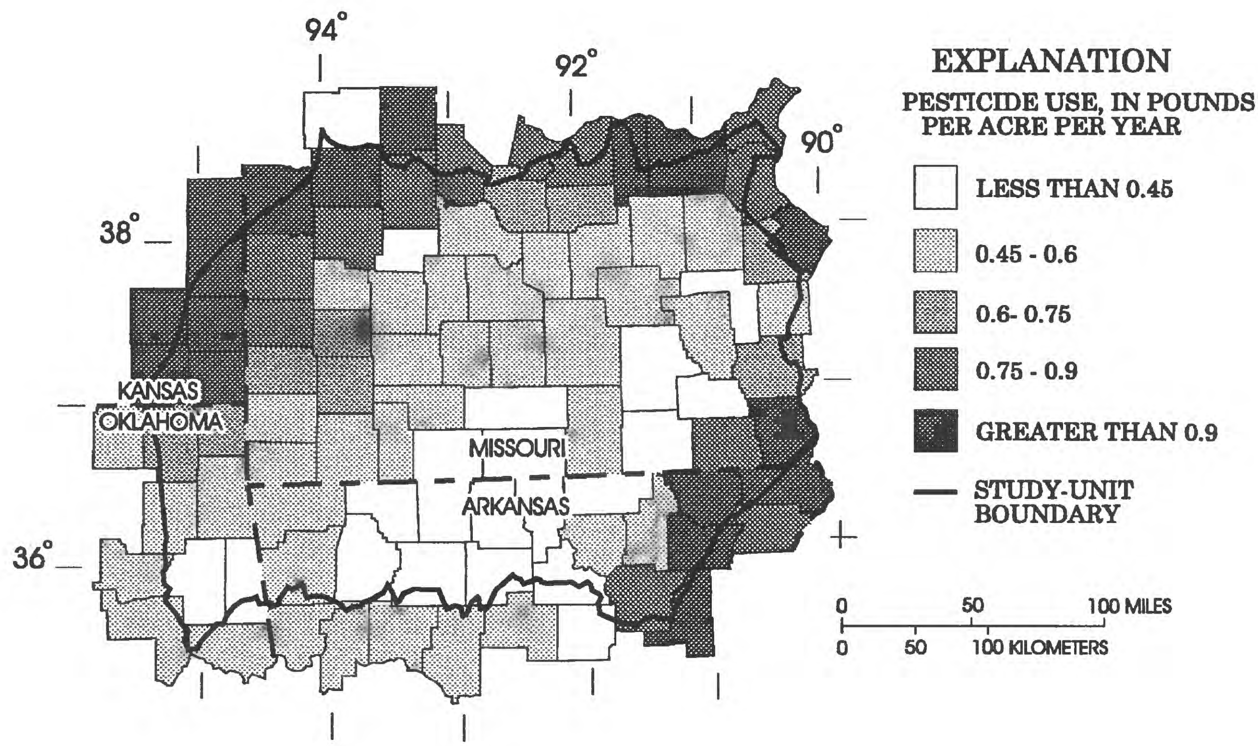


Figure 3. Pesticide application rate for counties within the study unit (calculated from data in Gianessi and Puffer, 1991; 1992a; 1992b).

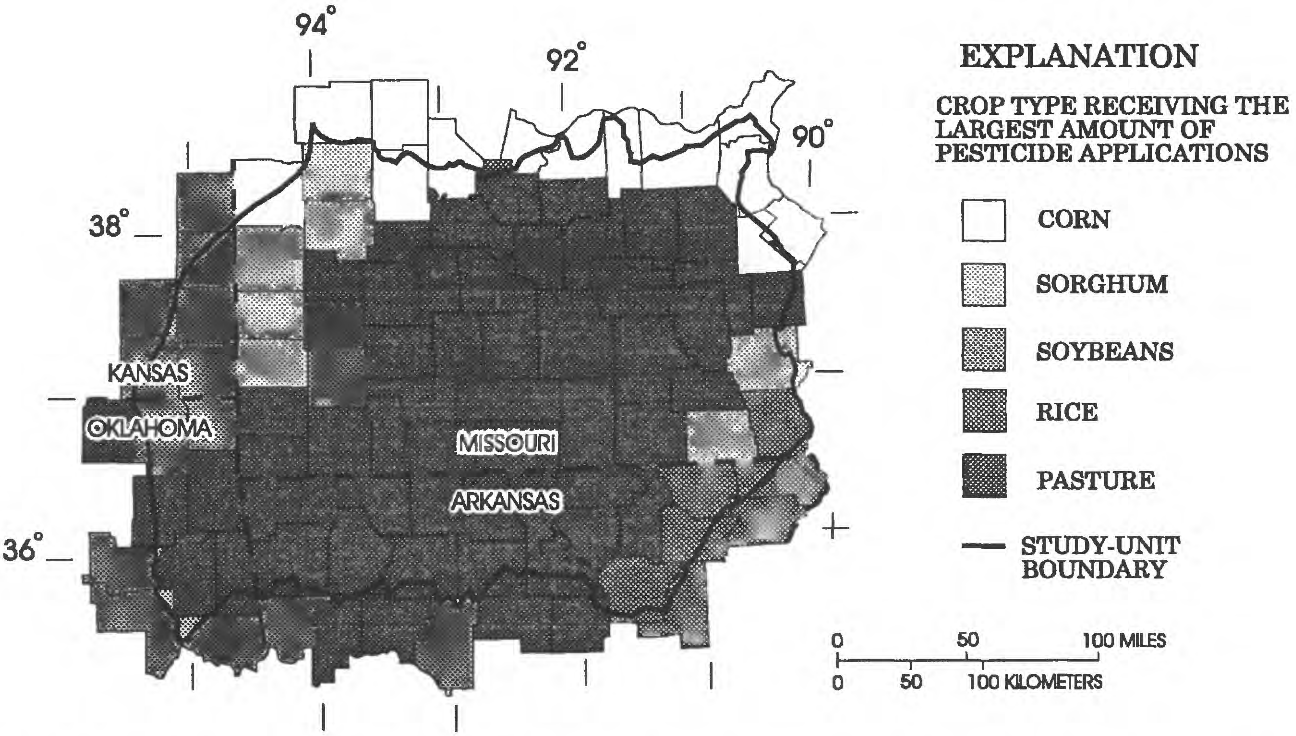


Figure 4. Crop types receiving the largest pesticide applications for counties within the study unit (calculated from data in Gianessi and Puffer, 1991; 1992a; 1992b).

Springfield and Salem Plateaus. Corn, sorghum, and soybeans received the greatest amounts of pesticides in Osage Plains; rice received the greatest amount of pesticides in the Mississippi Alluvial Plain.

DESCRIPTION OF SAMPLING NETWORK

Fifty-one surface-water (basic-fixed, intensive-fixed, and synoptic), bed-sediment, and biological-tissue sampling sites comprise the sampling network within the study unit (fig. 5; table 3). The sampling network for each component was designed based on factors including physiography, land use, and drainage area. The drainage basins of most sites are located in the Salem (22 sites) and Springfield (15 sites) Plateaus; drainage basins of fewer sites are located in the Boston Mountains (4 sites) and Osage Plains (3 sites). The drainage basins of seven sites cover parts of two or more physiographic areas. The predominant land use of basins in the sampling networks is forest (22 sites) and agricultural (21 sites); fewer sites are designated as multiple land uses (7 sites) and mining (1 site).

Surface Water

The surface-water sampling network is comprised of 12 basic-fixed, 2 intensive-fixed, and 29 synoptic sites. The sampling network was established, from a list of about 60 potential sites, to monitor water-quality effects in the study unit on a long-term basis and to assess the occurrence and temporal distribution of pesticides.

Basic-Fixed and Intensive-Fixed Sites

The network of basic-fixed and intensive-fixed sites (fig. 5; table 3) was established to monitor water-quality of sites representative of basins with several combinations of land use, basin size, and physiography within the study unit on a long-term basis. Basic-fixed and intensive-fixed sites drain basins of small (30.5 to 58.1 mi^2) or medium (294 to 959 mi^2) size with near-homogenous land use (indicator sites) and one basin (527 mi^2) that integrates forest and agricultural land uses, instream gravel mining, and discharge from an upstream wastewater-treatment facility, and several physiographic areas. An additional site (site 24; Current River at Van Buren, Mo.) draining a large basin

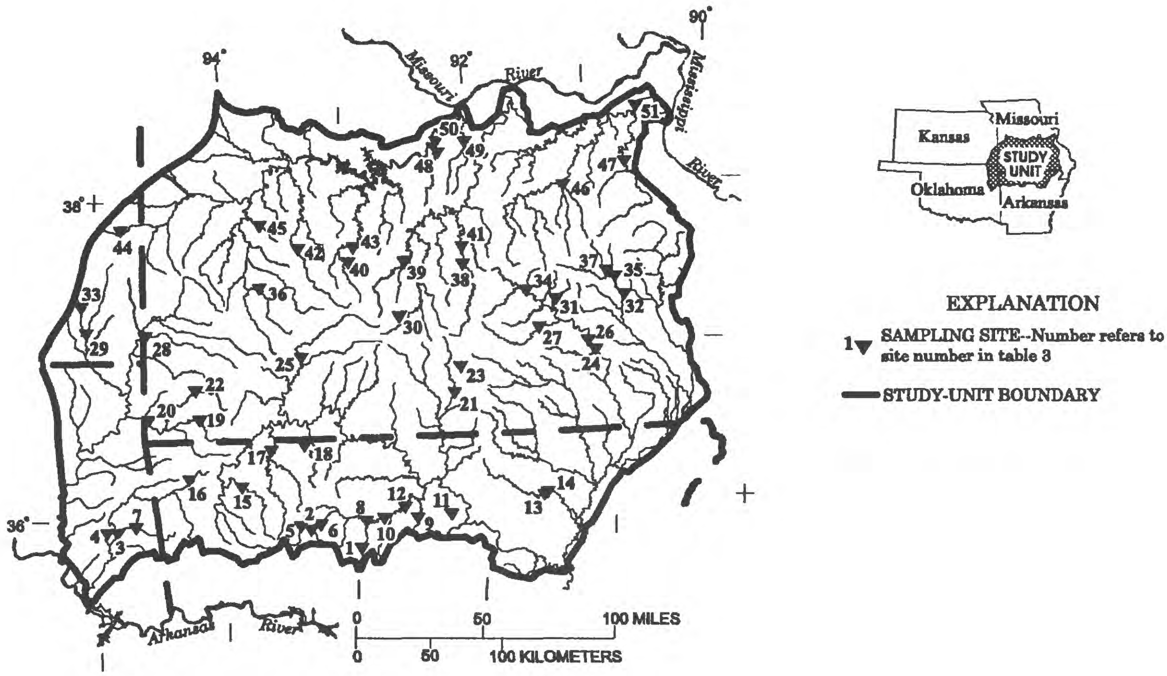


Figure 5. Location of sampling sites comprising the sampling network.

