Transport of Agricultural Chemicals in Surface Flow, Tileflow, and Streamflow of Walnut Creek Watershed near Ames, Iowa, April 1991–September 1993

By PHILIP J. SOENKSEN

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square kilometer (km^2)	0.3861	square mile
hectare (ha)	2.471	acre
milliliter (mL)	0.0338	fluid ounce
kilogram (kg)	2.205	pound
megagram (Mg) or tonne	2,205	pound
	1.102	ton
gram per hectare (g/ha)	0.01427	ounce per acre
kilogram per hectare (kg/ha)	0.8922	pound per acre
cubic meter per second (m^3/s)	35.3145	cubic foot per second
cubic hectometer (hm^3)	810.7	acre-foot
millimeter per day (mm/d)	0.3937	inch per day
millimeter per hour (mm/hr)	0.03937	inch per hour

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ABSTRACT

The U.S. Geological Survey, in cooperation with the National Soil Tilth Laboratory of the U.S. Department of Agriculture, Agricultural Research Service, conducted a study as part of the multi-scale, interagency Management Systems Evaluation Area (MSEA) program to evaluate the effects of agricultural management (farming) systems on water quality. Data on surface flow, tileflow, and streamflow in the Walnut Creek watershed just south of Ames, Iowa, were collected during April 1991–September 1993 at five sites with drainage areas ranging from 366 to 5,130 hectares. Precipitation, flow discharge, and concentration, loads, and yields of nitrate as nitrogen, atrazine, and metolachlor were analyzed to relate the transport of agricultural chemicals to major water-flow processes and to examine flow and transport differences among three subwatersheds.

Antecedent conditions and basin-characteristic differences had significant effects on the flow response from the subwatersheds. Monthly streamflow-to-precipitation ratios were greater than 1.0, as a result of snowmelt, and negative when streamflow was lost to the ground-water system in the downstream subwatershed. Dry antecedent conditions resulted in ratios less than 0.3 (July 1992), whereas wet antecedent conditions resulted in ratios from 0.7 to almost 1.0 (July 1993) during months with similar large rainfall amounts.

Most of the streamflow from the upland subwatersheds came from tileflow. Surface flow (surface runoff, interflow, and return flow) was highly variable and intermittent, usually lasting for only a few days after a storm, although it could be the dominant source of flow when stormflow was large. Tileflow was less variable and much more persistent, ceasing only after prolonged dry periods.

Large quantities of nitrate as nitrogen were transported in Walnut Creek, with concentrations often greater than the Maximum Contaminant Level of 10 milligrams per liter established by the U.S. Environmental Protection Agency for finished drinking water. In the upland subwatersheds, ground-water flow from the tiles appears to have been the primary means of transport to the streams. Concentrations in tileflow and streamflow generally were 4 to 16 milligrams per liter, with the lower concentrations often the result of dilution by surface runoff. Loss ratios, chemical yields expressed as a percentage of average application rates of nitrate as nitrogen for October 1992–September 1993, were about 10 percent for surface flow and more than 100 percent for tileflow from the 366-hectare basin and were more than 200 percent for streamflow from the downstream subwatershed.

Concentrations of atrazine and metolachlor in streamflow, typically, were less than the Maximum Contaminant Level of 3.0 micrograms per liter, but were as high as 59 and 80 micrograms per liter, respectively, during stormflow.

Concentrations as high as 170 micrograms per liter occurred in tileflow, but these were related to surface flow through surface inlets. The transport of herbicides was extremely variable, with most of the loads occurring during stormflow. Atrazine appeared more susceptible to transport losses to streamflow than did metolachlor. Loss ratios for streamflow from the subwatersheds for April–September periods were 0.3 to 20 percent for atrazine and 0.1 to 2.9 percent for metolachlor.

Chemical loss ratios indicated differences in the transport characteristics of the three subwatersheds. The downstream subwatershed, which has steeper terrain, a more-developed natural drainage system, and fewer tiles than the two upland subwatersheds, had the largest loss rates for all three chemicals—206 percent for nitrate as nitrogen (October 1992–September 1993) and 20 percent for atrazine and 2.9 percent for metolachlor (April–September 1993). For May–July 1993, when most of the herbicides were transported, the downstream subwatershed also had the largest cumulative unit discharge and the largest streamflow-to-precipitation ratios.

INTRODUCTION

Background

The Management Systems Evaluation Area (MSEA) program is part of a multi-scale, interagency initiative to evaluate the effects of agricultural management (farming) systems on water quality. The program resulted from the integration of the U.S. Department of Agriculture (USDA) Research Plan for Water Quality and the U.S. Geological Survey (USGS) Mid-Continent Herbicide Initiative and is part of the President's Water Quality Initiative (Onstad and others, 1991). The USGS cooperates in the MSEA program through its Toxic Substances Hydrology Program.

The midcontinental Corn Belt was selected for study because about 60 percent of the Nation's pesticides and nitrogen fertilizers are used there (Gianessi and Puffer, 1990; U.S. Environmental Protection Agency, 1990). Five MSEAs were selected to represent the principal hydrogeologic settings and geographic diversity of prevailing farming systems in the Corn Belt. MSEAs in sand and gravel settings are in Minnesota, Nebraska, and Ohio. Those in loess and till are located in Iowa and Missouri. Research is focused on ground-water processes in all areas, but stream processes also are a major consideration at areas in Iowa and Missouri.

In Iowa, the USGS, the Agricultural Research Service's National Soil Tilth Laboratory (NSTL) of the USDA, Iowa State University (ISU) through the Cooperative State Research Service of the USDA, and the U.S. Environmental Protection Agency are collaborating on research at scales ranging from laboratory to small watersheds with the following objectives: (1) measure the effects of prevailing and modified farming systems on ground-water and surface-water quality; (2) understand the processes and factors affecting the fate of selected agricultural chemicals; (3) assess the effects of selected agricultural chemicals on ecosystems; (4) assess the projected benefits to water quality of implementing modified farming systems; (5) evaluate the socioeconomic impacts of using modified farming systems; and (6) transfer appropriate technology for use on the land.

The Iowa MSEA project involves four research areas with three different hydrogeologic settings—thin till over bedrock, thick loess, and thick till. The focus of the USGS study within the Iowa MSEA was to understand the general hydrologic system of Walnut Creek watershed, near Ames in central Iowa (fig. 1), as it relates to the transport of agricultural chemicals. Walnut Creek watershed is an area of thick till that will be described in a later section of this report. Brief descriptions of each of the other Iowa MSEA areas, including the terrain, soils, and study layout, are given below.

Tillage Water-Quality Site near Nashua (northeast Iowa)—The area covers gently rolling terrain of weathered till overlying a carbonate-rock aquifer. The soils have a low to moderate permeability and a high water-holding capacity. Depth to bedrock is greater than 15 m at the site but can be less than 5 m a few kilometers away. The study area consists of thirty-six 0.4-ha (hectare) plots with a number of replications of various farming systems.

Deep Loess Research Station near Treynor (southwest Iowa)—This area consists of four field-sized watersheds, 30 to 40 ha each, in steep, dissected terrain of thick loess soil overlying till. Surface drainage patterns are well defined, and shallow subsurface flow

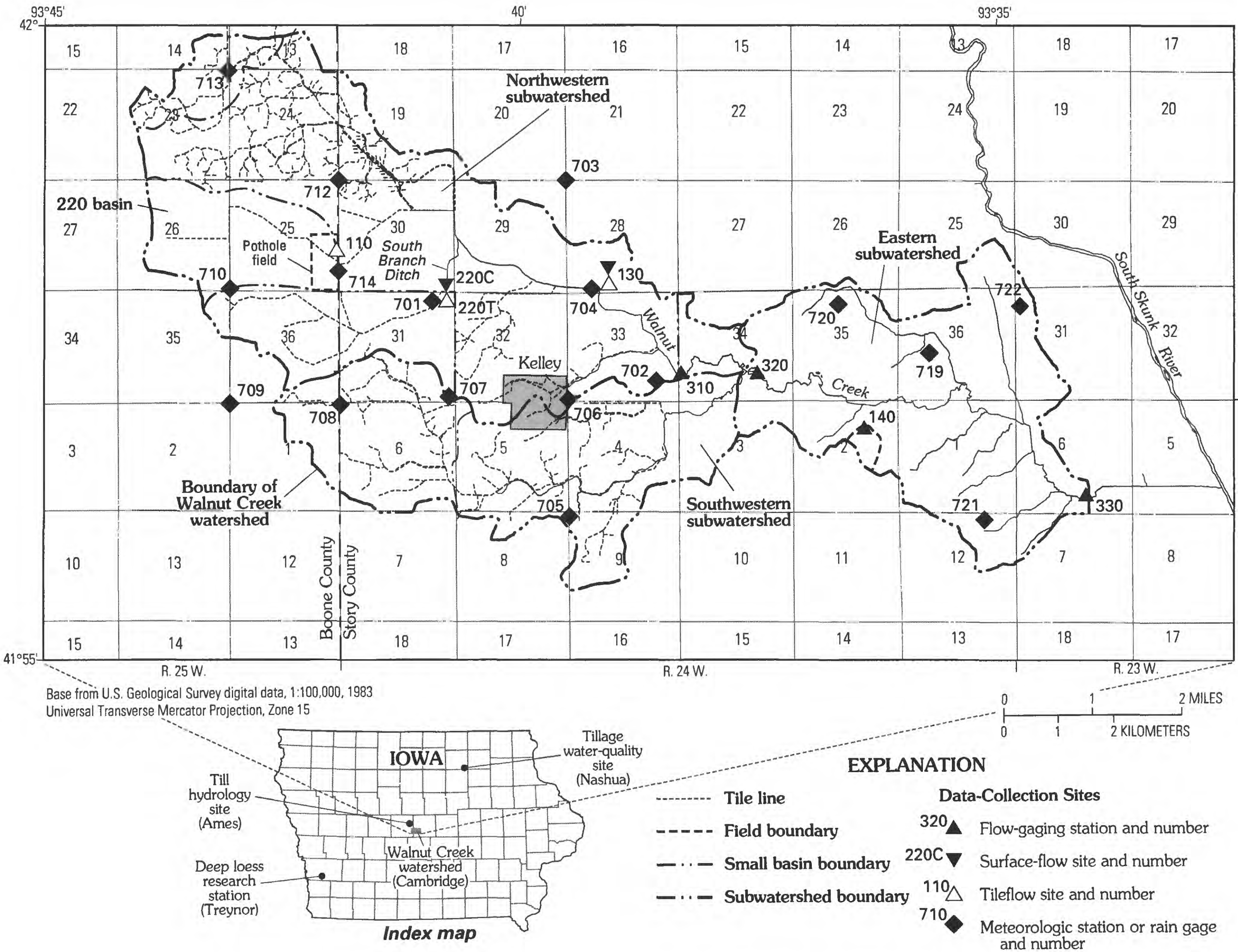

Figure 1. Walnut Creek watershed and location of data-collection sites near Ames, Iowa.

generally is to streams. The soils are highly erodible and have a high water-holding capacity. One watershed is terraced.

Till Hydrology Site near Ames (central Iowa)—The site is on nearly level to gently rolling terrain of till 60 to 90 m thick. Soil permeabilities are low to moderate. The study site consists of eight 0.4-ha plots.

Purpose and Scope

Because water can transport agricultural chemicals in both the dissolved and particulate phases, the USGS study consisted of three specific objectives directed at understanding the hydrologic system of the Walnut Creek watershed:

Objective 1—Define ground-water flow paths and movement in the saturated zone for selected basins.

Objective 2—Evaluate the ability of the USGS's Precipitation-Runoff Modeling System (PRMS) to simulate the major water/sediment flow processes in the watershed and compare simulations with results from other models.

Objective 3—Relate the loadings of agricultural chemicals and sediment in watershed, streamflow and tileflow to the major transport processes.

This report deals with objective 3. The amounts of the agricultural chemicals nitrate as nitrogen (nitrate-N), atrazine, and metolachlor transported by surface flow, tileflow, and streamflow within the Walnut Creek watershed from April 1991 through September 1993 are documented. Comparative analyses are made of the amounts of chemicals applied and the amounts of chemicals transported by the various flow processes from three subwatersheds. Chemical concentrations, discharges, loads and yields (load per unit area) are presented along with rainfall and flow data. Results for alachlor and metribuzin are not presented because they were detected much less frequently and at lower concentrations than the other herbicides, atrazine and metolachlor.

Acknowledgments

The author acknowledges the NSTL and its Director, Jerry Hatfield, for their interagency support of the Iowa MSEA project. Without the hundreds of chemical analyses that were provided by the NSTL, at no cost to the USGS, this study would not have been possible. In addition, Donna Schmitz, who was the author's primary operational contact with the NSTL, participated in almost all aspects of this project including gage construction, onsite measurements and sampling, equipment servicing and repair, and data compilation and analysis. The author also thanks Ed Fischer of the USGS, who helped with special programming needs vital to the computation of data for this project.

DESCRIPTION OF WALNUT CREEK WATERSHED

Walnut Creek watershed is located in Boone and Story Counties of central Iowa. It is part of Major Land Resource Region 103 (U.S. Department of Agriculture–Soil Conservation Service, 1981, p. 76), which covers much of central and north-central Iowa and southern Minnesota. In Iowa, Region 103 covers nearly the same area as the Des Moines Lobe landform region described by Prior (1991, p. 36–47). It is characterized by low relief and poorly developed natural surface drainage. Channel slopes generally are not great except where smaller streams have cut down from uplands near a larger stream. Flood peaks are not as large as for the other landform regions in the State, and low flows are not well sustained in most of the region.

Physical Characteristics

The terrain of the Walnut Creek watershed is typical of the Des Moines Lobe; it is nearly level with numerous potholes (closed depressions) in the upstream one-third of the watershed, nearly level or gently rolling in most of the other uplands, and steeper in the downstream part of the watershed where streams have cut down to the South Skunk River Valley. Surficial deposits of till overlie carbonate bedrock. Till thickness is 60 to 90 m on the uplands, and total relief is about 60 m. Soils are in the Clarion-Nicollet-Webster association (Oshwald and others, 1965, p. 28–31; Andrews and others, 1981; DeWitt, 1984). Clarion soils are well drained, moderately permeable, and located on upland highs and ridges with typical slopes of 2 to 5 percent. Nicollet soils are somewhat poorly drained, moderately permeable, and located on upland intermediate highs with typical slopes of 0 to 5 percent. Webster soils are poorly drained, moderately permeable, and located on low-lying upland flats with typical slopes of 0 to 2 percent. Natural drainage is poorly developed in the upper part of the watershed, requiring the use of subsurface drainage (tile lines)—many with surface inlets in potholes—and drainage ditches. Surface drainage areas are difficult to determine because of the nearly level terrain and subtle drainage features. In some cases, tile lines transport ground water to an adjacent surface drainage basin. Large parts of some drainage areas, especially in the upstream part of the watershed, may not contribute to surface flow but may contribute to tileflow through surface inlets and subsequently to streamflow.

Walnut Creek flows into the South Skunk River from the west about 11 km southeast of Ames and about 4 km north of Cambridge. At the outlet point of the study area (site 330, fig. 1), where Walnut Creek flows from the uplands and onto the South Skunk River alluvial plain, the watershed has a drainage area of 5,130 ha. As shown in figure 1, the watershed can be divided into three subwatersheds. The northwestern subwatershed, about 2,630 ha, and the southwestern subwatershed, about 1,170 ha, are nearly level to gently sloping with numerous potholes in their upstream reaches. In their downstream reaches, the terrain becomes more rolling but is steeper near the channels. Perennial (woody) vegetation is more prevalent in the steeper terrain. Drainage ditches, tile lines, and surface inlets connected to tile lines have been added throughout the watershed to increase the naturally poor drainage. The southwestern subwatershed is mostly tile drained with a well-defined channel or ditch extending only about one-fifth of the way up the basin, which contrasts with the channel and ditch in the northwestern subwatershed that extends about one-half of the way up the basin. Relief of the eastern subwatershed, draining about 1,330 ha, is greater than for the northwestern and the southwestern subwatersheds, and the terrain is steeper and more dissected with streams and drainageways. Natural drainage is better, but some tile lines have been installed. A few terraces also have been built. The northwestern and the southwestern subwatersheds are used almost entirely for row-crop agriculture, and there is little perennial vegetation. The eastern subwatershed also is used primarily for agriculture but has more perennial vegetation, mostly where the terrain is steeper.

Types of Flow

Flow (or runoff) types can be classified as to pathway and as to time of response to rainfall. A conceptual diagram of flow types, which are defined in the "Glossary" and which will be referred to for the remainder of the report, is shown in figure 2. Overland flow, depression overflow, surface runoff, matrix flow, preferential flow, interflow, ground-water flow, and return flow are examples of flow classification by pathway(s). Base flow and stormflow are classifications by time of response; each can consist of flow from a variety of pathways. Some flows by pathway(s) can provide a rapid or delayed response depending on basin and climatic characteristics and lengths of the pathways. For a given length of pathway, surface runoff usually will be rapid compared to other flow types; preferential flow through large solution channels could be more rapid under certain circumstances. For a given soil-rock system and length of pathway, preferential flow always should be more rapid than matrix flow.

It is usually quite difficult, if not impossible, to gather data at a given location such that flow from any one pathway can be isolated from all other pathways. Water readily moves from one pathway to another, splits from one to several pathways, or converges from several pathways to one. Apportioning flow based on time of response, though somewhat easier, is still rather subjective because delayed and rapid are relative not absolute terms and because their periods of response for a given location will overlap depending on many factors. The concepts and most of the terms presented above and used throughout this report are based on a number of sources (Langbein and Iseri, 1960; Chow, 1964, p. 14–1 to 14–5; Viessman and others, 1972, p. 4–8, 25–29, 61–72; Linsley and others, 1982, p. 204–214, 234–240; Bras, 1990, p. 284–290, 368–385; Wolock, 1993, p. 1–6). The specific use and definition of the term "surface flow" in this report was necessitated by the flow and water-quality data obtained at one of the data-collection sites, discussed in following sections of this report.

