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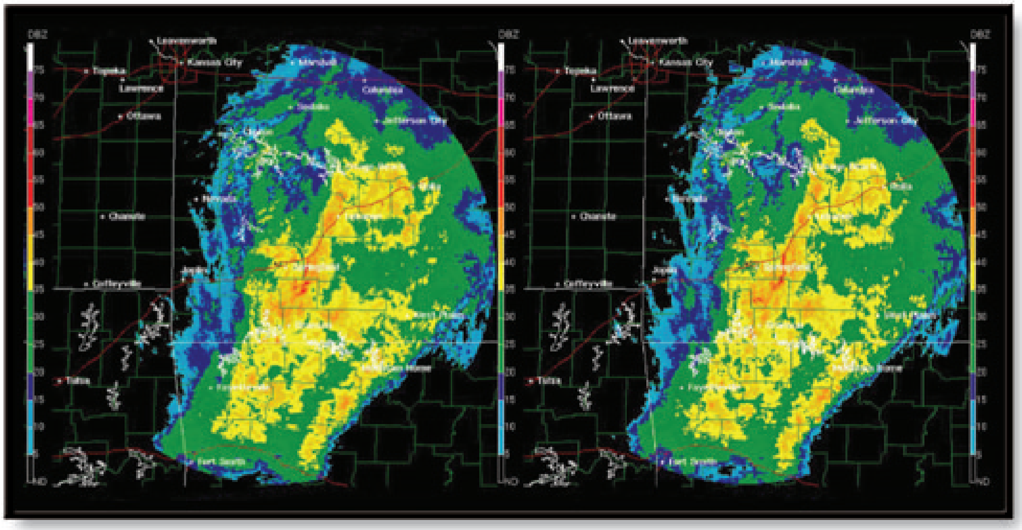
Water Quality, Selected Chemical Characteristics, and Toxicity of Base Flow and Urban Stormwater in the Pearson Creek and Wilsons Creek Basins, Greene County, Missouri, August 1999 to August 2000

Water-Resources Investigations Report 02–4124



Prepared in cooperation with the
Missouri Department of Natural Resources,
Division of Environmental Quality

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

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Water Quality, Selected Chemical Characteristics, and Toxicity of Base Flow and Urban Stormwater in the Pearson Creek and Wilsons Creek Basins, Greene County, Missouri, August 1999 to August 2000

By Joseph M. Richards *and* B. Thomas Johnson

Abstract

The chemistry and toxicity of base flow and urban stormwater were characterized to determine if urban stormwater was degrading the water quality of the Pearson Creek and Wilsons Creek Basins in and near the city of Springfield, Greene County, Missouri. Potentially toxic components of stormwater (nutrients, trace metals, and organic compounds) were identified to help resource managers identify and minimize the sources of toxicants.

Nutrient loading to the James River from these two basins (especially the Wilsons Creek Basin) is of some concern because of the potential to degrade downstream water quality. Toxicity related to dissolved trace metal constituents in stormwater does not appear to be a great concern in these two basins. Increased heterotrophic activity, the result of large densities of fecal indicator bacteria introduced into the streams after storm events, could lead to associated dissolved oxygen stress of native biota. Analysis of stormwater samples detected a greater number of polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) than were present in base-flow samples. The number and concentrations of pesticides detected in both the base-flow and stormwater samples were similar.

Genotoxicity tests were performed to determine the bioavilability of chemical contaminants and determine the potential harmful effects on aquatic biota of Pearson Creek and Wilsons Creek. Genotoxicity was determined from dialysates from both long-term (approximately 30 days) and storm-event (3 to 5 days) semipermeable membrane device (SPMD) samples that were collected in each basin. Toxicity tests of SPMD samples indicated evidence of genotoxins in all SPMD samples. Hepatic activity assessment of one long-term SPMD sample indicated evidence of contaminant uptake in fish. Chemical analyses of the SPMD samples found that relatively few pesticides and pesticide metabolites had been sequestered in the lipid material of the SPMD; however, numerous PAHs and VOCs were detected in both the long-term and the storm-event exposures. It is suspected, based on the compounds detected in the SPMDs and the water samples, that the observed genotoxicity is largely the result of PAHs and VOCs that were probably derived from petroleum inputs or combustion sources. Therefore the water quality and thus the aquatic environments in the Pearson Creek and Wilsons Creek Basins are being degraded by urban derived contaminants.

INTRODUCTION

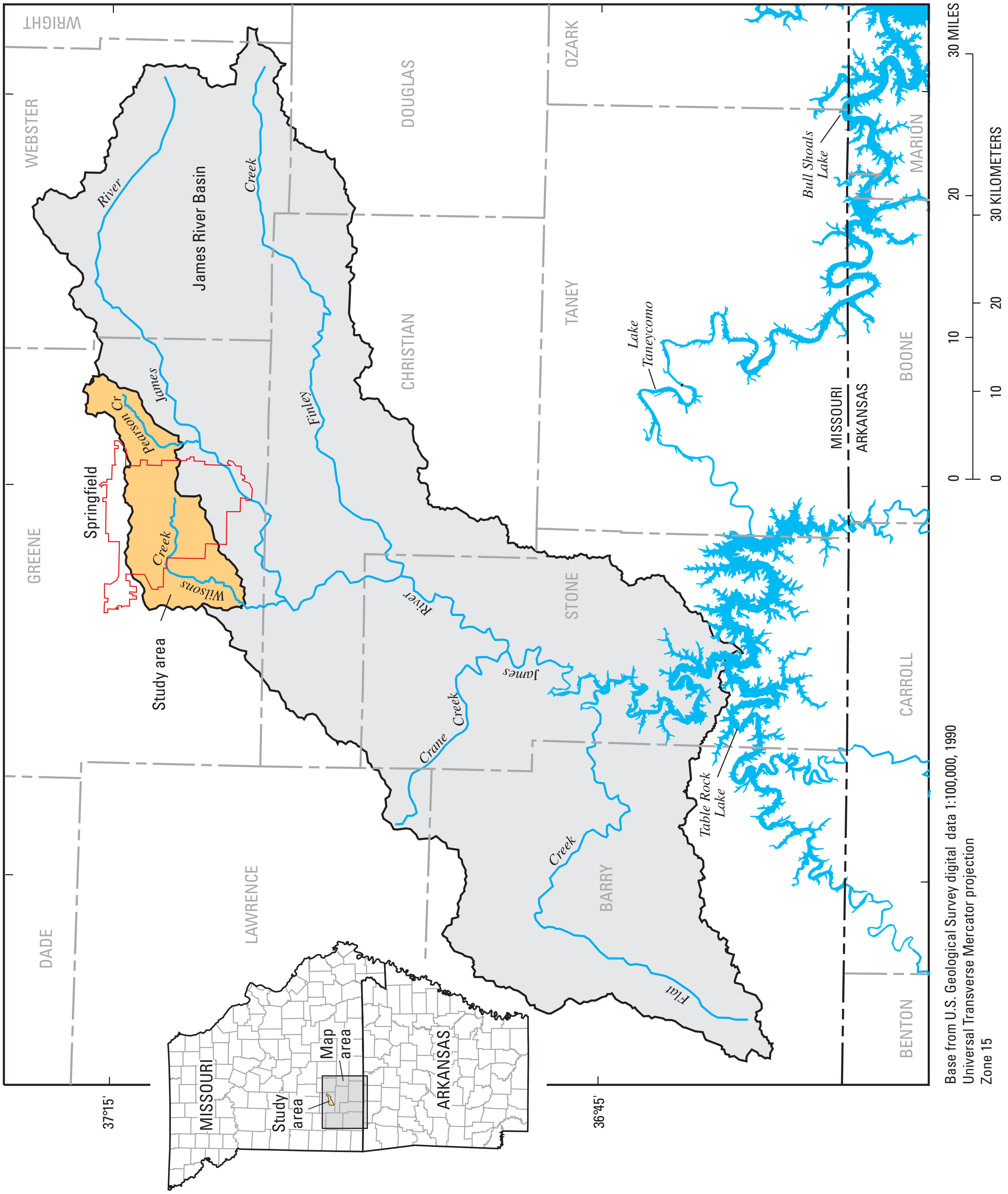
Urban areas affect the hydrologic characteristics and water quality of streams in many ways. The large amounts of impervious surface (for example, roof tops, parking lots, and roads) in urban areas increases the amount of runoff to urban streams because of the decreased infiltration capacity of the surface and because of the lack of obstructions to block the flow of water. In addition, the large population concentrated in urban areas means more automobiles with corresponding emissions, more construction, industrial effluent, wastewater effluent, more chemicals used for pest control, maintenance of road sides, golf courses, and utility rights of way. Because of the accumulation of chemicals on impervious surfaces, home lawns and gardens, golf courses, parks, and recreation areas, storm events could potentially move large amounts of chemicals into surface waters and degrade the water quality of those surface waters. Storm events can improve water quality by diluting point sources such as wastewater treatment plants or industrial effluents. Water-resource managers need reliable information on the effects of urban areas on water quality to manage those resources wisely.

Springfield is the third largest city in Missouri with a 2000 population of 151,580, and has grown 7.9 percent during the last 10 years (U.S. Census Bureau, 2001a). The surrounding Greene County has a 2000 population of 240,391 and has grown 15.6 percent since 1990 (U.S. Census Bureau, 2001b). Greene County is expected to have a population increase of about 65,000 by the year 2020 (Vision 20/20, City of Springfield, written commun., 1996). Springfield is located in southwest Missouri and lies mostly within the James River Basin (fig. 1). Pearson Creek and Wilsons Creek, both tributaries of the James River, receive most of the Springfield urban stormwater runoff. Based on the expansion in urban areas and the increasing population in the Springfield area, streams and rivers receiving stormwater and other discharges may show adverse water-quality effects.

Section 303(d) of the Federal Clean Water Act requires that each state identify those stream segments with documented pollution problems for which existing required pollution controls are not adequate to implement the state water-quality standards. For these impaired stream segments, states are required to establish total maximum daily loads (TMDLs) of the identified pollutant. A TMDL specifies the maximum amount of the identified pollutant allowed to be present in a water body, allocates allowable pollutant loads among sources, and provides the basis for attaining or maintaining water-quality standards within the affected water body. Pearson Creek, Wilsons Creek, and the James River are listed on Missouri's 303 (d) list for development of TMDLs. Pearson Creek and Wilsons Creek are listed as having unknown toxicity with affected reach lengths of 1.5 and 14 river miles, respectively, and are major contributors to the James River water budget. If these streams carried a substantial load of contaminants this could lead to serious water-quality concerns for the James River. The James River is one of the main water sources for Table Rock Lake and has been implicated as a source of increased nutrient loading to the lake (D. Sheridan, James River Basin Partnership, oral commun., 2000). A 57-river-mile reach of the James River is considered a high priority by the Missouri Department of Natural Resources for establishing TMDLs for nutrients and other unknown toxic constituents.

Pearson Creek is on the eastern side of Springfield in an area of growing urbanization. Because of the karst nature of the area, runoff from the commercialized areas to the west is captured by sinkholes and routed through complex natural conduits to Jones Spring, which becomes a tributary to Pearson Creek. Studies of the diversity of macroinvertibrate fauna in Pearson Creek suggest a decline in overall ecosystem health (N.W. Youngsteadt, City Utilities of Springfield, written commun., 1995, 1999). Whereas the sensitivity of this stream has been noted, no studies have been done to directly assess the water quality of Pearson Creek and to determine the nature of the alleged unknown toxicity.

Wilsons Creek and its tributaries drain a large part of Springfield and have shown adverse water-quality effects over the last several decades. Harvey and Skelton (1968) described the hydrology of Wilsons Creek and its relation to Rader Spring during base-flow and stormflow conditions. Results of this study indicate that a substantial part of the discharge from Rader Spring contains effluent from the Southwest Wastewater Treatment Plant (SWWWTP). This study also notes that seismic testing indicates numerous caves and fissures not apparent from topography that can carry and store large quantities of water and contaminants. A Federal Water Pollution Control Administration (now known as the U.S. Environmental Protection Agency) report (1969) stated that the initial runoff during a storm event contained inorganic chemicals, nutrients, and oxygen consuming material from urbanized areas that contributed to odor problems and fish kills in Wilsons Creek. A study by Emmett and others (1978) found that summer storms combined with the wastewater effluent resulted in severe depletion of dissolved oxygen in Wilsons Creek and the James River downstream from Wilsons Creek. The results of the investigation also concluded that the upstream reach of



Base from U.S. Geological Survey digital data 1:100,000, 1990
Universal Transverse Mercator projection
Zone 15

Figure 1. Location of study area.

Wilsons Creek is affected by runoff from the city of Springfield; the downstream reach is additionally affected by wastewater effluent. Upgrades were performed to the SWWWTP in 1977 and improvements in dissolved oxygen concentrations downstream were reported by the U.S. Geological Survey (USGS; Berkas, 1980, 1982). A study in 1989 by the National Park Service determined that chronic toxicity as indicated both by community studies and by toxicity tests was confirmed in tributaries and springs in the Wilsons Creek Basin (D.R. Nimmo, National Park Service, written commun., 1993). It further concluded that the chronic toxicity was from unknown contaminants from both point sources such as the SWWWTP and nonpoint sources such as urban stormwater. Since that time, little has been done to address water-quality conditions of the urban stormwater to Wilsons Creek.

From August 1, 1999, through August 1, 2000, the USGS, in cooperation with the Missouri Department of Natural Resources, conducted a water-quality investigation that focused on nutrients, indicator bacteria, trace metal constituents, organic compounds, and toxicity in Pearson Creek and Wilsons Creek. The data were used to calculate loads of selected constituents in Pearson Creek and Wilsons Creek. The toxicity part of the study was designed to determine the bioavailability of organic chemical constituents and determine their potential harmful effects on aquatic biota of Pearson Creek and Wilsons Creek. This report presents results of the study. These results provide needed information to the regulatory community for implementing sound resource management practices.

STUDY AREA

The study area includes most of the Pearson Creek Basin and the Wilsons Creek Basin (fig. 2). The following sections describe the data collection stations, and the physiography, geology, land use/land cover, and climate of the study area.

Data Collection Stations

Six sampling sites were chosen in two different basins (Pearson Creek and Wilsons Creek) to evaluate the base-flow and stormwater quality (fig. 2, table 1). Two sites were chosen in the Pearson Creek Basin, and four sites were chosen in the Wilsons Creek Basin. All sampling sites are located in Greene County, Missouri, and in hydrologic unit 11010002. Gaging stations were collocated at the sampling sites to provide the necessary flow information needed to calculate the constituent loads.

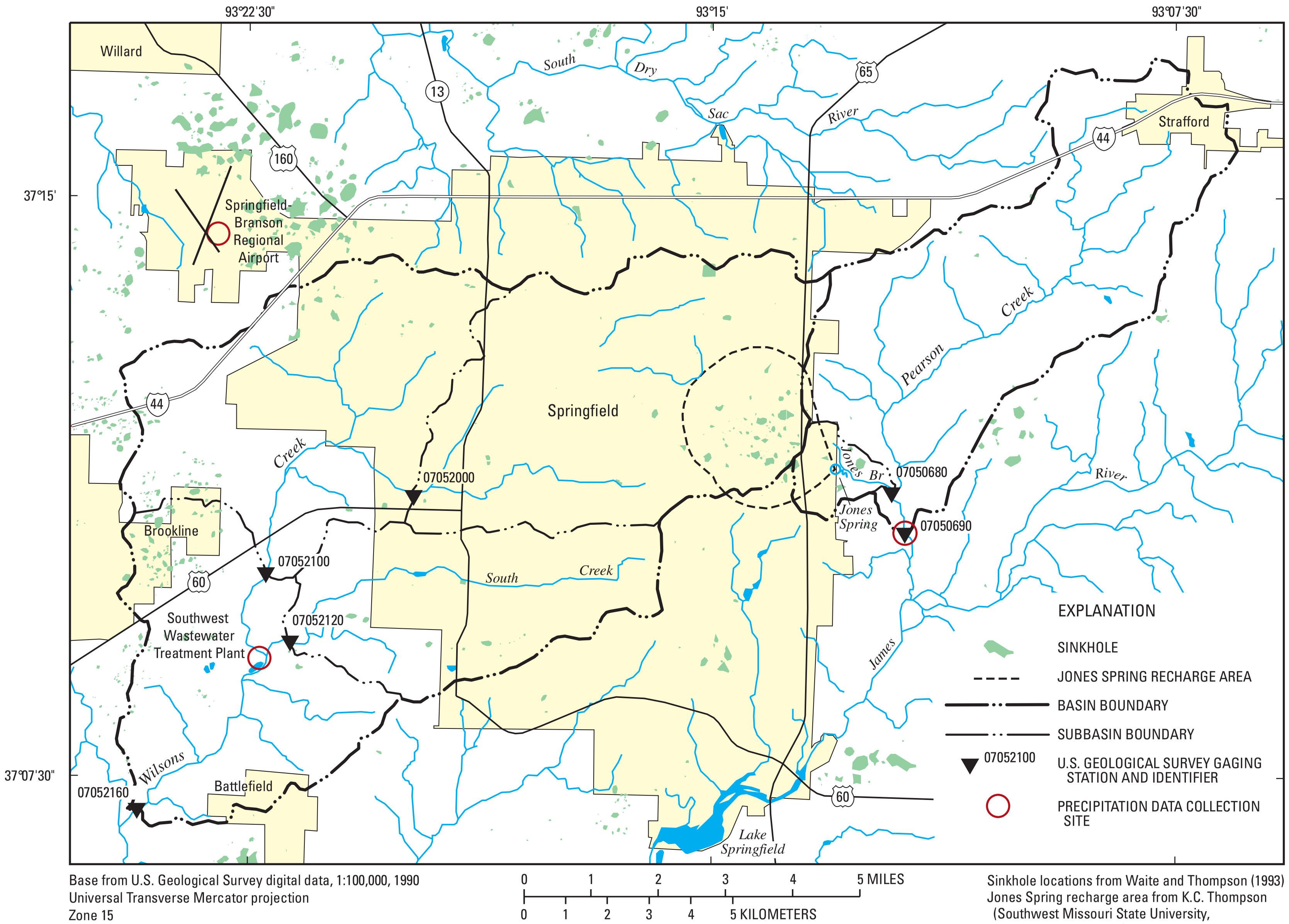
The Jones Branch continuous streamflow gaging station (hereinafter referred to as gaging station) (07050680, fig. 2, table 1) was established July 22, 1999. The control is a concrete dam at the outlet of the pond. Jones Spring provides most of the flow that passes the Jones Branch gage.