(1,667 mi²) was added to the basic-fixed site network in 1995.

The 14 fixed sites have drainage basins in the Boston Mountains (1 site), Salem Plateau (5 sites), and Springfield Plateau (5 sites) physiographic areas. Three basic-fixed sites have drainage basins that cover parts of two or more physiographic areas. The basic-fixed and intensive-fixed sites include agricultural (pasture and confined animal; 6 sites), forest (7 sites), and multiple (1 site) land uses. Pesticide samples were collected at the basic-fixed sites once in 1994 (May or June) and three times in 1995 (April, May, and June) when pesticides are most intensively applied and the likelihood of detecting them is greatest.

The intensive-fixed network was established to assess the occurrence and temporal distribution of pesticides (also nutrients and bacteria) in small agricultural land-use basins in the Springfield and Salem Plateaus. The intensive-fixed sites (fig. 5; table 3), Yocum Creek near Oak Grove, Ark. (site 18) and Dousinbury Creek near Wall Street, Mo. (site 40), had an increased sample-collection frequency to evaluate variations in the number of pesticide detections and concentrations during the time of most intense pesticide application and to determine if pesticides were present in measurable concentrations throughout the year. The drainage basin of site 18 is located in the White River Basin in the Springfield Plateau; land use in the basin is about 75 percent agricultural, predominantly poultry and beef cattle operations. The drainage basin of site 40 is located in the Osage River Basin in the Salem Plateau; the land use in the basin is about 60 percent agricultural, predominantly dairy operations and pasture. The animal waste (manure) and litter from these operations are used to fertilize pasturelands. Crops such as alfalfa, corn, soybean, and milo also are grown in these basins. Biweekly samples were collected at the two intensive-fixed sites in February, March, and July 1994; weekly samples were collected in April, May, and June 1994 (to coincide with the application of manure, commercial fertilizer, and pesticides to pasturelands and crops); and monthly samples were collected August through December 1994 and in January, April, May, and June 1995.

Table 3. Site and basin characteristics of sampling sites within the sampling network

[mi^2, square mile; SYN, Synoptic; BST, Bed Sediment and Tissue; BF, Basic Fixed; INT, Intensive Fixed; Sampling-network land use shown in parenthesis indicates a specialized land use that represents a minor part of the basin]

Site number (fig. 5)	Site Name	Latitude	Longi-tude	Drainage area (mi^2)	Sampling network	Physiographic area	Predominant land use in the sampling network
1	Richland Creek near Witts Springs, Ark.	354749	925543	67.4	SYN, BST	Boston Mountains	Forest
2	Little Buffalo River at Murray, Ark.	355509	931916	45.2	SYN	Boston Mountains	Forest
3	Baron Fork at Eldon, Okla.	355516	945018	312	SYN	Springfield	Agriculture
4	Illinois River near Tahlequah, Okla.	355522	945524	959	BF, BST	Springfield	Agriculture
5	Buffalo River near Boxley, Ark.	355643	932412	57.4	BF, BST	Boston Mountains	Forest
6	Shop Creek at Parthenon, Ark.	355709	931435	25.4	SYN	Boston Mountains	Forest
7	Peacheater Creek at Christie, Okla.	355717	944146	23.6	SYN	Springfield	Agriculture
8	Buffalo River near Eula, Ark.	355811	925310	603	SYN	Boston Mountains and Springfield	Forest
9	Big Creek near Big Flat, Ark.	355843	922853	89.5	SYN	Springfield	Forest and agriculture
10	Buffalo River near St. Joe, Ark.	355902	924444	829	BF, BST	Boston Mountains and Springfield	Forest
11	North Sylamore Creek near Fifty Six, Ark.	355943	921245	58.1	BF, BST	Springfield	Forest
12	Water Creek near Evening Star, Ark.	360259	923434	38.6	SYN	Springfield	Forest
13	Strawberry River north of Poughkeepsie, Ark.	360547	912836	380	BST	Salem	Forest
14	Strawberry River near Poughkeepsie, Ark.	360637	912659	473	SYN	Salem	Agriculture
15	War Eagle Creek near Hindsville, Ark.	361202	935120	266	SYN	Springfield	Forest and agriculture
16	Little Osage Creek at Healing Springs, Ark.	361513	941612	39.3	SYN, BST	Springfield	Agriculture
17	Kings River near Berryville, Ark.	362536	933715	527	BF, BST	Springfield, Salem, and Boston	Forest and agriculture
18	Yocum Creek near Oak Grove, Ark.	362714	932123	52.8	INT, BST	Springfield	Agriculture
19	Mikes Creek at Powell, Mo.	363735	941052	64.4	SYN	Springfield	Forest
20	Elk River near Tiff City, Mo.	363750	943512	872	BF, BST	Springfield	Agriculture
21	North Fork White River near Dora, Mo.	364535	920912	404	SYN	Salem	Forest
22	North Indian Creek near Wanda, Mo.	364840	941236	46.6	SYN	Springfield	Agriculture
23	Noblett Creek near Willow Springs, Mo.	365516	920544	20.6	SYN	Salem	Forest
24	Current River at Van Buren, Mo.	365929	910053	1,667	BF, BST	Salem	Forest
25	James River near Boaz, Mo.	370025	932150	464	SYN, BST	Springfield	Agriculture, (urban)
26	Rogers Creek near Van Buren, Mo.	370257	910418	17.9	SYN	Salem	Forest
27	Jacks Fork River at Alley Spring, Mo.	370840	912727	305	BF, BST	Salem	Forest
28	Center Creek near Smithfield, Mo.	370920	943610	294	BF, BST	Springfield	Agriculture, (urban and mining)

Table 3. Site and basin characteristics of sampling sites within the sampling network--Continued

[mi^2, square mile; SYN, Synoptic; BST, Bed Sediment and Tissue; BF, Basic Fixed; INT, Intensive Fixed; Sampling-network land use shown in parenthesis indicates a specialized land use that represents a minor part of the basin]

Site number (fig. 5)	Site Name	Latitude	Longi-tude	Drainage area (mi^2)	Sampling network	Physiographic area	Predominant land use in the sampling network
29	Lightning Creek near Oswego, Kans.	371049	950411	248	BST	Osage Plains	Mining
30	Woods Fork near Hartville, Mo.	371443	923404	45.6	SYN	Salem	Agriculture
31	Big Creek at Mauser Mill, Mo.	371847	911900	41.6	SYN, BST	Salem	Forest
32	Black River below Annapolis, Mo.	371930	904550	495	BF	Salem and St. Francois	Forest, (mining)
33	Neosho River near Parsons, Kans.	372024	950635	4,905	BST	Osage Plains	Agriculture
34	Current River below Akers, Mo.	372235	913251	294	SYN	Salem	Forest
35	Black River near Lesterville, Mo.	372626	904957	430	BST	Salem and St. Francois	Forest (mining)
36	Sac River near Dadeville, Mo.	372635	934105	257	SYN	Springfield	Agriculture
37	Middle Fork Black River near Lesterville, Mo.	372850	905410	160	BST	Salem	Forest (mining)
38	Paddy Creek above Slabtown Spring, Mo.	373329	920255	30.5	BF, BST	Salem	Forest
39	Osage Fork near Russ, Mo.	373518	923054	351	SYN	Salem	Agriculture
40	Dousinbury Creek near Wall Street, Mo.	373540	925800	40.9	INT, BST	Salem	Agriculture
41	Big Piney River near Big Piney, Mo.	373958	920302	551	SYN	Salem	Forest and agriculture
42	Pomme de Terre River near Polk, Mo.	374056	932212	276	SYN, BST	Salem	Agriculture
43	Niangua River at Windyville, Mo.	374103	925527	338	BF, BST	Salem	Agriculture
44	Marmaton River near Marmaton, Kans.	374903	944730	292	BST	Osage Plains	Agriculture
45	Brush Creek above Collins, Mo.	375005	934022	55.1	SYN	Salem	Agriculture
46	Huzzah Creek near Scotia, Mo.	380144	911248	486	SYN	Salem	Forest, (mining)
47	Big River near Richwoods, Mo.	380934	904222	735	SYN, BST	Salem and St. Francois	Forest and agriculture (mining)
48	Little Tavern Creek near St. Elizabeth, Mo.	381608	921250	47.8	SYN	Salem	Agriculture
49	Maries River near Freeburg, Mo.	382001	915934	186	SYN	Salem	Agriculture
50	Osage River near St. Thomas, Mo.	382020	921334	14,500	BST	Springfield, Salem, and Osage Plains	Multiple
51	Meramec River near Eureka, Mo.	383020	903530	3,788	BST	Salem	Multiple

Synoptic Sites

The 29-site synoptic network was established to increase the spatial coverage of the basic-fixed and intensive-fixed networks; the basin characteristics (basin size, physiography, and land-use) for each site in the synoptic network is similar to the basin characteristics of a basic-fixed or intensive-fixed site. The synoptic sites (fig. 5; table 3) drain basins of small (17.9 to 89.5 mi^2) or medium (185 to 735 mi^2) size in the Boston Mountains (3 sites), Salem Plateau (14 sites), and Springfield Plateau (10 sites) physiographic areas. The drainage basins of two synoptic sites cover parts of two physiographic areas. The synoptic sites include agricultural (pasture and confined animal; 13 sites), forest (12 sites), and multiple (4 sites) land uses. Pesticide samples were collected at the synoptic sites during a high-flux period (May or June) in 1994 and 1995.