Tileflow typically consists of ground water draining into a tile line when the surrounding soil is saturated. This process drains soils more quickly than would occur naturally because the tile lines serve as preferential flow paths to the surface-water system. A network of such tile lines allows integrated samples of shallow ground water to be collected from the area drained by the tiles. In Walnut Creek watershed,

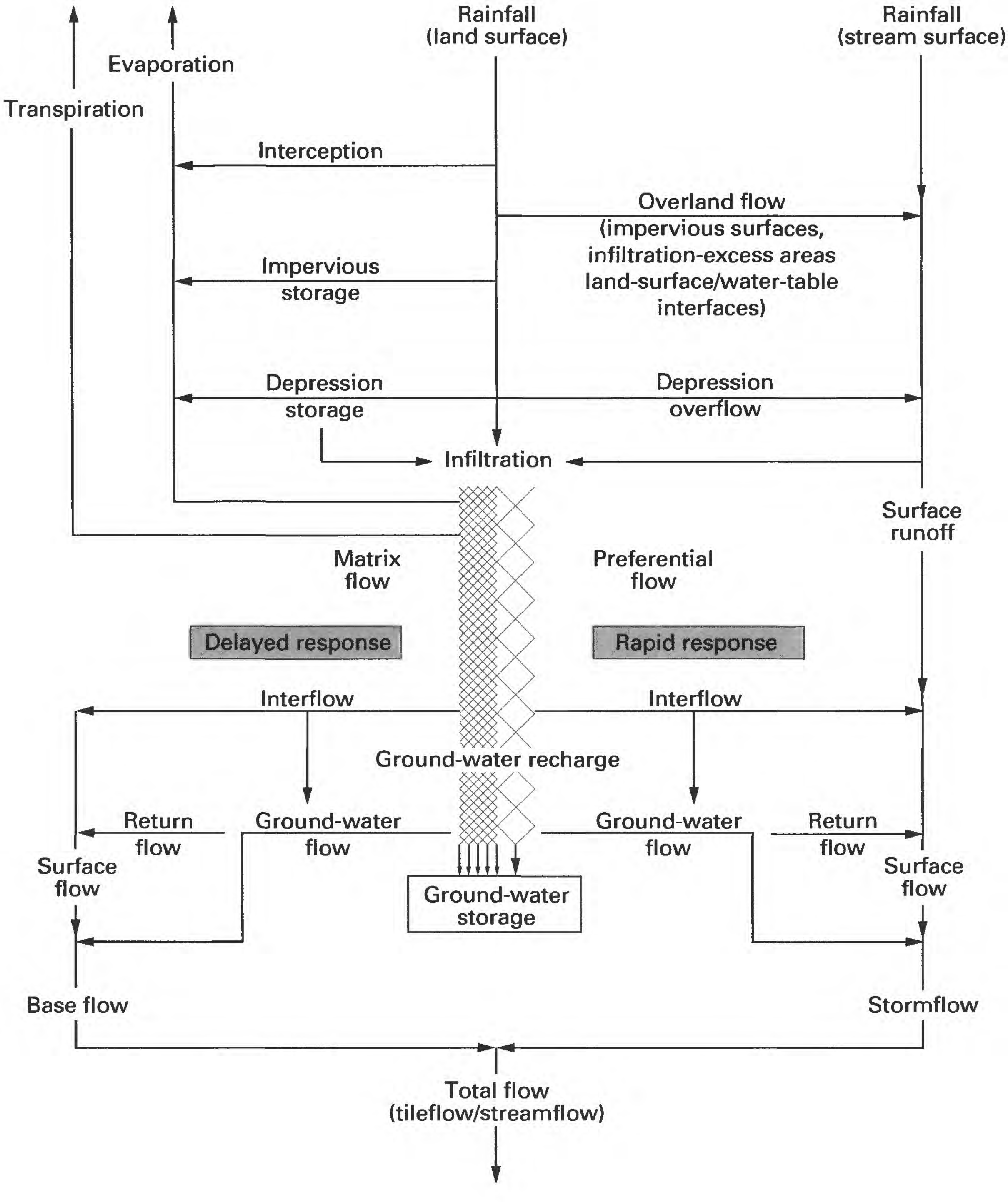

Figure 2. Conceptual diagram showing flow types, from rainfall to tileflow/streamflow, by pathway and time of response to rainfall (modified from Chow, 1964).

however, many tile lines also transport surface runoff from storms because the tiles are connected to inlets in surface depressions that have no surface outlets.

For quantification purposes, flow discharge can be reported as a rate (volume per time), such as cubic meters per second, or as a total volume, such as cubic hectometers. Instantaneous flow, at a specific point in time, is referred to as a rate. Over a period of time (hourly, daily, annually), flow can be expressed as an average rate or as a volume. For comparing the relative amounts of flow from different sized basins, flow also can be expressed per unit of area. The flow per unit area can be the same for two different sized basins, whereas the total flow (unit flow multiplied by drainage area) will be different. Unit flows can be reduced to equivalent depths of flow from the basin by dividing the volume term by the area term. For example, a daily flow expressed in hectare-millimeters (volume) per hectare (area) reduces to millimeters by canceling the hectares. A daily flow of 10 mm is equivalent to a volume of water 10 mm deep over the entire drainage basin flowing past the basin outlet during that day. The same can be done with flows reported as rates. In this report, flows are reported as equivalent depths of flow, expressed as both an instantaneous rate (millimeters per day) for each recording interval and as a volume over a given period (daily flow in millimeters, 15-minute flow in millimeters).

FLOW AND PRECIPITATION DATA

Data Collection

Flow-gaging stations were installed at points along Walnut Creek (sites 310, 320, and 330) to allow comparative studies of streamflow and chemical loadings from the three subwatersheds and at the surface-flow and tileflow outlets to one small basin (sites 220C and 220T) to allow comparisons between major flow pathways. As part of the overall Walnut Creek MSEA study, two meteorological stations—701 and 702—and a network of 15 other rain-gage sites—703–710, 712–714, and 719–722—were installed by the NSTL on or near the watershed to measure rainfall. The locations of the streamflow, surface-flow, tileflow, and rainfall sites referred to in this study are shown in figure 1. The sites are listed in table 1, along with the type of data, surface drainage area, beginning date of operation, and agencies involved. The meteorological stations became operational in March 1991; the other rainfall sites became operational from March 1991 to April 1992.

Surface-Flow Site 220C

Surface-flow site 220C (fig. 1) is located in the northwestern subwatershed at a culvert on an east-west road at the head of South Branch Ditch of Walnut Creek. There is no defined channel in the fields

Table 1. Data-collection sites in Walnut Creek watershed near Ames, Iowa

[NSTL, National Soil Tilth Laboratory; USGS, U.S. Geological Survey]

Site number and name (see fig. 1 for location)	Data type	Surface drainage area (hectares)	Beginning date of flow or rainfall record	Agencies involved
220C—Culvert at South Branch Ditch of Walnut Creek at Kelley	Surface flow	[1]366	August 1991	USGS NSTL
220T—County Tile at South Branch Ditch of Walnut Creek at Kelley	Tileflow [2]	366	July 1991	NSTL
310—Walnut Creek at Kelley	Streamflow	2,550	April 1991	USGS NSTL
320—Walnut Creek near Kelley	Streamflow	3,820	April 1991	USGS NSTL
330—Walnut Creek near Cambridge	Streamflow	5,130	May 1991	USGS NSTL
701–710, 712–714, and 719–722—meteorological station or rain-gage site	Rainfall	not applicable	March 1991 to April 1992	NSTL

[1]About one-third of the drainage area (upper end of basin) may be noncontributing to surface flow.
[2]Includes some surface flow from surface inlets in upstream part of basin.

upstream of the site, and flow is almost entirely storm related. This location was selected because a main tile line also empties into South Branch Ditch of Walnut Creek a few meters away (220T), thus allowing separate measuring and sampling of the major surface- and ground-water components of flow from the same basin.

Stilling wells with float gages were installed upstream and downstream of the culvert. The sensors were 10-turn potentiometers. Stage readings were recorded electronically every 5 minutes on a datalogger located in the main gaging/sampling structure at the downstream edge of the road right-of-way. This structure also contained the automatic water samplers for this and the adjacent tileflow site and the flowmeter for the tileflow site. Instrument stage readings were checked by measurements to water surface from reference points (RPs) during gage inspections and from surveyed high-water marks after large storms. The site was not operated during periods when temperatures were normally expected to be below freezing.

Current-meter and portable-flume discharge measurements were not made at this site because flows were almost entirely storm related and short lived and because measuring conditions were poor. There was no defined channel upstream of the culvert, and downstream the flow included tileflow. When study personnel were present during stormflow, it was not possible to measure the extreme velocities through the culvert; conditions were also unsafe because the culvert was usually submerged at both ends.

Two sets of theoretical ratings, based on approach conditions and culvert geometry and roughness, were developed to convert stage readings to flow discharge—one for unsubmerged outlet conditions and the other for submerged outlet conditions. Each consisted of a stage-discharge rating for the culvert inlet, with stage-fall and fall/discharge ratio ratings used to account for backwater effects. A theoretical road-overflow rating also was developed from approach conditions, profile of road centerline, and embankment geometry.

Tileflow Site 220T

Tileflow site 220T is located in the northwestern subwatershed at a main tile outlet on the north side of an east-west road crossing at the head of South Branch Ditch of Walnut Creek. This location was selected because storm-related surface flow from the same basin also empties into South Branch Ditch of Walnut Creek through a culvert in the road just a few meters away (site 220C).

To reduce turbulence for flow measurements in the corrugated-metal-pipe tile outlet, a slightly smaller, smooth-walled polyvinyl-chloride pipe (PVC) was inserted into the tile outlet and sealed to the outer tile with an inflatable device. A combination pressure transducer and electromagnetic sensor to measure stage and velocity was installed inside the PVC pipe near the bottom. It was connected to a flowmeter located in the main gaging/sampling structure. Stage and velocity readings were recorded electronically every 5 minutes by the internal datalogger and used to compute real-time values of discharge (Schmitz, 1994, p. 1–6). The area of flow was computed from the stage reading and the known geometry of the PVC flow section. Average velocity in the flow section was determined from the point velocity reading near the bottom of the flow section, a flow equation, and a theoretical site calibration coefficient. Area was multiplied by average velocity to determine discharge. The flowmeter could not measure extremely small flows. During such periods, manual measurements were made in the channel downstream of the tile outlet using a 7.6-cm modified Parshall flume or a pygmy current meter (Schmitz, 1994, p. 4–9).

Streamflow Site 310

Streamflow site 310 is located on Walnut Creek near the outlet of the northwestern subwatershed just upstream of a north-south road crossing with a concrete, single-box culvert. This location was selected because it is at the last road crossing upstream from where the southwestern subwatershed tributary enters Walnut Creek and because the culvert could be used as a discharge-measuring device at medium and high stages. The gaging/sampling structure is located on the upstream side of the road embankment, north of the culvert.

Stage was measured initially with a balanced-beam manometer and later with a pressure sensor as the primary gage. The gages sensed the pressure required to bubble nitrogen gas through a single line of polyethylene tubing anchored in the stream about 30 m upstream of the culvert. A weir was installed about 1 to 2 m downstream of the bubbler orifice to stabilize the low-flow stage-discharge relation and to minimize the effects of backwater from ice. An auxiliary stilling well equipped with float gage and potentiometer, similar to those used at site 220C, was installed on the north upstream wingwall of the culvert. A crest-stage gage (CSG) was installed on the north downstream wingwall to obtain high-water marks. Stage readings were recorded electronically every 5 minutes on a datalogger located in the main gaging/sampling structure. During gage inspections, recorded stage readings were compared with staff gage readings and with manual measurements to water surface from RPs. After large storms, recorded stage readings were compared with surveyed high-water marks. Stage data from the two culvert gages were used to compute peak flow of storms.

Thirty-four discharge measurements were made at this site from March 1991 through October 1993, and four stage-discharge ratings were developed. Theoretical weir computations were made for the low end of all ratings except the first rating, which was developed for natural channel conditions prior to construction of the weir. Theoretical culvert computations were made for the high end of all the ratings. Flume, current-meter, and indirect culvert measurements were used to verify or adjust the theoretical parts of the ratings and to define the remainder of the ratings.

Streamflow Site 320

Streamflow site 320 is located on Walnut Creek near the juncture of the northwestern and the southwestern subwatersheds just upstream of a northeast-southwest road crossing with a concrete, single-box culvert. This location was selected because it is at the first road crossing downstream from where the southwestern subwatershed tributary enters Walnut Creek, there is rock riffle with a deep pool to control low stages upstream of the culvert, and the culvert could be used as a discharge-measuring device at medium and high stages. The gaging/sampling structure is located just upstream of the road embankment, northeast of the culvert.

Stage was measured, recorded, and checked manually as described for site 310. The bubbler orifice is located in the pool above the rock riffle about 15 m upstream of the culvert. CSGs were installed 15 m upstream of the culvert and on the southeast downstream wingwall of the culvert to verify recorded peak flows and to aid in computation of peak flows from storms. The rock riffle provided a stable, low-flow stage-discharge relation and minimized the effects of backwater from ice except during extremely cold weather.

Thirty-four discharge measurements were made at this site from April 1991 through October 1993, and two stage-discharge ratings were developed. Theoretical culvert computations were made for the high end of both ratings. Flume, current-meter, and indirect culvert measurements were used to verify or adjust the theoretical parts of the ratings and to define the remainder of the ratings.

Streamflow Site 330

Streamflow site 330 is located where Walnut Creek flows from the uplands onto the South Skunk River alluvial plain, just downstream of a north-south road crossing with a concrete, triple-box culvert. This location was selected because it is at the last road crossing upstream from the mouth of Walnut Creek. The culvert was not used as the high-flow control because of considerable sand deposition in the culvert and the presence of a small north-bank tributary immediately upstream of the culvert. About 25 to 30 m downstream of the culvert, the channel is more uniform and constricted by comparison to the channel just downstream of the culvert and provides a fairly stable high-flow control. The gaging/sampling structure is located about 15 m downstream of the road embankment, north of the culvert.

Stage was measured, recorded, and checked manually as described for site 310. The orifice was located in the channel about 15 m downstream of the culvert. A CSG was located on the north downstream wingwall of the culvert to verify recorded peaks. A weir was installed at the constriction to stabilize the low-flow stage-discharge relation. The weir was kept low to minimize scour of the sand-bottom channel from fall over the weir; however, combined with the relatively flat downstream channel slope across the alluvial plain, this kept the weir from preventing the effects of backwater from ice.

Thirty-seven discharge measurements were made at this site from March 1991 through October 1993, and three stage-discharge ratings were developed. Theoretical weir computations were used for the low end of all ratings except the first rating, which was developed for natural channel conditions. Flume, current-meter, and indirect culvert measurements were used to verify or adjust the theoretical part of the ratings and to define the remainder of the ratings.

Precipitation

Tipping-bucket rain gages with dataloggers were installed by NSTL during March–April of 1991 and 1992 at two meteorological stations and 15 rain-gage network sites distributed throughout or near the Walnut Creek watershed. Dataloggers recorded 5-minute total rainfall and computed total daily rainfall. Equipment and preliminary data at the sites were checked weekly; rain gages were cleaned with distilled water (Hart, 1994a, p. 1–4; Hart, 1994b, p. 1–5). The rain gages are not heated and were not expected to record frozen precipitation; therefore, all gages then in place (13) were initially deactivated November 6, 1991, for the winter. On November 23, 1991, gages 708 and 712 were reactivated to record winter rainfall; the remaining gages were reactivated in March 1992. All gages were operated during the winter of 1992–93.

Data Computations

Flow Discharge

Data at the sites first were downloaded onto a portable computer or data storage module and from there onto a larger computer at the NSTL. Copies of stage data for sites 220C, 310, 320, and 330 were transferred to the USGS office in Iowa City, Iowa, for processing. The USGS computed 5-minute values of discharge for site 220C and 15-minute values of discharge for streamflow sites 310, 320, and 330 using standard techniques (Rantz and others, 1982; Kennedy, 1983). Periods of missing or poor data were reconstructed or estimated from reference readings, high-water marks, weather data, and comparison with data from other nearby sites. During some periods of backwater effect, discharge was computed from estimated backwater-free stage records. All discharge data processed and stored by the USGS also were sent to the NSTL for entry into their data base.

The NSTL computed 5-minute values of discharge for site 220T. Final screening of discharge values computed by the flowmeter was done manually before the data were entered into the NSTL data base. Four-hour values of discharge then were computed from the 5-minute values. For missing periods, values were estimated by interpolation and comparison to other sites and then flagged accordingly in the data base (Schmitz, 1994, p. 9–10).

Precipitation

Data from the climatological stations and rain gages first were downloaded onto a portable computer and from there onto a larger computer at the NSTL. After screening for missing or suspect values, data were summarized in daily tables with hourly and daily rainfall totals. The data then were entered into the NSTL data base (Hart, 1994a, p. 4; Hart, 1994b, p. 5).

Daily values of rainfall for the 17 sites were obtained from the NSTL and entered into USGS computer files in Iowa City. For November–March, daily values of precipitation from surrounding National Oceanic and Atmospheric Administration (NOAA) climatological stations were obtained and entered into the USGS files (National Oceanic and Atmospheric Administration, 1991–93). The NOAA data were used to estimate daily precipitation on the watershed during days of below-freezing temperatures. Daily values of area-weighted total rainfall were computed for the watershed and each of the subwatersheds using the Thiessen polygon method (Viessman and others, 1972, p. 162–164). Daily cumulative totals were computed by summing all the previous daily totals.

AGRICULTURAL-CHEMICAL DATA

Chemical-Application Data

Data on the amount and distribution of agricultural-chemical applications to fields in the watershed were collected by the NSTL from landowners or tenant farmers and entered into a geographic information system (GIS) at the NSTL. Computations were made to determine the amount of each chemical applied for each crop year to the various basins under study. Crop years are different for nitrate-N and the two herbicides, atrazine and metolachlor, because of when the chemicals are normally applied. For a given crop year, the application amounts of nitrate-N include those back to the previous fall harvest because nitrogen fertilizers are often applied at that time as well as in the spring. However, because herbicides are not applied until spring and summer, their crop year is based on the period from April of the specific year through March of the following year. The application data for nitrate–N, atrazine, and metolachlor are shown in table 2. Data for 1991 and 1992 were computed from the GIS, and those for 1993 were estimated manually.