The Pearson Creek gaging station (07050690, fig. 2, table 1) was established July 21, 1999. During low flow the channel is split and is composed of rocks and gravel. The control is a gravel riffle, and both banks are low and subject to overflow.

The Wilsons Creek at Scenic Drive in Springfield gaging station (07052000, fig. 2, table 1) was established May 6, 1932, discontinued in November 1939, re-established June 28, 1973, discontinued September 23, 1982, and re-established May 27, 1998. Wastewater from commercial plants enters the creek upstream from the gaging station. The low water control is a gravel riffle downstream from the gaging station. The channel is the control for medium and high stages. The left bank is forested and sufficiently high to prevent overflow onto the road; the right bank is cultivated, and water will overflow at an extremely high stage.

The Wilsons Creek near Springfield gaging station (07052100, fig. 2, table 1) was established September 21, 1972, discontinued September 20, 1982, and re-established May 27, 1998. The gaging station is approximately 1 river mile upstream from the SWWWTP. The low water control is a solid rock riffle about 100 ft (feet) downstream from the gaging station, and the channel is the control for medium and high stages. The left bank is high, brush covered, and is not subject to overflow; the right bank is low with scattered trees, and water will overflow at about an 8-ft stage.

The South Creek gaging station (07052120, fig. 2, table 1) was established May 29, 1998. The low water control is a gravel riffle, and the channel is the control for medium and high stages. The left bank is high and is not subject to overflow; the right bank is low with some trees, and water will overflow at about an 8-ft stage.



Base from U.S. Geological Survey digital data, 1:100,000, 1990
Universal Transverse Mercator projection
Zone 15
City boundaries from U.S. Census data, 2000

Sinkhole locations from Waite and Thompson (1993)
Jones Spring recharge area from K.C. Thompson
(Southwest Missouri State University,
written commun., 1987)

Table 1. Location, drainage area, and dominant land cover type for the sampling sites in the Pearson Creek and Wilsons Creek Basins

Station name	Station number	Latitude (degrees-minutes-seconds)	Longitude (degrees-minutes-seconds)	Drainage area (square miles)	Dominant land cover type (fig. 3)
Jones Branch	07050680	37º11'12"	93º12'04"	1.29	Cool-season grassland
Pearson Creek	07050690	37º10'40"	93º11'53"	20.9	Cool-season grassland
Wilsons Creek at Scenic Drive	07052000	37º11'12"	93º19'52"	19.4	Urban impervious
Wilsons Creek near Springfield	07052100	37º10'06"	93º22'14"	35.3	Cool-season grassland
South Creek	07052120	37º09'16"	93º21'51"	10.5	Cool-season grassland
Wilsons Creek near Battlefield	07052160	37º07'02"	93º24'14"	58.2	Cool-season grassland

The Wilsons Creek near Battlefield gaging station (07052160, fig. 2, table 1) was established March 14, 1968, discontinued October 14, 1970, re-established September 20, 1972, discontinued September 16, 1982, and re-established July 22, 1999. It is downstream from the SWWWTP. The low water control is a gravel riffle in a rock bottom channel, and the channel is the control for medium and high stages. The left bank is high and is not subject to overflow; the right bank is low with some trees, and water will overflow at about a 6-ft stage.

Physiography and Geology

The study area lies on the eastern edge of the Springfield Plateau physiographic province (Fenneman, 1938). Mississippian-age carbonate rocks (mainly limestone) dominate the surficial geology of the Springfield Plateau in the study area. Small, isolated, erosional remnants of Pennsylvanian-age sandstone and shale crop out in the southwest part of the study area. Land-surface altitudes range from near 1,095 ft above sea level to more than 1,500 ft. A topographic ridge that trends from east-central Greene County to western Christian County and passes through Springfield forms a main drainage divide (figs. 1 and 2). Streams in the study area generally follow courses that trend to the southwest. The headwaters of Wilsons Creek are in the city of Springfield, and the headwaters of Pearson Creek are east of Springfield near the city of Strafford.

The bedrock limestones and cherty limestones are fractured and extensively weathered. Photolineament interpretations suggest probable joint structure and fracture patterns in a northwest to southeast and northeast to southwest orientation (Waite and Thompson, 1993). Locally, these joint patterns have been observed to have some solutional enlargement and are suspected to be conduits for subsurface water (K.C. Thompson, Southwest Missouri State University, written commun., 1987).

Surface expressions of the weathering of the carbonate rocks are most prominently displayed as karst topography. The karst topography in the study area consists of features such as springs, sinkholes, caves, solution enlarged fractures, and losing streams. An area with a sinkhole density of greater than 10 sinkholes per 100 mi^2 (square miles) is classified by Harvey (1980) as an area of primary karst, such as the Pearson and Wilsons Creek Basins. Sinkholes are so prevalent in the Springfield urbanized area that they are sometimes used as stormwater conduits. All of the subbasins in the study area contain sinkholes (fig. 2) and have the potential of rerouting surface flow from one surface drainage to another through the ground-water system.

An example of this phenomenon was identified by a study conducted on the Jones Spring recharge area (K.C. Thompson, Southwest Missouri State University, written commun., 1987, 1988). Most of the surface flow in the Jones Branch subbasin of the Pearson Creek Basin (fig. 2), comes from Jones Spring. The surface drainage area of Jones Branch determined from a topographic map is 1.29 mi^2. The approximate recharge area of Jones Spring (fig. 2) determined from dye trace experiments was 3.95 mi^2 (K.C. Thompson, Southwest Missouri State University, written commun., 1987, 1988). As a result of the karst recharge to Jones Spring, Jones Branch captures some runoff from the adjacent Pearson Creek, Wilsons Creek, and James River Basins.

Land Use/Land Cover and Climate

The study area consists of most of two main Basins (Pearson Creek and Wilsons Creek) that drain the city of Springfield and surrounding rural areas. In 1999, the National Aeronautics and Space Administration contracted Positive Systems, of Whitefish, Montana, to collect 1-m (meter)-resolution multispectral imagery using the Airborne Data Acquisition and Registration (ADAR) 5500 system as part of a scientific data purchase. Part of the acquired data is for the metropolitan area of Springfield. The impervious features in the study area were mapped using the ADAR imagery in combination with Landsat thematic mapper satellite imagery acquired between 1991 and 1993 and classified by Missouri Resource Assessment Partnership (MoRAP) (1999). To supplement the Landsat data outside the ADAR data area, 1:24,000-scale digital road data were buffered to a width of 10 m (32.8 ft) and added as impervious surface to the final map. The majority of the urban area was mapped using the ADAR data, and the surrounding rural area was mapped with the lower resolution (30-m) Landsat data supplemented with the digital road data. The Landsat data were used to provide a general land use/land cover classification (fig. 3) and to determine the approximate relative percentage of the various land cover classes in each subbasin (table 2). An impervious surface map using the higher resolution ADAR data in the urban area of the city is shown in figure 4. The proportion of impervious surface for each basin derived from the combination of the ADAR and Landsat data is shown at the bottom of table 2. On table 2, two additional columns (Jones Spring and Jones Spring plus Jones Branch) were added to account for the capture of surface runoff by the sinkhole recharge area of Jones Spring.

The four dominant land cover classes (fig. 3) in the study area are urban impervious, urban vegetated, cool-season grassland, and deciduous forest. The subbasin with the largest percentage of impervious surface derived from a combination of ADAR and Landsat data is the Wilsons Creek at Scenic Drive site (32.0 percent). The Jones Spring recharge area is approximately 3.95 mi^2 and is 32.9 percent impervious surface. When combined, the Jones Branch drainage area and the Jones Spring recharge area collectively are 31.1 percent impervious surface. The least urbanized subbasin is the Pearson Creek site (14.7 percent impervious surface).

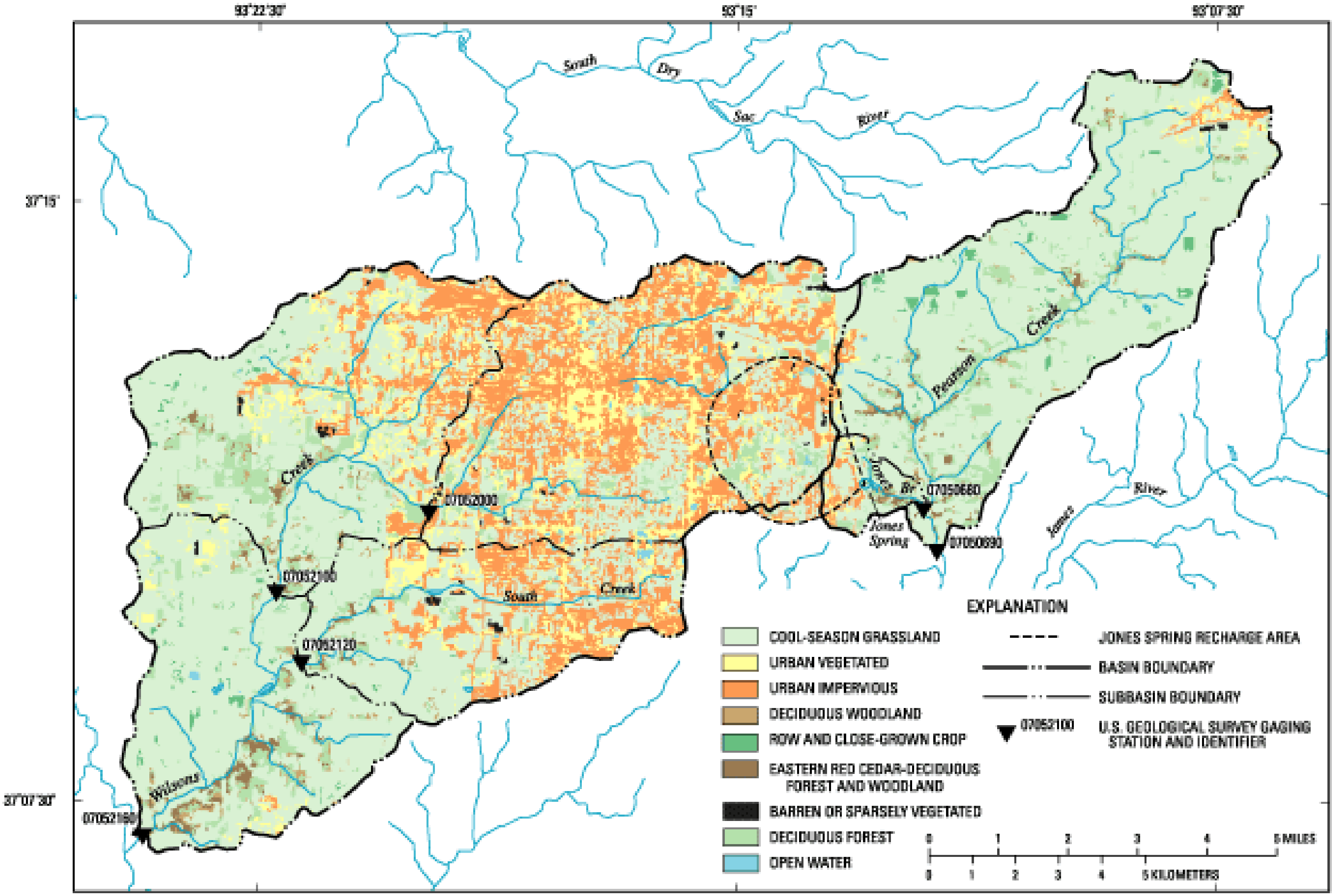
The area is located in a temperate region that is characterized by moderate temperatures and rainfall. The mean annual rainfall is approximately 40 in/yr (inches per year), the mean annual runoff for the area is approximately 12 in/yr, and the estimated mean annual evapotranspiration is approximately 29 in/yr (Missouri Department of Natural Resources, 1997).

DATA COLLECTION METHODS

Samples were collected during base-flow conditions and during storm events at six sites (table 3, fig. 2) between August 1999 and August 2000. All streams were measured for physical properties such as dissolved oxygen, pH, specific conductance, and temperature; samples were analyzed for major inorganic constituents, nutrients, fecal indicator bacteria densities, selected trace metal constituents, and selected organic constituents using a total ion chromatogram (TIC) scan (tables 4 and 5, at the back of this report). Two sites, Pearson Creek and Wilsons Creek near Battlefield, were sampled, and the samples were analyzed for selected pesticides and pesticide degradation products or metabolites (table 6, at the back of this report). Additionally at these two sites, toxicity was determined using sample dialysates from semipermeable membrane devices (SPMD) that were deployed in the creeks. The SPMD sequesters lipophilic compounds from the environment immediately and continuously on exposure to those compounds. The SPMD dialysates also were analyzed for selected general pesticides and selected metabolites (table 7, at the back of this report), selected organochlorine pesticides, selected organochlorine pesticide metabolites, total polychlorinated biphenyls (PCBs) (table 8, at the back of this report), polycyclic aromatic hydrocarbons (PAHs), and selected volatile organic compounds (VOCs) (table 9, at the back of this report).

Base-Flow Samples

Site visits during base flow and storm events involved obtaining quantitative stream data. Gage height was recorded by a gaging station that is referenced to a wire weight suspended from the bridge, a staff gage on the stream bank, or a reference point cut into a permanent structure near the gage control structure.



Base from U.S. Geological Survey digital data 1:100,000, 1980
Universal Transverse Mercator projection
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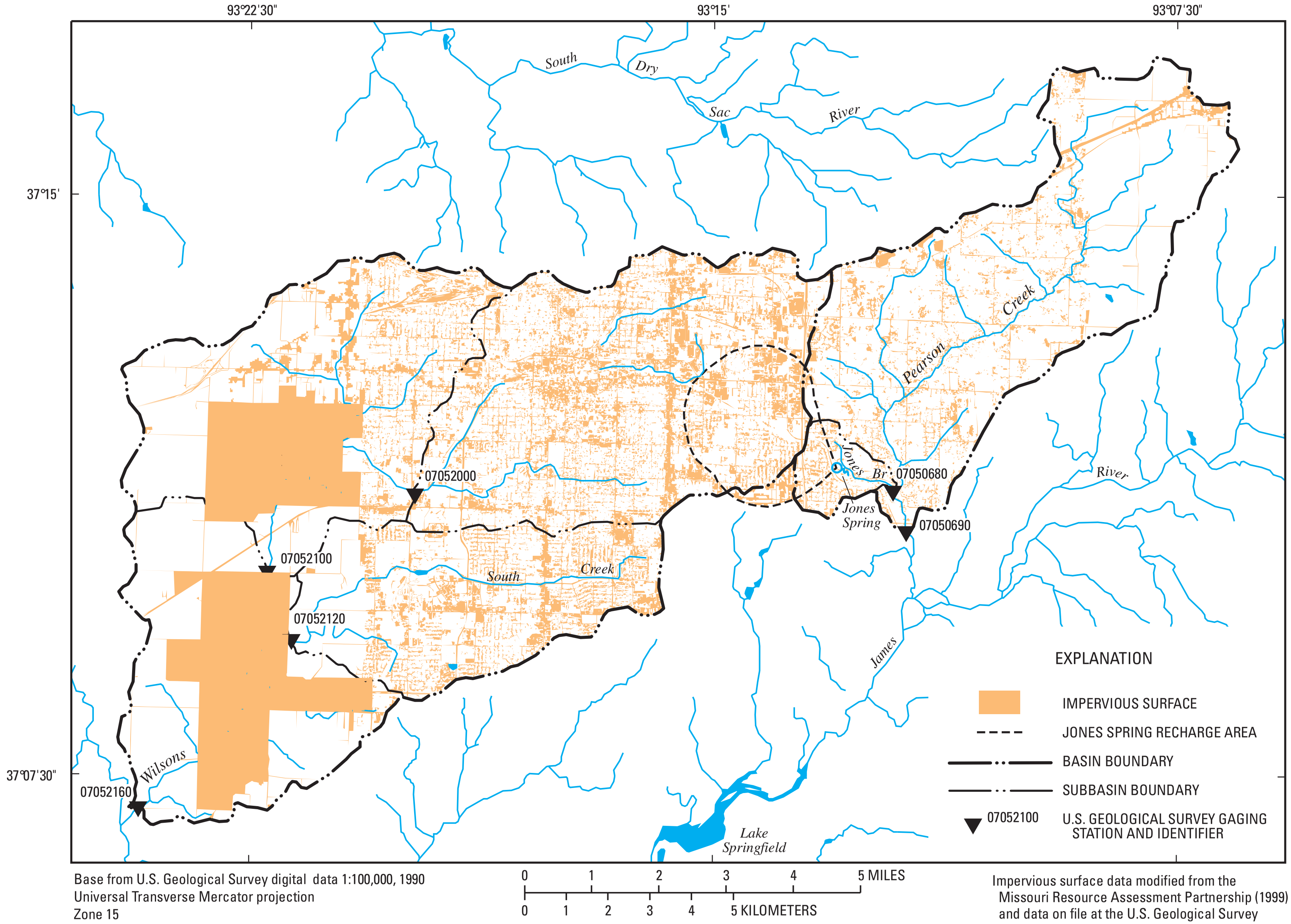
Land use from Missouri Resource Assessment Partnership (1999)

Figure 3. Land use/land cover in the Pearson Creek and Wilsons Creek Basins.