Bed Sediment and Biological Tissue

The bed-sediment and biological-tissue network (fig. 5; table 3), comprised of 27 sites, was established to survey the occurrence and distribution of organic compounds (and trace elements) and to establish a base-line data set from which long-term trends can be determined. The strategy for site selection was to optimize the possibility of detecting targeted organic compounds and to then determine the spatial distribution of these compounds. Sites drain basins of small (30.5 to 58.1 mi^2) or medium (294 to 959 mi^2) size with near-homogenous land use and one basin (527 mi^2) that integrates several major land uses and physiographic areas. An additional site (site 24; Current River at Van Buren, Mo.) draining a large basin (1,667 mi^2) was added to the bed-sediment site network in 1995.

The 27 sites selected for bed-sediment and biological-tissue sampling are located in the Boston Mountains (2 sites), Osage Plains (3 sites), Salem Plateau (10 sites), and Springfield Plateau (7 sites) physiographic areas. Five bed-sediment and biological-tissue sites have drainage basins that cover parts of two or more physiographic areas. The bed-sediment and biological-tissue sites include agricultural (pasture and confined animal; 11 sites), forest (9 sites), lead-zinc mining (3 sites), and multiple (4 site) land uses. Organic-compound samples were collected once at most bed-sediment and biological-tissue sampling sites; samples were collected twice at Niangua River near Windyville, Mo. (site 43), North Sylamore Creek near Fifty Six, Ark. (site 11), and Strawberry River north of Poughkeepsie, Ark. (site 13).

ASSESSMENT OF CONDITIONS

The following sections provide an assessment of the conditions of organic compounds in surface water, bed sediment, and biological tissue. For an assessment of the conditions of pesticides in ground water in the study unit, the reader is referred to Adamski (1997). The following sections include descriptions of the study approaches used for sample collection and presentations of the results of the organic-compound assessment.

Surface Water

Study Approach

Water samples analyzed for pesticides (157 samples) were collected at 43 surface-water sites in the study unit from February 1994 through June 1995. Samples collected from February 1994 through January 1995 were analyzed for 82 pesticides (fig. 6); after January 1995, samples were analyzed for 47 pesticides. Representative samples (composites of depth-integrated samples from multiple verticals in the stream cross section) were collected, split into sub-samples, and filtered using equipment that will not contaminate or sorb analytes and is suitable for use with organic solvents. Samples were analyzed by the USGS's National Water-Quality Laboratory (NWQL) in Denver, Colo. The surface-water collection strategy and methods are described in Shelton (1994).

Forty-three quality-assurance samples were collected at the 2 intensive-fixed sites and at 7 synoptic sites. The quality-assurance samples included 19 field equipment blanks collected at six sites to monitor for contamination and carry over between environmental samples, 7 replicate environmental samples collected at three sites to monitor analytical precision, and 17 "spiked" samples (in which a pesticide solution was added to the environmental sample) collected at four sites to monitor accuracy of analyte recovery in the sample matrix. No pesticide concentration exceeded the method detection limit (MDL) in any of the 19 field equipment blanks. Pesticide concentrations in the replicate environmental samples were mostly below, or so close to, the MDL, that differences were not practically

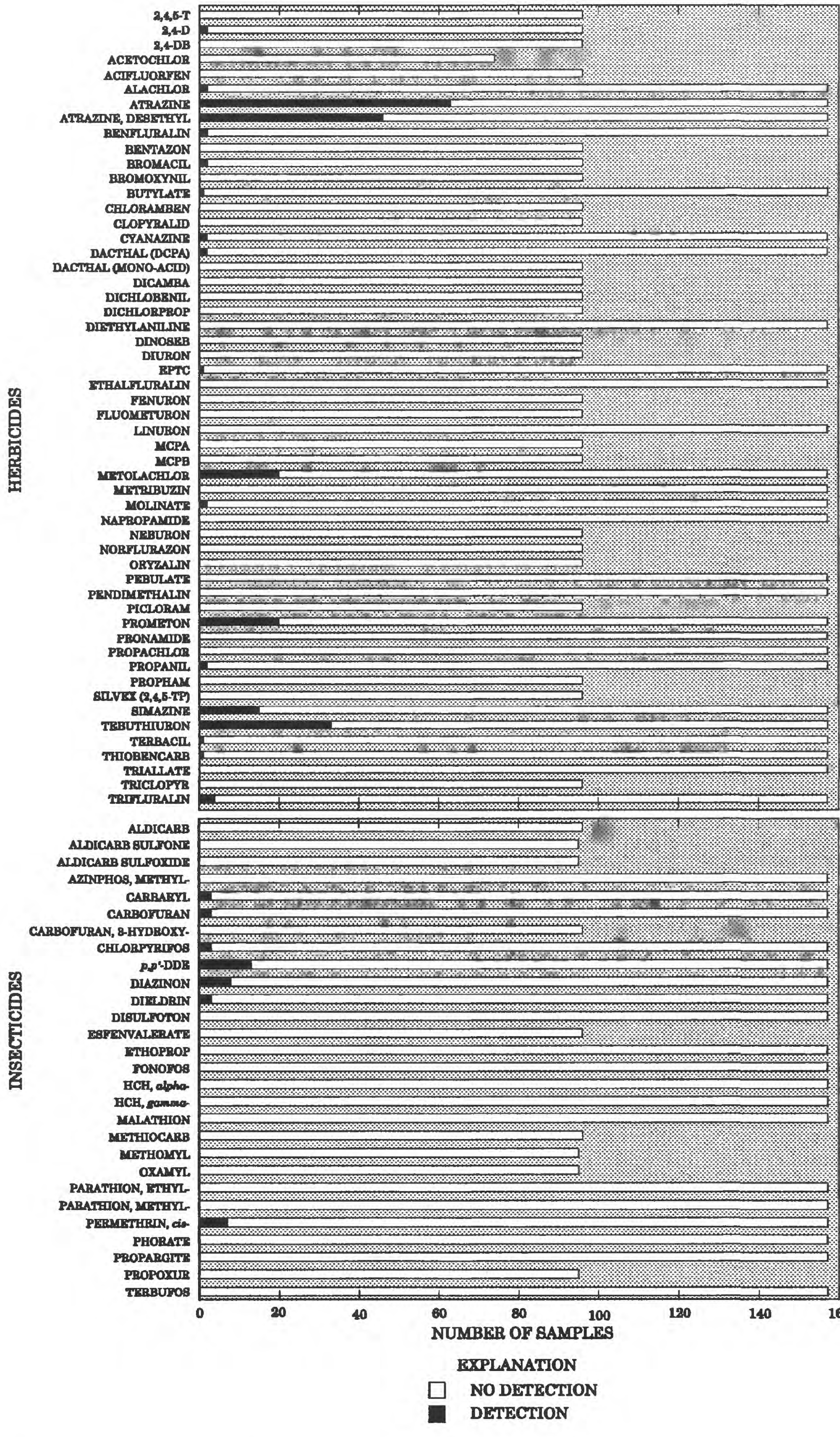


Figure 6. Pesticides analyzed and detected in surface-water samples, 1994-95.

significant. The spiked samples had recoveries that ranged from 5 to 490 percent with a median value of 58 percent for samples analyzed using a high-performance liquid chromatograph method and 94 percent for samples analyzed using a gas chromatography/mass spectrometry method; concentrations of pesticides in surface-water samples were not adjusted based on these percent recoveries.

In addition to the analyses for pesticides, water samples from all the sites were analyzed for major ions (calcium, magnesium, sodium, potassium, chloride, fluoride, bromide, and silica), nutrients (nitrite plus nitrate, nitrite, ammonia, ammonia plus organic nitrogen, orthophosphate, and phosphorus), organic carbon, selected trace elements, and indicator bacteria (fecal coliform, fecal streptococcus, and *Escherichia coli*). Field measurements at each site included water and air temperatures, alkalinity, dissolved oxygen, pH, and specific conductance. Water-quality data collected during water years 1994-95 at the 43 basic-fixed, intensive-fixed, and synoptic sites are available in the Arkansas, Missouri, and Oklahoma annual data reports (U.S. Geological Survey, 1995-96a; 1995-96b; 1995-96c).

The pesticide data were analyzed to determine factors affecting pesticide occurrence in streams in the study unit. Data were grouped according to physiographic area (Boston Mountains, Salem, or Springfield Plateaus), land use (forest or agricultural), drainage area (small, medium, or large), and number of pesticide detections. The Kruskal-Wallis test was used to determine whether the proportion of pesticide detections was significantly different among the groups at a significance level of 0.05. If a statistically significant difference was detected among groups, Tukey's Multiple Comparison Test (MCT) on the ranks of the data was performed to determine which group differed from the others (Helsel and Hirsch, 1992). Seasonal variations in pesticide detections at the two intensive-fixed sites also were considered.

Results

Of the 54 herbicides and 28 insecticides analyzed, 19 herbicides and 7 insecticides were detected in at least 1 sample (fig. 6). The most commonly detected herbicides (figs. 6 and 7) were atrazine (63 samples), desethylatrazine (a metabolite of atrazine; 46 samples), tebuthiuron (33 samples), prometon (20 samples), metolachlor (20 samples), and simazine (15 samples); the most commonly detected insecticides were *p,p'*-DDE (a metabolite of DDT; 13 samples), diazinon (8 samples), and *cis*-permethrin (7 samples). (Desethylatrazine was not included in figure 7 because, in most cases, it was detected only when atrazine also was detected.) The other 13 herbicides and 4 insecticides detected were found in less than five samples.

Pesticides were detected at 39 of the 43 sites sampled (fig. 8 and table 4). The largest number of compounds detected was 13 at Yocum Creek near Oak Grove, Ark. (site 18), an intensive-fixed site located in a small agricultural basin in the Springfield Plateau where poultry and beef cattle are raised. The largest number of compounds detected in a single sample was 10 in a sample collected at Woods Fork near Hartville, Mo. (site 30), a synoptic site located in a small agricultural basin in the Salem Plateau where dairy cattle are raised.