Table 2. Average chemical-application rates of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor for basins in Walnut Creek watershed, 1991–93 crop years

[Source: National Soil Tilth Laboratory of the U.S. Department of Agriculture, Ames, Iowa. Crop year for nitrate-N, October–September; crop year for atrazine and metolachlor, April–March. ha, hectares; kg/ha, kilograms per hectare]

Basin identification (sites located in fig. 1)	Drainage area (ha)	Crop year	Nitrate-N (kg/ha)	Atrazine (kg/ha)	Metolachlor (kg/ha)
Site 220 basin	366	1991	66	0.10	0.68
		1992	95	.34	.56
		1993	57	.10	.79
Site 310 basin (northwestern subwatershed)	2,550	1991	65	.20	.72
		1992	53	.20	.42
		1993	63	.16	.51
Site 310–320 basin (southwestern subwatershed)	1,270	1991	56	.20	.42
		1992	76	.26	.63
		1993	62	.14	.23
Site 320–330 basin (eastern subwatershed)	1,310	1991	41	.09	.56
		1992	51	.15	.77
		1993	27	.04	.32

Basin boundaries were based on the locations of flow-gaging stations, not the locations of stream junctions. For example, site 310 basin refers to the drainage area upstream of site 310, and site 310–320 basin refers to the drainage area downstream of site 310 and upstream of site 320. Although the boundaries are not exactly contiguous with those for the subwatersheds already described, they are nearly identical because sites 310 and 320 are located near the stream junction that determines the subwatershed boundaries; the basin application rates will be considered representative of the specific subwatersheds.

Collection and Analyses of Flow Samples

The water-quality sampling systems at each of the above sites consisted of a peristaltic-pump sampler with 24 glass bottles (350 mL each), and a sample line of Teflon-coated tubing. The sample lines were installed inside of metal pipe or plastic tubing that extended from the samplers to anchored points in the flow. Samplers were triggered by dataloggers or flow-meter (220T only) on the basis of real-time data. Samples were removed and taken to the NSTL laboratory weekly and after stormflows. Except at site 220C, manual samples also were collected weekly throughout the year by dipping sterilized glass bottles into the flow. Samplers were serviced weekly except during periods when the samplers were shut down because temperatures were expected to be below freezing. All water-quality sampling and equipment servicing were done by the NSTL.

Datalogger Sampling

Programmed automatic sampling based on real-time data and user-set decision criteria allowed for efficient use of personnel resources and a sampler's limited bottle capacity, while still obtaining enough samples when they were most needed—during rapidly changing flow. A datalogger sampling program was developed by the USGS and used to initiate sampling at sites 220C, 310, 320, and 330. The decision criteria were set independently for each site on the basis of individual conditions. Below trigger stage (user set), the program was in base mode, and routine low-flow samples were collected whenever elapsed time in base mode exceeded the base sample interval (set to 7 days). Upon exceeding trigger stage, an initial sample was collected. Above trigger stage, thereafter, samples were collected whenever one of two criteria (user set) was exceeded—stage change since the previous sample or elapsed time since the previous sample. Samples were collected as frequently as the minimum-allowed sample interval (set to 15 minutes) during rapidly changing flow or as infrequently as the maximum-allowed sample interval (user set) during slowly changing flow. Occasionally, when a problem occurred with either the datalogger or the relay-driver trigger interface, initiation of sampling was switched directly to a sampler's internal timer until the problem was corrected.

Flowmeter Sampling

For site 220T, sampling was done on a flow-proportional basis. The flowmeter computed flow discharge and cumulative flow volume in real time. When a user-set value of flow volume was exceeded, the sampler was triggered by the flowmeter. Because every sample represents an equal amount of flow, computations of chemical loads can be simplified when the chemical concentrations in the samples are assumed to be averages for those flow amounts. This may not be the case if concentrations are changing rapidly. When malfunctions occurred with the flowmeter, initiation of sampling was switched directly to the sampler's internal timer (Schmitz, 1994, p. 7–9).

Laboratory Sample Analyses

Water samples were analyzed for concentrations of nitrate-N, atrazine, metolachlor, alachlor, and metribuzin at the NSTL in Ames, Iowa, using methods described by Pfeiffer (1994). Nitrate-N concentrations were determined using a colorimetric method. The quantification limit was 1.0 mg/L (milligram per liter). Herbicide analytes were extracted by use of a ^{18}C solid-phase extraction technique and analyzed by gas chromatograph/mass spectrometer using selective ion monitoring. Quantification limits were 0.2 µg/L (microgram per liter) for atrazine and metolachlor, and 0.5 µg/L for alachlor and metribuzin.

Chemical Concentrations, Loads, and Yields

Chemical-concentration and flow-discharge data were used to compute chemical discharges for nitrate-N, atrazine, and metolachlor. Chemical loads were computed from the chemical-discharge data for selected time periods. Chemical yields were computed from the chemical-load and drainage-area data. Alachlor and metribuzin were detected much less frequently and at lower concentrations than were the other herbicides, atrazine and metolachlor; therefore, no discharges, loads, or yields were computed for these chemicals.

Values of chemical discharge—a transport rate expressed as mass per unit time—were computed by multiplication of flow-discharge rates (volume per unit time) by chemical concentrations (mass per volume) and units-conversion factors for each 15-minute time step. Time-concentration curves were developed from the discrete sample concentrations; then values of 15-minute chemical concentration were computed by linear interpolation between samples to match the times of the discharge data. Samples with concentrations less than the quantification limit were arbitrarily assigned a value of one-half the quantification limit. Outliers were eliminated or additional values were added on the basis of data trends and comparison with flow records. For example, additional data points often were added to the last time step prior to a stormflow period to represent the continuation of base-flow concentrations until after stormflow had started. The automatic sampling program usually allowed sufficient samples to be collected during stormflow periods, but there were some periods with few or no samples due to limited bottle supply or equipment malfunction. These periods of limited data were estimated, whenever possible, by additional comparison with concentration data from an upstream or downstream station(s), rainfall data, and data from previous stormflows. The sample concentrations, time-concentration curves, and the U.S. Environmental Protection Agency's (1994) Maximum Contaminant Level (MCL) for drinking water for each chemical and the daily values of flow discharge are shown in figures 3–7 for each site.

Values of chemical load—the total amount of material transported for a given period of time, used here in terms of mass—were computed by multiplication of chemical discharges (mass per time) by the 15-minute time-step intervals (time) and units-conversion factors. This process produced the 15-minute values of load that were then summed to obtain the daily loads for the gaging stations. Daily loads for the subwatersheds were computed by adjusting daily loads at the gaging stations for differences in drainage area and subtracting the loads from other subwatersheds as needed. The loads at site 310 were assumed representative of the northwestern subwatershed and were increased by the drainage-area ratio of 2,630:2,550 to account for the larger drainage area for the northwest-

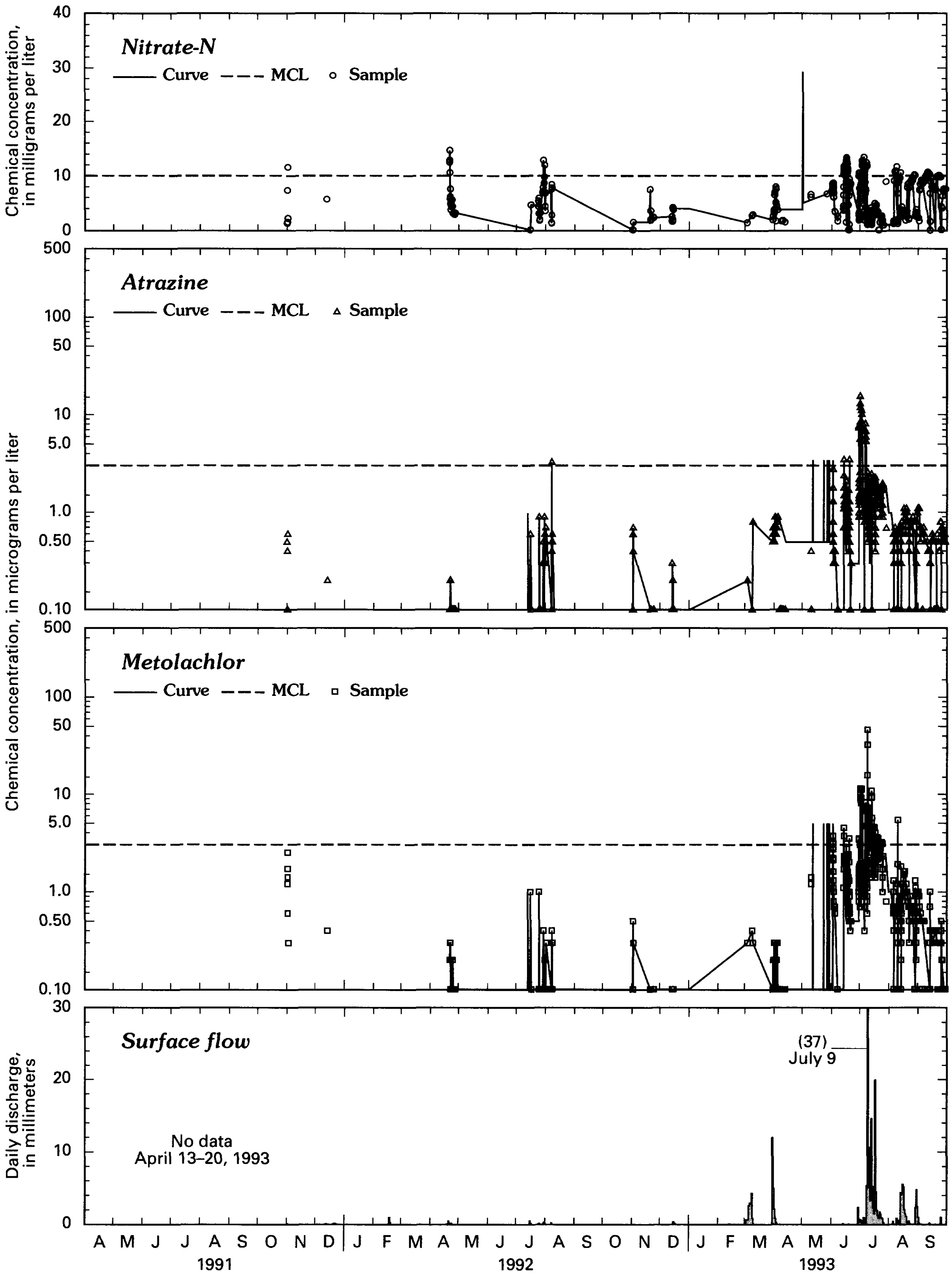

Figure 3. Discrete sample concentrations, time-concentration curves, and Maximum Contaminant Levels (MCLs) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily discharge for surface flow at data-collection site 220C during April 1991–September 1993.

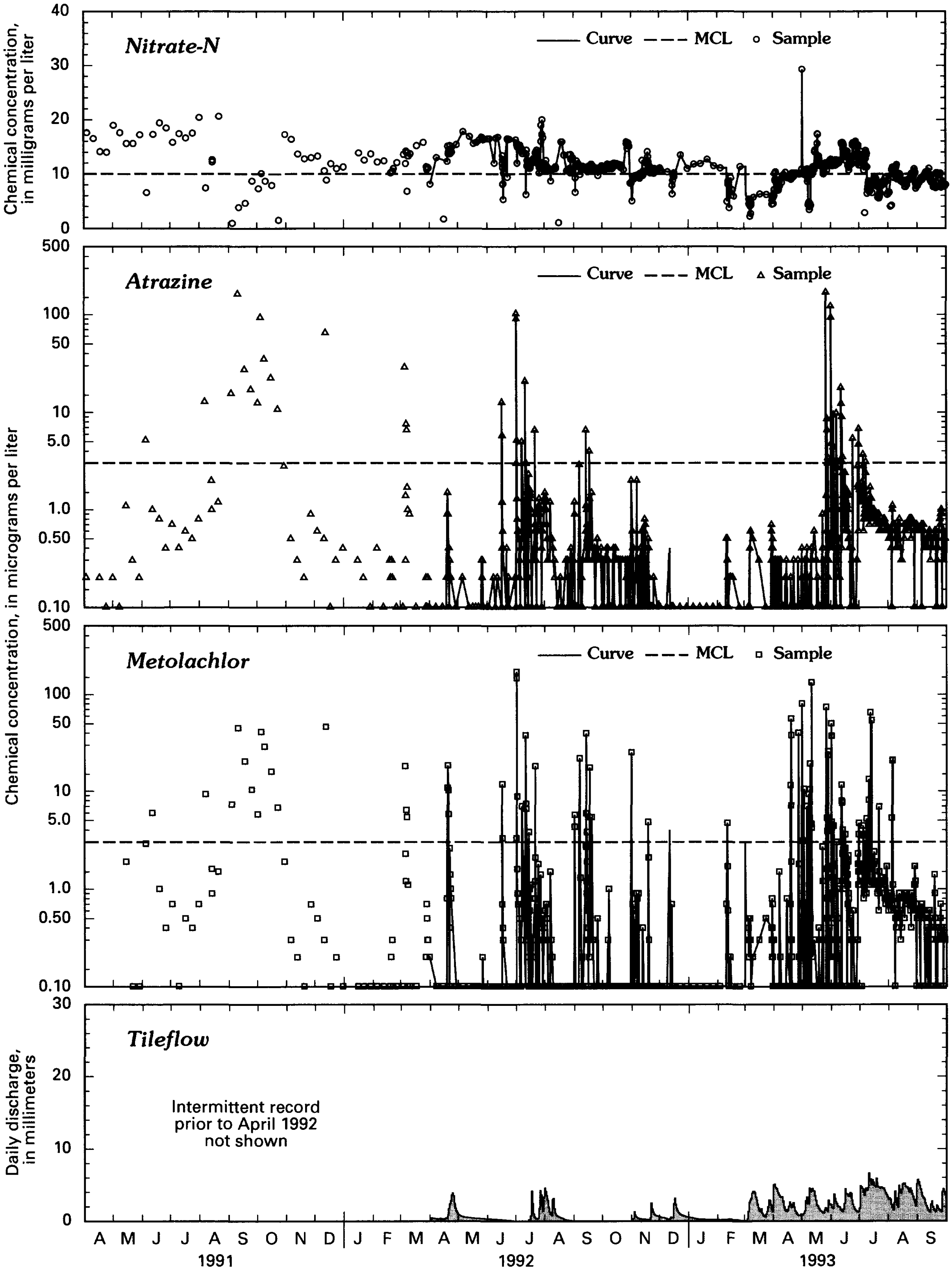

Figure 4. Discrete sample concentrations, time-concentration curves, and Maximum Contaminant Levels (MCLs) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily discharge for tileflow at data-collection site 220T during April 1991–September 1993.

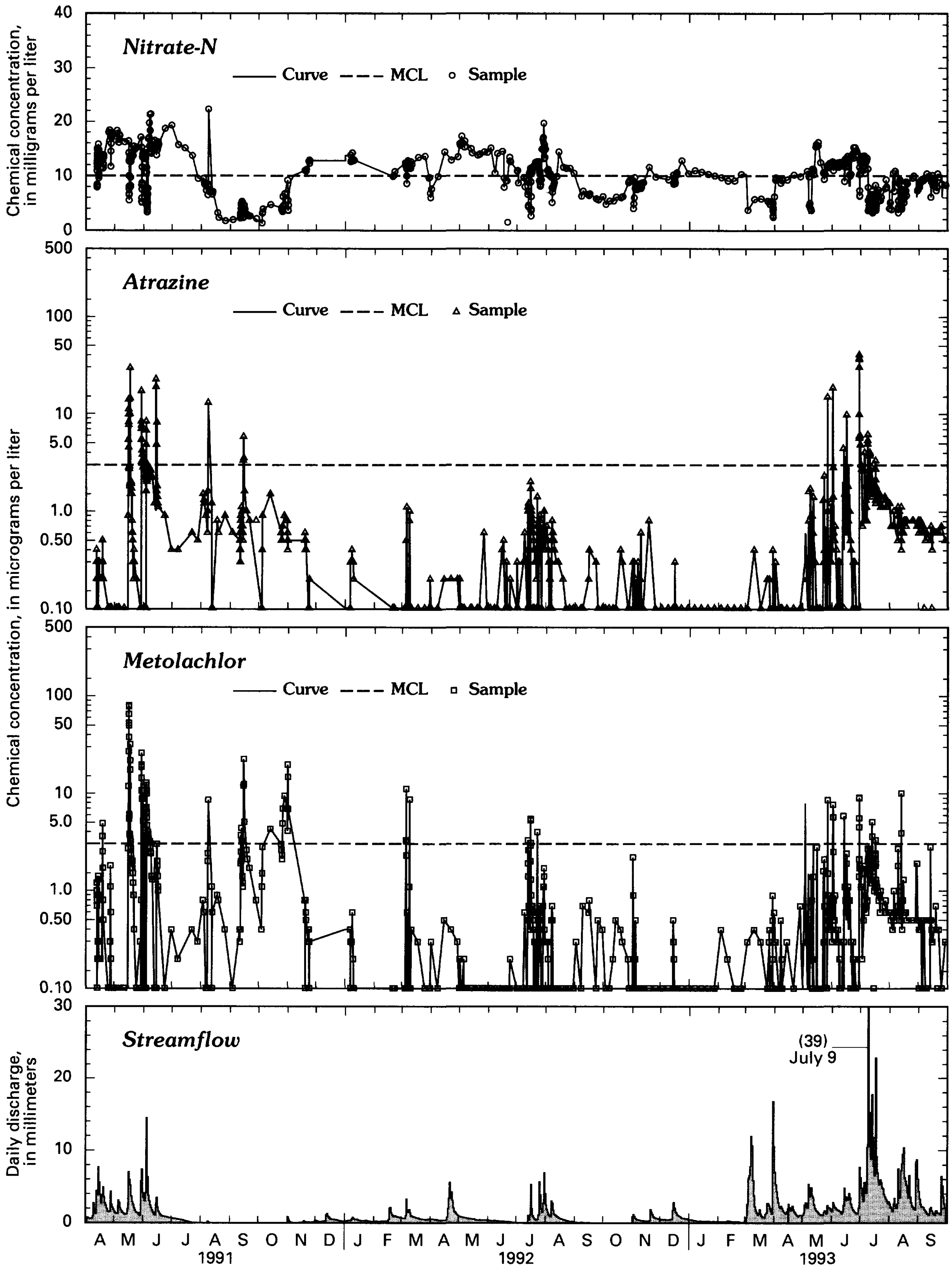

Figure 5. Discrete sample concentrations, time-concentration curves, and Maximum Contaminant Levels (MCLs) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily discharge for streamflow at data-collection site 310 during April 1991–September 1993.

