Pesticides in Surface Water in Agricultural and Urban Areas of the South Platte River Basin, from Denver, Colorado, to North Platte, Nebraska, 1993–94

By Robert A. Kimbrough and David W. Litke

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FOREWORD

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

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

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

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

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

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
acre	4,047	square meter
acre-foot (acre-ft)	1,233	cubic meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
cubic foot per second per mile [(ft^3/s)/mi]	0.01676	cubic meter per second per kilometer
foot (ft)	0.3048	meter
foot per day (ft/d)	0.3048	meter per day
mile (mi)	1.609	kilometer
pound (lb)	0.4536	kilogram
pound per day (lb/d)	0.1825	ton per year
square mile (mi^2)	2.590	square kilometer

Temperature in degree Celsius (°C) can be converted to degree Fahrenheit (°F) as follows:

°F = 1.8 (°C) + 32

ADDITIONAL ABBREVIATIONS

μg/L	microgram per liter
μm	micrometer
L	liter
HA	health advisory
MCL	maximum contaminant level
MDL	method detection limit

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By Robert A. Kimbrough *and* David W. Litke

ABSTRACT

Results of two studies are presented in this report. The first part of the report presents results of pesticide data collected at surface-water sites in the agricultural areas along the South Platte River from Henderson, Colorado, to North Platte, Nebraska, during the 1994 growing season. Samples were collected at 16 to 20 sites on three occasions from May through August 1994 (synoptic samples) and at 2 sites approximately biweekly during the same period (anchor-site samples). The second part of the report presents results of pesticide data collected at two surface-water sites in the Denver metropolitan area. One site was located on the main-stem South Platte River in Denver, whereas the second was located on a tributary (Cherry Creek) at its confluence with the South Platte River, 0.4 mile upstream from the main-stem site. Eighteen samples were collected at each site from December 1993 through November 1994.

Thirty-nine pesticides were detected at least once during the agricultural study. Ten pesticides accounted for about 80 percent of the synoptic sample detections. Of the 10 pesticides, 6 commonly are used for irrigated agriculture in the study area (atrazine, metolachlor, DCPA, cyanazine, EPTC, and carbofuran); one (desethylatrazine) is a metabolite of atrazine; two (prometon, simazine) primarily are used for long-term weed control in noncropped areas; and one (diazinon) is an insecticide used around households and commercially on some vegetable crops.

Of the 39 pesticides detected during the agricultural study, only 8 had median concentrations greater than their respective method detection limits (the 8 median concentrations ranged from 0.004 to 0.15 microgram per liter). Collectively, there were 22 detections of 10 pesticides that were measured at concentrations greater than 1 microgram per liter. The herbicide DCPA was measured at the highest concentration of 30 micrograms per liter. Pesticide concentrations generally were less than standards or guidelines for drinking water and aquatic life.

Atrazine, desethylatrazine, and prometon were detected throughout the agricultural study area, and each persisted throughout the growing season at consistent concentrations. Ground-water discharge may transport atrazine, desethylatrazine, and prometon to surface waters in the study area because these three compounds also have been detected at equivalent concentrations in alluvial ground water in the study area. Other commonly detected pesticides occurred less frequently and had geographic or temporal fluctuations in their occurrence, indicating that pesticide use varies throughout the study area. For example, occurrences of metolachlor, which commonly is applied to corn, primarily were limited to sites located in corn production areas. Occurrences of diazinon, which is used in urban areas and on vegetables, primarily were limited to

sites in the upper one-half of the study area where major urban centers are located and where most vegetable production occurs. The timing of pesticide applications resulted in temporal variations of concentrations. For example, the concentrations of the herbicide DCPA were highest in May, following early season application, and steadily declined throughout the growing season. The insecticide propargite was detected only for several weeks following its application to corn in July, and the insecticide carbofuran was only detected in June following its application to alfalfa and corn.

Twenty-eight pesticides were detected at the two sampling sites during the urban study. Nine pesticides accounted for about 80 percent of the detections at both sites, indicating that pesticide use is similar in each basin. Of the nine most commonly detected pesticides, five (carbaryl, chlorpyrifos, DCPA, diazinon, and malathion) commonly are used by homeowners or commercial applicators in urban areas of the South Platte River Basin. Three (prometon, simazine, and tebuthiuron) are herbicides generally associated with nonagricultural uses in Colorado and are used for long-term, nonselective weed control; and one (atrazine) has had nonagricultural uses in Colorado limited to roadside and turf application since 1992.