Some differences in pesticide detections at individual sites appear to be related to land use and drainage area. The four sites where no detections occurred (fig. 8 and table 4; sites 1, 6, 32, and 46) varied in drainage-area categories, but had predominantly forest land use and are located in either the Boston Mountains or Salem Plateau. Only 3 sites had greater than 15 pesticide detections, including the 2 intensive-fixed sites (sites 18 and 40) where 24 to 26 samples were collected. The 4 samples collected at the Illinois River near Tahlequah, Okla. (site 4), had a total of 20 pesticide detections. Land use in the Illinois River Basin is about 59 percent agricultural, which includes poultry, beef cattle, and a large number of landscape nurseries. Seventeen sites had 6 or more pesticide detections. Of these, 11 have greater than 50 percent agricultural land use, 4 have 30 to 50 percent agricultural land use, and 2 have less than 30 percent agricultural land use (table 4). The James River near Boaz, Mo. (site 25; 10 pesticide detections) also has about 10 percent urban land use. The Current River at Van Buren, Mo. (site 24), a large, predominantly forest basin, had 12 pesticide detections in four samples. This is the only basin with less than 20 percent agricultural land use that has more than four pesticide detections. The number of detections probably is related to the drainage area, which is at least twice as large as any of the other basins sampled (table 4). Nine basins with greater than 30 percent agricultural land use had five or less pesticide detections.

After considering the pesticide data results at the individual sites, the data were grouped according to land use (forest or agricultural) and drainage area (small or medium; tables 4 and 5) for further analysis.

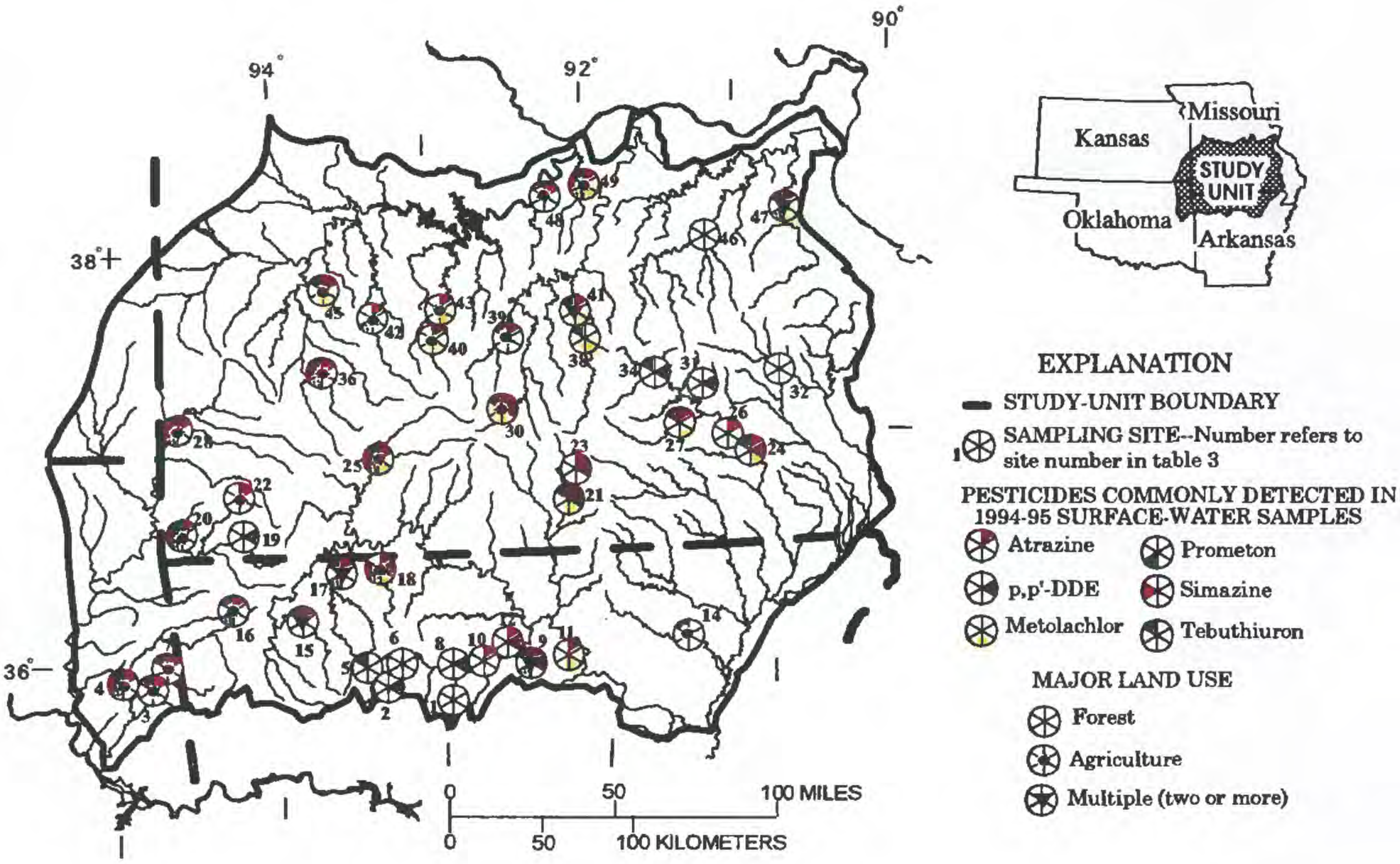


Figure 7. Pesticides commonly detected in surface-water samples, 1994-95.

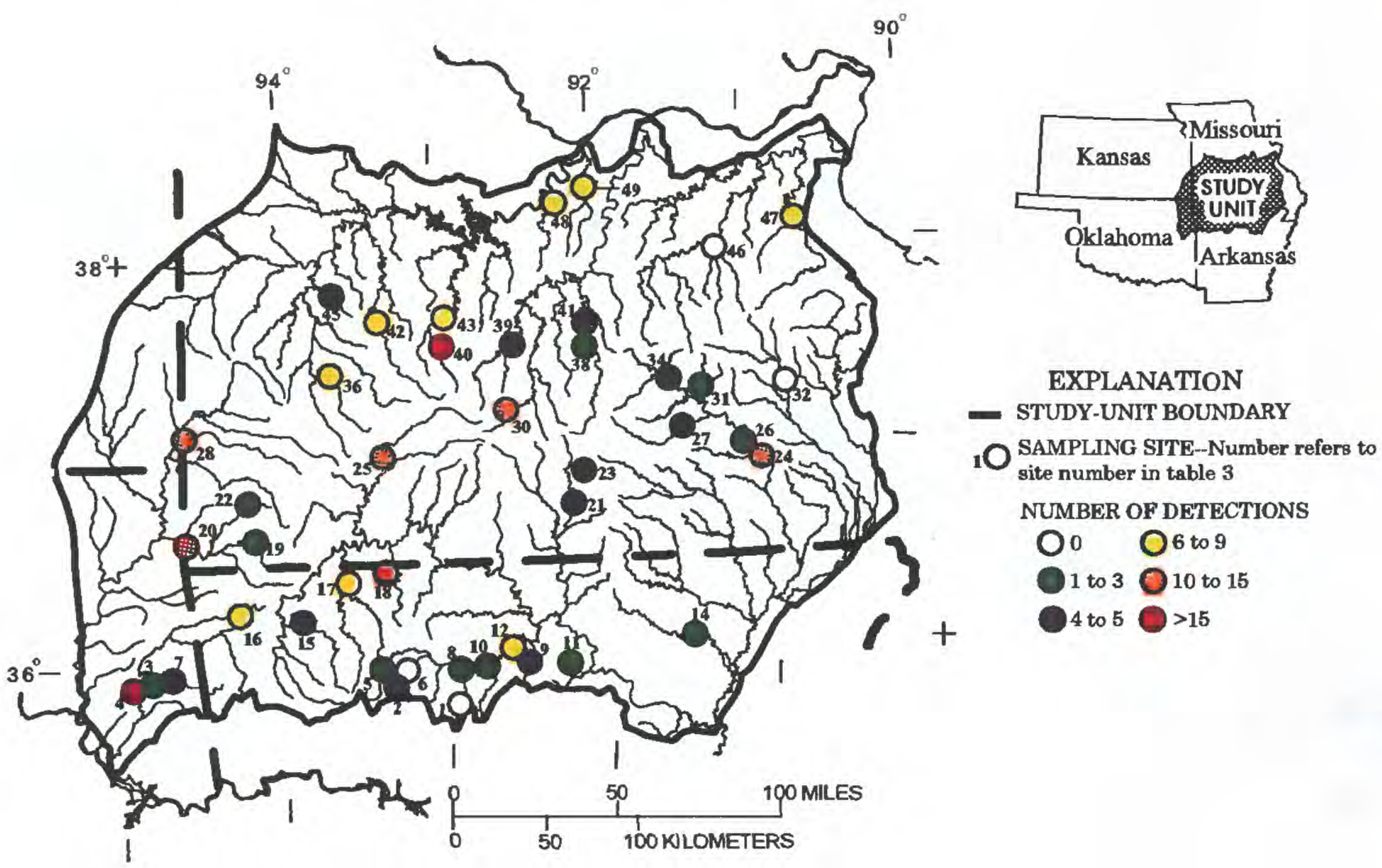


Figure 8. Number of pesticide detections at surface-water sites, 1994-95.