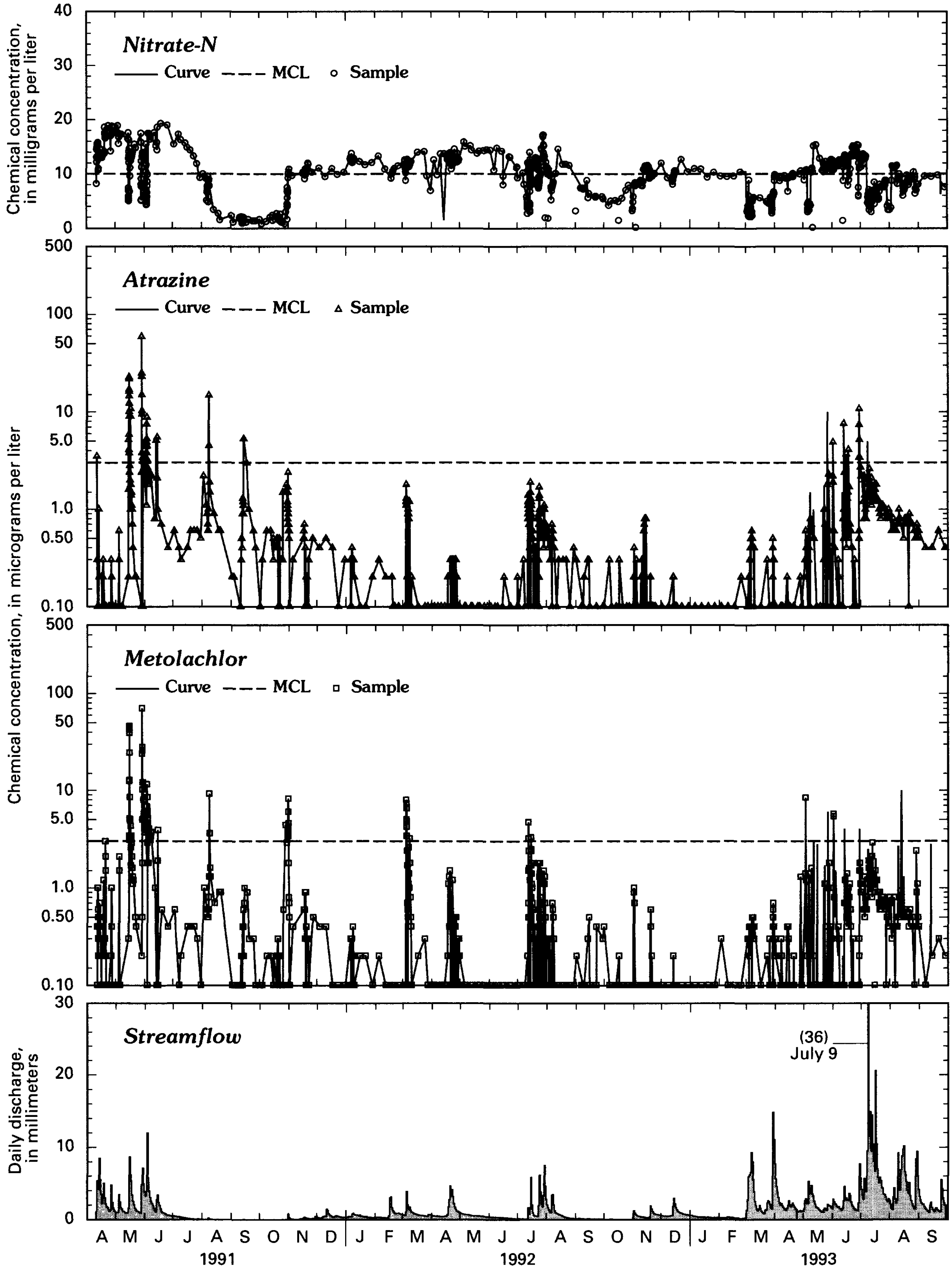

Figure 6. Discrete sample concentrations, time-concentration curves, and Maximum Contaminant Levels (MCLs) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily discharge for streamflow at data-collection site 320 during April 1991–September 1993.

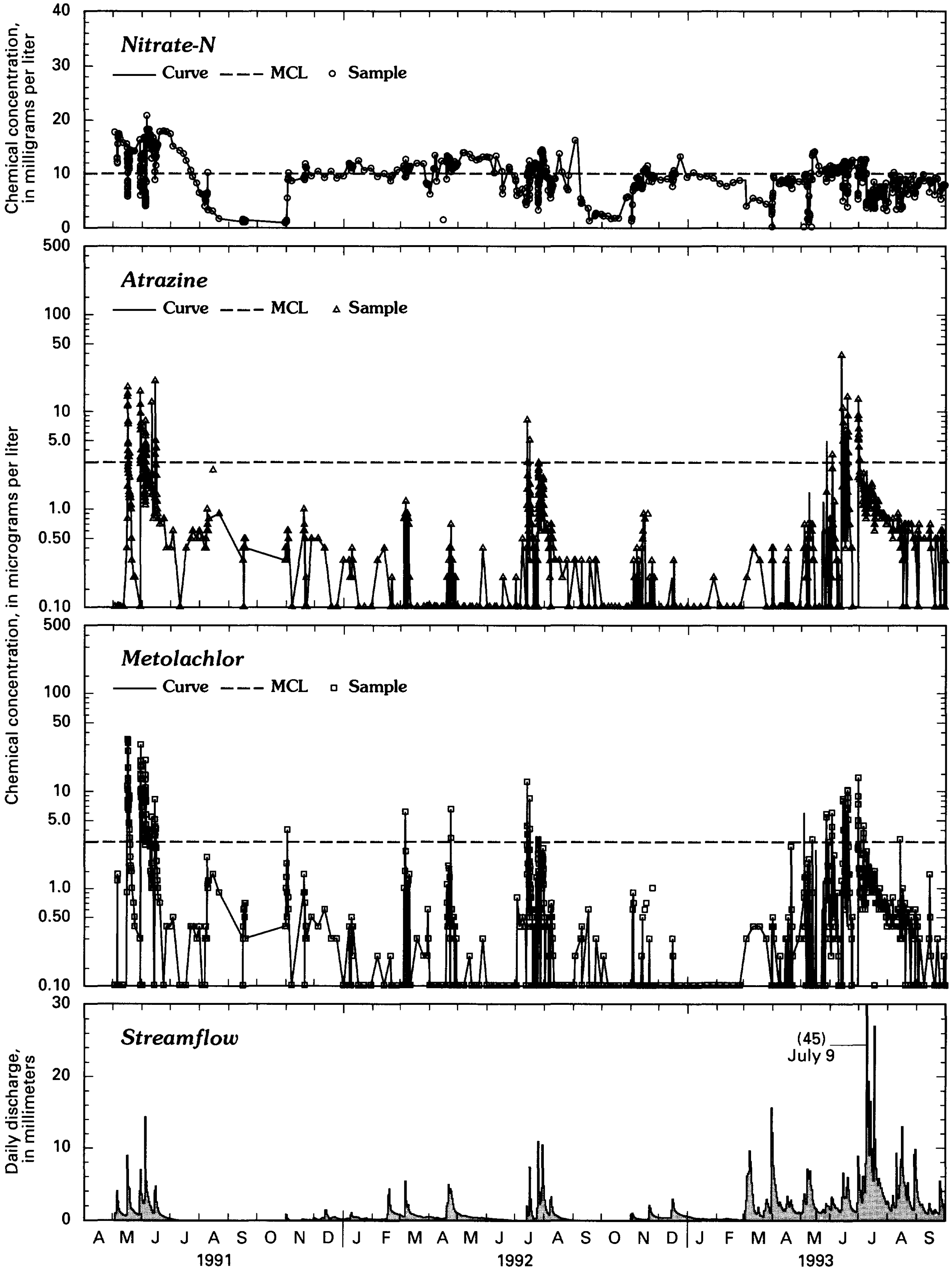

Figure 7. Discrete sample concentrations, time-concentration curves, and Maximum Contaminant Levels (MCLs) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily discharge for streamflow at data-collection site 330 during April 1991–September 1993.

ern subwatershed compared to the drainage area for the gaging station at site 310. The loads at site 320 were assumed representative of the northwestern plus the southwestern subwatersheds and were decreased by the drainage-area ratio of 3,800:3,820. The loads of the southwestern subwatershed were computed by subtraction of the northwestern subwatershed from the northwestern plus the southwestern subwatersheds. Loads for the eastern subwatershed were computed by subtraction of the northwestern plus the southwestern subwatersheds from loads determined at site 330. Combined loads for the three subwatersheds in the Walnut Creek watershed are represented by loads at site 330. Daily cumulative loads were computed by summing all the previous daily loads. The daily and cumulative loads for each chemical at each site and the daily and cumulative values of flow discharge are shown in figures 8–12.

Values of chemical yield—discharge or load per unit of area, used here as mass per unit area—were computed by division of daily loads, daily cumulative loads, or total loads by the appropriate drainage area for each value. Yields allow for relative comparisons between or among different-sized basins because the values are per unit area and not totals. Most of the herbicides were transported during three high-flow periods that include May–June 1991, July–August 1992, and May–July 1993. The cumulative chemical yields for nitrate-N, atrazine, and metolachlor from each subwatershed and the site 220 basin and the cumulative discharge for the three high-flow periods are shown in figure 13. The cumulative yield curves for the southwestern and the eastern subwatersheds, which are computed from two sites instead of one, occasionally show negative cumulative values because the upstream site values are larger than the downstream site values for those periods. These could be the result of either improper definition of the concentration curves from insufficient data or the occurrence of large yields at the upstream site just before midnight that do not reach the downstream site until after midnight that day.

Chemical loss rates for nitrate-N, atrazine, and metolachlor were computed for the site 220 basin and the subwatersheds for crop years and the periods April–September and October–March (table 3). The cumulative yield for the given chemical, basin/subwatershed, and period was divided by the appropriate application rate (table 2) and multiplied by 100. The crop-year loss rates for nitrate-N are based on the period from October of the previous year through September of the crop year. The crop-year loss rates for atrazine and metolachlor are based on the period from April of the crop year through March of the following year. The 6-month periods (April–September and October–March) are given for comparison purposes because they can be combined to make up either crop year and because most herbicide losses occurred during the April–September periods.

TRANSPORT OF AGRICULTURAL CHEMICALS

Flow Processes

A comparison of precipitation and streamflow data indicate that antecedent conditions have a large effect on the flow response from a specific subwatershed and that the flow response to similar precipitation can vary among the three subwatersheds. Average monthly precipitation (based on the Thiessen polygon method of area weighting), streamflow from the Walnut Creek watershed and the three subwatersheds, and the streamflow-to-precipitation ratios for the watershed and the three subwatersheds for April 1991–September 1993 are shown in figure 14. The ratio was greater than 1.0 for the eastern subwatershed during February 1992 and for all subwatersheds during March–April 1993 as stored precipitation (snow, ice) was released to streams when temperatures increased. The negative streamflow and streamflow-to-precipitation ratio for the eastern subwatershed during July–October 1991 and September–October 1992 are a result of less water flowing out of the eastern subwatershed than flowed into it. Streamflow was observed to completely disappear along the streambed of Walnut Creek during the 1991 period, first along the South Skunk River flood plain downstream of the eastern subwatershed and then along reaches of the eastern subwatershed itself. The water-quality implications of recharge to the alluvial aquifer in the South Skunk River flood plain could be important; Buchmiller (1995) suggests that Walnut Creek, downstream of site 330, almost always loses water to the alluvial aquifer.

Different amounts of streamflow resulted from similar large amounts of rainfall during July 1992 and July 1993 (see also figs. 8–12). July 1992 was preceded by two relatively dry months with few cloudy days and normal crop development, which reduced

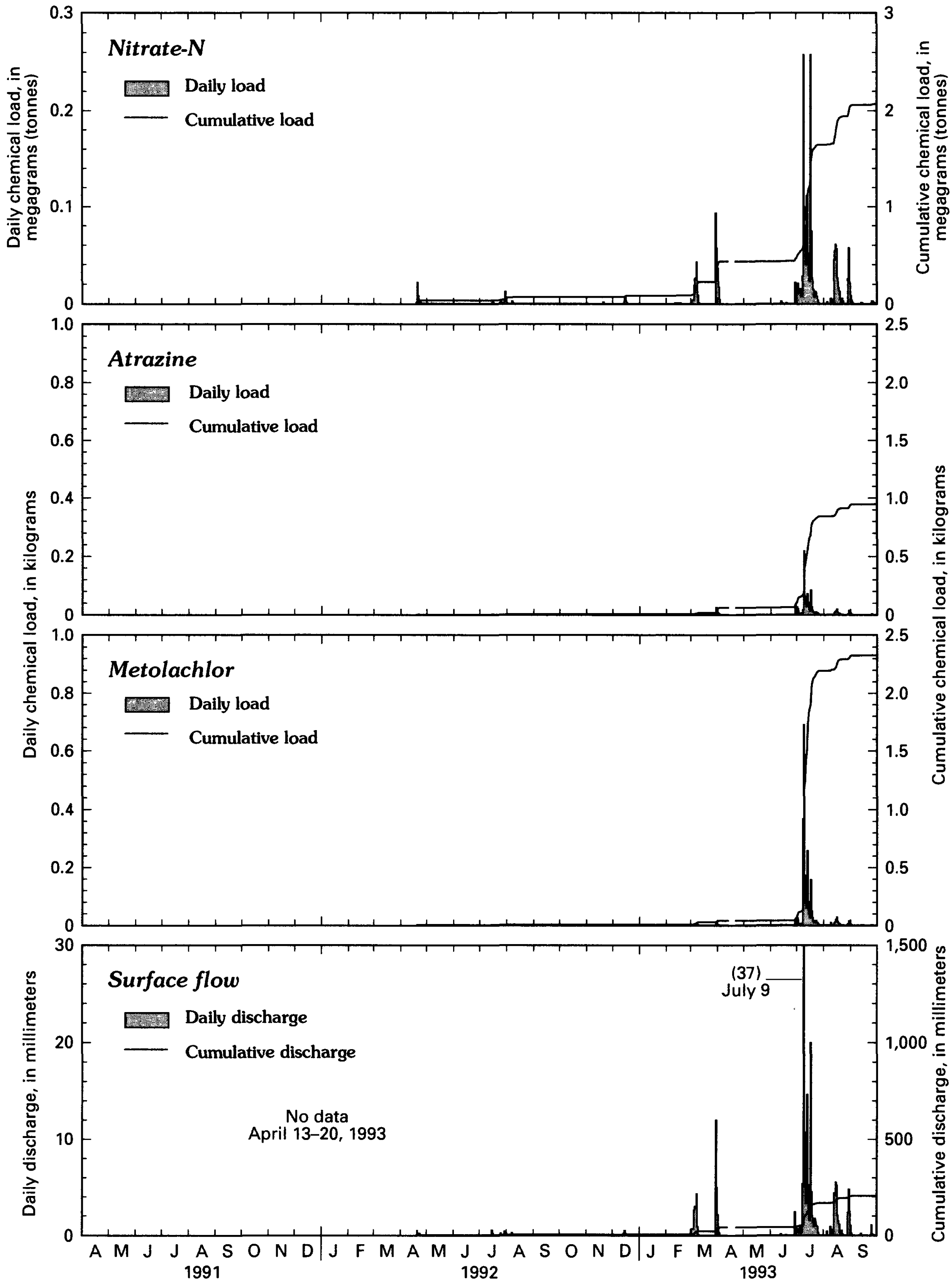

Figure 8. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily and cumulative discharge of surface flow at data-collection site 220C during April 1992–September 1993.

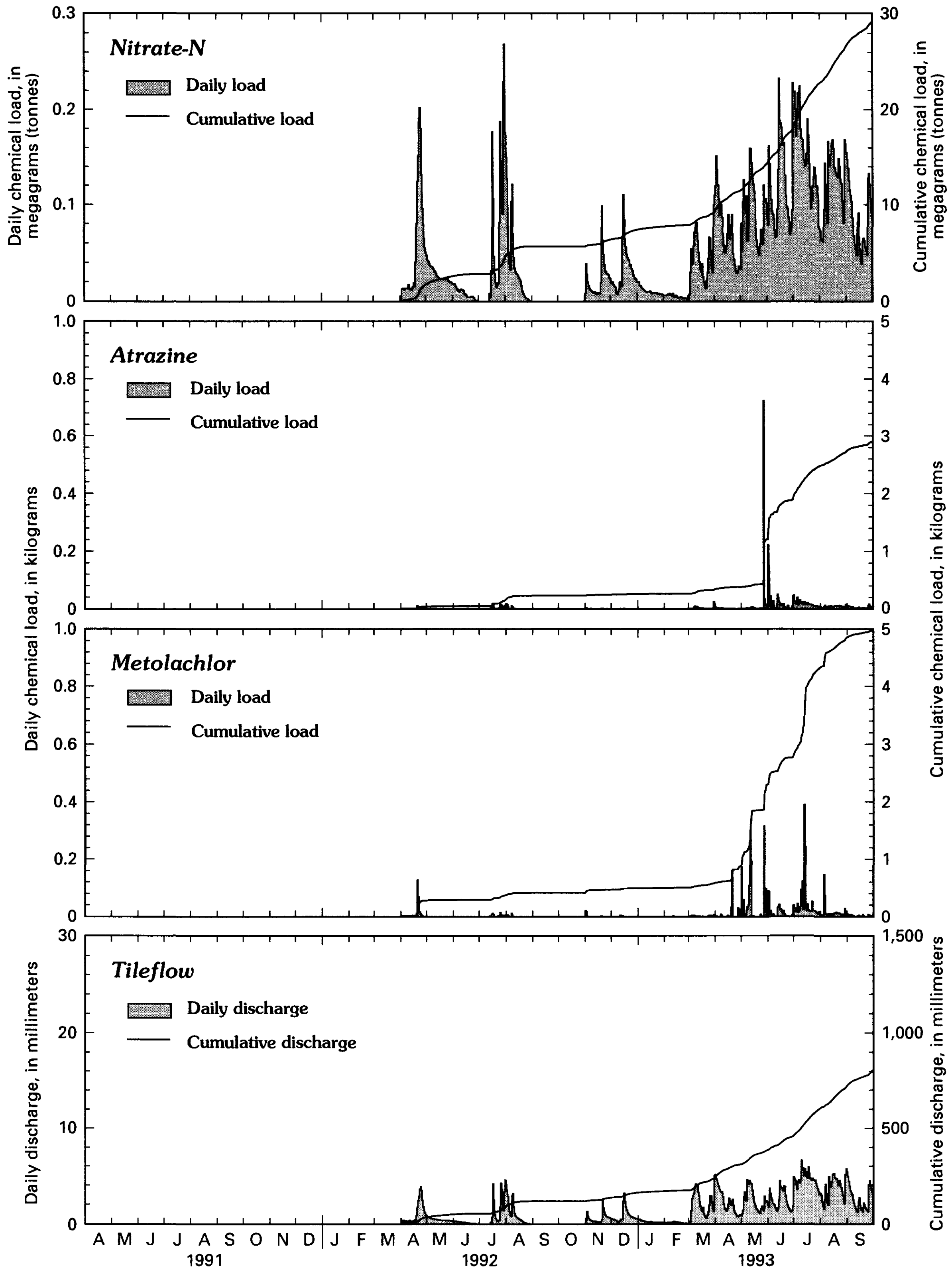

Figure 9. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily and cumulative discharge of tileflow at data-collection site 220T during April 1992–September 1993.