Base from U.S. Geological Survey digital data 1:100,000, 1990
Universal Transverse Mercator projection
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Impervious surface data modified from the Missouri Resource Assessment Partnership (1999) and data on file at the U.S. Geological Survey office, Rolla, Missouri

Figure 4. Impervious surface in the Pearson Creek and Wilsons Creek Basins.

Table 2. Land cover distribution and impervious surface in percent of total area draining to each location

Land cover class	Jones Branch	Pearson Creek	Wilsons Creek at Scenic Drive	Wilsons Creek near Springfield	South Creek	Wilsons Creek near Battlefield	Jones Spring	Jones Spring plus Jones Branch
Landsat data[1]								
Cool-season grassland	51.1	77.1	27.7	40.2	51.5	50.3	36.9	40.0
Urban vegetated	11.7	2.6	26.4	21.5	15.3	16.5	19.2	16.9
Urban impervious	15.6	2.3	39.7	28.3	25.3	21.8	34.0	29.5
Deciduous woodland	4.3	2.6	0	.8	1.6	1.6	0	1.2
Row and close-grown crops	0	2.3	0	.4	.3	.7	0	0
Eastern red cedar - deciduous forest and woodland	4.2	1.9	0	.5	.7	1.2	0	1.1
Barren or sparsely vegetated	0	.1	.5	.4	.6	.4	.6	.5
Deciduous forest	13.0	10.9	5.2	7.6	4.1	7.2	8.7	10.4
Open water	0	.1	.5	.3	.5	.4	.4	.4
ADAR and Landsat data[2]								
Impervious surface	25.5	14.7	32.0	24.1	25.0	19.8	32.9	31.1

[1] Data derived from Landsat imagery.

[2] Data derived from Airborne Data Acquisition and Registration (ADAR) imagery in combination with Landsat imagery.

Table 3. Dates of base-flow and stormwater sample collection

[B, base flow; S, stormwater; X, stormwater semipermeable membrane device (SPMD) was deployed; --, no data]

	Summer										
Station name	**08/18-19/1999**	**08/23/1999**	**10/09/1999**	**11/22-23/1999**	**02/17/2000**	**05/01/2000**	**05/09/2000**	**06/07-08/2000**	**06/28/2000**	**07/12/2000**	**07/20/2000**
Jones Branch	B	--	S				--	B	S		--
Pearson Creek	B	--	--				--	B	S X		--
Wilsons Creek at Scenic Drive	B	S	--				--	B	--		S
Wilsons Creek near Springfield	--	S	--				--	--	--		--
South Creek	--	--	--				S	--	--		S
Wilsons Creek near Battlefield	B	--	--				--	B	S		--

Base-flow water samples were collected at a cross section within the stream that could be waded. If there was sufficient depth, these samples were collected with a DH-81 hand-held isokinetic sampler constructed of Teflon using the equal-width increment method (Wilde and others, 1999a). The sample was composited in a churn splitter (pre-cleaned polyethylene container) from which aliquots were drawn for processing before shipment to the laboratory. If there was insufficient depth (less than 0.5 ft) to use the DH-81, base-flow samples were collected at 5 equal width increments using a 2-L (liter) glass bottle and composited in a churn splitter. Samples for the TIC organic scan (collected at all sites) were collected in a 1-L amber glass bottle from the centroid of flow. Samples for pesticide analysis, collected at Pearson Creek and Wilsons Creek near Battlefield, were composited in an organic-free glass container.

The pH and alkalinity were determined from an aliquot of the composited sample. Generally, a 50-mL (milliliter) aliquot of sample was measured for pH using a Ross combination ion-specific electrode connected to a meter. Alkalinity was determined on the same 50-mL aliquot by titrating the sample with 0.16-N (normal) sulfuric acid. Temperature, specific conductance, and dissolved oxygen were determined in the stream using procedures described by Wilde and Radtke (1997). Preservation and processing techniques for all samples are described in Wilde and others (1999b).

During the sample collection process, a 500-mL grab sample was collected at midstream for the determination of indicator bacteria. The bacteria sample was processed onsite within 6 hours of collection using the membrane filtration technique for *Escherichia coli* (*E. coli*), fecal coliform (FC), and fecal streptococci (FS). Before the sampling event, fresh media for plating bacteria were prepared. To ensure that the media and the membrane filtration equipment were not causing false positive results, blank samples were prepared and processed. Bacteria collection, plating, incubation, and enumeration were conducted as outlined by Greenberg and others (1985) and Myers and Wilde (1997).

The SPMDs were used for long-term and storm event sampling of organic constituents at the farthest downstream sampling points in each of the basins (Pearson Creek and Wilsons Creek near Battlefield). Five SPMDs were placed in a clean stainless steel carrier and deployed in the stream. The long-term base-flow SPMD samples were left in the water for approximately 30 days before being removed, packaged, and shipped to Environmental Sampling Technologies (EST) of St. Joseph, Missouri, for dialysis and cleanup. The SPMD dialysates were split and transferred in either dimethylsulfoxide (DMSO) (for toxicity determination) or hexane (for quantitative chemical analysis) to glass vials, sealed, and sent to the USGS Environmental Microbiology Laboratory at the Columbia Environmental Research Center (CERC) in Columbia, Missouri, for toxicity determination and to the USGS National Water Quality Laboratory (NWQL), Denver, Colorado, for quantitative chemical analysis.

Stormwater Samples

An attempt was made to collect samples of stormwater from all of the sites once during each season (table 3); however, because the study was conducted during an unusually dry year and because rainfall intensities and quantities vary greatly even over relatively short distances, it was nearly impossible to collect samples at every site during any particular storm event. As a result, the sampling period was divided into seasons during which samples were to be collected once at each site. Even then, because rainfall events often were too far apart or too close together, each site could not be sampled during each season.

More than one storm usually was sampled during each season. However, samples were not collected from some sites for every season either because there was not enough runoff at the site to meet the minimum sampling requirements, or the rainfall events that did meet the requirements were missed.

Because of the potential danger of wading in a rain-swollen stream, stormwater samples were collected from the bank as far out into the flow as practical. Samples obtained during storm events were collected in clean 2-L glass bottles and composited in a churn splitter. Samples for the TIC organic scan (collected at all sites) were sampled in a 1-L amber glass bottle. Samples for pesticide analysis, collected at Pearson Creek and Wilsons Creek near Battlefield, were composited in a pre-cleaned glass container. All field measurements, sample processing, and indicator bacteria procedures were identical to those used for the base-flow samples.

To ensure storm samples would be representative of the initial stormwater runoff, sites were sampled only after meeting specific requirements. Based on the size of the basin and the relative amount of impervious surface in the basin, gage-height (water-level stage in the stream) thresholds for sampling were established. The gage-height requirement initially was set to a 1-ft change in gage height from pre-storm conditions for all sites except for Jones Branch and Wilsons Creek near Battlefield. Jones Branch, because of the small drainage area, initially was set to a 0.2-ft change in gage height from pre-storm conditions, but was later changed (based on field observations) to 0.4-ft change. Wilsons Creek near Battlefield was set at a 2-ft change in gage height from pre-storm conditions. Because of the relatively high proportion of pervious surface in the Pearson Creek Basin and after a number of storm events were observed, the Pearson Creek sampling requirement was decreased to 0.8-ft change in gage height from pre-storm conditions. Stormwater sampling was, as far as practical, conducted following at least a 72-hour period of no runoff.

After the gage-height requirement was satisfied, sampling was initiated on the rising limb of the storm hydrograph, and samples were collected as follows: the first bottle was collected, 5 minutes later the second bottle was collected, 5 minutes later the third bottle was collected, 7 minutes later the fourth bottle was collected, and 10 minutes later the fifth bottle was collected. The 10 L of sample (five 2-L sub-samples) were composited and processed the same as the base-flow samples. Gage height and physical properties values were recorded when the third sub-sample was collected. A 500-mL grab sample was collected at the same time as the third sub-sample for the determination of fecal indicator bacteria. A 1-L amber glass bottle for the TIC organic scan (all sites) also was collected at the same time as the third sub-sample.

The SPMDs were used for stormwater sampling of bioavailable organic constituents at the Pearson Creek and Wilsons Creek near Battlefield sites. Five SPMDs were placed in a clean stainless steel carrier and deployed in the stream at each site on the rising limb of the storm hydrograph. The stormwater SPMD samples were left in place until the gage height returned to approximately the pre-storm level (usually 3 to 5 days). The SPMD was then removed, packaged, and shipped as described for base-flow samples.

Surface-Water Data

The gaging stations continuously record gage-height information that can be related to discharge by the use of a stage-discharge (rating) table. The rating table is created using information such as channel geometry, flow conditions, and discharge measurements for a range of different gage heights.

Two types of equipment are used to measure gage-height data: pressure sensor and float. Both types were used for the gaging stations included in this study. A pressure sensor type operates by measuring the static pressure head above the level of the sensor. The pressure head is then converted to gage height using the density of water, and the gage height is recorded electronically every 15 minutes. A float type operates by setting a data recorder to the gage height of the water surface. A float is connected to a metal tape that is suspended over a specific-size pulley with a counter weight attached to the other end of the tape. As the float rises or falls an encoder attached to the pulley records the distance traveled. The distance is added or subtracted from the original gage height, and the computed gage height is electronically recorded every 15 minutes. In the case of the Pearson Creek and Wilsons Creek near Springfield sites, the gage heights are transmitted by satellite to the USGS computer database every 4 hours. The data at the remaining sites are downloaded to laptop computers during routine site visits.

Discharge measurements are made periodically to relate the gage height to the discharge for a range of gage-height values. Discharge measurements are made by subdividing the stream into discrete sections. The discharge of each subsection is computed by multiplying the depth and width of that subsection and multiplying the resultant area by the velocity, measured with a current meter, in that section. The total discharge is the sum of the discharge for each subsection. Procedures used for current-meter measurements are discussed in detail in Carter and Davidian (1968), Buchanan and Somers (1969), and Rantz and others (1982).

The measurements are plotted relative to the gage heights and a curve relating the two is fitted to the points for each site. The curve is used to compute a rating table. The procedures for the development, modification, and application of rating tables are described in Rantz and others (1982) and in Kennedy (1983, 1984).

Rating tables for the six sites are in tables 10 to 15, at the back of this report. The creation of a stage-discharge relation is a dynamic process. As more measurement data and field observations are collected, the ratings are updated and changed to represent the current stream conditions. Environmental factors, such as storm events redistributing bed material or the accumulation of debris on the control, change the stage-discharge relation periodically. The rating tables presented in this report are the most up-to-date (April 2001) representation of the stage-discharge relation that existed for these six sites.

Toxicity

The SPMD is designed to mimic the key aspects of the bioconcentration process and to passively sample bioavailable organic compounds. Short-term toxicity tests can rapidly detect substances potentially harmful to the aquatic biota that are sequestered in SPMDs (Johnson, 1998; Johnson and others, 2000).

Fluoroscan

The fluoroscan is a test that can help to identify the compounds that may be present in SPMD sample dialysates. If the sample fluoresces when it is exposed to ultraviolet light, then aromatic organic compounds are likely present in the sample. In a darkened room, SPMD sample dialysates were placed about 3 centimeters from a portable light with emissions at wavelengths of 280 nanometers. To detect the presence of fluorescent compounds, each sample was viewed under ultraviolet light for about 1 minute, and then compared with solvent controls, trip blanks, and positive controls. The appearance of a distinctive glow was considered a “positive” response and evidence of aromatic compounds, probably a PAH with three or more rings. Two-ringed PAHs do not fluoresce under ultraviolet light of this wavelength.

Acute Toxicity

Acute toxicity was determined using the Microtox acute toxicity test according to the standard protocol described in Microbics Corporation (1992). Validation of Microtox acute toxicity test in single and complex mixtures of pesticides, PCBs, petroleum products, and PAHs has been previously reported by Kaiser and Palabrica (1991) and Johnson and Long (1998).

The carrier solvent, DMSO, used by EST of St. Joseph, Missouri, for the SPMD dialysates for use in toxicity determinations was contaminated. The values of the solvent blanks were “toxic” with values several orders of magnitude less than those of the normal trip blank and SPMD controls. The dialysates contaminated with DMSO negated the Microtox acute toxicity test.

Genotoxicity

In the last few decades, genetic toxicology has emerged with the generally accepted view that some chemicals (genotoxins) can induce deoxyribonucleic acid (DNA) damage in cells that may result in lethality, mutagenesis, and carcinogenesis (Wurgler and Kramers, 1992). The Mutatox bioassay is a method to measure the genotoxicity of an environmental sample. Mutatox bioassays were conducted according to the protocol described by Johnson (1992a, 1992b, 1993, 2000). For the Mutatox bioassay, a nonglowing or dark mutant strain of luminescent bacteria is exposed to a test substance, and the amount of light emitted is measured with a luminometer; sample-induced reversion from the nonglowing to glowing type bacteria is used to indicate the genotoxicity of the sample. Because most simple organism cells, such as the dark mutant strain of *Vibrio* bacteria, fail to duplicate vertebrate metabolism of contaminants into potential DNA-damaging agents, a mammalian metabolic activation system was incorporated (Johnson, 1992a, 1992b, 1993, 2000). Mammalian S9 is the post-mitochondrial supernatant fraction obtained after centrifugation of a cellular homogenate (usually livers of rats; which is a mammalian surrogate for humans) at 9,000 times gravity (S9). The subcellular fraction contains enzymes that are important in detoxification reactions in mammals. Mammalian S9 is used frequently to activate promutants to the active mutant forms in genotoxicity tests. Validation of Mutatox in single and complex mixtures of pesticides, PCBs, petroleum products, and PAHs has been previously reported by Johnson and Long (1998). Test samples were serially diluted in a mixture of bacteria—1 percent mammalian S9—buffer over a 100-fold dose range, incubated in a water bath at 37 ºC (degrees Celsius) for 15 minutes to activate the mammalian S9, and then incubated at 27 ºC overnight. DMSO, a known compatible carrier solvent with Mutatox (Johnson, 1992a), was used as the standard solvent in this study. Benzo[a]pyrene was used as the standard positive control and DMSO was used as the negative control. A genotoxic response of the luminescent bacteria was determined by measuring the light intensity. A positive response was defined as a light value of at least three times the light intensity of the solvent control blank. The dose-response number was defined as the number of positive responses recorded at different concentrations per dilution series. A dilution series that contained two or more positive responses at two or more different concentrations was designated as “genotoxic”. When the series contained only one positive response, it was designated “suspect”. When the series contained no positive response, it was designated “negative”. Each test sample was determined to be genotoxic, suspect, or negative only after replicate dilution series were performed on different days.

Hepatic Activity Assessment

Hepatic activity assessment, a measure of the simulation of specific enzyme production in the livers of living organisms, can be used to indicate the presence and amounts of foreign substances in environmental samples and their potential role in toxic effects. Mixed function oxygenase, a liver enzyme that is part of the S9 fraction, is essential for the metabolism of PAHs and PCBs in living organisms. Exposure of fish to PAHs and PCBs stimulates the production of these enzymes. Cytochrome P450-dependent 7-ethoxyresorufin-O-deethylase (EROD) activity is a highly sensitive indicator of contaminant uptake in fish and provides evidence of the stimulation of the production of specific enzymes, cytochrome P450-dependent monooxygenases, by foreign compounds (Whyte and others, 2000).

Channel catfish (*Ictalurus punctatus*), obtained from a commercial source, were maintained in a flow-through raceway at 15 ºC and cultured according to the methods of Brauhn and Schoettger (1975). The fish were mixed sexes, healthy, and vigorous; each weighed between 750 and 1,000 grams. Water conditions were pH of 7.8, alkalinity of 255 mg/L (milligrams per liter), and total hardness 283 mg/L. To increase liver enzymatic activity, catfish were injected once intraperitoneally with a dialysate from the long-term SPMD that was deployed on August 19, 1999, at Wilsons Creek near Battlefield. The dialysate was dissolved in corn oil, warmed, and sonicated a few minutes to increase solubility before injection. After injection, each fish was segregated for 5 days in a flow-through aquarium at 20 ºC without feeding. Control fish received either a corn oil injection or no injection.

After 5 days, the S9 fraction was prepared from each fish. The liver was immediately removed through a ventral incision avoiding gut and bile contamination, placed on a cold pre-weighed beaker, covered with aluminum foil, and weighed. The fish S9 fraction was prepared as described by Johnson (1989), who modified the rodent activation method of Maron and Ames (1983). All steps of the procedures were carried out at 0 to 3 ºC: cold solutions, chilled glassware, and refrigerated equipment. The liver was minced with sterile scissors and washed 5 to 6 times with 0.15-M (molar) potassium chloride (KCl) solution to remove pooled nucleated red blood cells and hemoglobin. The minced liver was covered with 0.15-M KCl at a ratio of 2 to 1 (KCl volume to liver volume) and rapidly homogenized. Tissue grinding was minimal to avoid excessive heat production and possible loss of enzymatic activity. The homogenate was centrifuged 10 minutes, and the supernatant, the S9 fraction, saved. This fraction was immediately placed in sterile disposable cryogenic tubes, labeled, frozen, and stored in liquid nitrogen. The standard EROD method (Pohl and Fouts, 1980) was used to measure the changes in mixed function oxygenase activity of the S9 fraction.