Table 4. Pesticide detections by site in the surface-water sampling network

[mi^2, square miles; Springfield, Springfield Plateau; Salem, Salem Plateau; Boston, Boston Mountains; St. Francois, St. Francois Mountains; <, less than; --, no land use in the category]

Site number (fig. 5)	Site name	Number of pesticide samples	Number of pesticide compounds detected	Number of pesticide detections	Drainage area (mi^2)	Physiographic area	Percent land use in basin: Forest	Agriculture[1]	Urban	Other[2]
	Basic-fixed sites									
4	Illinois River near Tahlequah, Okla.	4	7	20	959	Springfield	35.9	58.9	4.9	<1
5	Buffalo River near Boxley, Ark.	4	1	1	57.4	Boston	96.1	3.9	--	--
10	Buffalo River near St. Joe, Ark.	4	2	3	829	Boston and Springfield	86.3	13.1	<1	<1
11	North Sylamore Creek near Fifty Six, Ark.	4	3	3	58.1	Springfield	97.3	2.7	--	--
17	Kings River near Berryville, Ark.	4	6	7	527	Boston, Salem, and Springfield	67.5	31.9	<1	<1
20	Elk River near Tiff City, Mo.	4	5	12	872	Springfield	50.8	46.7	1.9	<1
24	Current River at Van Buren, Mo.	4	9	12	1,667	Salem	82.6	17.1	<1	--
27	Jacks Fork River at Alley Spring, Mo.	4	4	5	305	Salem	77.9	21.7	<1	<1
28	Center Creek near Smithfield, Mo.	4	6	15	294	Springfield	17.4	76.8	3.4	2.4
32	Black River below Annapolis, Mo.	4	0	0	495	Salem and St. Francois	93.2	6.2	<1	<1
38	Paddy Creek above Slabtown Springs, Mo.	5	3	3	30.5	Salem	90.1	9.6	<1	--
43	Niangua River at Windyville, Mo.	6	4	8	338	Salem	42.2	56.3	1.4	<1
	Intensive-fixed sites									
18	Yocum Creek near Oak Grove, Ark.	26	13	26	52.8	Springfield	22.1	76.2	1.7	--
40	Dousinbury Creek on Highway JJ near Wall Street, Mo.	24	7	20	40.9	Salem	40.1	59.4	<1	--
	Synoptic sites									
1	Richland Creek near Witts Spring, Ark.	1	0	0	67.4	Boston	96.6	3.2	<1	--
2	Little Buffalo River at Murray, Ark.	2	4	4	45.2	Boston	94.6	5.0	<1	--
3	Baron Fork at Eldon, Okla.	2	3	3	312	Springfield	52.3	46.4	1.3	--
6	Shop Creek at Parthenon, Ark.	2	0	0	25.4	Boston	91.6	8.4	--	--
7	Peacheater Creek at Christie, Okla.	2	3	5	23.6	Springfield	42.3	57.1	<1	--
8	Buffalo River near Eula, Ark.	2	2	2	603	Boston and Springfield	87.8	11.6	<1	<1
9	Big Creek near Big Flat, Ark.	2	5	5	89.5	Springfield	64.1	35.7	<1	--
12	Water Creek near Evening Star, Ark.	2	6	6	38.6	Springfield	72.3	27.7	--	12
14	Strawberry River near Poughkeepsie, Ark.	2	1	1	473	Salem	57.2	41.2	1.2	14

Table 4. Pesticide detections by site in the surface-water sampling network--Continued

[mi^2, square miles; Springfield, Springfield Plateau; Salem, Salem Plateau; Boston, Boston Mountains; St. Francois, St. Francois Mountains; <, less than; --, no land use in the category]

Site number (fig. 5)	Site name	Number of pesticide			Drainage area (mi^2)	Physiographic area	Percent land use in basin			
		samples	compounds detected	detections			Forest	Agriculture[1]	Urban	Other[2]
15	War Eagle Creek near Hindsville, Ark.	2	4	4	266	Springfield	61.2	38.1	<1	15
16	Little Osage Creek at Healing Springs, Ark.	2	5	6	39.3	Springfield	5.6	91.3	3.1	16
19	Mikes Creek at Powell, Mo.	2	1	1	64.4	Springfield	71.9	28.1	--	19
21	North Fork White River near Dora, Mo.	2	5	5	404	Salem	70.9	29.0	<1	21
22	North Indian Creek near Wanda, Mo.	2	2	2	46.6	Springfield	4.7	94.1	1.2	22
23	Noblett Creek near Willow Springs, Mo.	2	4	4	20.6	Salem	90.7	9.3	--	23
25	James River near Boaz, Mo.	2	6	10	464	Springfield	21.4	68.2	9.7	25
26	Rogers Creek near Van Buren, Mo.	2	2	2	17.9	Salem	99.5	<1	--	26
30	Woods Fork near Hartville, Mo.	2	10	10	45.6	Salem	42.9	57.1	--	30
31	Big Creek at Mauser Mill, Mo.	2	2	2	41.6	Salem	94.7	4.9	<1	31
34	Current River below Akers, Mo.	2	5	5	294	Salem	73.9	26.0	<1	34
36	Sac River near Dadeville, Mo.	2	5	8	257	Springfield	14.9	82.6	2.4	36
39	Osage Fork near Russ, Mo.	2	4	5	351	Salem	48.3	51.3	<1	39
41	Big Piney River near Big Piney, Mo.	2	4	5	551	Salem	63.5	35.7	<1	41
42	Pomme de Terre River near Polk, Mo.	2	7	7	276	Salem	28.0	71.2	<1	42
45	Brush Creek above Collins, Mo.	2	4	4	55.1	Salem	36.6	61.7	1.7	45
46	Huzzah Creek near Scotia, Mo.	1	0	0	486	Salem	86.5	12.1	<1	46
47	Big River near Richwoods, Mo.	2	6	6	735	Salem and St. Francois	64.3	31.0	1.4	47
48	Little Tavern Creek near St. Elizabeth, Mo.	2	4	6	47.8	Salem	49.7	50.3	--	48
49	Maries River near Freeburg, Mo.	2	7	8	186	Salem	58.9	40.5	<1	49

[1]Agriculture includes pasture and cropland.
[2]Other includes barren land, rangeland, and water.

For the two intensive-fixed sites (sites 18 and 40), only data collected in May 1994 and April, May, and June 1995 were included. These data coincide with the pesticide data collected at all the other basic-fixed and synoptic sites. Site 25, which has about 68 percent agricultural land use, was included with the medium, agricultural sites. Big Creek near Big Flat, Ark. (site 9), Water Creek near Evening Star, Ark. (site 12), War Eagle Creek near Hindsville, Ark. (site 15), Kings River near Berryville, Ark. (site 17), Mikes Creek at Powell, Mo. (site 19), Current River at Van Buren, Mo. (site 24), Big Piney River near Big Piney, Mo. (site 41), and Big River near Richwoods, Mo. (site 47), were not included in the analysis. These sites have multiple land uses with no predominant land use, much less percent forest land use, or larger drainage area.

The percent detections and median and maximum concentrations of the 21 detected pesticides for the data grouped by land use and drainage area are shown in table 5. The largest variety of pesticides detected (18) was in small, agricultural basins, and the largest percentage (about 80) of detections of a single pesticide (atrazine) was in medium, agricultural basins. Pesticide concentrations were small, and in most cases, at or near the MDL (table 5). Maximum concentrations ranged from 0.001 (*cis*-permethrin) to 0.007 micrograms per liter (µg/L; tebuthiuron) at small, forest sites; 0.001 (*cis*-permethrin) to 0.029 µg/L (tebuthiuron) at medium, forest sites; 0.001 (*cis*-permethrin and dachtal) to 0.079 µg/L (carbaryl) at small, agricultural sites; and 0.003 (EPTC) to 0.29 µg/L (prometon) at medium, agricultural sites. No pesticide concentration exceeded the maximum contaminant level (MCL) or the lifetime health-advisory (HA) level for drinking water or the ambient water-quality criteria for the protection of aquatic life, set by the U.S. Environmental Protection Agency (USEPA), described in Nowell and Resek (1994).

The Kruskal-Wallis test was used to determine whether the proportion of pesticide detections was significantly different among groups at a significance level of 0.05. The data were divided into nine groups: (1) small Boston Mountains forest, (2) small Springfield Plateau forest, (3) small Salem Plateau forest, (4) medium Springfield Plateau forest, (5) medium Salem Plateau forest, (6) small Springfield Plateau agriculture, (7) small Salem Plateau agriculture, (8) medium Springfield Plateau agriculture, and (9) medium Salem Plateau agriculture. The Kruskal-Wallis test indicated that the proportion of pesticide detections was significantly different among the groups (p-value was 0.03). The data were further analyzed using Tukey's MCT on the ranks of the data to determine which group(s) differed from the others. Tukey's MCT indicated that pesticides were detected significantly more often in streams in medium Springfield Plateau agricultural basins. This does not mean that the other treatment groups had the same proportion of pesticide detections, but the evidence is insufficient to determine if the difference was statistically significant.

As described previously, pesticide sampling was done at an increased frequency at the two intensive-fixed sites, Dousinbury Creek near Wall Street, Mo. (site 40; 24 samples), and Yocum Creek near Oak Grove, Ark. (site 18; 26 samples), to look at variations in the number of pesticide detections and concentrations through the time of most intense pesticide usage and to determine if pesticides were present throughout the year in detectable concentrations. Although samples were collected during a 1-year period (February 1994 through January 1995), most pesticide detections and maximum concentrations (fig. 9) occurred in the spring (April, May, and June). This coincides with the time of most intense pesticide usage, as well as maximum precipitation and runoff. The sample collected at site 18 in September had five pesticide detections and four maximum concentrations. This sample was collected during a rainfall-runoff event after an extended period of dry weather.