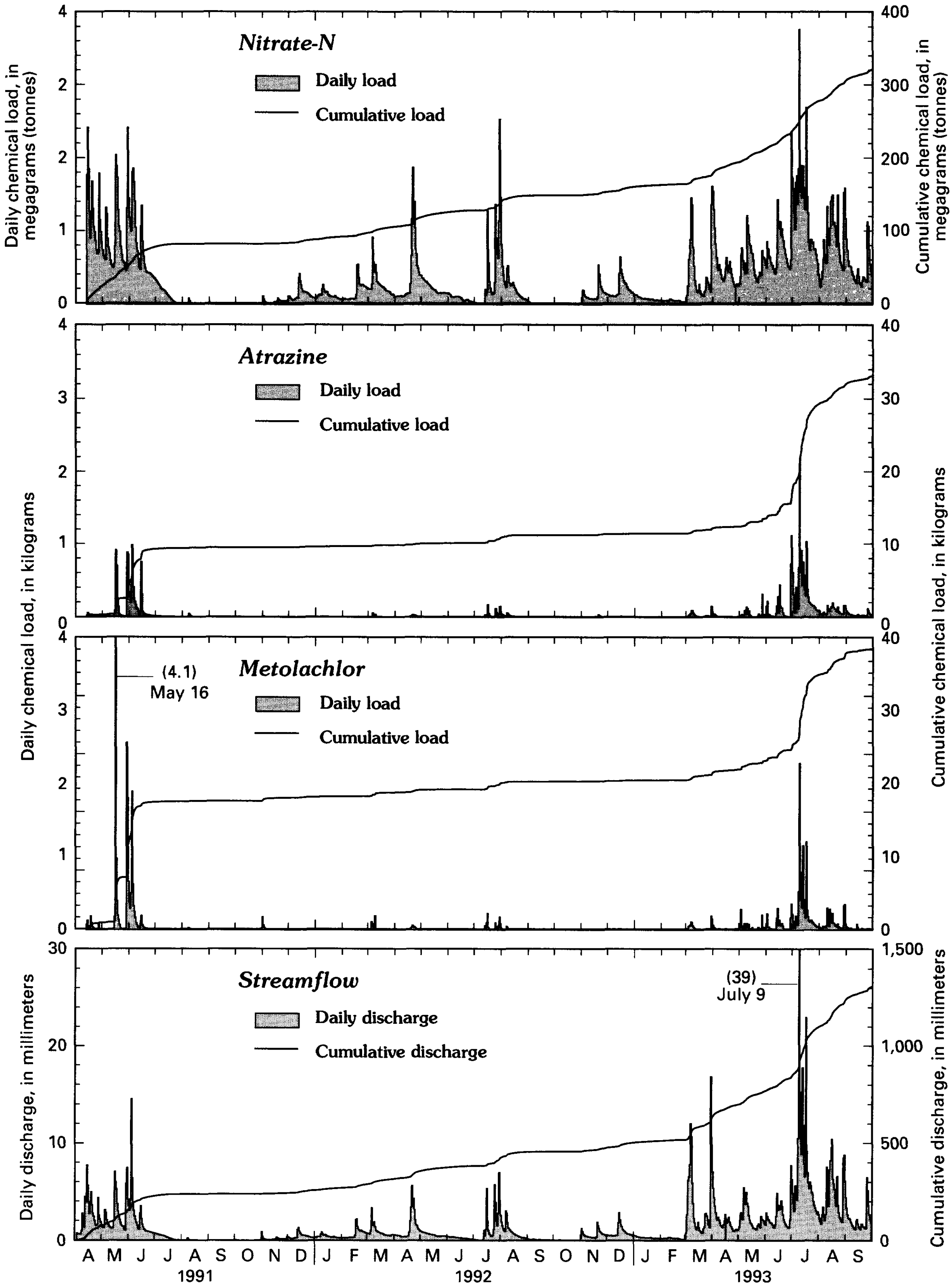

Figure 10. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily and cumulative discharge of streamflow at data-collection site 310 during April 1991–September 1993.

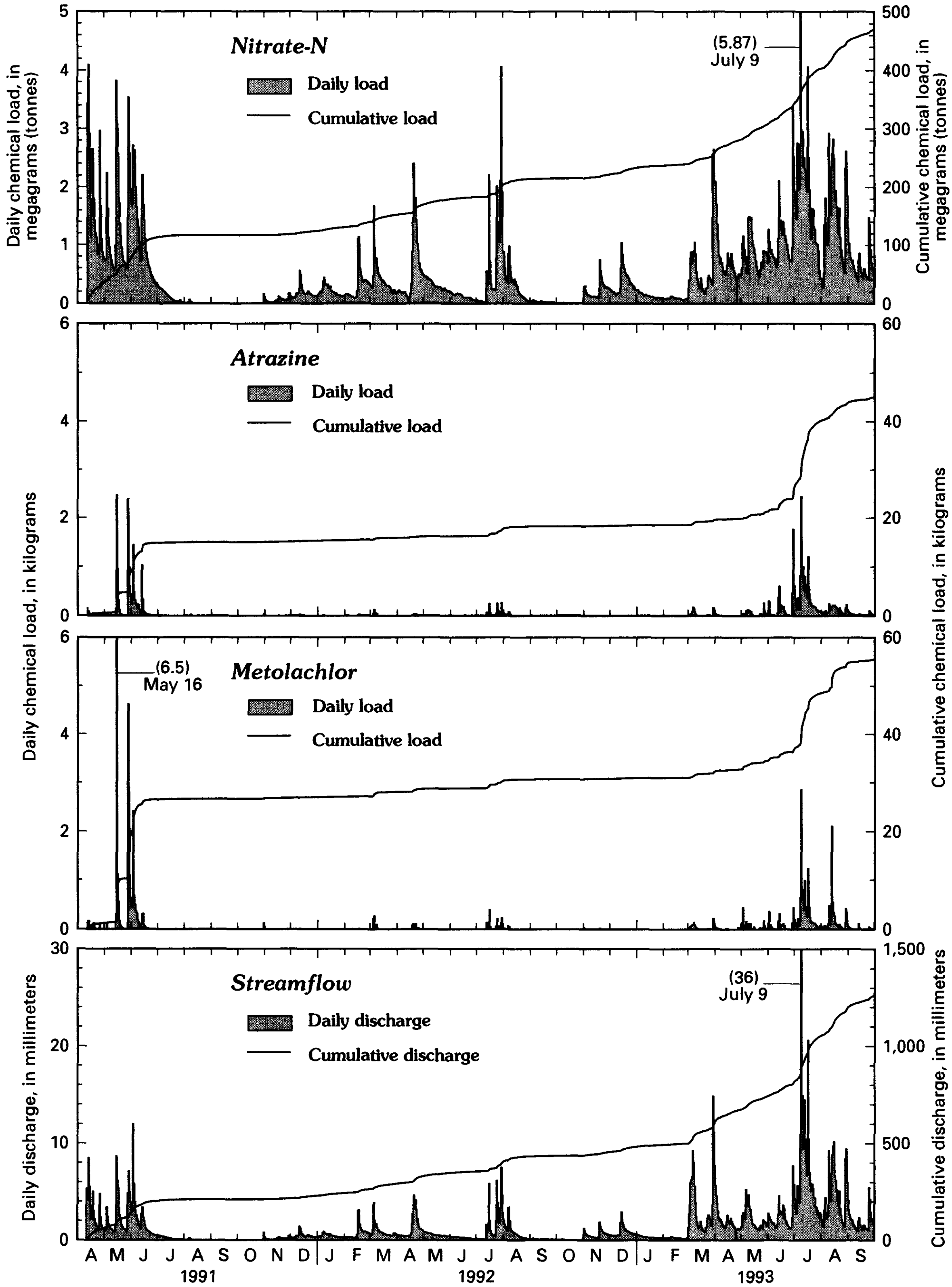

Figure 11. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily and cumulative discharge of streamflow at data-collection site 320 during April 1991–September 1993.

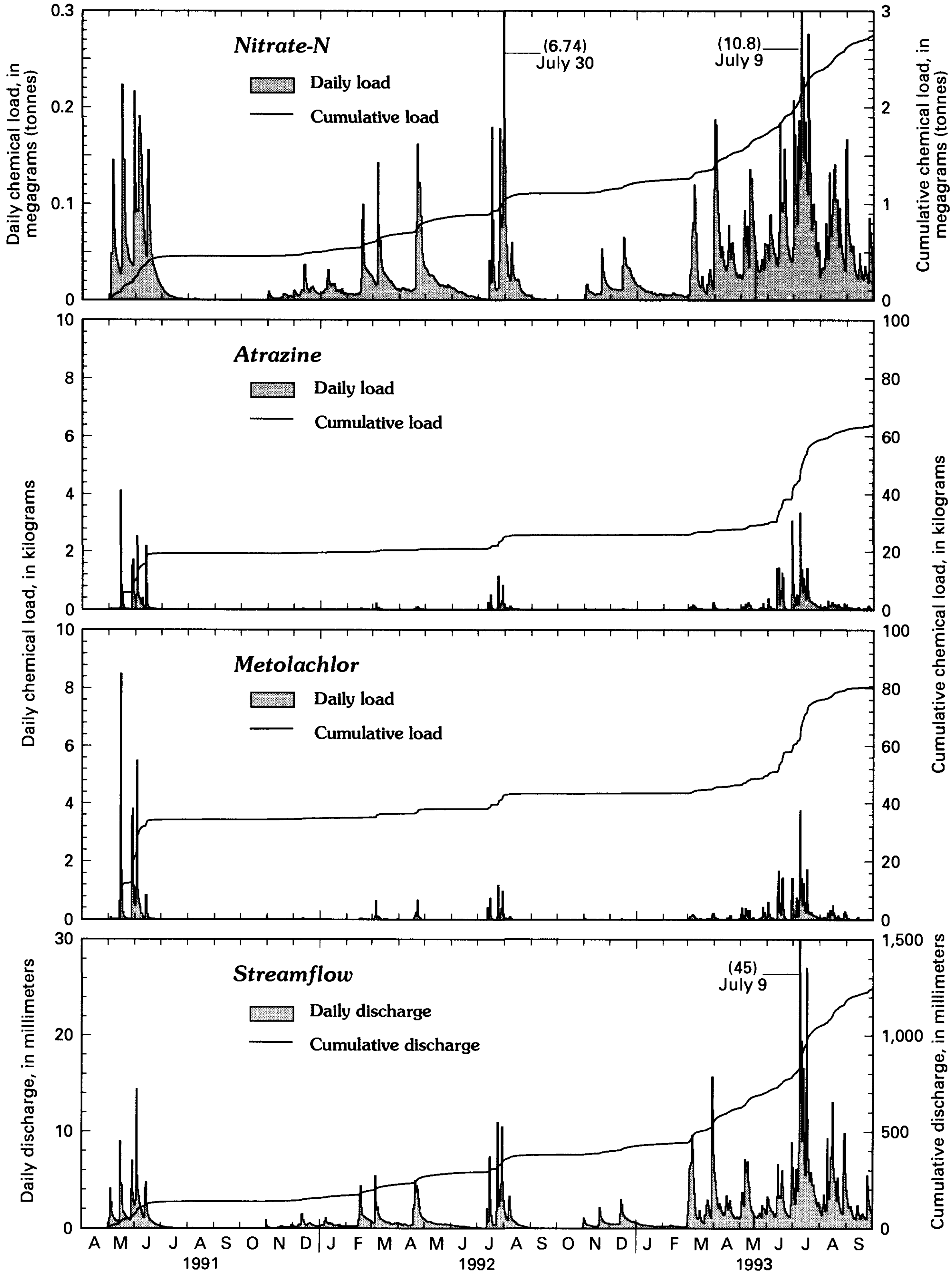

Figure 12. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and daily and cumulative discharge of streamflow at data-collection site 330 during April 1991–September 1993.

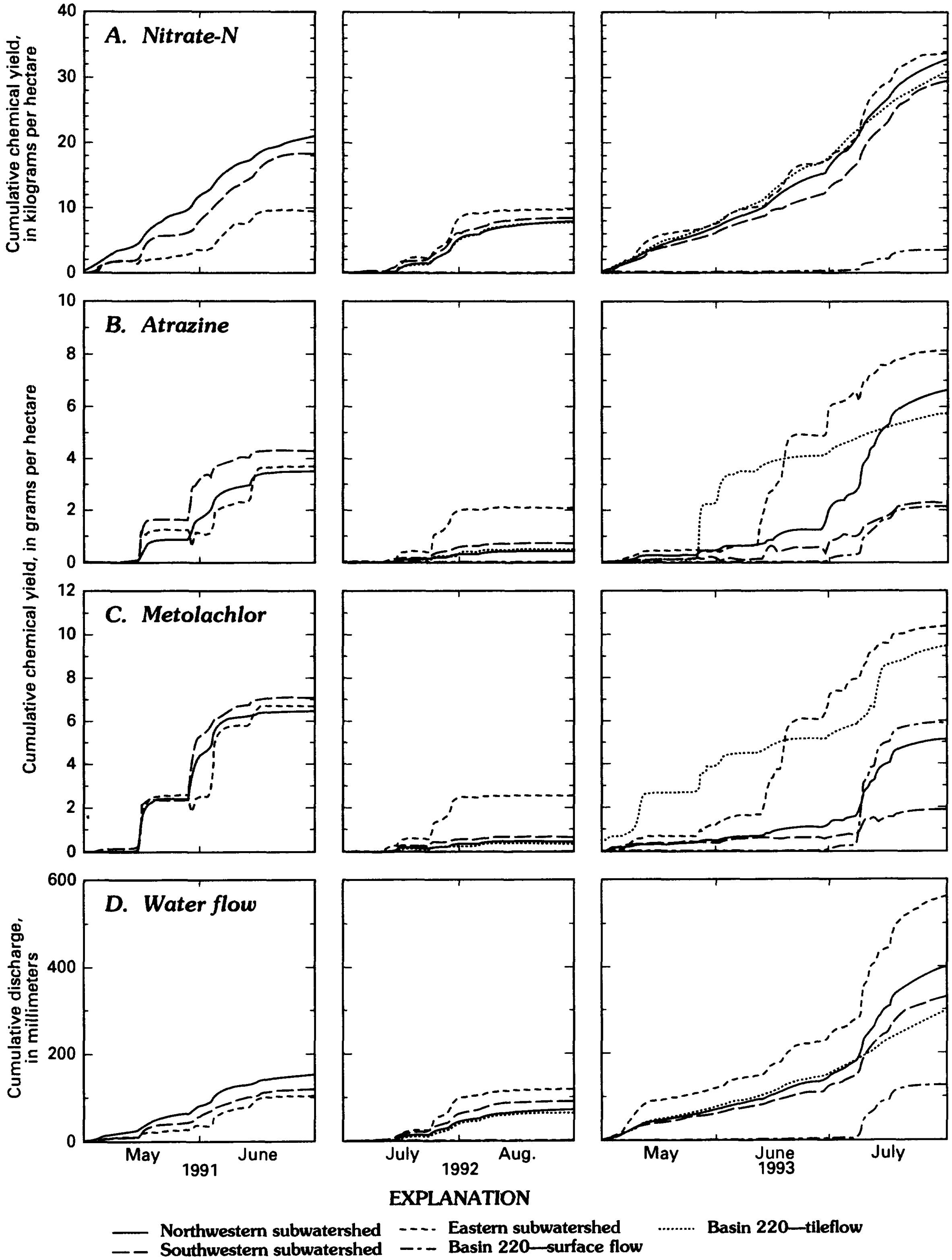

Figure 13. Cumulative chemical yields of (*A*) nitrate as nitrogen (nitrate-N), (*B*) atrazine, and (*C*) metolachlor and (*D*) cumulative discharge of water flow for three subwatersheds (streamflow) and one small basin (surface flow and tileflow) in Walnut Creek watershed during selected high-flow periods, 1991–93.