Quality Assurance/Quality Control

The components of analytical variability (uncertainty) can be estimated when quality-assurance (QA) and quality-control (QC) samples of the correct types and quantities are incorporated into measurement procedures. The USGS NWQL incorporates numerous QA/QC samples to ensure that the measurement system is functioning properly. In addition to the laboratory QA/QC procedures, QA/QC samples were collected onsite.

The most common error attributable to field procedures is contamination of the sample matrix. Two general forms of contamination occur—systematic and erratic. The goal of the QA program is to decrease the systematic component and provide evidence of the erratic component by collecting replicate samples and filtration, equipment, field, and trip blank samples. The QA/QC samples made up approximately 10 percent of all samples collected for the study.

Replicate Samples

Replicate samples were collected and analyzed to determine the precision of sampling, processing, and onsite analysis. Generally, a replicate sample was collected immediately after an environmental sample using the same equipment and sampling techniques. Both the replicate and environmental samples were analyzed at the NWQL using identical analytical techniques. Analysis of the replicate samples indicated that the laboratory analysis and the sampling procedure were producing consistent results.

Blank Samples

Water-quality blank samples were collected to determine the cleanliness of the filtration and sampling equipment and to ensure that the sample collection procedures were free from contamination. Analysis of all water-quality blank samples indicated that minimal contamination occurred during the base-flow and stormwater sampling process.

Blank SPMD samples were collected onsite to ensure that the SPMDs were not affected by atmospheric contamination. The nature of the SPMD device allows it to sequester lipophilic compounds from the environment immediately on exposure to those compounds. The device can sequester compounds from any environmental media (air, water, and/or sediment) that it contacts. During the deployment and recovery of a base-flow or stormwater SPMD, a blank SPMD was exposed to the atmosphere onsite. A total of seven SPMD blank samples were collected.

Because of the sensitivity of the SPMD sampling device and the precision of the analysis, target compounds were detected in some of the blank samples. Most all of the detections were less than the reporting limits of the analyses, and the concentrations were estimated by the laboratory. The pesticide 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) was detected twice in the blank samples at concentrations of 1.24 and 1.98 μg/kg (micrograms per kilogram; reporting limit 1.0 μg/kg). Cis-chlordane was detected twice in blank samples at concentrations of 2.9 and 3.1 μg/kg (reporting limit 5.0 μg/kg). Trans-chlordane was detected three times in blank samples at concentrations from 2.9 to 4.0 μg/kg (reporting limit 5.0 μg/kg). Acridine was detected once in blank samples at a concentration of 76.9 μg/kg (reporting limit 250 μg/kg). Bis(2-ethylhexyl)phthalate and di-n-butylphthalate were detected in every blank sample, and concentrations ranged from 65.6 to 221 μg/kg and 30.4 to 113 μg/kg, respectively (reporting limit 250 μg/kg). Butylbenzylphthalate was detected twice in blank samples at concentrations of 87.8 and 90.1 μg/kg (reporting limit 250 μg/kg). Diethylphthalate was detected twice in blank samples at concentrations of 85.6 and 91.3 μg/kg (reporting limit 250 μg/kg). 4,5-Methylenephenanathrene was detected once in blank samples at a concentration of 47.6 μg/kg (reporting limit 250 μg/kg). Phenanthrene was detected twice in blank samples at concentrations of 73.8 and 74.3 μg/kg (reporting limit 250 μg/kg). With the exception of di-n-butylphthalate and bis(2-ethylhexyl)phthalate, which were detected in every blank sample and every environmental sample, the compounds detected in the SPMD blank samples do not negate detections in environmental samples. However, because DDE was detected in two blank samples at concentrations larger than the reporting limit, detections in environmental samples could be suspect.

Surface-Water Data

The surface-water data are checked, reviewed, and subjected to QC procedures before the data are published. A complete analysis of data collected, procedures used in processing the data, and the logic on which the computations were based is documented for each year of record for each station to provide a basis for review and as a reference for questions about the records in the future. The station analysis includes a description of equipment, hydrologic conditions, gage-height record, datum corrections, rating, discharge, special computations, remarks, and recommendations. Discharge measurement notes are checked before the values are entered into the database. Rating curves are reviewed and revised before the discharge data are computed and accepted into the database.

WATER-QUALITY, SURFACE-WATER, AND PRECIPITATION DATA

The water was clear and colorless in appearance during base-flow sampling events at all sites sampled. This contrasts greatly with the opaque, nearly black in color, initial runoff that was observed at the Wilsons Creek sites (Wilsons Creek at Scenic Drive, Wilsons Creek near Springfield, South Creek, and Wilsons Creek near Battlefield) during storm events. The black color probably was from oil and grease, particulates from ground-up tires, or other sources. The runoff from the Pearson Creek sites (Jones Branch and Pearson Creek) usually was opaque and brownish-red during storm events. The color at these sites probably was from the brownish-red sediment that is washed out of the karst system through springs during high flow, and from sediment picked up by overland flow. Storm events that were sampled generally were high-intensity, short-duration storms that usually produced about 1 to 2 in. (inches) of rain. One storm event on July 12, 2000, produced more than 5 in. of rainfall in about 6 hours. Much of the city of Springfield and the surrounding area of Greene County were flooded, causing extensive property damage.

Inorganic Constituent, Nutrient, Bacteria, and Trace Metal Data

Base-Flow Samples

Base-flow samples were collected at four sites (Jones Branch, Pearson Creek, Wilsons Creek at Scenic Drive, and Wilsons Creek near Battlefield, fig. 2) twice during the study (tables 3 to 5). Two sites (Wilsons Creek near Springfield and South Creek) had zero flow and were not sampled. The concentrations of the inorganic constituents calcium, magnesium, potassium, sodium, chloride, fluoride, and sulfate are shown on table 4. The concentrations of calcium ranged from 60.1 to 91.6 mg/L, magnesium ranged from 2.53 to 8.12 mg/L, potassium ranged from 1.4 to 13.1 mg/L, sodium ranged from 8.7 to 137 mg/L, chloride ranged from 18.6 to 143 mg/L, fluoride ranged from less than 0.1 to 0.6 mg/L, and sulfate ranged from 9.1 to 78.2 mg/L.

Nutrient concentrations in the base-flow samples generally were greatest at the Wilsons Creek near Battlefield site. The concentrations of the nitrite plus nitrate as nitrogen (because the majority of nitrite plus nitrate is nitrate, nitrite plus nitrate as nitrogen will hereinafter be referred to as nitrate), dissolved phosphorus, orthophosphorus, and total phosphorus were several times the concentrations of the base-flow samples from other sites. The concentrations of nitrate ranged from 0.786 to 8.29 mg/L, dissolved phosphorus ranged from less than 0.05 to 1.916 mg/L, orthophosphorus ranged from less than 0.01 to 1.84 mg/L, and total phosphorus ranged from less than 0.05 to 2.03 mg/L.

Indicator bacteria densities in base-flow samples for *E. coli* ranged from 23 to greater than 1,600 col/100 mL (colonies per 100 milliliters), for FC ranged from 20 to 12,000 col/100 mL, and for FS ranged from 37 to 1,340 col/100 mL. All sites sampled except for Jones Branch exceeded the FC whole-body-contact state standard of 200 col/100 mL (Missouri Department of Natural Resources, 1996) in both base-flow samples.

The dissolved trace metal concentrations generally were less than the detection limit, with the exception of iron, which ranged from less than 10 to 40 μg/L (micrograms per liter) and manganese, which ranged from 4 to 107 μg/L. Total metal concentrations of cadmium, lead, mercury, and zinc were mostly less than their respective detection limits. The concentration of total aluminum ranged from an estimated 16 to 136 μg/L, and total lead ranged from less than 1 to 2 μg/L.

Stormwater Samples

The median concentrations of the inorganic constituents (calcium, magnesium, potassium, sodium, chloride, fluoride, and sulfate) in stormwater samples generally were less than the median concentrations of base-flow samples. In stormwater samples, the concentrations of calcium ranged from 19.3 to 92.9 mg/L, magnesium ranged from 1.06 to 8.47 mg/L, potassium ranged from 1.6 to 8.1 mg/L, sodium ranged from 2.4 to 58.5 mg/L, chloride ranged from less than 0.3 to 102 mg/L, fluoride ranged from less than 0.1 to 0.3 mg/L, and sulfate ranged from 3 to 36.2 mg/L.

The nitrogen species median concentrations generally were greater than the median concentrations of the base-flow samples, and the median concentrations of the phosphorus species generally were less than the median concentrations of the base-flow samples. The largest concentrations (ammonia plus organic nitrogen as nitrogen, 5.9 mg/L, and ammonia as nitrogen, 0.544 mg/L) of the reduced nitrogen species occurred at the Wilsons Creek at Scenic Drive site. That site had consistently larger concentrations of reduced nitrogen species than the other sites. The largest concentration (4.62 mg/L) of nitrate occurred at the Wilsons Creek near Battlefield site. However, the concentrations of nitrate were much lower at that site than the concentrations in base-flow samples. In Jones Branch, nitrate concentrations were larger in stormwater samples than base-flow samples. The largest stormwater total phosphorus concentration occurred at Wilsons Creek near Battlefield on November 23, 1999, with a value of 1.57 mg/L.

Fecal indicator bacteria densities generally were several orders of magnitude greater in stormwater samples than in base-flow samples. *E. coli* densities ranged from less than 1,000 (South Creek) to 140,000 (Wilsons Creek at Scenic Drive) col/100 mL. Fecal coliform densities ranged from 1,000 (South Creek) to 150,000 (Wilsons Creek at Scenic Drive) col/100 mL. Fecal streptococcus densities ranged from 1,980 to 290,000 col/100 mL at Jones Branch.

The concentrations of the dissolved metals generally were less than the detection limit with the exception of iron, which ranged from less than 10 to 60 μg/L; manganese, which ranged from an estimated 2 to 322 μg/L; and zinc, which ranged from an estimated 10 to 24 μg/L. Total mercury concentrations were mostly below the detection limit of 0.3 μg/L. The concentration of total aluminum ranged from an estimated 133 to

12,500 µg/L, total cadmium ranged from an estimated 0.1 to 2.9 µg/L, total lead ranged from 1 to 245 µg/L, and total zinc ranged from an estimated 19 to 472 µg/L.

Organic Constituent Data

Base-Flow Samples

A sample for the TIC scan was collected for each base-flow sample. The TIC scan can be used as an organic compound screening tool. The TIC scan technique is useful for detecting compounds that are amenable to extraction by dichloromethane and detection by gas chromatograph-mass spectrometer. These compounds may include certain pesticides, industrial pollutants, petroleum products, and natural organic compounds. Compounds not usually determined by this technique include highly volatile or nonvolatile compounds, and very polar or thermally labile compounds (including many pesticides and their metabolites). A total of 13 compounds were detected in the TIC scans of the base-flow samples (table 5). The compounds isophorone, phenanthrene, and anthracene were the most frequently detected in base-flow samples. These 3 compounds were detected in more than 63 percent of the base-flow samples.

Samples collected at Pearson Creek and Wilsons Creek near Battlefield were analyzed for an extensive list of general pesticides and pesticide metabolites (table 6). Pesticides detected in the base-flow samples included atrazine, carbaryl, chlorpyrifos, cyanazine, diazinon, diuron, lindane, metolachlor, prometon, and tebuthiuron. Prometon was detected at both sites during both base-flow sampling periods and ranged from 0.056 to 0.225 µg/L. More pesticides were detected during the June 2000 base-flow sampling period (5 at Pearson Creek, 8 at Wilsons Creek) than during the August 1999 sampling period (2 at Pearson Creek, 2 at Wilsons Creek). Most of the pesticide concentrations were near the detection limits. The highest base-flow concentrations for cyanazine (0.554 µg/L), diuron (0.13 µg/L), and prometon (0.225 µg/L) occurred at the Wilsons Creek near Battlefield site during the June 2000 sampling period. For the protection of aquatic life, the Missouri Department of Natural Resources (1996) established a state standard (0.04 µg/L) on the concentration of chlorpyrifos in water. The chlorpyrifos concentration at the Wilsons Creek near Battlefield site was 0.035 µg/L during the June 2000 sampling period. Chlorpyrifos, an insecticide often applied to turf, is not a restricted-use pesticide and approximately 50 percent of its use is in agricultural settings and 50 percent is in non-agricultural settings (U.S. Environmental Protection Agency, October 2001). All of the pesticide concentrations detected were less than their respective state standards for the protection of aquatic life (Missouri Department of Natural Resources, 1996).

Stormwater Samples

A TIC scan sample was collected for each stormwater sample. A total of 27 compounds were detected in the TIC scans of the stormwater samples (table 5). Seventeen of these compounds were detected in more than one-half of the samples collected. Isophorone, fluoranthene, pyrene, and chrysene were detected in more than 75 percent of the stormwater samples. The Pearson Creek Basin had a maximum of 17 compounds detected by the TIC scan, whereas the Wilsons Creek Basin had a maximum of 25 compounds detected.

Stormwater samples collected at Pearson Creek and Wilsons Creek near Battlefield were analyzed for an extensive list of general pesticides and metabolites (table 6). Those detected in the stormwater samples included 2,4-dichlorophenoxyacetic acid (2,4-D), atrazine, carbaryl, chlorpyrifos, deethyl atrazine, diazinon, diuron, malathion, metolachlor, molinate, pendimethalin, picloram, prometon, simazine, and tebuthiuron. Diazinon was detected in 86 percent of the stormwater samples; atrazine and prometon were detected in 71 percent of the stormwater samples. The concentration of diazinon ranged from less than 0.002 to 0.384 µg/L, atrazine ranged from less than 0.001 to 0.017 µg/L, and prometon ranged from less than 0.018 to 0.408 µg/L. Diuron was detected once in stormwater samples at a concentration of 8.03 µg/L.

Semipermeable Membrane Device (SPMD) Chemical Data

Long-Term Samples

Three long-term (30-day) SPMD samples were collected, and the dialysates analyzed for selected general and organochlorine pesticides (and metabolites), total PCBs, PAHs, and VOCs (tables 6 to 8). Toxicity was determined for the dialysates in addition to the analysis of the water-quality constituents. The long-term samples were collected at Wilsons Creek near

Battlefield (fig. 2) from August 19 to September 19, 1999, and from June 11 to July 11, 2000, and at Pearson Creek near Springfield from May 12 to June 12, 2000.

Numerous compounds were detected in the long-term SPMD samples (tables 7 to 9). The general pesticides (table 7) benfluralin, DDE, and lindane were detected in the base-flow samples. DDE was detected in all long-term SPMD samples, but because of detections in SPMD blanks, its environmental detections are suspect. Eleven organochlorine pesticides and metabolites (table 8) were detected in the long-term SPMD samples. Of those 11, 10 were detected in the Pearson Creek sample and 8 were detected in each of the Wilsons Creek samples. Seven organochlorine pesticides and metabolites (cis-chlordane, trans-chlordane, dieldrin, p,p’-DDE, heptachlor epoxide, cis-nonachlor, and pentachloroanisole) were consistently detected in the long-term SPMD samples. A total of 26 PAH and VOC compounds (table 9) were detected in the long-term SPMD samples. Wilsons Creek had the greatest number of detections (24) of PAH and VOC compounds in the long-term sample collected from June 11 to July 11, 2000, while the Pearson Creek long-term sample had 8 detections. Eight PAH and VOC compounds [acenaphthene, diethylphthalate, di-n-butylphthalate, bis(2-ethylhexyl)phthalate, fluoranthene, 9h-fluorene, phenanthrene, and pyrene] were consistently detected in the long-term SPMD samples. Because of detections in every SPMD blank sample, di-n-butylphthalate and bis(2-ethylhexyl)phthalate detections were not considered reliable.

Storm-Event Samples

Storm-event SPMD samples were collected at Pearson Creek from June 28 to July 1, 2000, and July 12 to July 17, 2000, and at Wilsons Creek near Battlefield (fig. 2) from February 17 to February 21, 2000, and July 12 to July 17, 2000. The general pesticides (table 7) that were detected in storm-event SPMD samples were chlorpyrifos (once at Pearson Creek) and DDE (once at Pearson Creek and once at Wilsons Creek near Battlefield). A total of 10 organochlorine pesticides and metabolites (table 8) were detected in the storm-event SPMD samples. The pesticides and metabolites cis-chlordane, trans-chlordane, heptachlor epoxide, and pentachloroanisole were detected in three of the four storm-event SPMD samples. There were six organochlorine pesticides and metabolites detected in storm-event SPMD samples from Pearson Creek (June 28, 2000) and Wilsons Creek (July 12, 2000). The other two SPMD samples had four or fewer organochlorine pesticides detected. Thirty-one PAHs and VOCs (table 9) were detected in storm-event SPMD samples. Nine compounds [acenaphthene, di-n-butylphthalate, chrysene, diethylphthalate, bis(2-ethylhexyl)phthalate, fluoranthene, naphthalene, phenanthrene, and pyrene] were consistently detected in all storm-event SPMDs. Because of detections in every SPMD blank sample, di-n-butylphthalate and bis(2-ethylhexyl)phthalate detections are not considered reliable. The greatest numbers of PAH and VOC detections occurred at Wilsons Creek near Battlefield with 28 detections in the February 17, 2000, sample and 24 detections in the July 12, 2000, sample. At Pearson Creek, there were 9 PAH and VOC detections in storm event SPMD samples on June 28, 2000, and 10 on July 12, 2000.