Bed Sediment

Study approach

Bed-sediment samples were collected in 1992-95 at 27 sites during the low-flow season, in late summer or early fall, to avoid effects of seasonal variability. The sample-collection design targeted fine sediments found in depositional zones of the sampling reach. No attempt was made to collect a representative cross-sectional bed-sediment sample. At least five subsamples were collected from at least 5 to 10 depositional zones at each site. These subsamples were collected using a Teflon scoop to remove the top 1 to 10 millimeters (mm) of fine sediments. All subsamples were then composited in a glass bowl for processing onsite. The composited sample was then thoroughly mixed and sieved through a stainless steel 2-mm sieve into a baked glass jar. Duplicate sediment samples were collected at three sites to assess quality control of sam-

Table 5. Occurrence of selected pesticides in small and medium, forest and agricultural basins, 1994-95

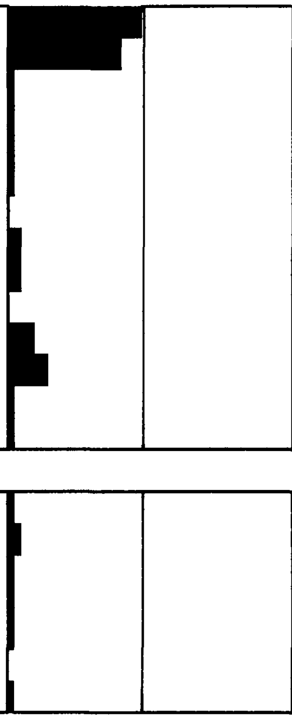
[MDL, method detection limit, in micrograms per liter; --, herbicide or insecticide not detected; <, less than; all concentrations expressed in micrograms per liter]

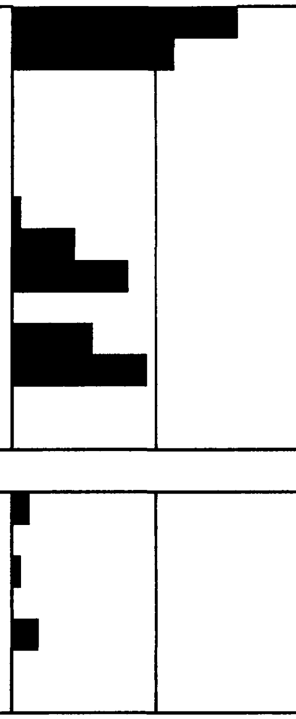
Compound		Small forest basins (9 basins; 24 samples)[1]			Medium forest basins (7 basins; 19 samples)[2]		
		Percent detections	Concentration		Percent detections	Concentration	
Herbicides	MDL	0 50 100	Median	Maximum	0 50 100	Median	Maximum
Atrazine	.001		<0.001	0.003		<0.001	0.022
Atrazine, Desethyl	.002		<.002	.004		<.002	.004
Benfluralin	.002		--	--		--	--
Butylate	.002		--	--		--	--
Cyanazine	.004		--	--		--	--
Dacthal (DCPA)	.002		--	--		--	--
EPTC	.002		--	--		--	--
Metolachlor	.002		<.002	.002		<.002	.005
Prometon	.018		--	--		--	--
Propanil	.004		--	--		<.004	.006
Simazine	.005		--	--		--	--
Tebuthiuron	.01		<.01	.007		<.01	.029
Terbacil	.007		--	--		--	--
Trifluralin	.002		<.002	.004		--	--
Insecticides							
Carbaryl	.003		--	--		--	--
Carbofuran	.003		--	--		--	--
Chlorpyrifos	.004		--	--		--	--
p,p'-DDE	.006		<.006	.005		<.006	.004
Diazinon	.002		<.002	.003		--	--
Dieldrin	.001		<.001	.004		--	--
cis-Permethrin	.005		<.005	.001		<.005	.001

Table 5. Occurrence of selected pesticides in small and medium, forest and agricultural basins, 1994-95—Continued

[MDL, method detection limit, in micrograms per liter; --, herbicide or insecticide not detected; <, less than; all concentrations expressed in micrograms per liter]

Compound	MDL	Small agricultural basins (8 basins; 26 samples)[3] Concentration Median	Small agricultural basins Concentration Maximum	Medium agricultural basins (11 basins; 32 samples)[4] Concentration Median	Medium agricultural basins Concentration Maximum
Herbicides					
Atrazine	.001	0.002	0.033	0.012	0.086
Atrazine, Desethyl	.002	<.002	.009	.002	.017
Benfluralin	.002	<.002	.009	--	--
Butylate	.002	<.002	.022	--	--
Cyanazine	.004	<.004	.005	--	--
Dacthal (DCPA)	.002	<.002	.001	--	--
EPTC	.002	--	--	<.002	.003
Metolachlor	.002	<.002	.003	<.002	.047
Prometon	.018	<.018	.006	<.018	.29
Propanil	.004	--	--	--	--
Simazine	.005	<.005	.014	<.005	.14
Tebuthiuron	.01	<.01	.026	<.01	.04
Terbacil	.007	<.007	.004	--	--
Trifluralin	.002	<.002	.008	--	--
Insecticides					
Carbaryl	.003	<.003	.079	<.003	.044
Carbofuran	.003	<.003	.008	--	--
Chlorpyrifos	.004	<.004	.007	<.004	.009
p,p'-DDE	.006	<.006	.003	--	--
Diazinon	.002	<.002	.026	<.002	.017
Dieldrin	.001	--	--	--	--
cis-Permethrin	.005	<.005	.001	--	--





[1] These basins have greater than 90 percent forest land use.
[2] These basins have greater than 70 percent forest land use.
[3] These basins have greater than 50 percent agricultural land use.
[4] These basins have greater than 40 percent agricultural land use.

Pesticide	F / 2	M / 2	A / 4	M / 5	J / 4	J / 2	A / 1	S / 1	O / 1	N / 1	D / 0	J / 1
	Yocum Creek near Oak Grove, Ark. (site 18, figure 5 and table 3)											
Herbicides												
Alachlor								**1**				
Atrazine			1	1				**1**				
Atrazine, Desethyl				1				**1**	1			
Benfluralin			**1**									
Bromacil						**1**			1			
2,4-D			**1**									
Metolachlor								**1**				
Prometon					**3**							
Simazine			**1**	3	1			1				
Trifluralin			**1**									
Insecticides												
Carbaryl					**1**							
p,p'-DDE		1	**1**									
Diazinon					**1**							

Pesticide	F / 2	M / 2	A / 4	M / 4	J / 5	J / 2	A / 1	S / 1	O / 0	N / 1	D / 1	J / 1
	Dousinbury Creek near Wall Street, Mo. (site 40, figure 5 and table 3)											
Herbicides												
Alachlor			**1**									
Atrazine			**2**	1	4							
Atrazine, Desethyl			**1**	2	1							
2,4-D						**1**						
Metolachlor			**2**									
Molinate			**1**									
Insecticides												
Carbofuran			**1**	2								
Diazinon			**1**									

Column headings: Month/Number of Samples

EXPLANATION

1 — Number of pesticide detections

1 (shaded) — Month during which maximum concentration of indicated pesticide occurred

Figure 9. Pesticide detections by month at intensive-fixed sites, 1994-95.

ple collection and laboratory procedures. Organic-compound concentrations in the duplicate samples were mostly below, or so close to, the MDL that differences were not practically significant. The bed-sediment collection strategy and methods are described in Shelton and Capel (1994).

Results

Bed-sediment samples were analyzed for 95 organic compounds (tables 6 and 7). Forty-six organic compounds were detected in 30 samples from the 27 sampling sites (table 6); 49 compounds had concentrations below the method detection limit for all samples (table 7). Two compounds, bis-2-ethylhexyl-phthalate and di-n-butylphathalate, were detected in every sample and are probably laboratory or field processing contaminants, except for the samples that had concentrations well above background levels: sample having a bis-2-ethylhexyl-phthalate concentration of 260 micrograms per kilogram (µg/kg) collected at the Illinois River near Tahlequah, Okla. (site 4) and samples having a bis-2-ethylhexyl-phthalate concentration of 230 µg/kg and a di-n-butylphathalate concentration of 120 µg/kg collected at the Marmaton River near Marmaton, Kans. (site 44).

Most of the organic compounds (63 percent) detected at the sites had maximum concentrations less than 100 µg/kg. Eleven of the 18 compounds detected at five or more sites were polycyclic aromatic hydrocarbons (PAH). The compound 2,6-dimethylnaphthalene, one of the PAH having the greatest number of detections, was detected in samples from 12 of 27 sites. The maximum concentration of 2,6-dimethylnaphthalene was 130 µg/kg, collected in a sample from site 4. Three compounds detected in samples from site 4 had concentrations that exceeded 250 µg/kg: p-cresol (2,800 µg/kg), butylbenzylphthalate (420 µg/kg), and bis-2-ethylhexyl-phthalate (260 µg/kg). These compounds are generally found in coal tar, crude oils, incomplete combustion products of fossil fuels or forest fires, or in machinery such as vacuum pumps.

Sites with detected compounds show no apparent systematic distribution, with respect to both physiography and land use, throughout the study unit. Sites with 12 or more organic compounds detected (fig. 10) are located in each physiographic area and major land-use category. Seventeen or more compounds were

Table 6. Summary of organic compounds detected at bed-sediment sampling sites for water years 1992-95

[µg/kg, micrograms per kilogram; MAH, monocyclic aromatic hydrocarbon; PAH, polycyclic aromatic hydrocarbon; OC, organochlorine; E, estimated value]

Compound		Number of		Maximum	
Name	Class	sites	sites with a detectable concentration	concentration (µg/kg)	method detection limit[1]
1,2 Dimethylnaphthalene	PAH	27	2	E6.0	50
1,6 Dimethylnaphthalene	PAH	27	3	160	50
1, Methyl 9H fluorene	PAH	27	1	E20	50
1, Methylphenanthrene	PAH	27	5	150	50
1, Methylpyrene	PAH	27	2	E47	50
2,3,6 Trimethylnaphthalene	PAH	27	3	E22	50
2,6 Dinitrotoluene	MAH	27	1	E14	500
2,6 Dimethylnaphthalene	PAH	27	12	130	50
2, Ethylnaphthalene	PAH	27	3	E12	50
2, Methylanthracene	PAH	27	2	E32	50
4,5 Methylenephenanthrene	PAH	27	2	63	50
4, Bromophenyl phenylether	Brominated ether	27	1	E26	50
4, Chloro-3,methylphenol	Phenol	27	1	E30	50

Table 6. Summary of organic compounds detected at bed-sediment sampling sites for water years 1992-95--Continued

[µg/kg, micrograms per kilogram; MAH, monocyclic aromatic hydrocarbon; PAH, polycyclic aromatic hydrocarbon; OC, organochlorine; E, estimated value]