Table 3. Chemical loss rates (chemical yields expressed as a percentage of average application rates) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor in surface flow, tileflow, and streamflow for nitrate as nitrogen and herbicide crop years and 6-month periods April–September and October–March, April 1991–September 1993

[--, no data; <, less than]

<table>
<tr><th rowspan="4">Basin/sub-watershed and flow type</th><th rowspan="4">Chemical</th><th colspan="5">Chemical loss rate, in percent</th></tr>
<tr><th></th><th colspan="2">Nitrate-N crop year</th><th colspan="2">Nitrate-N crop year</th></tr>
<tr><th>April 1991–September 1991</th><th>October 1991–March 1992</th><th>April 1992–September 1992</th><th>October 1992–March 1993</th><th rowspan="2">April 1993–September 1993</th></tr>
<tr><th colspan="2">Atrazine and metolachlor crop year</th><th colspan="2">Atrazine and metolachlor crop year</th></tr>
<tr><td rowspan="6">Site 220C basin
Surface flow</td><td rowspan="2">Nitrate-N</td><td>--</td><td>--</td><td>0.2</td><td>1.5</td><td>8.2</td></tr>
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<tr><td rowspan="2">Atrazine</td><td>--</td><td>--</td><td><0.1</td><td><0.1</td><td>2.6</td></tr>
<tr><td colspan="2">--</td><td colspan="2"><0.1</td><td></td></tr>
<tr><td rowspan="2">Metolachlor</td><td>--</td><td>--</td><td><0.1</td><td><0.1</td><td>0.8</td></tr>
<tr><td colspan="2">--</td><td colspan="2"><0.1</td><td></td></tr>
<tr><td rowspan="6">Site 220T basin
Tileflow</td><td rowspan="2">Nitrate-N</td><td>--</td><td>--</td><td>16</td><td>18</td><td>96</td></tr>
<tr><td></td><td colspan="2">--</td><td colspan="2">113</td></tr>
<tr><td rowspan="2">Atrazine</td><td>--</td><td>--</td><td>0.2</td><td>0.1</td><td>7.3</td></tr>
<tr><td colspan="2">--</td><td colspan="2">0.3</td><td></td></tr>
<tr><td rowspan="2">Metolachlor</td><td>--</td><td>--</td><td>0.2</td><td>0.1</td><td>1.5</td></tr>
<tr><td colspan="2">--</td><td colspan="2">0.3</td><td></td></tr>
<tr><td rowspan="6">Northwestern subwatershed
Streamflow</td><td rowspan="2">Nitrate-N</td><td>49</td><td>18</td><td>32</td><td>19</td><td>88</td></tr>
<tr><td></td><td colspan="2">50</td><td colspan="2">106</td></tr>
<tr><td rowspan="2">Atrazine</td><td>1.8</td><td>0.1</td><td>0.3</td><td>0.2</td><td>5.1</td></tr>
<tr><td colspan="2">1.9</td><td colspan="2">0.5</td><td></td></tr>
<tr><td rowspan="2">Metolachlor</td><td>1.0</td><td>0.1</td><td>0.1</td><td>0.1</td><td>1.3</td></tr>
<tr><td colspan="2">1.0</td><td colspan="2">0.3</td><td></td></tr>
<tr><td rowspan="6">Southwestern subwatershed
Streamflow</td><td rowspan="2">Nitrate-N</td><td>34</td><td>11</td><td>21</td><td>17</td><td>88</td></tr>
<tr><td></td><td colspan="2">32</td><td colspan="2">104</td></tr>
<tr><td rowspan="2">Atrazine</td><td>2.1</td><td>0.2</td><td>0.3</td><td>0.1</td><td>2.6</td></tr>
<tr><td colspan="2">2.3</td><td colspan="2">0.4</td><td></td></tr>
<tr><td rowspan="2">Metolachlor</td><td>1.7</td><td>0.1</td><td>0.10</td><td><0.1</td><td>2.0</td></tr>
<tr><td colspan="2">1.7</td><td colspan="2">0.1</td><td></td></tr>
</table>

Table 3. Chemical loss rates (chemical yields expressed as a percentage of average application rates) for nitrate as nitrogen (nitrate-N), atrazine, and metolachlor in surface flow, tileflow, and streamflow for nitrate as nitrogen and herbicide crop years and 6-month periods April–September and October–March, April 1991–September 1993—Continued

Basin/sub-watershed and flow type	Chemical	Chemical loss rate, in percent				
			Nitrate-N crop year		Nitrate-N crop year	
		April 1991–September 1991	October 1991–March 1992	April 1992–September 1992	October 1992–March 1993	April 1993–September 1993
		Atrazine and metolachlor crop year		Atrazine and metolachlor crop year		
Eastern subwatershed Streamflow	Nitrate-N	20	17	31	36	169
			48		206	
	Atrazine	4.0	0.3	1.6	0.2	20
		4.3		1.7		
	Metolachlor	1.2	0.1	0.4	<0.1	2.9
		1.3		0.5		

soil moisture. July 1993 was preceded by two relatively wet months with many cloudy days and slower crop development, which kept soil moisture greater compared to July 1992. Soil and depression storage were available in 1992, and streamflow was not large, which resulted in streamflow-to-precipitation ratios of about 0.2 to 0.3 for the subwatersheds. But, in July 1993, little soil storage was available, and much of the rainfall became streamflow, which resulted in streamflow-to-precipitation ratios of about 0.7 to almost 1.0. The ratio for the eastern subwatershed, which has more relief and a more extensive natural drainage network than the other subwatersheds, was almost 1.0 in July 1993. The ratios for the northwestern and the southwestern subwatersheds, which have more depression storage than the eastern subwatershed, were lower than for the eastern subwatershed. The southwestern subwatershed, which has the most limited surface drainage network, had the lowest ratio. The steeper terrain of the eastern subwatershed suggests a larger potential for surface runoff, interflow, and possibly return flow. This could result in increased transport of chemicals susceptible to these flow processes.

Although the records for the Walnut Creek watershed are relatively short, it is probable that the high streamflow-to-precipitation ratios for 1993 are extreme. Severe flooding occurred during the spring and summer of 1993 throughout the upper Mississippi River Basin, including the South Skunk River Basin (Parrett and others, 1993). These floods were caused by an unusual combination of wet antecedent conditions, persistent wet weather patterns, and large-rainfall storms (Wahl and others, 1993), just as with the 1993 high flows in the Walnut Creek watershed.

Examination of the flow graphs in figures 8–10 indicates that most of the streamflow from the northwestern subwatershed comes from tileflow. Cumulative streamflow at site 310 for April 1992–September 1993 was equal to about 1,000 mm (a volume of flow equivalent to a depth of the specified amount over the entire basin). For the same period, surface flow at site 220C was equivalent to about 200 mm, and tileflow at site 220T was equivalent to about 800 mm. These flows do not have to "balance," but they do. The fact that the flows per unit area at the 220 sites and the 310 site were the same is an indication that the flows from the 220 basin are representative of the entire northwestern subwatershed. Surface flow is highly variable and intermittent, usually lasting for only a few days after a storm. Tileflow is less variable and much more persistent, ceasing only after prolonged dry periods.

Although the flow graphs show that tileflow is the primary source of flow to streams during most periods, surface flow can be dominant for short periods of as much as a few days. In July 1993, large and repeated rains saturated soils and eventually produced very

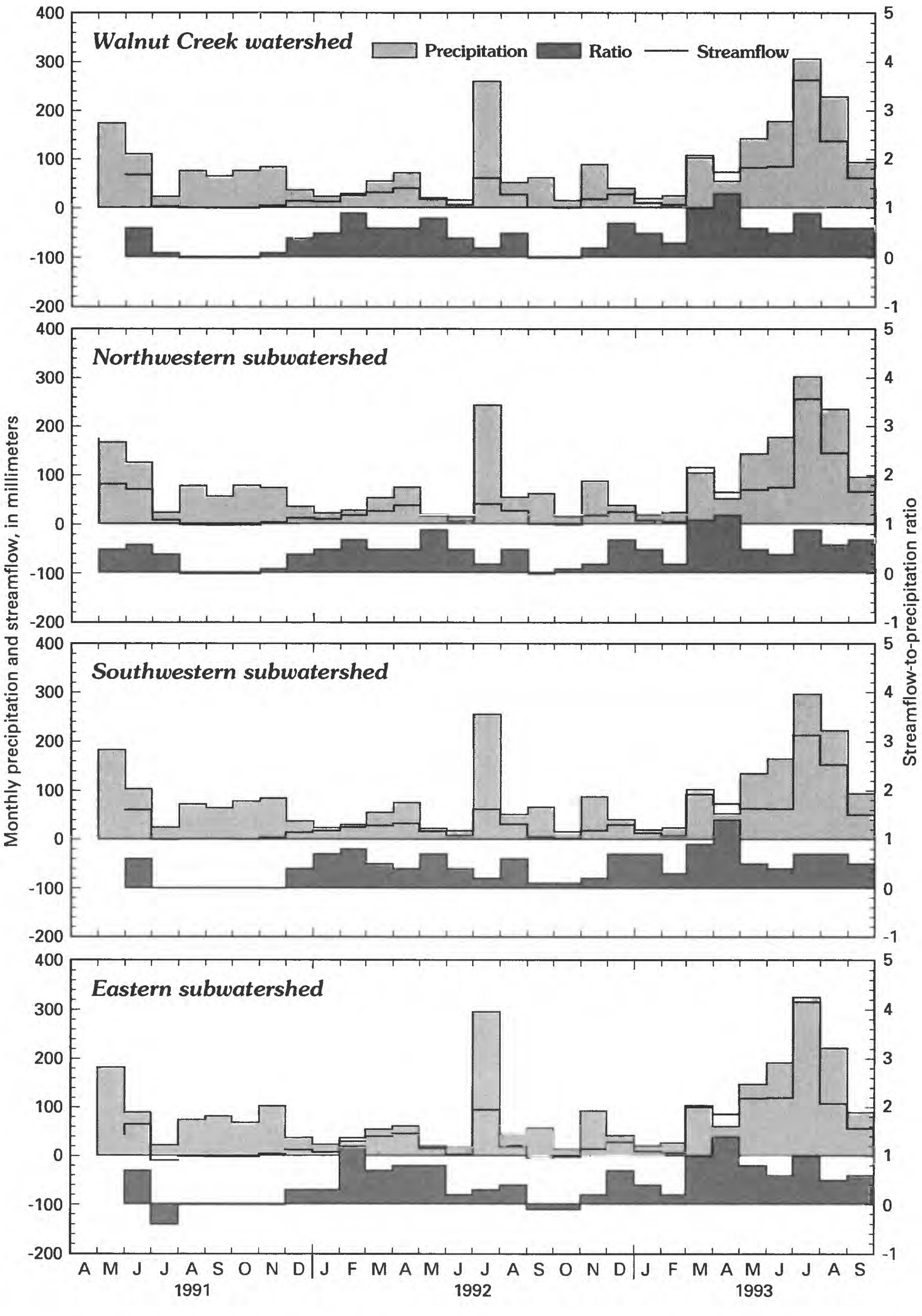

Figure 14. Monthly precipitation, streamflow, and streamflow-to-precipitation ratios for Walnut Creek watershed and three subwatersheds, May 1991–September 1993.

large amounts of surface flow. The variations in surface flow (fig. 8) and streamflow (figs. 10–12) during this period are much greater than the variations in tileflow (fig. 9). The ability of the tile system to rapidly deliver increased amounts of flow in response to large rainfall is constrained by the limited flow area of the tiles themselves; once the tiles are full, only greater velocities from increased heads can increase the tileflow. There is no such limit on surface flow or streamflow. The slopes of the cumulative flow-discharge graphs in figure 13 are another indicator of the differences in flow response during July 1993. For tileflow, the slope remains fairly steady during July, indicating fairly steady flows. For surface flow from the 220 basin and streamflow from the subwatersheds, the slopes become steeper for short periods on several occasions, indicating increases in flow at those times. This is especially true for the eastern subwatershed, which has a better natural drainage system and steeper terrain than the northwestern and the southwestern subwatersheds.

Chemical-Transport Processes

The data indicate that large amounts of nitrate-N are transported in Walnut Creek with concentrations often greater than the MCL of 10 mg/L and that ground-water flow from tiles, at least in the northwestern subwatershed, is the primary means of transport to the streams. The amounts of the herbicides atrazine and metolachlor transported in Walnut Creek are extremely variable, with concentrations typically less than the MCL of 3.0 μg/L but as large as 59 and 80 μg/L, respectively, during stormflow. Both surface flow and tileflow contribute to the herbicide load in the streams, but surface flow appears to be the primary means of transport. The amounts of rainfall, timing of rainfall relative to application of chemicals, and basin characteristics affect the amounts of chemicals transported to and by the streams.

Nitrate-N—Surface Flow, Tileflow, and Streamflow

Nitrate-N was present in surface flow, tileflow, and streamflow during all flow regimes (figs. 3–7). In surface flow, concentrations were usually less than the MCL of 10 mg/L. In streamflow and tileflow, concentrations were often greater than the MCL of 10 mg/L for extended periods. Concentrations in tileflow and streamflow generally were 4 to 16 mg/L, with a few samples greater than 20 mg/L. A comparison of data for sites 310 and 330 indicates that concentrations were slightly lower at the downstream site 330 than at the upstream site 310. During snowmelt over frozen ground in March 1993, tileflow and streamflow concentrations were notably lower than in adjacent months; this indicates that base flow was diluted by surface runoff containing lesser concentrations.

Nitrate-N concentrations also decreased in surface flow and streamflow during stormflow. Rainfall, flow discharge, and chemical concentration data are presented for the series of stormflows in 1993 on June 29–July 1, and July 5, 8–9, 11, 13, and 17 in figures 15–17. The nitrate-N concentrations in tileflow show small decreases during the June 29–July 1 and July 5 stormflows, but during the extremely large stormflow of July 8–9, a larger, sustained decrease in concentration of at least 1 mg/L is apparent. Surface inlets in the 220 basin probably contributed surface runoff for days after this stormflow, which maintained lower nitrate-N concentrations, as large areas were inundated throughout the watershed.

Nitrate–N concentrations also decreased as streamflow decreased during July–August 1991 and September–October 1992. This was not apparent in tileflow, possibly suggesting a degradation process that was occurring in the stream channels but not in the tile lines. At various times during August–October 1991, no flow was recorded at every site except site 320 where small flows were always present— apparently seepage from a pond immediately upstream and adjacent to the stream. Samples collected at sites other than 320 during this period were from ponded areas of water in the stream channels.

The patterns of daily and cumulative nitrate-N loads closely follow the corresponding patterns of flow as would be expected with the fairly stable concentrations (figs. 8–12). Because of the intermittent and variable nature of surface flow, the cumulative flow discharge and nitrate-N load curves have a stepped appearance. By contrast, the same curves for tileflow have a smoother appearance because of the less variable nature of the flow. The curves for streamflow are a composite of the other two—smooth, gentle slope during base-flow periods and stepped features during stormflow periods. Most of the flow and nitrate-N load to streams come from ground-water flow as opposed to surface flow, as indicated by the much larger cumulative values from site 220T than

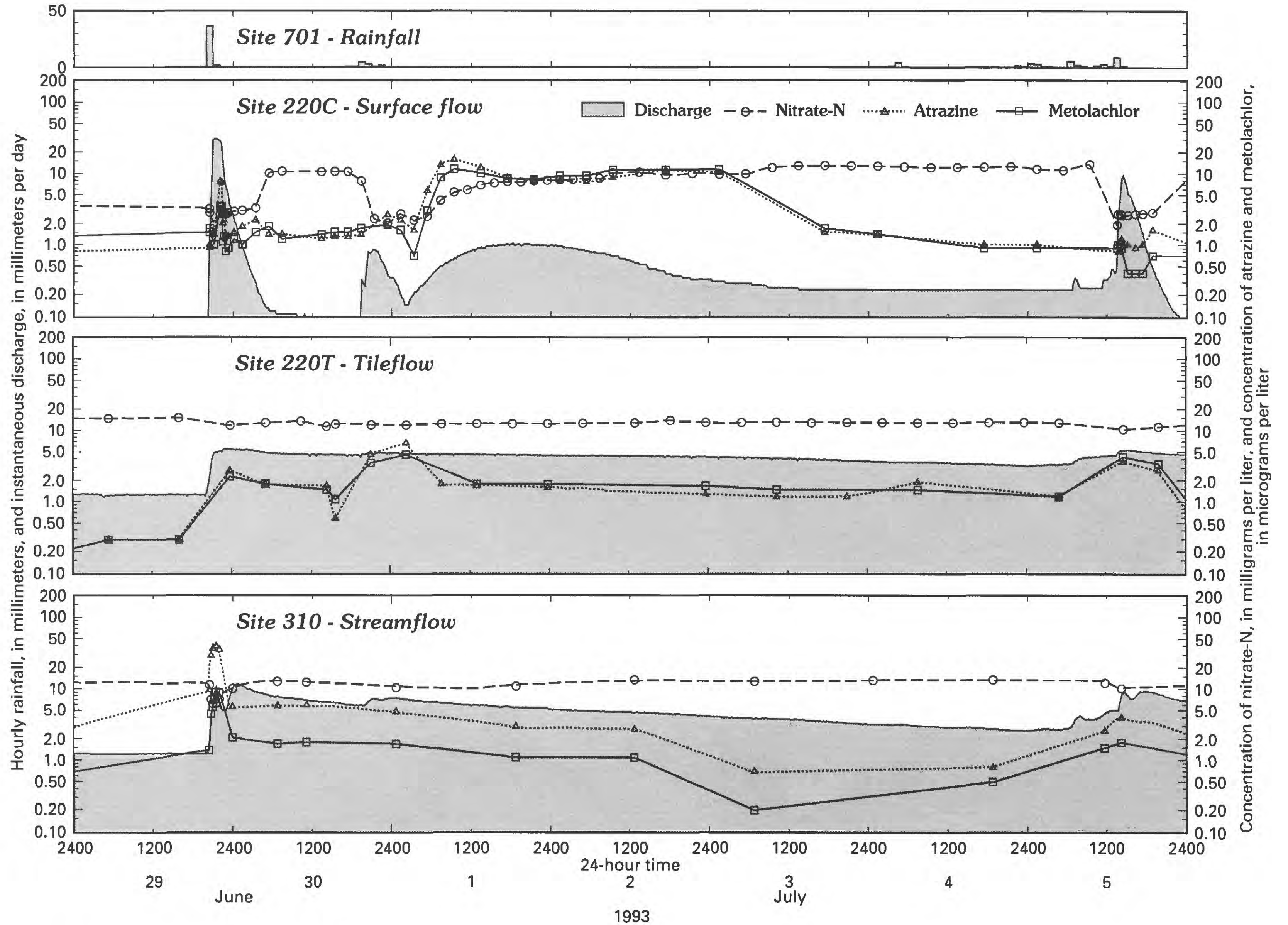

Figure 15. Rainfall for data-collection site 701 and discharge of water flow and sample concentrations of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor for data-collection sites 220C (surface flow), 220T (tileflow), and 310 (streamflow) during high-flow periods, June 29–July 5, 1993.