Surface-Water and Precipitation Data

Surface-water gages were collocated at each water-quality sampling site and recorded gage-height data throughout the period of study. The discharge was computed from the gage-height record using the stage-discharge relation developed for each station. Discharge hydrographs for the sites sampled during the period of the study are shown in figures 5 through 10. Discharge data were used to calculate the load (mass per unit time) of a particular water-quality constituent passing a fixed point. Gage heights were recorded during water-quality sampling and were later converted to discharge using the discharge hydrographs shown in figures 5 to 10.

A flow-duration curve is a cumulative frequency curve that shows the percentage of time during which specified discharges were equaled or exceeded in a given period. It is another means of representing streamflow data combining, in one curve, the flow characteristics of a stream throughout the range of discharge. Flow-duration curves often are useful for estimating discharges for simulation purposes. The flow-duration curve for each site based on the period of record that data were collected at each site is shown in figure 11. However, the curves for Jones Branch, Pearson Creek, and South Creek are based on less than 2 years of record.

Predicted peak discharge data often are useful for simulation purposes. Becker (1986) developed equations for urbanized basins that use the characteristics of drainage area and percent impervious surface to

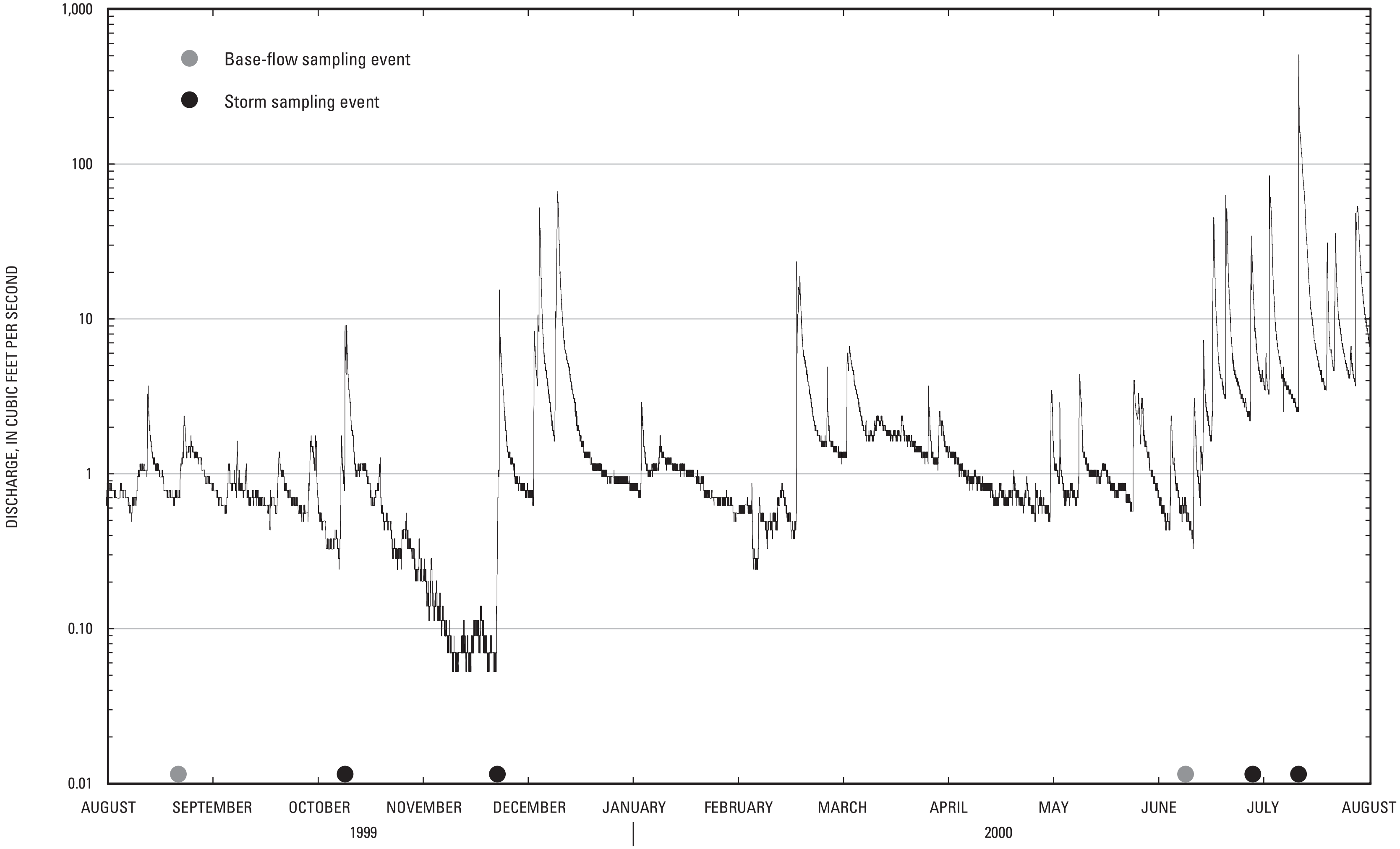

Figure 5. Discharge hydrograph at Jones Branch (07050680), August 1, 1999, through August 1, 2000.

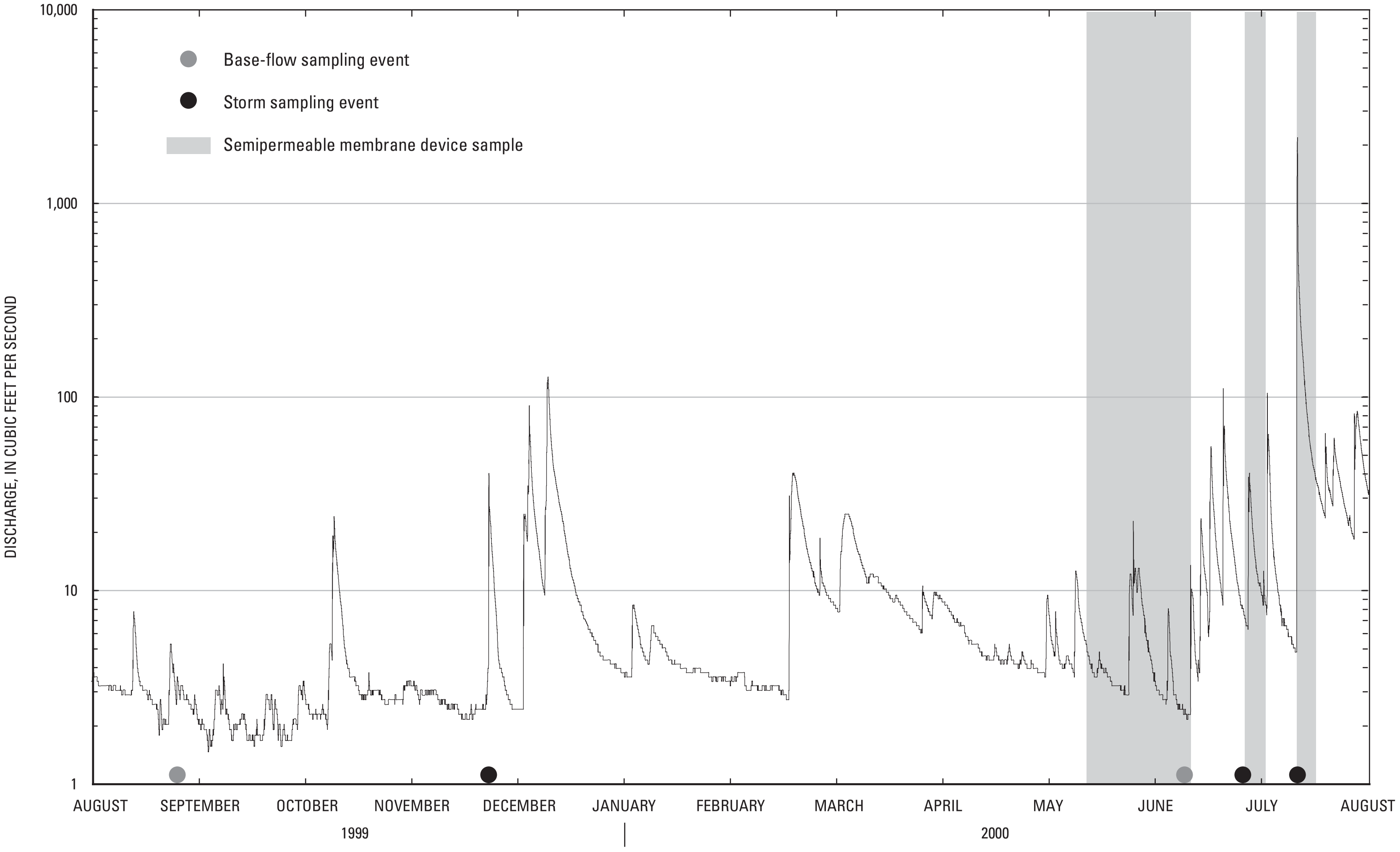

Figure 6. Discharge hydrograph at Pearson Creek (07050690), August 1, 1999, through August 1, 2000.

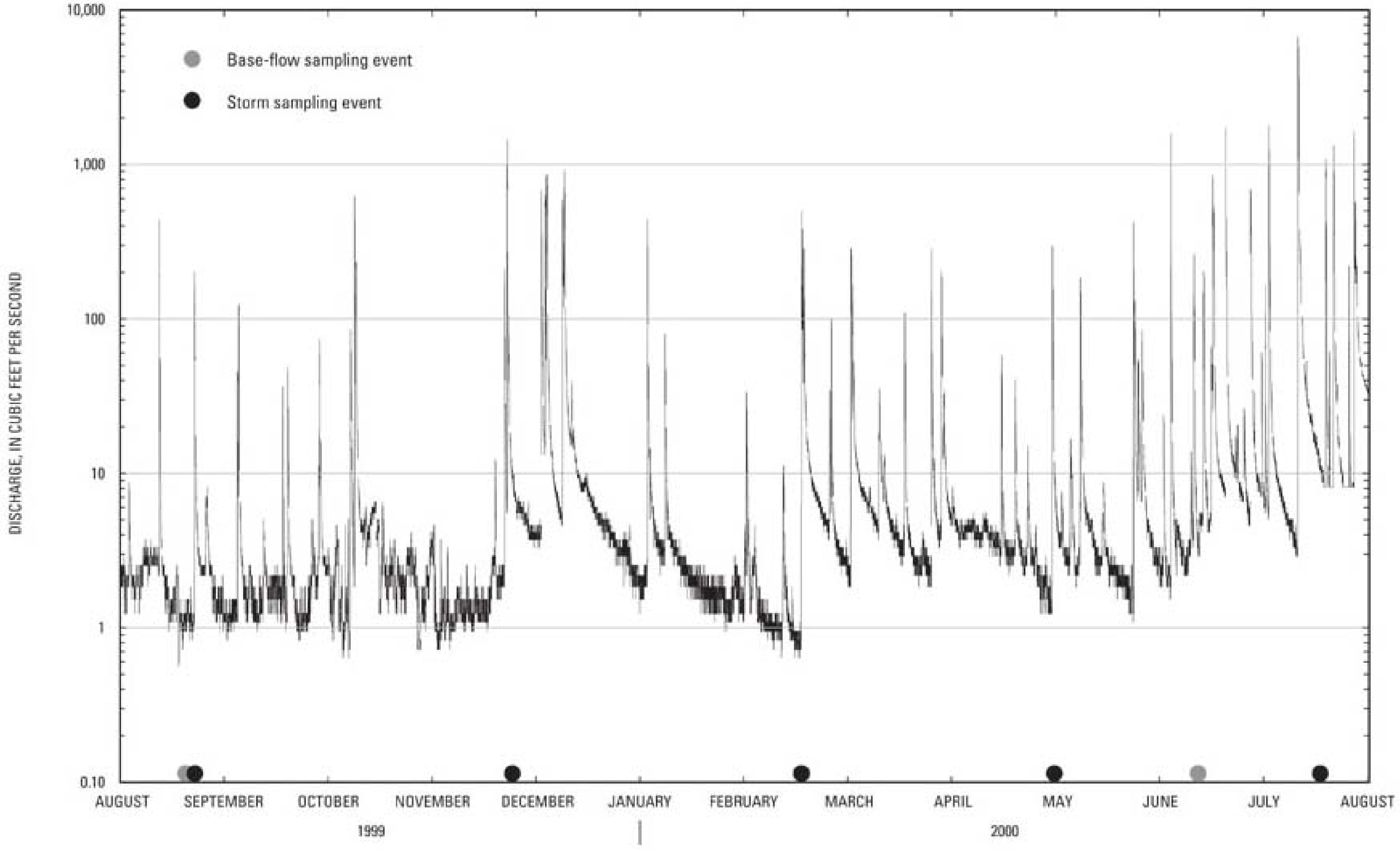

Figure 7. Discharge hydrograph at Wilsons Creek at Scenic Drive (07052000), August 1, 1999, through August 1, 2000.

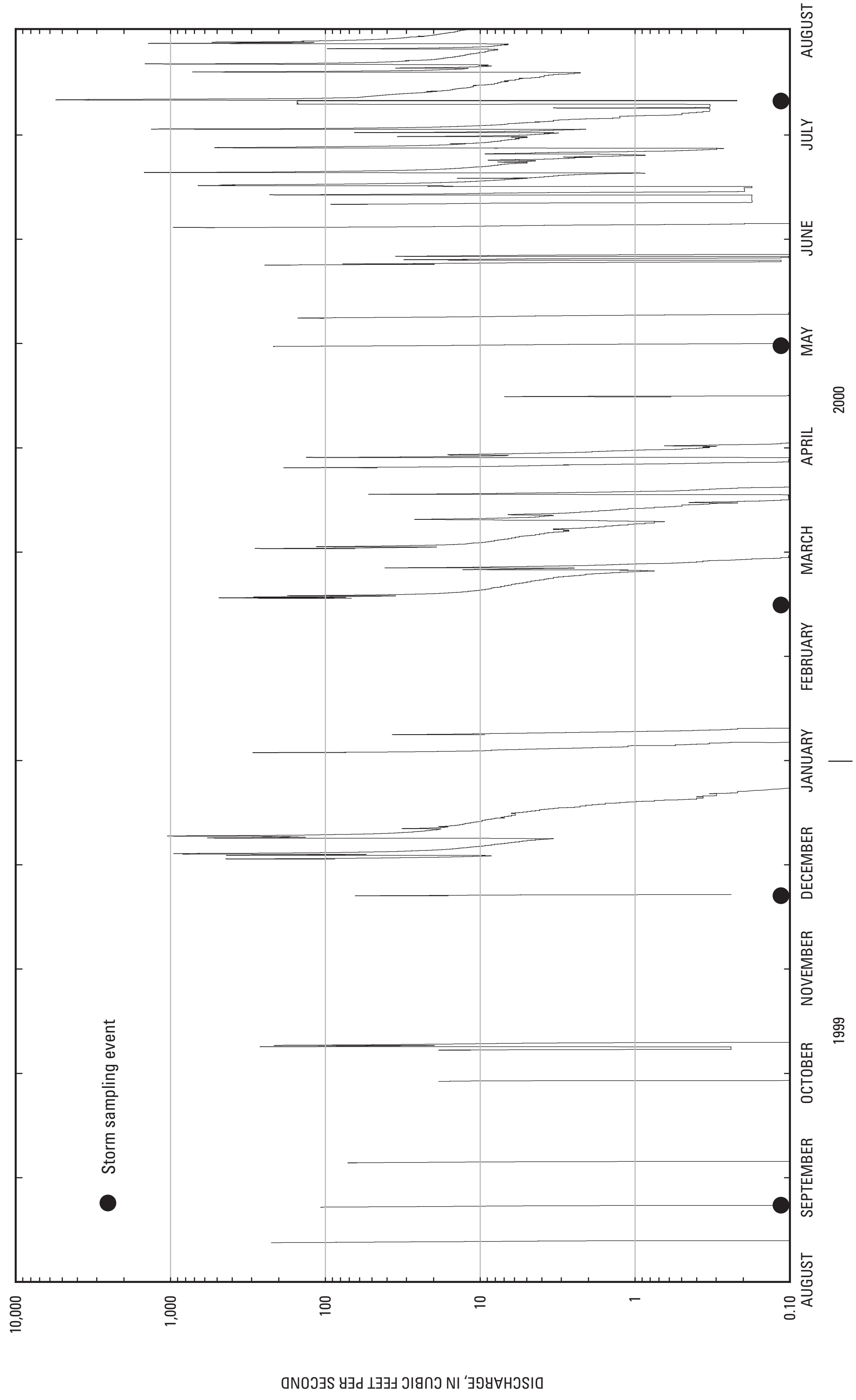

Figure 8. Discharge hydrograph at Wilsons Creek near Springfield (07052100), August 1, 1999, through August 1, 2000.