Compound		Number of		Maximum	
Name	Class	sites	sites with a detectable concentration	concentration (µg/kg)	method detection limit[1]
4, Chlorophenyl-phenylether	Chlorinated ether, OC	27	1	E24	50
9H, Carbazole	PAH	27	1	E20	50
9H, Fluorene	PAH	27	2	E20	50
Acenaphthene	PAH	27	2	E11	50
Acenaphthylene	PAH	27	2	E22	50
Anthracene	PAH	27	5	50	50
Anthraquinone	PAH	27	1	E44	50
Azobenzene	Mono-aromatic nitrogen	27	1	E29	50
Benzo(a) anthracene	PAH	27	9	84	50
Benzo(b) fluoranthene	PAH	27	10	110	50
Benzo(g,h,i) perylene	PAH	27	1	88	50
Benzo(k) fluoranthene	PAH	27	8	94	50
Benzo(a) pyrene	PAH	27	5	180	50
Bis-2-ethylhexyl-phthalate	Phthalate	27	27	260	50
Butylbenzylphthalate	Phthalate ester	27	16	420	50
Cis-chlordane	OC	27	1	1.1	1.0
Trans-chlordane	OC	27	1	1.1	1.0
Chrysene	PAH	27	9	130	1.0
Dibenzothiophene	PAH	27	3	60	50
Di-n-butylphthalate	Phthalate ester	27	27	120	50
Dibenzo(a,h) anthracene	PAH	27	1	64	50
Diethyl phthalate	Phthalate ester	27	8	E23	50
Dimethyl phthalate	Phthalate ester	27	2	E7	50
Di-n-octyl phthalate	Phthalate ester	27	2	120	50
Fluoranthene	PAH	27	12	130	50
Indeno(1,2,3-c,d) pyrene	PAH	27	6	110	50
N-nitrosodiphenylamine	Nitrosoamine	27	2	E27	50
Nitrobenzene	MAH	27	1	E14	50
Trans-nonachlor	OC	27	1	1.7	1.0
p-Cresol	Phenol	27	15	2,800	50
Phenanthrene	PAH	27	9	190	50
Phenol	Phenol	27	19	140	5.0
Pyrene	PAH	27	12	120	50

[1]The method detection limit (MDL) is the smallest concentration of a compound that can be reliably detected by a particular analytical method.

Table 7. Organic compounds analyzed for, but not detected in samples collected at bed-material sampling sites for water years 1992-95

[MAH, monocyclic aromatic hydrocarbon; PAH, polycyclic aromatic hydrocarbon; OC, organochlorine; PCB, polychlorinated biphenyl]

Compound		Compound	
Name	**Class**	**Name**	**Class**
1,2 Dichlorobenzene	MAH	*o,p*'-DDT	OC
1,3 Dichlorobenzene	MAH	Dieldrin	OC
1,4 Dichlorobenzene	MAH	Endosulfan I	OC
1,2,4 Trichlorobenzene	MAH	Endrin	OC
2,2' Biquinoline	PAH	Heptachlor epoxide	OC
2,4 Dinitrotoluene	MAH	Heptachlor	OC
2, Chlorophenol	Phenol	Isoquinoline	Araarene
2, Chloronaphthalene	PAH	Isodrin	OC
3,5 Dimethylphenol	Phenol	Isophorone	Base neutral acid
Acridine	Araarene	Lindane	OC
Aldrin	OC	*o,p*'-Methoxychlor	OC
c8, Alkyl phenol	Phenol	*p,p*'-Methoxychlor	OC
Bis (2, chloroethoxy) methane	Ether, OC	Mirex	OC
Benzo(c) quinoline	PAH	N-nitroso-di-n-propylamine	Nitrosoamine
Alpha BHC	OC	Naphthalene	PAH
Beta BHC	OC	*Cis*-nonachlor	OC
Chlorneb	OC	*Cis*-permethrin	OC
Pentachloronitrobenzene	Aromatic, MAH, OC	*Trans*-permethrin	OC
Hexachlorobenzene	Aromatic, OC	Oxychlordane	OC
Dachtal (DCPA)	OC	PCB's, total	PCB
p,p'-DDD	OC	Pentachloroanisole	Aromatic, MAH, OC
o,p'-DDD	OC	Phenanthridine	PAH
o,p'-DDE	OC	Quinoline	Araarene
p,p'-DDE	OC	Toxaphene	OC
p,p'-DDT	OC		

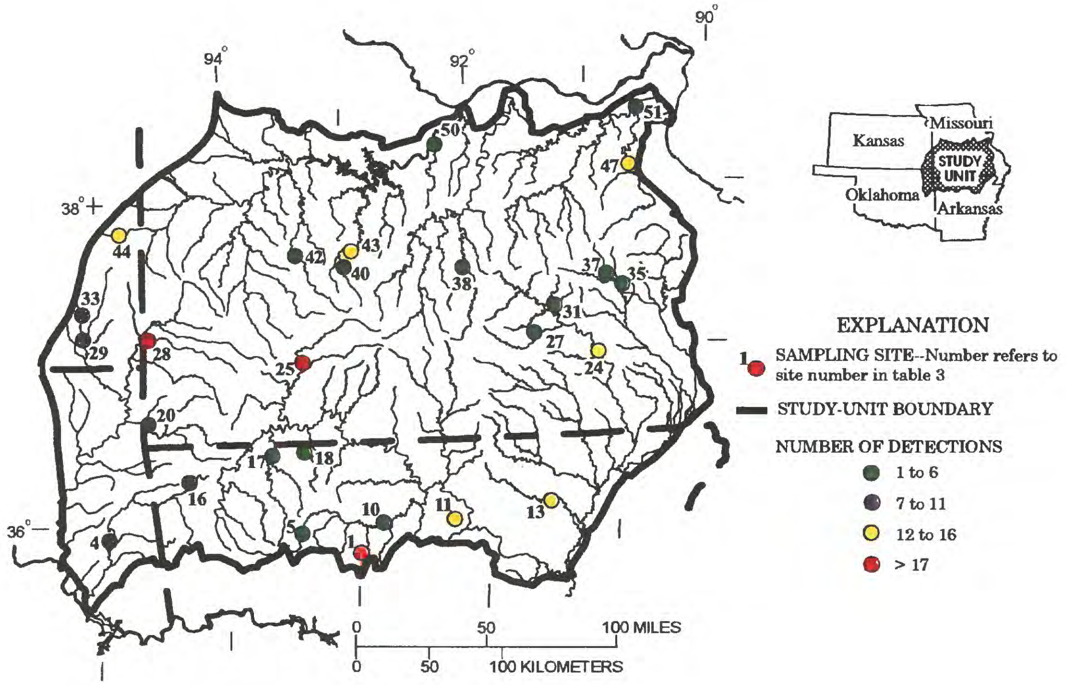


Figure 10. Number of organic compounds detected at bed-sediment sampling sites, 1992-95.

detected in samples from 3 of the 27 sites; the basins for 2 of the 3 sites have urban land uses.

The three sites with detections of 17 or more organic compounds are: James River near Boaz, Mo. (site 25), Richland Creek near Witts Spring, Ark. (site 1), and Center Creek near Smithfield, Mo. (site 28). Thirty-nine compounds were detected in samples collected at site 25; most of the detections were PAH and chlordane compounds. Five compounds with concentrations greater than 100 µg/kg were detected at site 25: p-cresol (130 µg/kg), fluoranthene (130 µg/kg), chrysene (120 µg/kg), indeno(1,2,3-c,d) pyrene (110 µg/kg), and pyrene (110 µg/kg). The drainage basin for site 25 is located in the Springfield Plateau and includes the city of Springfield, Mo., the largest urban area in the study unit. Twenty-three compounds, most frequently the mono- and polycyclic aromatic hydrocarbons compounds, were detected in the sample from site 1. Butylbenzylphthalate (50 µg/kg) was the compound having the maximum concentration in the sample collected at site 25. The drainage basin for site 1 is located in the Boston Mountains and the basin is 97 percent forest. A definitive explanation has not been determined for the large number of compounds detected at site 1; a possible explanation is that solvents associated with furniture refinishing were disposed of upstream from the location of the sampling site (J.L. Dixon, U.S. Forest Service, oral commun., 1996). Seventeen compounds, most frequently the PAH compounds, were detected in samples collected at site 28. The only compound detected at site 28 with a concentration greater than 100 µg/kg was p-cresol (1,300 µg/kg). The drainage basin for site 28 is located in the Springfield Plateau and the basin includes mining, urban, and industrial land uses.

No concentration of organic compounds detected in bed-sediment samples exceeded the sediment quality criteria set by the USEPA (Nowell and Resek, 1994).

Biological Tissue

Study Approach

Biological-tissue samples were collected once in 1992-1995 at 23 bed-sediment sampling sites and twice at 3 sites (sites 11,13, and 43) in conjunction with the bed-sediment sampling effort (biological tissue was not collected at site 42, Pomme de Terre River near Polk, Mo.). *Corbicula fluminea*, the Asiatic clam found throughout southern and western United States, was selected as the target organism for the NAWQA Program biological-tissue study. If *C. fluminea* was not found at a site, a fish species was selected for tissue sampling. Fish species on the NAWQA national target list (Crawford and Luoma, 1993) are not widespread or abundant at most sites in the study unit; therefore, the longear sunfish (an abundant and widespread invertivore) was sampled at several sites. *C. fluminea* tissue samples were collected at 11 sampling sites, whole-fish tissue samples from *Lepomis megalotis* (longear sunfish), *Micropterus dolomieu* (smallmouth bass), and *Hypentelium nigricans* (northern hog sucker), were collected at 17 sites, and a tissue sample from *Amblema plicata* (three-ridge mussel) was collected at 1 site. Samples using both *C. fluminea* and fish were collected at three sites to assess species-to-species variation at a site. No compounds exceeded their detection limits at the sites where both *C. fluminea* and fish were collected; therefore, the data were not sufficient to assess species-to-species variation. Duplicate tissue samples were collected at three sites to assess quality control of sample collection and laboratory procedures. No compounds exceeded their detection limits at the sites where duplicate tissue samples were collected; therefore, the data were not sufficient to statistically assess quality-control procedures. (However, replication of less-than-detection-limit concentrations for the duplicate tissue samples indicates that no sources of contamination were introduced by sampling or laboratory procedures). Each organism was identified, weighed, and measured as part of the collection process. Detailed procedures for collecting and processing of biological-tissue samples are described in Crawford and Luoma (1993).