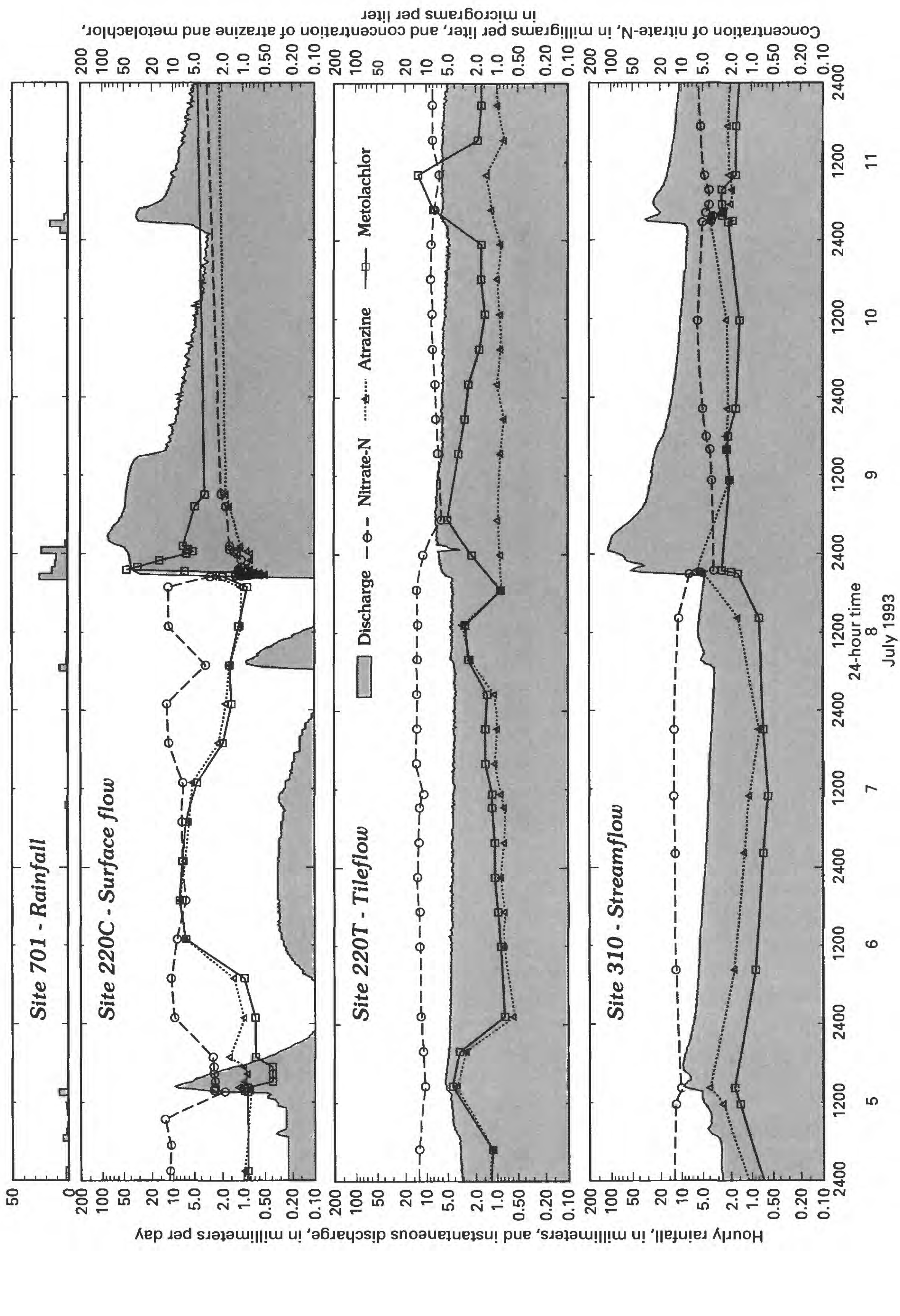

Figure 16. Rainfall for data-collection site 701 and discharge of water flow and sample concentrations of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor for data-collection sites 220C (surface flow), 220T (tileflow), and 310 (streamflow) during high-flow periods, July 5–11, 1993.

from site 220C, and from the more subdued nature of the steps in the nitrate-N cumulative load curves for the streamflow sites compared to the steps in the corresponding discharge curves.

The cumulative-yield graphs in figure 13 also show that ground-water flow, represented by the tileflow at site 220T, transports most of the nitrate-N load to streamflow at site 310 for July–August 1992 and May–July 1993. Only during periods of extremely large surface flow, such as July 8–9 and 17, 1993, did surface-flow loads exceed tileflow loads of nitrate-N. Even then, it may have been only because tileflow loads became limited by the ability of the tile system to deliver flow. The variability and dominance of surface flow during the July 8–17, 1993, period can be seen in the discharge graphs in figures 8–10 and in the cumulative-discharge graph of May–July 1993, in figure 13. The uniform nature of nitrate-N transport in tileflow for this same period can be seen in the cumulative-load plot for site 220T in figure 9.

The susceptibility of nitrate-N to transport is seen in the data of table 3. The chemical loss rate for October 1992 through September 1993 was about 10 percent in surface flow and more than 100 percent in tileflow for the 220 basin, more than 100 percent in streamflow from the northwestern and the southwestern subwatersheds, and more than 200 percent in streamflow for the eastern subwatershed. Nitrate-N stored in the soil from past years and mobilized by the much-greater-than-normal rainfall during 1993 (Lucey and Goolsby, 1993; Wahl, and others, 1993) and the release of nitrate-N by mineralization of organic matter in the soil probably contributed to the yields from the basins and subwatersheds with loss rates greater than 100 percent. The eastern subwatershed is very susceptible to nitrate-N transport losses. The steeper terrain and better natural drainage system in the eastern subwatershed probably results in more stormflow than in the northwestern and the southwestern subwatersheds. It is not clear whether the additional stormflow would be from surface flow, ground-water flow, or some combination of each.

Atrazine and Metolachlor—Surface Flow

Concentrations of the herbicides atrazine and metolachlor in surface flow usually were less than the MCL of 3.0 μg/L and often less than the detection limit of 0.2 μg/L, but for some short periods of time, concentrations were large and variable (figs. 3, 15–17). During late June and early July 1993, herbicide concentrations increased when surface runoff was, apparently, the dominant part of surface flow (June 29–30, July 8, figs. 15–16). Surface runoff is usually indicated when nitrate-N concentrations decrease during stormflow. As the rainfall continued into July (figs. 16–17), the concentrations started to show a dilution effect similar to that for nitrate-N. This indicates that more and more of the herbicides had been removed from the surface where they were no longer available for transport by surface runoff. This effect shows up first for atrazine and later and to a lesser extent for metolachlor and could be caused by the differences in the average amounts of the two chemicals applied to the 220 basin in 1993—0.10 kg/ha of atrazine compared to 0.79 kg/ha of metolachlor (table 2).

The largest concentrations of atrazine (5–16 μg/L) occurred during July 1–2 (fig. 15) and July 6–7 (fig. 16) when return flow appears to be the dominant part of surface flow. The second and more gradual rise of each high-flow period is not associated with rainfall but is a delayed response from return flow. Metolachlor concentrations (4–12 μg/L) were similar to atrazine concentrations during July 1–2 and 6–7 (figs. 15–16), but were larger (15–47 μg/L) during the initial part of the July 8–9 stormflow when surface runoff was dominant. The much larger average application rates of metolachlor compared to atrazine (table 2) for the site 220 basin may explain the larger concentrations (fig. 16) and loads (fig. 8) of metolachlor during July 8–9. The concurrent large concentrations of both herbicides and nitrate-N during July 1–2 and 6–7 may be explained by a rise in the water table to shallow depths, which allows the return of flow to the surface from shallow ground water. This probably allowed interaction of flow with the soil matrix at shallow depths, because of the saturated conditions, but without significant mixing with the main ground-water system since the flow was returned quickly to the surface. Return flow may have occurred during other stormflows, but it is not as evident, or return flow may only occur under certain conditions such as moderate-intensity rainfall shortly after other rains have saturated parts of the soil profile. The initial flow during these two stormflows was short and small enough that the return flow part was clearly evident.

The daily chemical load data in figure 8 and the cumulative chemical yield data in figure 13 show the highly variable nature of atrazine and metolachlor transport in surface flow. Most of the herbicide loads

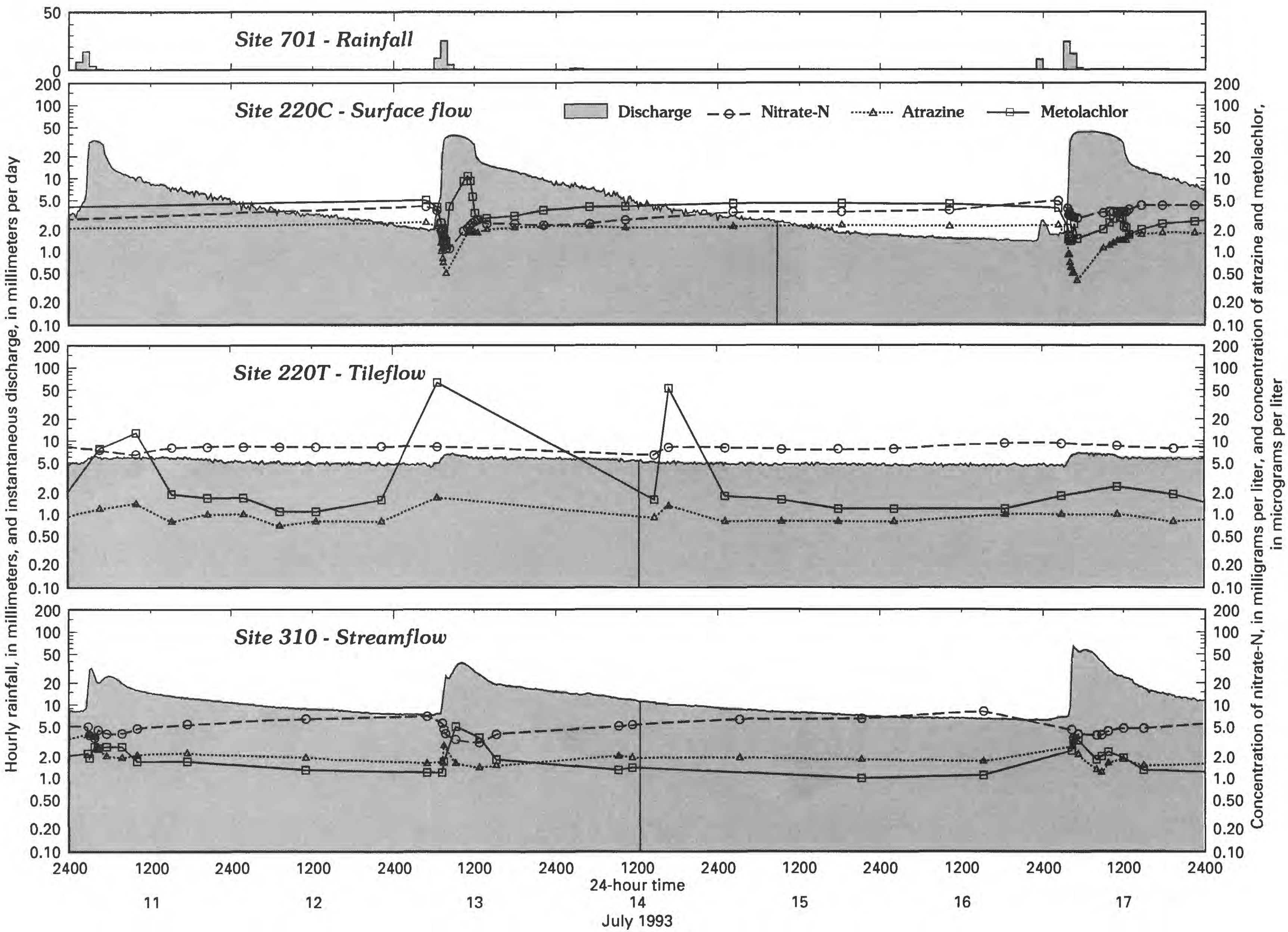

Figure 17. Rainfall for data-collection site 701 and discharge of water flow and sample concentrations of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor for data-collection sites 220C (surface flow), 220T (tileflow), and 310 (streamflow) during high-flow periods, July 11–17, 1993.

from April 1992 through September 1993 were transported during July 8–17, 1993. A comparison of figures 16–17 with figure 8 shows that most of the July 1993 herbicide loads occurred during periods when nitrate-N concentrations were lower than prestorm concentrations, which indicates transport by surface runoff. Although more metolachlor was applied and transported in 1993 compared to atrazine, the chemical loss rates (table 3) show that for April–September 1993, atrazine was transported at more than three times the rate of metolachlor—2.6 percent compared to 0.8 percent. Herbicide losses in surface flow during the 1992 growing season were small because of the dry spring, which allowed chemicals to be applied on schedule and also because of the relatively long time between chemical application and the onset of large runoff-producing rains in July. The dry conditions decreased the amount of flow, as discussed previously, and the time lapse allowed for vegetative uptake or degradation before the chemicals could be transported in larger quantities.

Atrazine and Metolachlor—Tileflow

Concentrations of both atrazine and metolachlor in tileflow (fig. 4) were larger and more frequently greater than the MCLs compared to surface flow (fig. 3) and to streamflow (figs. 5–7). The largest concentrations usually occurred when hydrologic conditions favored surface runoff into the tile system through surface inlets. In 1992, conditions generally were dry with no large rains until mid-July. On July 2, 12, and 22 there was little or no flow in the tile prior to about 25 mm of rainfall, which, in each case, produced a small increase in tileflow and a decrease in the concentration of nitrate-N. Data from the field tile at site 110 (Donna Schmitz, NSTL, written commun., 1992), which drains a pothole just across the road from the 220 basin but which has no surface inlets, show no apparent flow response for those same days. Although there was no surface flow at the outlet of the 220 basin (site 220C) on those days, surface flow did occur on July 13 after some additional rainfall. More localized surface flow could have occurred on July 12 and was most likely the source of the small flows and large herbicide concentrations in the 220 basin tile system. Concentrations at site 220T were 102, 21, and 6.6 μg/L for atrazine, and 171, 38, and 18 μg/L for metolachlor on July 2, 12, and 22, respectively. Because of the small amounts of flow on those days, the loads and yields were small (figs. 9 and 13).

In 1993, soil conditions generally were wet from frequent light and moderate rainfalls, and conditions were favorable for larger amounts of flow to surface inlets. Numerous large increases in herbicide concentration, followed by corresponding decreases in concentration in a relatively short amount of time, were detected in the tileflow at site 220T (fig. 4). With the exception of July 14, each increase in herbicide concentration is closely associated with rainfall. There is a corresponding decrease in nitrate-N concentration with most of the large herbicide concentrations, which indicates the presence of surface runoff in the tileflow. It seems unlikely that such rapid concentration changes could be produced by ground-water flow, even by preferential flow to ground water, considering the diffusion of chemicals that would occur in the saturated zone (saturated conditions are necessary for ground-water flow to occur in a tile drain). The largest 1993 daily loads of atrazine and metolachlor shown in figure 9 (April 20, May 1, 10–11, 27, June 1–2, July 13–14, August 5) are associated with the large concentration changes; these show up as steps in the cumulative-load (fig. 9) and yield graphs (fig. 13). It seems reasonable that when herbicide concentrations increase and decrease in response to stormflow, especially when nitrate-N concentrations also decrease, that the resultant increases in herbicide loads are from surface runoff into the surface inlets. Because the base-flow concentrations of atrazine and metolachlor between rains are less than the detection limit of 0.2 μg/L until after the large rainfall of May 27–June 2, virtually all of the 1993 tileflow loads to that time appear to be from surface sources. Much of the June and July loads, especially for metolachlor, also are associated with surface flow. It seems, therefore, that most of the atrazine and metolachlor loads and yields from April through September 1992 from the 220 basin are from surface flow directly to the basin outlet or indirectly through surface inlets to the tile-drainage system. More metolachlor than atrazine was applied in the 1993 crop year (table 2) and transported during April–September 1993 in tileflow. However, atrazine loss rates were much larger than for metolachlor—7.3 percent compared to 1.5 percent (table 3).

Atrazine and Metolachlor—Streamflow

Atrazine and metolachlor concentrations in streamflow (figs. 5–7) were generally less than the MCL of 3.0 μg/L and often less than the detection limit of 0.2 µg/L during base flow, but during stormflow, atrazine concentrations were as large as 59 µg/L at site 320 on May 29, 1991 (fig. 6), and metolachlor concentrations were as large as 80 µg/L at site 310 on May 16, 1991 (fig. 18). Concentrations were largest when stormflow occurred shortly after application of chemicals, as in May 1991 and June–July 1993; these peak concentrations generally would decrease with successive rainfall during a crop year. Concentrations were much lower during stormflow in 1992 because large rains did not occur until about 2 months after the application of chemicals. Increases of herbicide concentrations during stormflow usually were accompanied by decreases in nitrate-N concentrations (figs. 15–18), indicating that surface runoff was probably the dominant flow process and source of chemicals during that part of stormflow.

The stormflow-oriented nature of herbicide transport to streams is evident in the daily and cumulative loads of atrazine and metolachlor at sites 310, 320, and 330 (figs. 10–12). Note the stepped appearance of the cumulative-load graphs during stormflow compared to the same graplhs for nitrate-N. Large increases in cumulative loads for herbicides can be correlated to stormflow, whereas cumulative loads for nitrate-N can increase between stormflows. Most of the herbicide loads in streamflow occur when nitrate-N concentrations were low and surface runoff was dominant (figs. 10–12, 15–18). Despite the lack of surface flow and tileflow data in 1991, it seems most likely that surface runoff was the major source of atrazine and metolachlor loads to streamflow during 1991 on the basis of similar stepped appearance of the cumulative-load graphs.