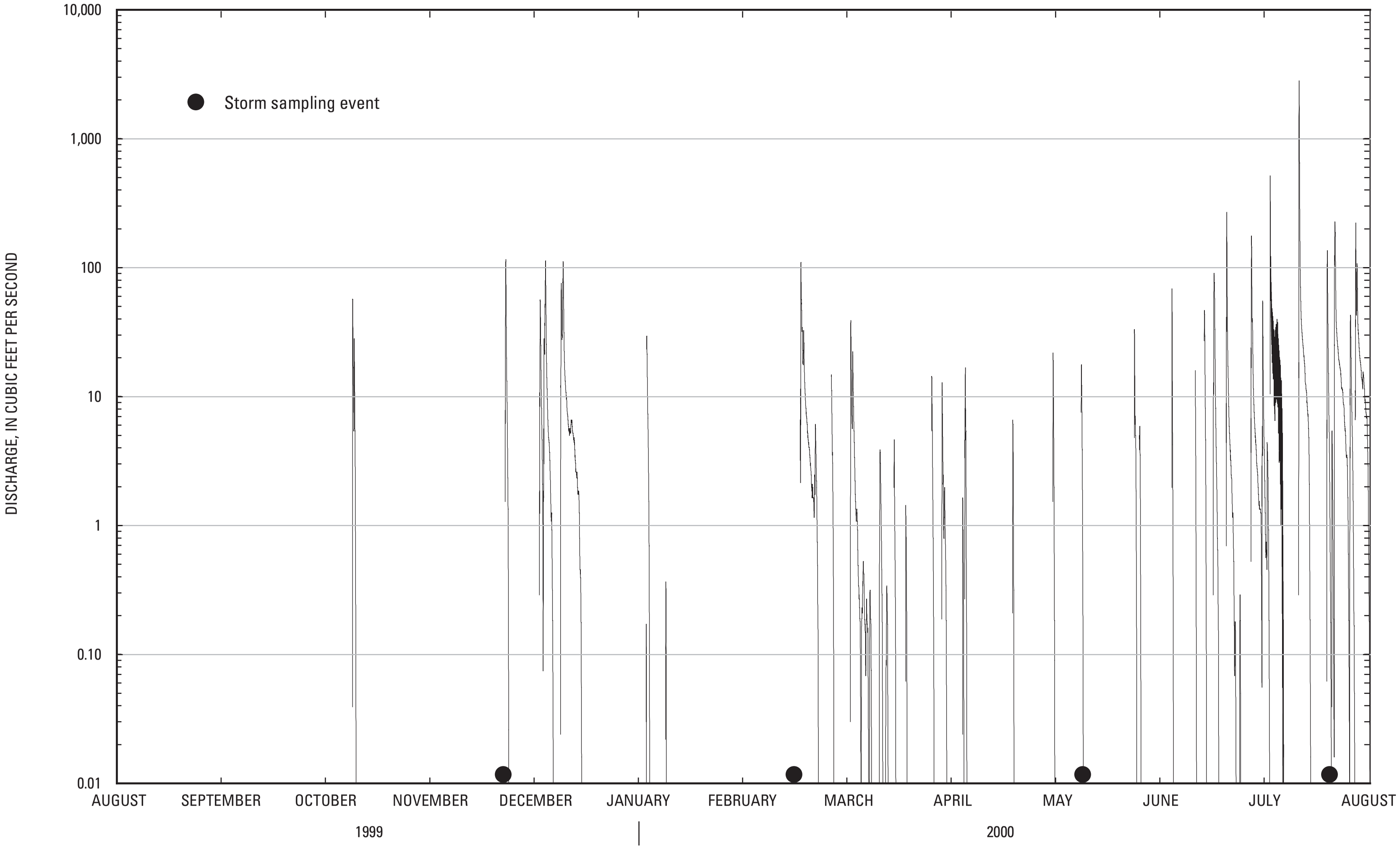

Figure 9. Discharge hydrograph at South Creek (07052120), August 1, 1999, through August 1, 2000.

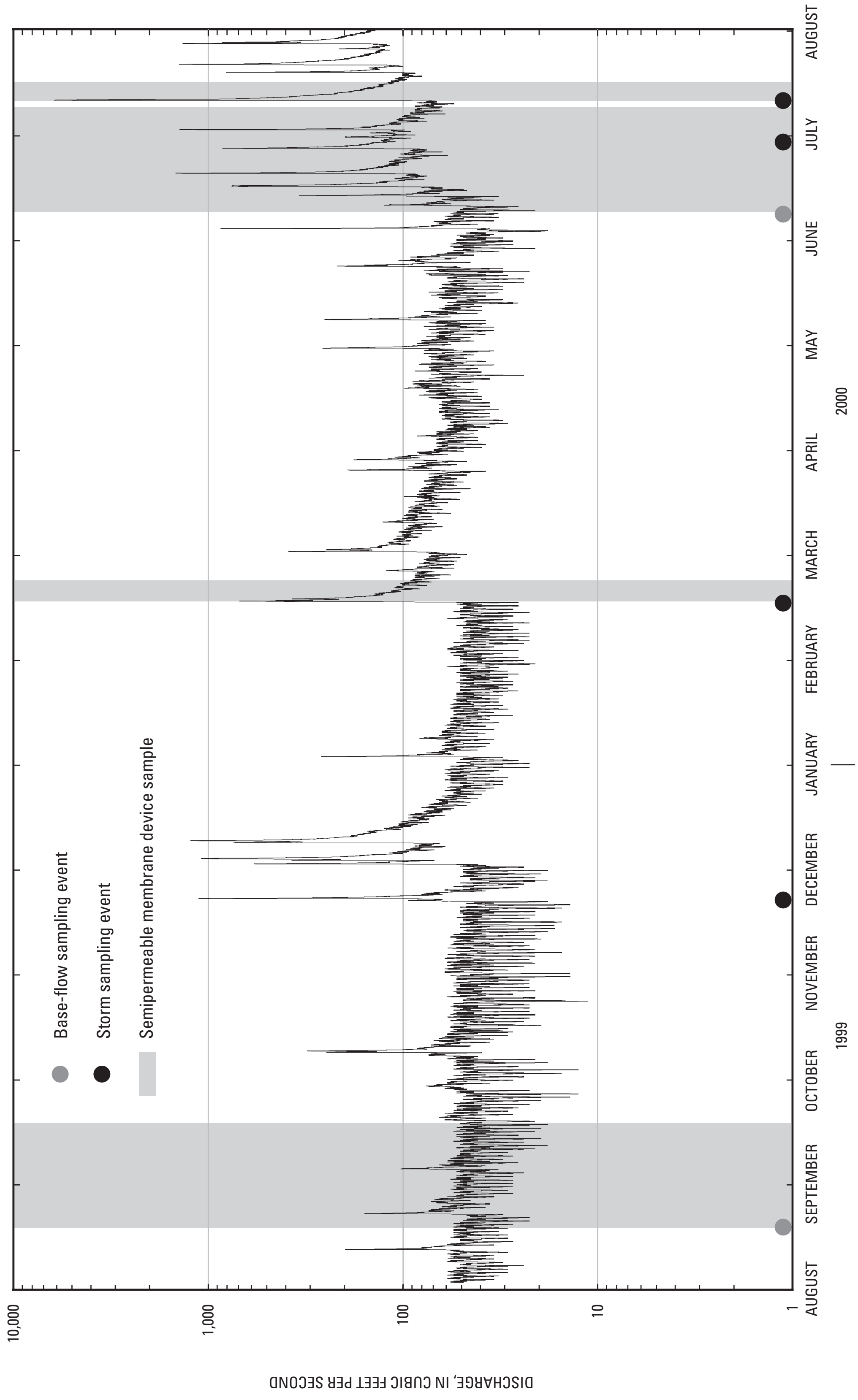

Figure 10. Discharge hydrograph at Wilsons Creek near Battlefield (07052160), August 1, 1999, through August 1, 2000.

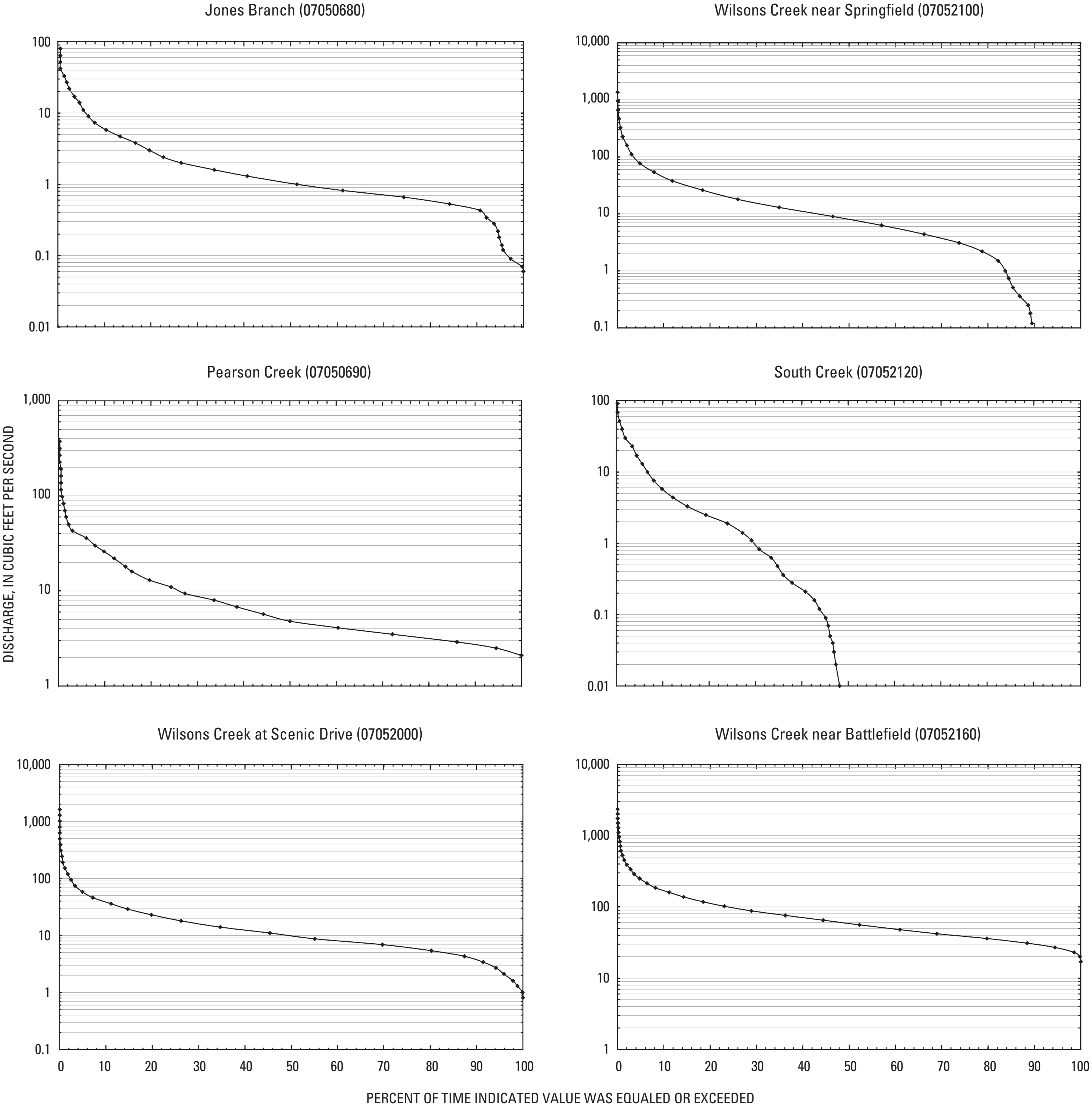

Figure 11. Flow-duration curves for the period of record at the gaging stations in the Pearson Creek and Wilsons Creek Basins.

estimate the 2-, 5-, 10-, 25-, 50-, and 100-year peak flood discharge. The drainage area and percent impervious surface in each basin were calculated using geographic information system techniques using 1:24,000-scale topographic maps, aerial photography, and satellite imagery (fig. 4) as the source data. The peak discharge observed during the period of study and the predicted flood peak discharges using the urbanized-basin equations are listed in table 16. The July 12, 2000, storm produced peak discharges consistent with a 2-year event. Despite the relatively high peaks observed during one storm, the sampling period was relatively dry.

The USGS collected precipitation data at one site (Pearson Creek) during the study (fig. 2). Because of equipment malfunctions, only a partial rainfall record (September 24, 1999, to August 1, 2000) is available for that site. Other supplemental precipitation data sets (one collected at the Springfield-Branson Regional Airport and one collected at the SWWWTP near the Wilsons Creek near Springfield site; fig. 2) are presented in figure 12 to show the variation in the rainfall over the study area and to fill gaps in the USGS precipitation data. Most of the storms sampled were short, high intensity rainfall events that developed quickly and delivered between 1 and 2 in. of rain.

CHEMICAL CHARACTERISTICS AND TOXICITY

Data Limitations

For SPMDs, the relation between the ambient water concentration of the constituent and the concentration of the constituent in the triolein-lipid of the SPMD is described by a first-order kinetics equation (J.N. Huckins, U.S. Geological Survey, written commun., 1996). Numerous rate constants and partition coefficients must be known to calculate ambient water concentration when the constituent is not at equilibrium with the triolein of the SPMD. Most of these parameters are not yet well known. At equilibrium, ambient water concentration can be calculated from the lipid-water partition coefficient (K_{lw}) and the concentration of the constituent in the SPMD. For hydrophobic compounds, the K_{lw} can be approximated by the octanol-water partition coefficient of the constituent (K_{ow}) (J.N. Huckins, U.S. Geological Survey, written commun., 1996). Unfortunately, the SPMDs probably were not given enough time to equilibrate (especially during storm events) with all of the compounds detected, and thus ambient water concentrations cannot be computed. The TIC scan concentrations do not con-

Table 16. Observed peak discharge between August 1, 1999, and August 1, 2000, and predicted flood peak discharges for the 2-, 5-, 10-, 25-, 50-, and 100-year flood events using equations for urbanized basins
[*, value from indirect measurement]

Station name	Station number	Drainage area (square miles)	Impervious surface (percent)	Observed peak discharge (cubic feet per second)	Predicted peak flood discharge (cubic feet per second)					
					2-year	5-year	10-year	25-year	50-year	100-year
Jones Branch	07050680	1.29	25.5	511	483	791	1,023	1,366	1,637	1,937
Pearson Creek	07050690	20.9	14.7	2,200	4,000	6,546	8,667	11,815	14,518	17,640
Wilsons Creek at Scenic Drive	07052000	19.4	32.0	*5,480	4,314	6,826	8,984	12,307	15,181	18,531
Wilsons Creek near Springfield	07052100	35.3	24.1	*6,700	6,600	10,517	13,928	19,144	23,715	29,083
South Creek	07052120	10.5	25.0	2,870	2,548	4,098	5,379	7,316	8,956	10,841
Wilsons Creek near Battlefield	07052160	58.2	19.8	6,160	9,481	15,172	20,191	27,839	34,619	42,630

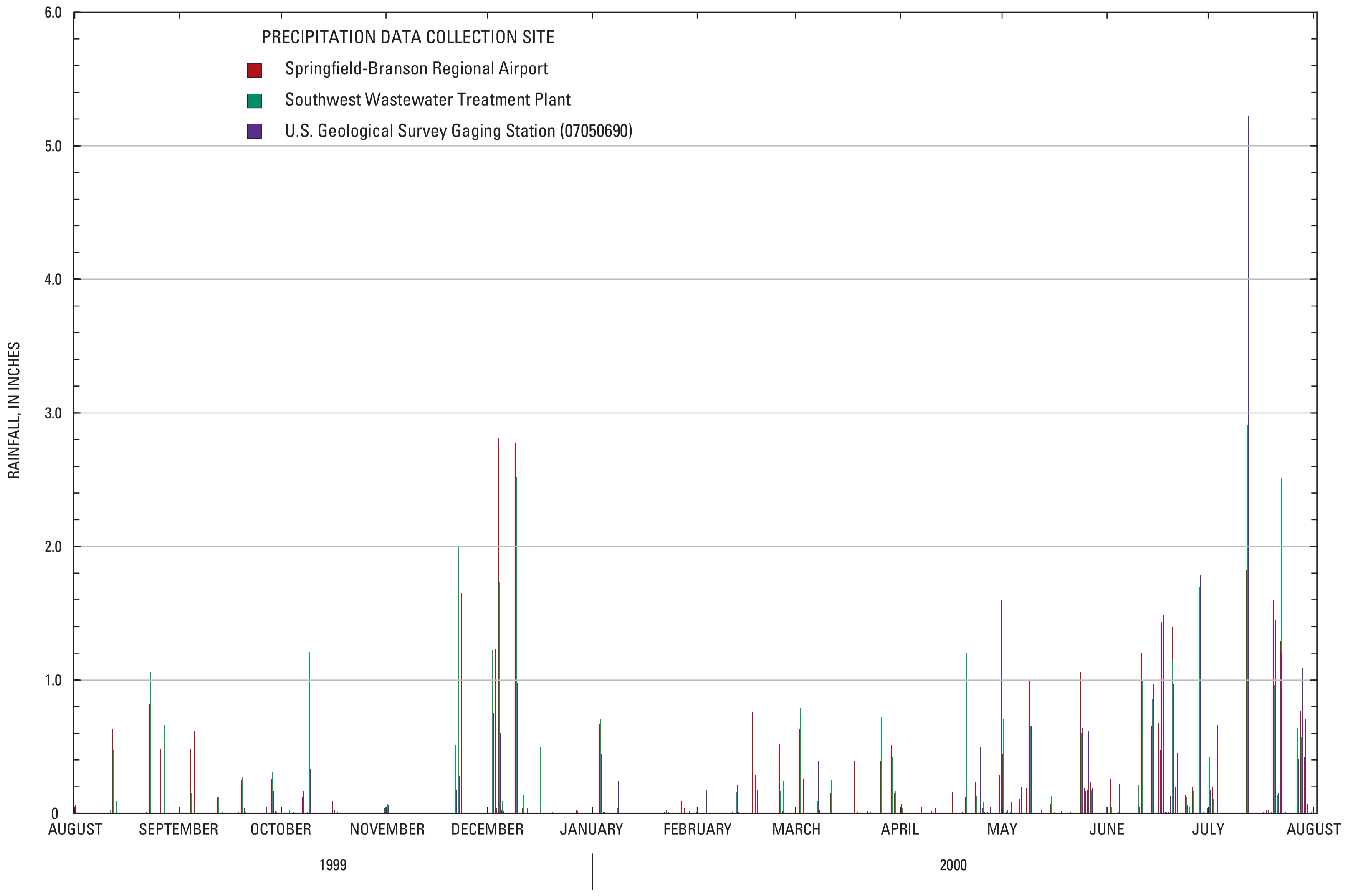

Figure 12. Daily precipitation near Springfield, between August 1, 1999, and August 1, 2000.

sider the differences in chemical properties of the constituents relative to the internal standard; therefore, the values are treated as semi-quantitative, and concentration values cannot be compared.