Results

Biological-tissue samples were analyzed for 26 organic compounds (table 8). Only four compounds, in samples from 2 of 26 sites, were detected. *C. fluminea* tissue from the Osage River near St. Thomas, Mo. (site 50) had a measurable concentration, 0.0052 milligram per kilogram (mg/kg), of *p,p'*-DDT. Because the Osage River site drains a portion of the Osage Plains (row crop agriculture), finding *p,p'*-DDT was not unexpected. The concentration of *p,p'*-DDT in tissue collected at site 50 is well below the recommended maximum concentration (1.0 mg/kg) for the protection

Table 8. Summary of organic compounds analyzed for, and detected, at biological-tissue sampling sites for water years 1992-95

[OC, organochlorine; compounds detected are shown in bold type]

Compound		Compound	
Name	**Class**	**Name**	**Class**
Aldrin	OC	Hepachlor	OC
Alpha BHC	OC	Hepachlor epoxide	OC
Beta BHC	OC	Hexachlorobenzene	Aromatic, OC
Delta BHC	OC	Lindane	OC
***Cis*-chlordane**	OC	*o,p'*-Methoxychlor	OC
***Trans*-chlordane**	OC	*p,p'*-Methoxychlor	OC
Dachtal (DCPA)	OC	Mirex	OC
o,p'-DDD	OC	*Cis*-nonachlor	OC
p,p'-DDD	OC	***Trans*-nonachlor**	OC
o,p'-DDE	OC	Oxychlordane	OC
o,p'-DDT	OC	Pentachloroanisole	Aromatic, MAH, OC
***p,p'*-DDT**	OC	PCB	PCB
Endrin	OC	Toxaphene	OC

of fish-eating wildlife set by the U.S. Environmental Protection Agency (Nowell and Resek, 1994).

C. fluminea tissue from the James River near Boaz, Mo. (site 25) had measurable concentrations of *cis*-chlordane (0.0051 mg/kg), *trans*-chlordane (0.0096 mg/kg), and *trans*-nonachlor (0.0076 mg/kg). These compounds are frequently found near urban areas such as the James River site. The concentration of total chlordane (*cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor) residues sum, 0.0223 mg/kg, in tissue collected at site 25 is less than the national standards and guidelines recommended maximum concentration (0.1 mg/kg) for the protection of fish-eating wildlife set by the USEPA (Nowell and Resek, 1994).

SUMMARY

This report includes an overview of the environmental setting of the Ozark Plateaus study unit, a summary of pesticide-use data for 1987-91, a description of the surface-water, bed-sediment, and biological-tissue sampling networks, and an assessment of conditions using statistical summaries of organic-compound data collected during water years (October 1 through September 30) 1992-95.

Approximately 4.9 million pounds of active ingredients per year from 130 pesticides were applied on 25 crop types within the study unit from 1987-91. Only 6 of the 130 pesticides were used extensively throughout the study unit and these account for approximately 56 percent of the total pesticides applied. Pesticide use generally was greatest in areas where the dominant land use was pastureland areas in the Springfield and Salem Plateaus and in cropland areas in the Osage Plains and Mississippi Alluvial Plain. The most frequently applied pesticide in the study unit was 2,4-D. Atrazine was the second most frequently applied pesticide.

Five crop types--corn, pasture, rice, sorghum, and soybeans--received approximately 85 percent of the pesticides applied within the study unit. The highest pesticide use on these crops occurred in the Mississippi Alluvial Plain and Osage Plains. Pastureland located in the Springfield and Salem Plateaus received moderate amounts of pesticides. Forestland and pastureland in the Boston and St. Francois Mountains received the least amounts of pesticides. Pastureland was the crop type that received the greatest amount of pesticides in 53 of the 96 counties in the study unit based on crop estimates accompanying the pesticide-use data.

The surface-water (basic-fixed, intensive-fixed, and synoptic), bed-sediment, and biological-tissue sampling networks are represented by 51 sites. The drainage basins of most sites are located in the Salem (22 sites) and Springfield (15 sites) Plateaus. The predominant land use of basins in the sampling networks is forest (22 sites) and agricultural (19 sites).

The basic-fixed network consists of 12 sites located primarily in small and medium drainage basins with near-homogenous land uses (primarily agricultural or forest). The drainage basins of most basic-fixed sites are located in the Salem Plateau (4 sites) and Springfield Plateau (4 sites). Samples for pesticide analysis were collected at the basic-fixed sites once in 1994 and three times in 1995.

The intensive-fixed network consists of two sites in small agricultural land-use basins in the Springfield and Salem Plateaus. The intensive-fixed sites had an increased sample-collection frequency in comparison with the other networks---biweekly samples were collected in February, March, and July 1994; weekly samples in April, May, and June 1994; and monthly samples in August through December 1994 and January, April, May, and June 1995.

The synoptic network consists of 29 sites located primarily in small and medium drainage basins with near-homogenous land uses (primarily agricultural or forest). The drainage basins of most synoptic sites are located in the Salem Plateau (14 sites) and Springfield Plateau (10 sites). Pesticide samples were collected at the synoptic sites during a high-flux period (May or June) in 1994 and 1995.

The bed-sediment and biological-tissue network consists of 27 sites located primarily in small and medium drainage basins with near-homogenous land uses (primarily agricultural or forest). The drainage basins of most bed-sediment and biological-tissue sites are located in the Salem Plateau (10 sites) and Springfield Plateau (7 sites). One sample for organic-compounds analysis was collected at most bed-sediment and biological-tissue sampling sites.

A total of 157 surface-water samples were analyzed for up to 82 pesticides. Of the 54 herbicides and 28 insecticides analyzed, 19 herbicides and 7 insecticides were detected in at least 1 sample. The most commonly detected herbicide (63 samples) was atrazine. Five other pesticides--desethylatrazine, tebuthiuron, prometon, metolachlor, and simazine--were detected in 15 or more samples. The most commonly detected insecticide (13 samples) was *p,p'*-DDE. Two other insecticides, diazinon and *cis*-permethrin, were detected in seven or more samples.

Pesticides were detected at 39 of 43 surface-water sites. Yocum Creek near Oak Grove, Ark., a small, agricultural basin in the Springfield Plateau, was the surface-water site that had the most pesticides (13) detected in the sampling network. Woods Fork near Hartville, Mo., a small, agricultural basin in the Salem Plateau, had the most pesticides (10) detected in a single sample. The Illinois River near Tahlequah, Okla., a medium, agricultural basin in the Springfield Plateau, had 20 pesticide detections in four samples. Seventeen other sites, predominantly in agricultural basins, had samples with 6 or more pesticide detections.

Pesticide data collected at surface-water sites were analyzed according to land use and drainage area. The largest number (18) of the 21 different pesticides detected was in small, agricultural basins; the largest percentage of detections (about 80) of a single pesticide (atrazine) was in medium, agricultural basins. Pesticide concentrations were small, and in most cases, at or near the detection limit. Maximum concentrations ranged from 0.001 to 0.007 micrograms per liter (µg/L) at small, forest sites; 0.001 to 0.029 µg/L at medium, forest sites; 0.001to 0.079 µg/L at small, agricultural sites; and 0.003 to 0.29 µg/L at medium, agricultural sites. Results from the Kruskal-Wallis test indicate the proportion of pesticide detections in groupings of stream basins (grouped by physiography, land use, and drainage area) was significantly different at a 0.05 significance level. Results from Tukey's Multiple Comparison Test indicate pesticides were detected significantly more often in streams in medium, Springfield Plateau agricultural basins.

Bed-sediment samples were analyzed for 95 organic compounds. Forty-six organic compounds were detected in samples from 27 sampling sites. Eleven of the 18 compounds detected at 5 or more sites were polycyclic aromatic hydrocarbons (PAH). The PAH compound 2,6-dimethylnaphthalene, which had the greatest number of detections in concentrations noticeably above background levels, was detected in samples from 12 of 27 sites. The maximum concentration of 2,6-dimethylnaphthalene was 130 micrograms per kilogram (µg/kg), detected in a sample collected at the Illinois River near Tahlequah, Okla. Most compounds (63 percent) had maximum concentrations less than 100 µg/kg. However, three compounds---p-cresol, butylbenzylphthalate, and bis-2-ethylhexyl-phthalate--all detected in samples collected at the Illinois River near Tahlequah, Okla. had concentrations that exceeded 250 µg/kg. Sites with detected compounds show no apparent systematic distribution, with respect to both physiography and land use, throughout the study unit. Seventeen or more compounds were detected in samples collected at three sites: 39 compounds, most frequently the PAH and the chlordane compounds, were detected in samples collected at the James River near Boaz, Mo.; 23 compounds, most frequently the mono- and polycyclic aromatic hydrocarbons compounds, were detected in samples collected at Richland Creek near Witts Spring, Ark.; 19 compounds, most frequently the PAH compounds, were detected in samples collected at Center Creek near Smithfield, Mo.

Biological-tissue samples were analyzed for 26 organic compounds. Four compounds, in samples from two sites, were detected in biological tissue. Biological-tissue samples at only 2 of the 25 sites had measurable concentrations of organic compounds: *C. fluminea* tissue from the Osage River near St. Thomas, Mo. had a concentration of 0.0052 mg/kg (milligram per kilogram) of *p,p'*-DDT; *C. fluminea* tissue from the James River near Boaz, Mo. had concentrations of *cis*-chlordane (0.0051 mg/kg), *trans*-chlordane (0.0096 mg/kg), and *trans*-nonachlor (0.0076 mg/kg).

No pesticides that were detected in surface-water samples exceeded the maximum contaminant level or the lifetime health-advisory level for drinking water, or the ambient water-quality criteria for the protection of aquatic life set by the U.S. Environmental Protection Agency (USEPA). No organic compounds that were detected in bed-sediment samples exceeded the sediment quality criteria set by the USEPA. No organic compounds that were detected in biological-tissue samples exceeded the recommended maximum concentrations for the protection of fish-eating wildlife set by the USEPA. Based on this information, organic compounds do not pose any widespread or persistent problems in the study unit.

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