Data for late May 1991 also illustrate the importance of surface flow in the transport of the herbicides atrazine and metolachlor. There are relative differences in cumulative chemical yields for atrazine and metolachlor for the southwestern, the northwestern, and the eastern subwatersheds (fig. 13). The southwestern subwatershed shows a large increase on May 29 followed by lesser increases on May 30–31. The northwestern subwatershed shows a similar pattern but of lesser magnitude, whereas the eastern subwatershed shows a decrease on May 29 followed by an almost equal increase on May 30 and then no change on May 31. Rainfall data show that the largest total (86 mm) and most intense (43 mm/hr) rainfall for May 29–31 occurred in the upstream end of the southwestern subwatershed, and the least total rain (35 to 46 mm) occurred over the eastern subwatershed. Streamflow data for sites 310 (fig. 18) and 320 both show double peaks; the first and sharper peak is an indicator of flow from the immediate vicinity of the site—mostly surface runoff, and the second peak represents delayed local flow and flow from the main part of the basin. Site 330 has only one peak similar to and lagging several hours behind the second peak of the other two sites. This indicates a lack of local surface flow at the extreme eastern end of the eastern subwatershed. Rainfall data indicate that this was probably true for most of the eastern subwatershed. This would explain the lack of cumulative herbicide yield from the eastern subwatershed for the period. The temporary declines in the cumulative herbicide yields for the eastern subwatershed (May 29) are the result of timing. Almost all of the herbicide loads had passed site 320 by midnight (May 29), whereas not as much of the loads had passed site 330. Because the loads (and yields) for the eastern subwatershed are computed by subtraction of loads at site 320 from those at site 330, this resulted in a negative value for that day. The remainder of the herbicide loads was accounted for the following day at site 330 and resulted in the apparent recovery of loads for the eastern subwatershed.

Atrazine appears more susceptible to transport losses to streamflow than is metolachlor. Herbicide loss rates in streamflow from the subwatersheds (table 3) for April–September period in 1991–93 ranged from 0.3 to 20 percent for atrazine and from 0.1 to 2.9 percent for metolachlor. The loss rates for atrazine were larger than for metolachlor for concurrent periods by factors ranging from 1.3 to 4 for the 1991 and 1992 crop years (April–March) and from 1.3 to 6.9 for the 1993, 6-month period (April–September). Herbicide losses from the 220 basin for the April–September periods in 1992–93 ranged from less than 0.1 to 2.6 percent in surface flow and from 0.2 to 7.3 percent in tileflow for atrazine and from less than 0.1 to 0.8 percent in surface flow and 0.2 to 1.5 percent in tileflow for metolachlor.

Subwatershed Transport Differences

Chemical loss rates in table 3 indicate differences in the transport characteristics of the three subwatersheds. The eastern subwatershed had the highest loss rates for all three chemicals—206 percent for nitrate-N (October 1992–September 1993), 20 percent for atrazine, and 2.9 percent for metolachlor (April–Sep-

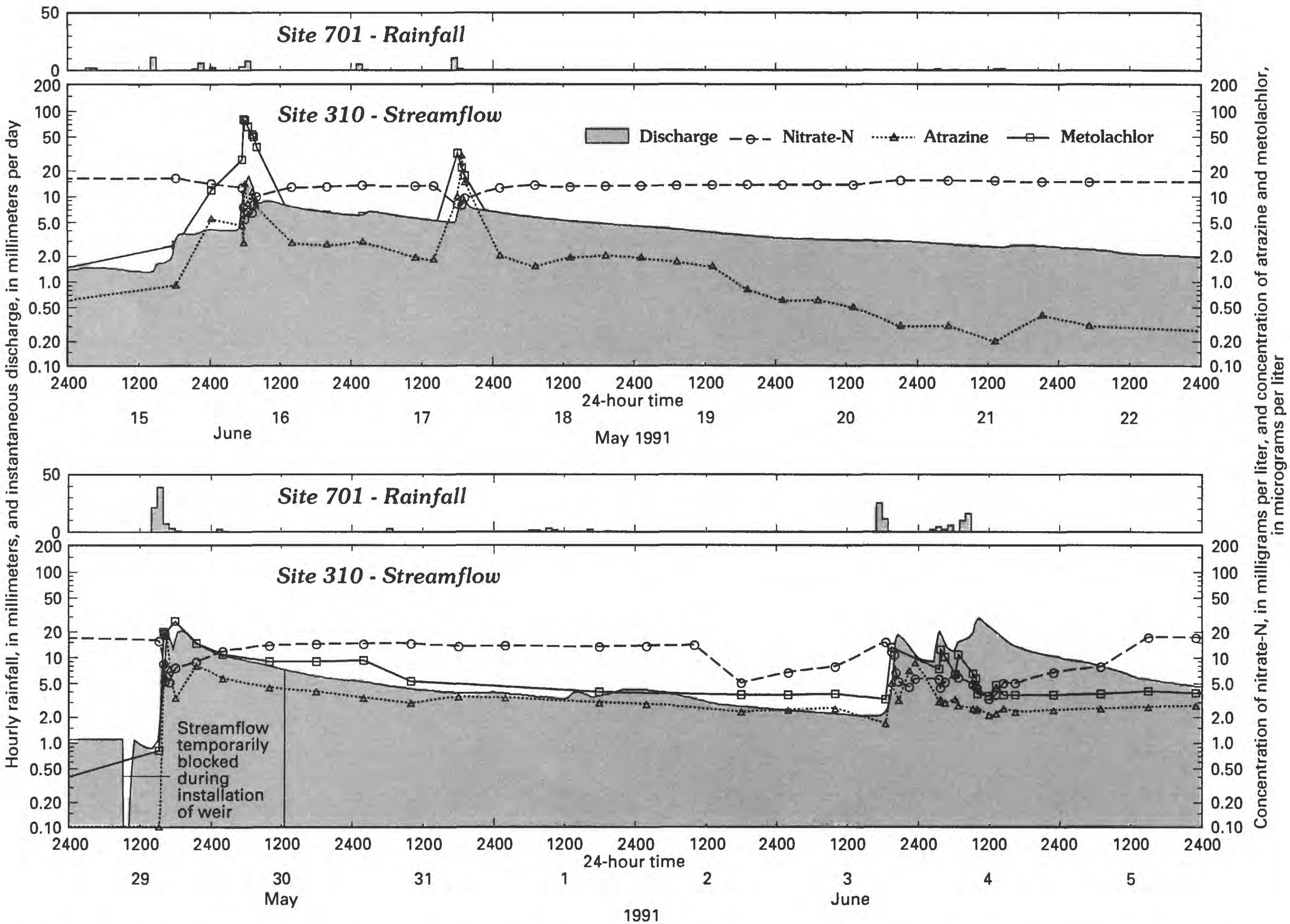

Figure 18. Rainfall for data-collection site 701 and discharge of water flow and sample concentrations of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor for data-collection site 310 during high-flow periods, May 15–June 5, 1991.

tember 1993). For May–July 1993, when most of the herbicides were transported from the subwatersheds, the eastern subwatershed also had the largest cumulative unit discharge (fig. 13) and the largest streamflow-to-precipitation ratios (fig. 14). The steeper terrain, better natural drainage network, and the larger streamflow-to-precipitation ratios during long periods of rainfall for the eastern subwatershed indicate that surface flow is probably greater than for the northwestern and the southwestern subwatersheds. Larger surface runoff and possibly interflow could account for the high loss rates of herbicides in surface flow. Larger return flow and possibly interflow could account for the high loss ratios of nitrate-N in surface flow, although surface runoff also could be contributing increased amounts.

SUMMARY AND CONCLUSIONS

Data on the quantity of precipitation and the quantity and quality of surface flow, tileflow, and streamflow were collected during April 1991–September 1993 at various sites within Walnut Creek watershed located south of Ames, Iowa. The study was part of the multi-scale, interagency Management Systems Evaluation Area (MSEA) project for Iowa to detemine the effects of farming practices on water quality. The U.S. Geological Survey (USGS) cooperated with the National Soil Tilth Laboratory(NSTL) of the U.S. Department of Agriculture, Agricultural Research Service, in collecting data at five sites in the watershed.

Walnut Creek is a tributary of the South Skunk River and has a drainage area of about 5,130 ha at the most downstream data-collection site. The terrain of Walnut Creek watershed is nearly level with numerous potholes in the upstream part, nearly level to rolling in the middle part, and steeper in the downstream part where streams cut down to the river valley. Surficial deposits of till overlie carbonate bedrock. Till thickness is 60 to 90 m on the uplands, and total reflief is about 60 m. Natural drainage is poor in the uplands, and subsurface tiles, some with surface inlets, and ditches have been added to improve drainage. The watershed can be divided into three subwatersheds. The northwestern subwatershed of 2,630 ha is drained by Walnut Creek upstream of the confluence with the major upland tributary. The southwestern subwatershed of 1,170 ha is drained by the major upland tributary. The eastern subwatershed of 1,330 ha is in the steeper part of the watershed between the major upland tributary and the watershed outlet.

Data on precipitation, flow discharge, and concentrations, loads, and yields of nitrate-N, atrazine, and metolachlor are presented. The data were evaluated to relate the tranport of chemicals to major flow processes and to examine flow and transport differences among the three subwatersheds. Stage or stage and velocity data were recorded at five flow sites. Surface flow and tileflow, sites 220C and 220T, were monitored separately at the outlet of a 366-ha basin in the northwestern subwatershed. Streamflow was monitored just upstream from the outlet of the northwestern subwatershed—site 310; just downstream from the combined outlets of the northwestern and the southwestern subwatersheds—site 320; and at the watershed outlet—site 330. Stage-discharge ratings were computed from theoretical equations and discharge measurements. Flow samples were collected frequently during stormflows by automatic samplers and weekly during base flows by manual and automatic methods. Samples were analyzed at the NSTL for concentrations of nitrate-N, alachlor, atrazine, metolachlor, and metribuzin. Precipitation data were recorded at 17 sites throughout the watershed.

Chemical application amounts (mass) for the various basins were computed for each crop year (1991–93) by the NSTL using a geographic information system (GIS). Daily values of areally weighted precipitation were computed for each subwatershed using the Theissen polygon method. Flow discharges were computed at each site for each set of recorded stage or stage and velocity measurements for April 1991–September 1993. Daily streamflows for the subwatersheds were computed from data for an individual site or a pair of sites. Streamflow-to-precipitation ratios were computed. Time-concentration curves were developed from sample concentrations at each site for the most frequently detected chemicals—nitrate-N, atrazine, and metolachlor. Concentrations were determined by linear interpolation on 15-minute time steps. Chemical-discharge rates (mass per time) were computed by multiplication of flow discharge and chemical concentration. Chemical loads (mass) were computed by summation of chemical discharges over specified time periods. Chemical yields (mass per area) were computed by division of loads by drainage area. Chemical loss rates were computed as yields expressed as a percentage of average application rates.

A comparison of precipitation and streamflow data indicates that antecedent conditions have a substantial effect on the flow response from a given subwatershed and that the flow response to similar precipitation can vary among the three subwatersheds. The streamflow-to-precipitation ratio was greater than 1.0 for some months as stored precipitation (snow, ice) was released due to increasing temperatures. Negative streamflow-to-precipitation ratios for the eastern subwatershed during July–October 1991 and September–October 1992 indicated a loss of streamflow to the ground-water system; disappearing streamflow was observed, first downstream of the eastern subwatershed and later within the eastern subwatershed itself. Streamflow differed substantially during July 1992 and July 1993 despite similar large amounts of rainfall. Antecedent conditions prior to July 1992 were dry, and the streamflow-to-precipitation ratios were less than about 0.3. Antecedent conditions prior to July 1993 were wet, and the ratios were about 0.7 for the southwestern subwatershed, which has the most limited surface drainage, to almost 1.0 for the eastern subwatershed, which has the most extensive natural drainage. This suggests a larger potential for surface and subsurface flow and chemical transport in the eastern subwatershed. It is probable that the high streamflow-to-precipitation ratios for 1993 are extreme.

Flow data indicate that most of the streamflow from the northwestern subwatershed comes from tileflow. Cumulative streamflow at site 310 for April 1992–September 1993 was equal to about 1,000 mm (a volume of flow equivalent to a depth of the given amount over the entire basin). For the same period, surface flow at site 220C was equivalent to about 200 mm, and tileflow at site 220T was equivalent to about 800 mm. Surface flow is highly variable and intermittent, usually lasting for only a few days after a storm. Tileflow is less variable and much more persistent, ceasing only after prolonged dry periods. Surface flow can be the dominant source of flow for as much as a few days after large storms.

Large amounts of nitrate-N are transported in Walnut Creek with concentrations often greater than the MCL of 10 mg/L. Ground-water flow from the tiles, at least in the northwestern subwatershed, is the primary means of transport to the streams. Concentrations in tileflow and streamflow generally were 4 to 16 mg/L, with the lower concentrations usually occurring during periods of surface runoff from snowmelt or rainstorms. Concentrations also decreased as streamflow decreased during July–August 1991 and September–October 1992. This was not apparent in tileflow, possibly suggesting a degradation process that was occurring in the stream channels but not in the tile lines. Daily and cumulative nitrate-N loads closely correspond to patterns of flow. Loss rates of nitrate-N for October 1992 through September 1993 show the susceptibility of nitrate-N to transport—about 10 percent in surface flow and more than 100 percent in tileflow from the 220 basin, more than 100 percent in streamflow from the northwestern and the southwestern subwatersheds, and more than 200 percent in streamflow for the eastern subwatershed.

Concentrations of the herbicides atrazine and metolachlor in streamflow typically are less than the MCL of 3.0 μg/L but are as much as 59 and 80 μg/L, respectively, during stormflow. Rapid concentration increases of herbicides to as much as 171 μg/L occurred in tileflow, but these are attributed to surface flow through surface inlets on the basis of rainfall data and a comparison with data for a tileflow site with no contributing surface inlets. The transport of herbicides is extremely variable, with most of the loads occurring during relatively short periods of surface flow. Both surface flow and ground-water flow contribute to the herbicide load in the streams, but surface flow appears to be the primary means of transport. Cumulative-yield data show tileflow contributing more herbicides to streamflow than surface flow; however, surface flows to the tile system through surface inlets appear to account for most of that load when stormflow is large, as in May–June 1991 and May–July 1993. The amounts of rainfall, timing of rainfall relative to application of chemicals, and basin characteristics affect the amounts of chemicals transported to and by the streams.

Atrazine appeared more susceptible to transport losses to streamflow than did metolachlor. Herbicide losses in streamflow from the subwatersheds for the April–September periods ranged from 0.3 to 20 percent for atrazine and from 0.1 to 2.9 percent for metolachlor. The loss rates for atrazine for the subwatersheds were larger than for metolachlor for concurrent periods by factors ranging from 1.3 to 4 percent for the 1991 and 1992 crop years and from 1.3 to 6.9 percent for the April–September 1993 period.

Chemical loss rates indicate differences in the transport characteristics of the three subwatersheds. The eastern subwatershed had the highest loss ratios for all three chemicals—206 percent for nitrate-N

(October 1992–September 1993), 20 percent for atrazine, and 2.9 percent for metolachlor (April–September 1993). For May–July 1993, when most of the herbicides were transported from the subwatersheds, the eastern subwatershed also had the largest cumulative unit discharge and the largest streamflow-to-precipitation ratios.

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GLOSSARY

Base flow. The part of **streamflow** or **tileflow** that enters stream channels or tile lines relatively slowly after **precipitation** and is sustained during dry periods from flow out of the soil-rock system. Generally, it is composed of **ground-water flow**, but it also can include delayed **surface flow** from **interflow** and **return flow**.

Depression storage. Water from **precipitation** stored in areas with no surface-runoff outlet.

Depression storage overflow. Flow of water from **precipitation** on a **depression storage** area that has become filled.

Evaporation. The process by which surface water and water from the soil-rock system are returned directly to the atmosphere as vapor.

Ground-water flow. Flow of water through the **saturated zone** of the soil-rock system.

Ground-water recharge. Flow of water from the **unsaturated zone** to the **saturated zone** of the soil-rock system.

Ground-water storage. Water in the **saturated zone** of the soil-rock system.

Impervious storage. Water from **precipitation** stored in areas that have no surface-flow outlets and that do not allow **infiltration**.

Infiltration. The movement of water from the land surface into the soil-rock system through pores, cracks, holes, and other openings.

Interception. **Precipitation** intercepted by vegetation that is returned to the atmosphere by means of **evaporation** or **sublimation**.

Interflow. Flow of water by gravity through the **unsaturated zone** toward drainageways and stream channels.

Matrix flow. The flow of water through the pores and other small pathways of the soil-rock matrix.

Overland flow. The flow of **precipitation** over the land surface toward stream channels; it is composed of flow from impervious surfaces where **infiltration** cannot occur, from areas where **precipitation** rate exceeds **infiltration** rate (**infiltration** excess), and from areas where the land surface is saturated and **infiltration** can no longer occur.

Precipitation. Water droplets and ice particles discharged from the atmosphere that fall to land or water surfaces in such forms as rain, snow, hail, and sleet.

Preferential flow. The flow of water within the soil-rock system along cracks, holes, and other pathways large enough to allow relatively rapid movement compared to the surrounding soil-rock matrix.

Rain/Rainfall. Liquid **precipitation**.

Return flow. Flow of water from the **saturated zone** of the soil-rock system to the land surface.

Saturated zone. That part of the soil-rock system below the **water table** where all spaces are filled with water. It is also known as the phreatic zone.

Stormflow. The flow of water from **precipitation** that enters stream channels or tile lines relatively rapidly. It includes **surface flow** and flow out of the soil-rock system along flow paths that are mostly preferential or relatively short, including **interflow**, **return flow**, and **ground-water flow**.

Streamflow. The flow of water from **precipitation** that eventually appears in surface stream channels.

Sublimation. The process by which frozen **precipitation** is returned directly to the atmosphere as vapor.

Surface flow. The flow of water from **precipitation** that directly or eventually appears on the land surface; it includes **surface runoff**, **interflow**, and **return flow**.

Surface runoff. The flow of water from **precipitation** that has not passed beneath the land surface.

Tileflow. The flow of water in a buried tile-drainage system, usually consisting of **ground-water flow** from the **saturated zone** but including **surface flow** if surface inlets are connected to the tile system.

Transpiration. The process by which water in the soil-rock system is returned to the atmosphere as vapor through living plants.

Unsaturated zone. That part of the soil-rock system above the **water table** where spaces may contain air or water. It is also known as the vadose zone or zone of aeration and includes the root zone, the intermediate zone, and the capillary fringe.

Water table. The upper surface of the **saturated zone** where hydrostatic pressure equals atmospheric pressure.

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