Load Calculations

Calculation of the load of the various constituents is important to determine the total quantity of the constituent that passes a certain point in a given amount of time. The calculations provide another tool to evaluate the water quality during storm events. Instantaneous discharge was determined from the most recent rating tables for the six sampling sites in this study. The gage height used to determine the instantaneous discharge for the base-flow samples was the gage height of the stream at the time of sampling. The gage height used to determine the instantaneous discharge during storm events was the gage height of the stream at the time the third bottle was filled for the water-quality sampling. Loads were not computed from SPMD data or from TIC scan data.

Selected constituents were chosen to highlight the nutrient, fecal indicator bacteria, metal, and pesticide loading in the Pearson Creek and Wilsons Creek Basins at the six sampling locations. Dissolved nitrate and total phosphorus were chosen to illustrate nutrient loading in Pearson Creek and Wilsons Creek Basins (fig. 13). Wilsons Creek near Battlefield carried the greatest nutrient load, an average (2 samples) of 74 lbs (pounds) of nitrogen and 17 lbs of phosphorus per hour during base flow. At the Wilsons Creek at Scenic Drive site, the creek carried an average (2 samples) of 0.5 lb of nitrogen and 0.03 lb of phosphorus per hour. Pearson Creek carried an average (2 samples) of 1 lb of nitrogen and 0.03 lb of phosphorus per hour during base flow. During storm events, nutrient loading generally was one or two orders of magnitude greater in Wilsons Creek than in Pearson Creek and South Creek generally was a small contributor of the total nutrient load of Wilsons Creek. During storm events, Jones Branch was a substantial contributor of nitrogen and a somewhat lesser contributor of phosphorus to Pearson Creek.

Fecal indicator bacteria loads in the base-flow samples typically were several orders of magnitude less than in stormwater samples (fig. 14). The bacteria load usually was higher at the Wilsons Creek near Battlefield site than at the Pearson Creek site during both base-flow and storm-event conditions. The bacteria load of Jones Branch was approximately one order of magnitude less than Pearson Creek during storm events and several orders of magnitude less during base flow. During storm events, South Creek appeared to be a minor contributor to the total bacteria load at Wilsons Creek near Battlefield, whereas Wilsons Creek at Scenic Drive and Wilsons Creek near Springfield carried a substantial part of the total bacteria load at Wilsons Creek near Battlefield.

Of the analyzed trace metals, only four (total aluminum, total zinc, dissolved manganese, and total lead) were present in sufficient amounts to calculate loads (figs. 15 and 16). These metals were present in nearly all base-flow and stormwater samples. In the past, the area was mined for lead and zinc, and remnants of mine tailings are present in several locations throughout the county. In the dissolved state, aluminum, zinc, manganese, and lead are all potentially detrimental to the aquatic environment at large enough concentrations, though the dissolved concentrations observed in the samples collected during this study were well below their state limits for the protection of aquatic life. During base flow, total aluminum and total zinc loads were low [less than 0.1 lb/hr (pound per hour)] in Pearson Creek, but were somewhat higher at Wilsons Creek near Battlefield. During storm events, the total aluminum load increased to between 1.2 and 2,400 lb/hr at Pearson Creek and between 276 and 1,900 lb/hr at Wilsons Creek near Battlefield. Total zinc loads were between 0.27 and 36 lb/hr at Pearson Creek and between 13 and 27 lb/hr at Wilsons Creek near Battlefield during storm events. Total lead and dissolved manganese loads during base-flow conditions were relatively low at all sites, but increased substantially during stormflow conditions. During storm events, the total lead loads ranged between 0.06 and 15.5 lb/hr at Pearson Creek and between 13 and 27 lb/hr at Wilsons Creek near Battlefield. The total manganese loads ranged from 0.05 to 0.62 lb/hr at Pearson Creek and between 0.9 to 6.3 lb/hr at Wilsons Creek near Battlefield during storm events.

Because trace metals usually are associated with the sediment and organic carbon in the water column, the observed increase in the trace metal concentrations/loads was likely a result of the increased sediment and organic carbon concentrations/load of the stream during storm events. During and after storm events, these sediments accumulate in streambeds and lakes. The bioavailability, and thus the toxic effects, of these trace

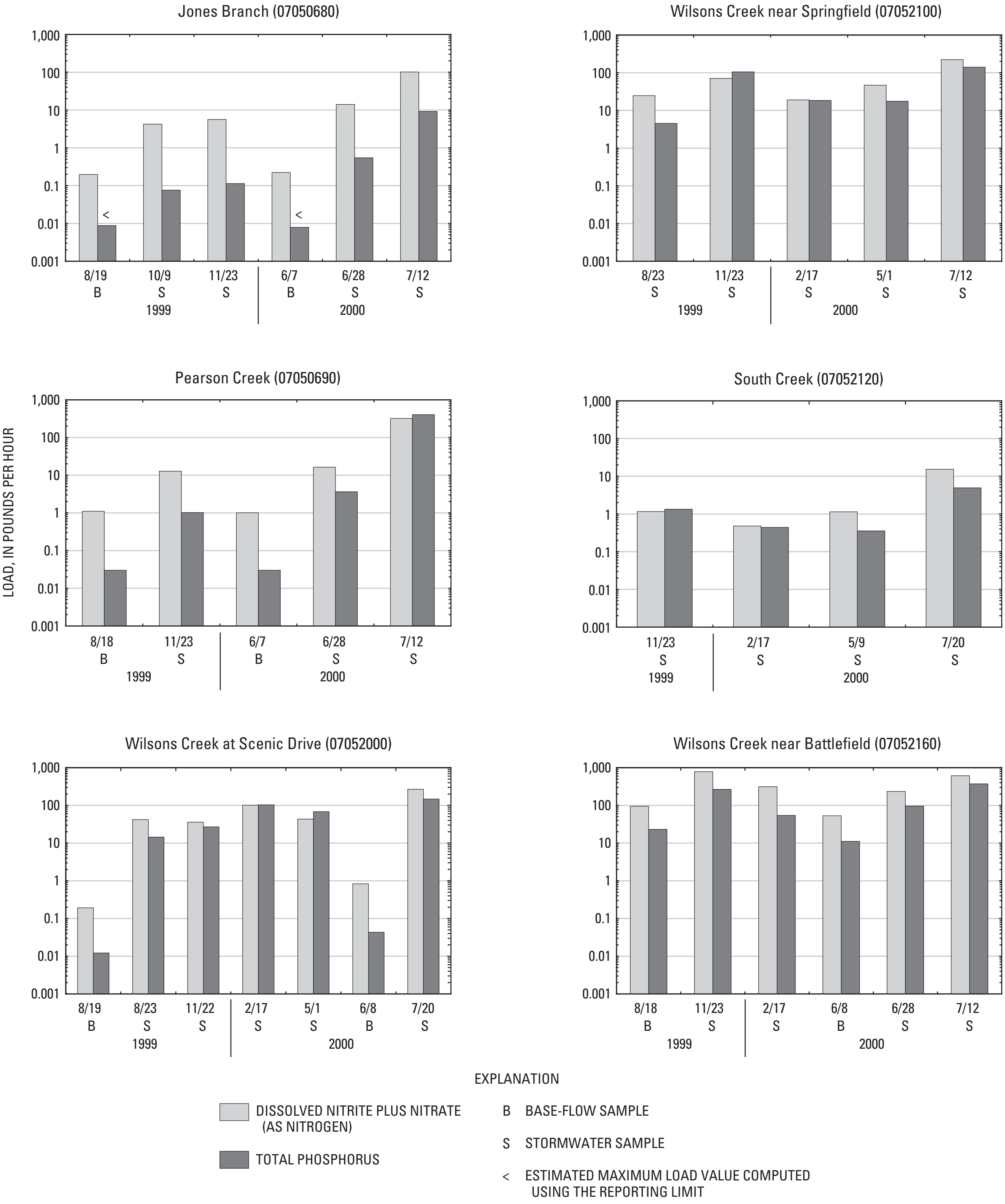

Figure 13. Dissolved nitrite plus nitrate (as nitrogen) and total phosphorus loads during base-flow and storm-event sampling periods in the Pearson Creek and Wilsons Creek Basins.

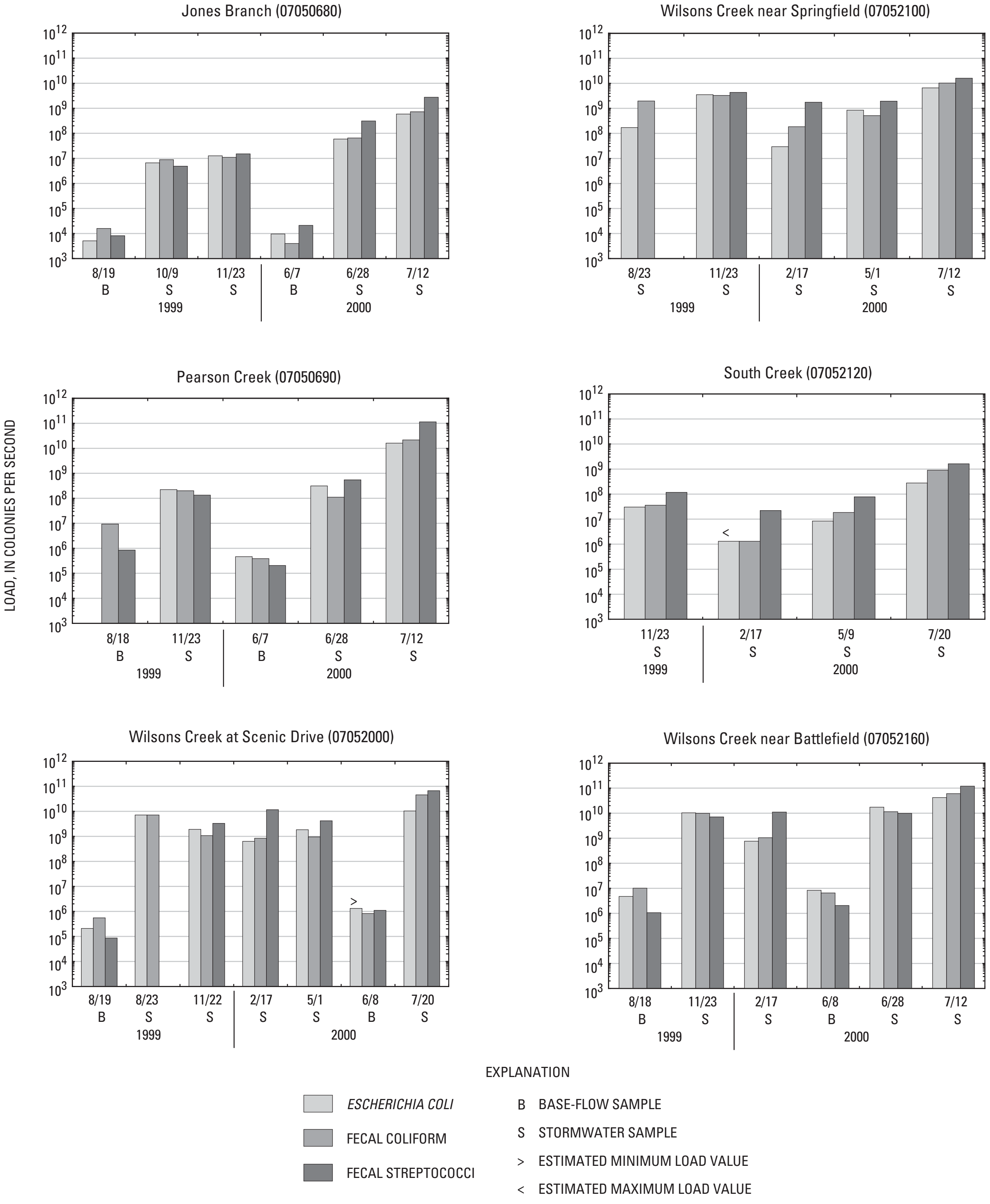

Figure 14. *Escherichia coli*, fecal coliform, and fecal streptococci loads during base-flow and storm-event sampling periods in the Pearson Creek and Wilsons Creek Basins.

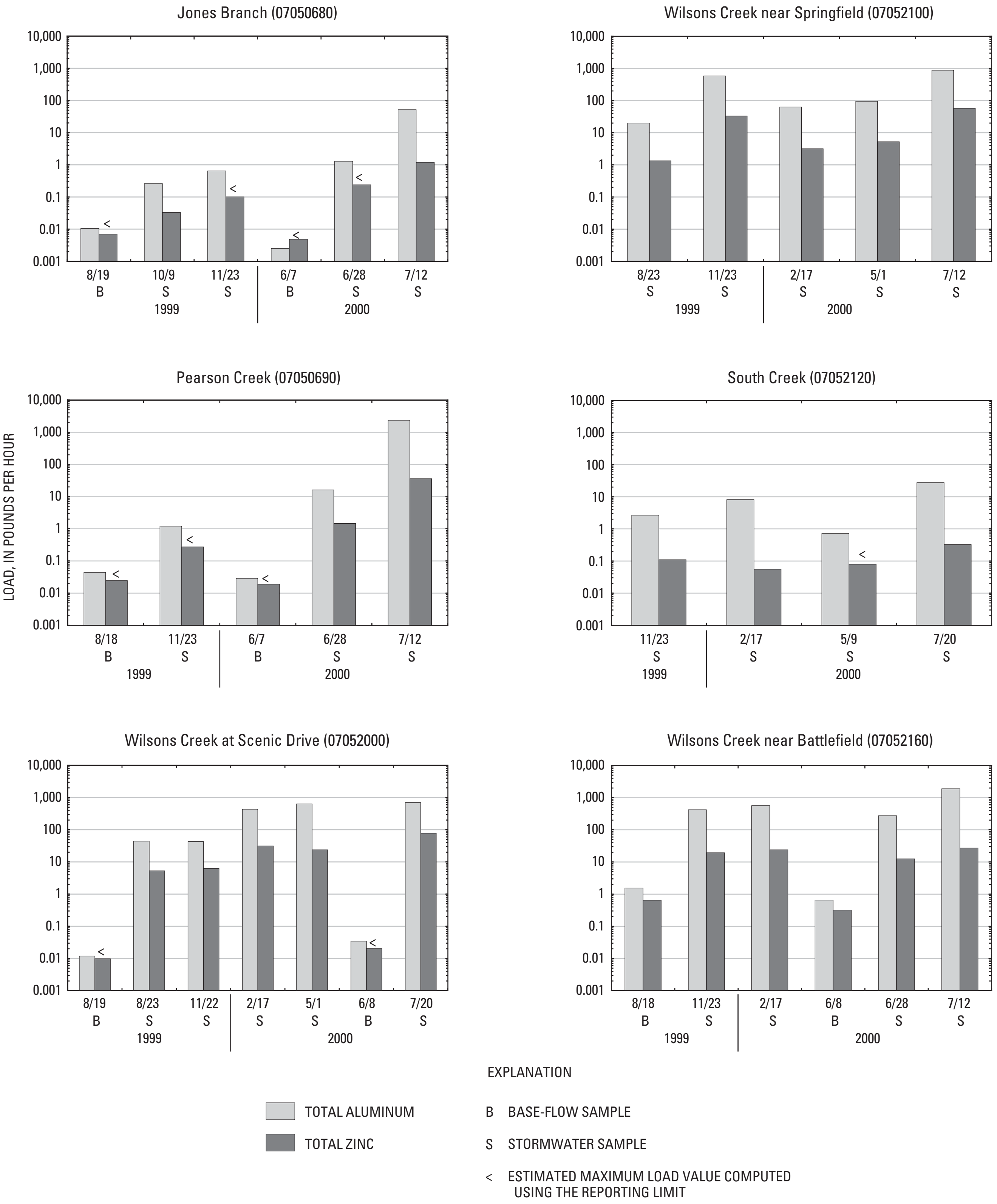

Figure 15. Total aluminum and total zinc loads during base-flow and storm-event sampling periods in the Pearson Creek and Wilsons Creek Basins.

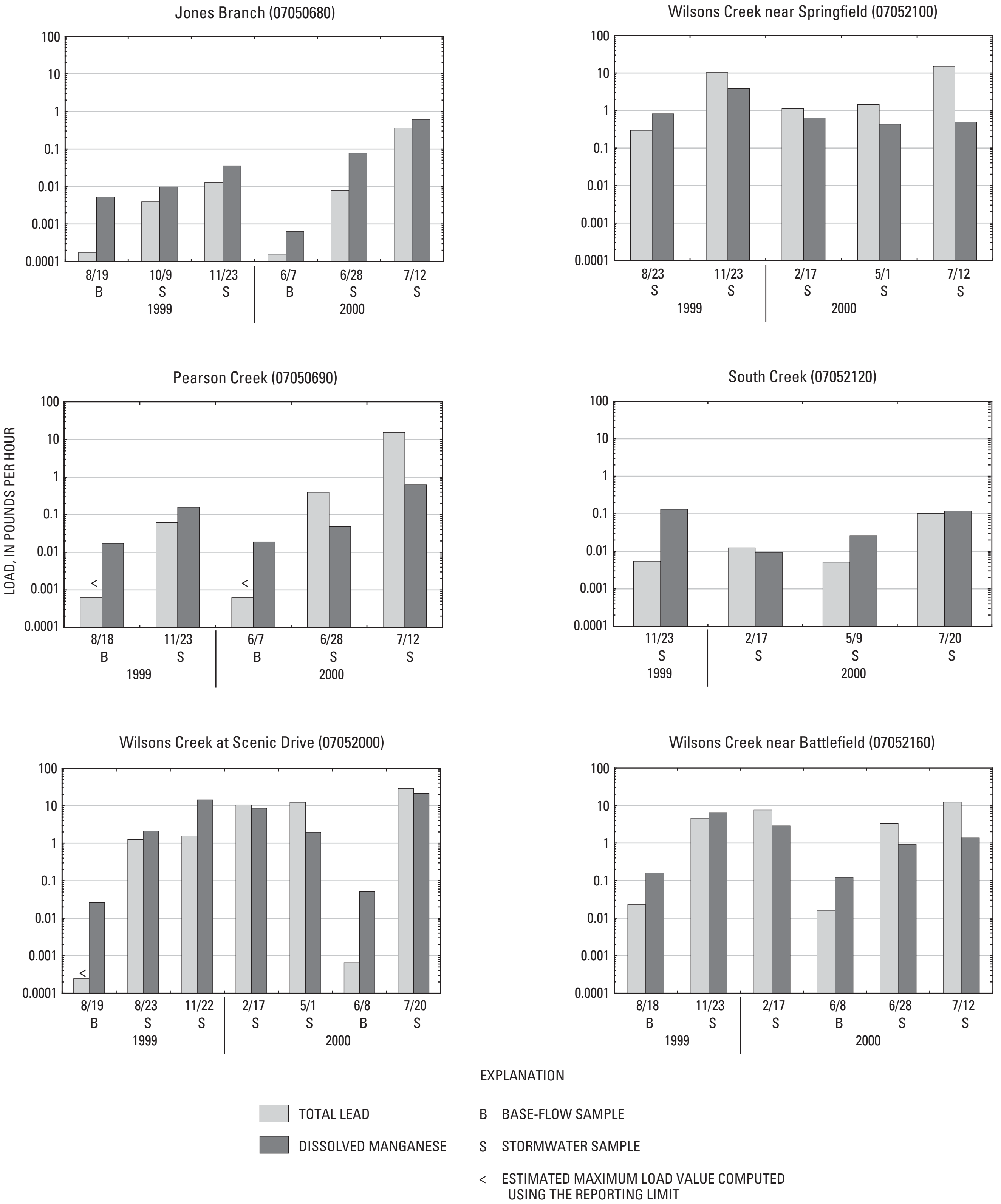

Figure 16. Total lead and dissolved manganese loads during base-flow and storm-event sampling periods in the Pearson Creek and Wilsons Creek Basins.

metals is likely controlled by the solubility and the adsorption properties of the constituent on the sediment.

Only four pesticides (atrazine, diazinon, metolochlor, and prometon) were present in sufficient amounts to calculate loads (fig. 17) at Pearson Creek and Wilsons Creek near Battlefield. The concentrations of all four pesticides were below their respective state limits for the protection of aquatic life in both baseflow and storm-event samples. Storm event loads of these pesticides were about 1 to 1,000 times the baseflow loads, and in general, the loads of the pesticides in the Pearson Creek Basin were less than those in the Wilsons Creek Basin.

The greatest pesticide load was for diazinon—0.12 lb/hr at Pearson Creek and 0.24 lb/hr at Wilsons Creek near Battlefield. Eighty percent of the use of diazinon in the United States is on turf and for residential control of various insects indoors and outdoors (U.S. Environmental Protection Agency, November 2001a). Diazinon is applied at rates ranging from 0.25 lb of active ingredient per acre to 4.35 lbs of active ingredient per acre (residential turf application rate) (U.S. Environmental Protection Agency, November 2001b). The U.S. Environmental Protection Agency is in the process of phasing out certain uses of diazinon (U.S. Environmental Protection Agency, 2000).

Toxicity Evaluation

Under visible light, all samples appeared uniformly clear and colorless. Short exposure to ultraviolet light showed that all dialysates from the long-term and storm-event SPMD samples fluoresced in a darkened room. The intensity of the fluorescence of the samples was similar, and neither reagent blanks nor the trip blanks fluoresced.

As mentioned earlier, the Microtox acute toxicity test results were invalid. The test showed that the solvent blanks were “toxic”, which indicated that the DMSO carrier solvent used by the lab was contaminated.

Mutatox analysis of all samples with metabolic activation (rat S9) showed clear evidence of genotoxins in waterborne chemicals sequestered with SPMDs. Tests of dialysates from all samples demonstrated that the light-emitting revertant bacteria of the Mutatox test exceeded the spontaneous light values of the controls. Each sample was designated genotoxic.

Catfish injected intraperitoneally with a dialysate from the long-term SPMD placed at Wilsons Creek near Battlefield (fig. 2) from August 19 to September 19, 1999, induced hepatic S9 activity as measured by an increase of P450 activity in the EROD assay. The S9 enzymatic activity was heat labile, inducible, and cofactor dependent. Evidence of EROD activity is an indicator of contaminant uptake in fish.

Evaluation of Water Quality in Base Flow and Stormflow

Analysis of the nutrient data indicate that the nutrient load from the Pearson Creek Basin can, during extremely high flow conditions, equal or exceed the load from the Wilsons Creek Basin. During normal flows or moderate storm events, the nutrient load from the Wilsons Creek Basin is much greater than the load from the Pearson Creek Basin. Overall, the effect on the water quality with respect to nutrients downstream from the study area probably is greater from the Wilsons Creek Basin.

Base-flow fecal indicator bacteria densities were relatively low, although coliform concentrations often exceeded the limit for whole-body contact. During storm events, fecal indicator bacteria densities can increase more than 100 times the density during baseflow, which could, for short periods after storm events, pose a potential health hazard to persons exposed to the water. The oxygen consuming metabolic processes of the large densities of heterotrophic bacteria in the stormwater could cause native biota to experience dissolved oxygen stress.

Concentrations and loads of trace metals were not determined to be of immediate concern in either the Pearson Creek or the Wilsons Creek Basin. However, this does not negate the possibility of detrimental effects of these constituents farther downstream in the James River, or when they are introduced into Table Rock Lake. Further sampling of base flow and stormwater in the rest of the James River would better indicate the potential for harmful effects to the basin because of trace metals.

Water sample analyses indicated the presence of pesticides or pesticide metabolites, PAHs, or VOCs at nearly every site during both base-flow and storm-event conditions. Relative concentrations, frequency of detection, and the number of organic compounds detected increased dramatically between during storm-event as compared to base-flow conditions. During

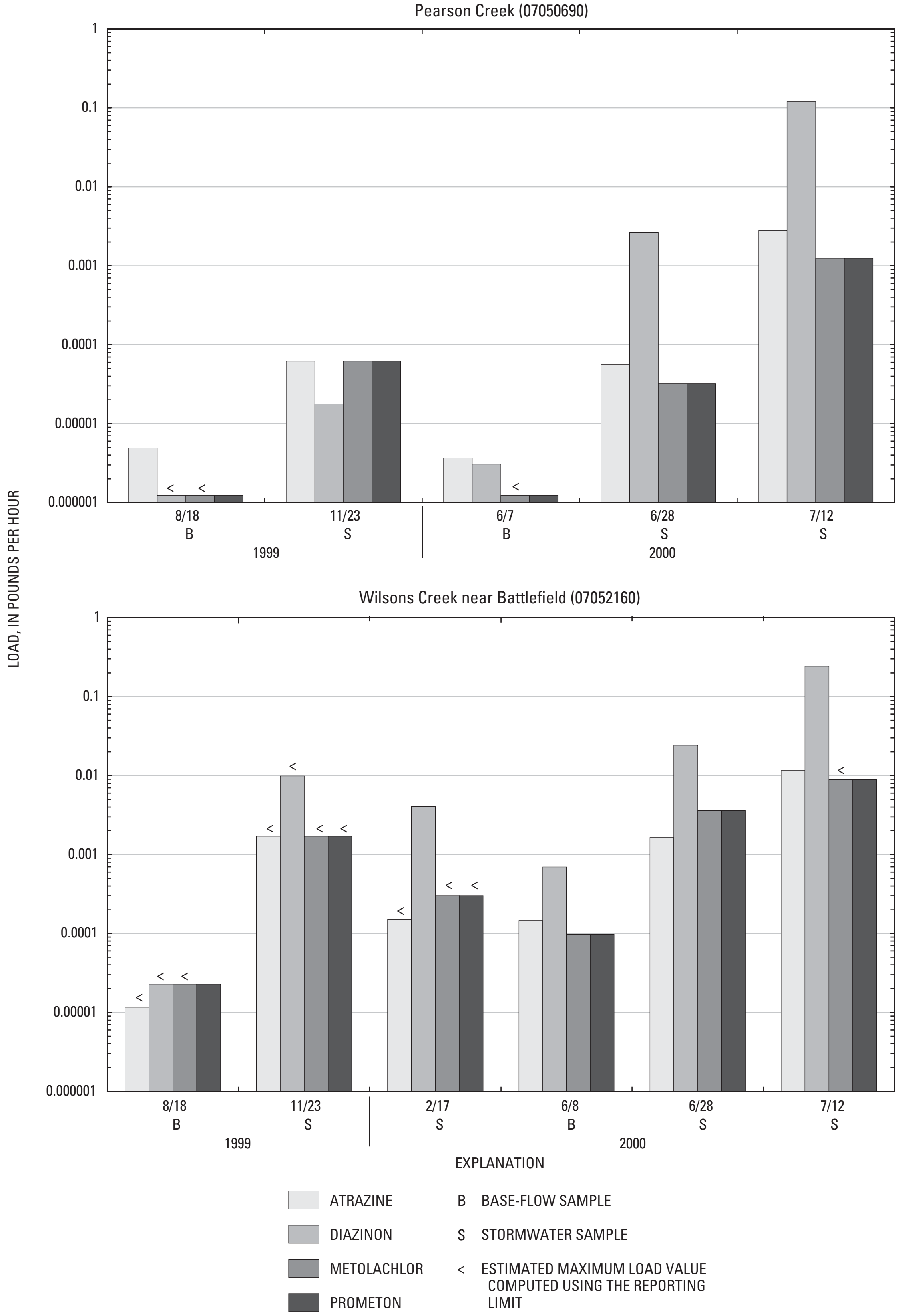

Figure 17. Atrazine, diazinon, metolachlor, and prometon loads during base-flow and storm-event sampling periods in the Pearson Creek and Wilsons Creek Basins.

base-flow conditions, concentrations of organic compounds were not determined to exceed their respective state limits for the protection of aquatic life, though in one sample the pesticide chlorpyrifos approached the state limit of 0.04 μg/L for the protection of aquatic life. Atrazine, diazinon, metolochlor, and prometon frequently were detected at both the Pearson Creek and Wilsons Creek near Battlefield sites during storm events.

Sample fluorescence indicated the presence of aromatic organic compounds in all SPMD samples collected in Pearson Creek and Wilsons Creek near Battlefield. Risk assessment from Mutatox and hepatic induction data indicated evidence of genotoxins, and suggested that multiple-ringed-substituted PAHs, common in petroleum or combustion sources, were the probable bioavailable agents.

The unique ability of the SPMD samplers to simulate the bioconcentration of organic compounds in aquatic biota enabled the detection of a number of compounds that may not have been detectable by standard water analyses. The organic compounds listed in tables 8 and 9 generally are more hydrophobic (less water soluble) than the pesticides (and metabolites) listed in table 7, and are less likely to be detected in water samples. The hydrophobic organic compounds are preferentially concentrated in the lipid material of the SPMD and can be detected on analysis of the dialysates. The presence of these compounds can affect the overall aquatic ecosystem health because many of them can be acutely toxic or genotoxic to aquatic biota.

Aquatic biota living in the Pearson Creek or Wilsons Creek Basin are potentially bioaccumulating the same complex organic mixture as was detected in the SPMDs. Because every base-flow and storm-event SPMD sample was determined to be genotoxic, the compounds that contribute to the genotoxic effects are likely present in both the base flow and the stormwater. The compounds cis-chlordane, trans-chlordane, heptachlor epoxide, and pentachloroanisole were the most frequently detected pesticides and pesticide metabolites in both base-flow and storm-event SPMD samples. The PAH and VOC compounds acenaphthene, diethylphthalate, fluoranthene, phenanthrene, and pyrene consistently were detected in both base-flow and storm-event SPMD samples. The petroleum hydrocarbon series PAHs fluoranthene, phenanthrene, and pyrene were also detected in at least 67 percent of the water samples (table 5).

The combination of the detection of many man-made organic compounds in water and SPMD samples during both base-flow and storm-event conditions and the determination that every SPMD sample was genotoxic leads to the conclusion that the water quality and thus the aquatic environments in the Pearson Creek and Wilsons Creek Basins are degraded by urban inputs. Both the Pearson Creek and Wilsons Creek Basins are affected by these organic compounds during base-flow and storm-event conditions. Based on the number and frequency of the organic compounds detected, the Wilsons Creek Basin appears to be impaired to a greater degree than the Pearson Creek Basin. The harmful effects of long-term exposure of aquatic biota to the compounds present during base flow is compounded by the short-term exposure to the myriad of compounds present in stormwater runoff. Conditions that could increase this likelihood are extended periods between storm events causing compounds to accumulate on the land surface, flushing of the compounds from the karst system from a period of high ground-water flow, and/or improper handling, storage, or disposal (either presently or in the past) of the compounds, thereby causing them to be exposed to the environment.

SUMMARY

The U.S. Geological Survey, in cooperation with the Missouri Department of Natural Resources, characterized the chemistry and toxicity of base flow and urban stormwater to determine if urban contaminants were degrading the water quality of the Pearson Creek and Wilsons Creek Basins in and near the city of Springfield, Missouri. Undesirable and potentially toxic phases of stormwater (nutrients, trace metals, and organic compounds) were identified to help resource managers identify and minimize the sources of these toxicants.

Selected constituents were analyzed from a total of 8 base-flow and 25 stormwater water-quality samples collected from six sites in the study area. Bioavailability of toxicants was determined from three base-flow and four stormwater semipermeable membrane devices (SPMD) samples collected at the furthest downstream sampling point in each of the two basins.

Concentrations of nutrients were generally higher in Wilsons Creek than in Pearson Creek, except during very high-flow storm events. Nutrient loading to the James River from these two basins (especially the Wilsons Creek Basin) is of some concern and has the potential to degrade the water quality. Fecal indicator bacteria densities exceeded the state limit for whole-body-contact recreation at all but one site during base-flow conditions and were orders of magnitude greater in stormwater samples. High indicator bacteria densities shortly after storm events and the associated increased heterotrophic activity could be degrading the aquatic environment in the two basins and potentially the James River downstream by increasing the dissolved oxygen stress on the native biota. Most trace metals dissolved in base-flow and stormwater samples were below the detection limits, but total recoverable trace metal concentrations were much greater, particularly in stormwater samples. Dissolved trace metal concentrations do not appear to be a major concern in the two basins in either base-flow or stormwater runoff.

A maximum of 8 non-pesticide organic compounds were detected in base-flow water samples, and a maximum of 25 non-pesticide organic compounds were detected in stormwater samples. These compounds were mostly polycyclic aromatic hydrocarbons (PAHs). A maximum of 8 pesticides were detected in both base-flow and stormwater samples. All pesticide and non-pesticide concentrations in water samples were below their state standards for the protection of aquatic life. Though pesticides were present in both base-flow and stormwater runoff, the concentrations were low and not substantially different. The presence of the pesticides is of some concern, but it is not likely that their presence alone is causing the observed toxicity.

A maximum of 14 pesticides and pesticide metabolites, and 24 PAHs and volatile organic compounds (VOCs) were detected in long-term SPMD samples. A maximum of 7 pesticides and pesticide metabolites, and 28 PAH and VOC compounds were detected in storm event exposed SPMDs. Toxicity tests of SPMD dialysates indicated evidence of genotoxins in all long-term and storm-event SPMD samples. Hepatic activity assessment of one long-term SPMD sample indicated evidence of contaminant uptake in fish. It is suspected, based on the compounds detected in the SPMDs and the water samples, that the observed toxicity is largely the result of PAHs and VOCs that are probably derived from petroleum inputs or combustion sources. The pesticides and pesticide metabolites that were detected probably compound the genotoxicity primarily caused by the PAHs and VOCs. Based on the organic compounds detected in the stormwater samples and SPMDs and the evidence of genotoxicity, the water quality and thus the aquatic environment in the Pearson Creek and Wilsons Creek Basins are being degraded by urban derived contaminants.

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