Pesticide concentrations measured in the urban samples were small. Seventy-eight percent of the pesticide detections were less than 0.1 microgram per liter, and about 94 percent were less than 0.5 microgram per liter. Carbaryl and 2,4-D were the only pesticides detected at concentrations greater than 1 microgram per liter, and carbaryl was measured at a maximum concentration of 5.5 micrograms per liter. Pesticide concentrations generally were less than standards and guidelines for drinking water and aquatic life, although the U.S. Environmental Protection Agency health advisory for diazinon was exceeded in one sample, and the aquatic-life guidelines for carbaryl, diazinon, and chlorpyrifos were exceeded in several samples. Multiple pesticides were detected in all of the samples.

Individual pesticide concentrations were higher in storm-runoff samples than in nonstorm-runoff samples. The insecticide carbaryl was the dominant pesticide in most of the storm-runoff samples. Carbaryl concentrations in storm-runoff samples generally were 1 to 2 orders of magnitude higher than other pesticide concentrations. DCPA, chlorpyrifos, and malathion generally were detected only during storm-runoff events. Several detections of atrazine, carbaryl, diazinon, prometon, and simazine during dry weather indicate that mechanisms other than storm runoff transport pesticides to streams in the urban environment. Prometon and simazine most likely are being transported by ground water in the Cherry Creek Basin. Prometon and simazine were consistently detected in dry-weather samples when ground water was the predominant source of streamflow in Cherry Creek.

Comparisons of drainage area, urban area, lawn area, and mean streamflow indicate that the small urban basin (Cherry Creek) is representative of the larger urban basin (South Platte River); however, the percentage of carbaryl load in the South Platte River at Denver attributed to Cherry Creek was not consistent and correlated poorly with the contribution of streamflow from Cherry Creek. Overall, the median percentage of pesticide load in the South Platte River at Denver that was attributed to Cherry Creek (equal to 21 percent) was greater than the median contribution of streamflow from Cherry Creek (12.5 percent).

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began to implement the full-scale National Water-Quality Assessment (NAWQA) Program. The goals of the NAWQA Program are to describe the status and trends in the quality of a large, representative part of the Nation's surface- and ground-water resources and to provide a sound, scientific understanding of the primary natural and human factors affecting the quality of these resources (Leahy and others, 1990). Pesticides were identified as a primary water-quality concern and of particular interest was the occurrence and distribution of pesticides in water, the relation of pesticide occurrence to land use, and the movement of pesticides through the hydrologic system. The South Platte River Basin was among the first 20 NAWQA study units selected for study under the full-scale implementation plan (Dennehy, 1991).

The South Platte River Basin (fig. 1) has a drainage area of about 24,300 mi^2; 79 percent of the basin is in Colorado, 15 percent in Nebraska, and 6 percent in Wyoming (Dennehy, 1991). The basin is located within two major physiographic provinces (Lobeck, 1922). The Southern Rockies province on the west is characterized by steeply sloping valleys that drain mountain ranges with peaks as high as 14,286 ft. The Great Plains province on the east is characterized by pediment surfaces sloping gently to the northeast from an altitude of about 5,500 ft at the base of the foothills to 2,788 ft at North Platte, Nebraska. The South Platte River originates in the Southern Rockies province and flows northeastward for about 450 mi across the Great Plains to its confluence with the North Platte River at North Platte, Nebraska. The major tributaries to the South Platte River (Clear Creek, St. Vrain Creek, Big Thompson River, Cache La Poudre River) are perennial streams that originate in the Rocky Mountains; plains streams (for example, Kiowa Creek, Bijou Creek, Beaver Creek, Lodgepole Creek) are ephemeral and contribute little water to the South Platte during most years. Within the South Platte River Basin, land use is 41 percent rangeland, 37 percent agriculture, 16 percent forest, 3 percent urban, and 3 percent other (Fegeas and others, 1983). For a more complete description of the environmental setting of the South Platte River Basin, see Dennehy and others (1993).

A study of existing water-quality data in the South Platte River Basin (Dennehy and others, 1995) revealed that pesticide data were scarce from 1980 to 1992. Ten of 29 surface-water sites having pesticide data had only one sample analyzed. Five sites had between 2 and 9 samples analyzed, and 14 sites had 10 or more samples analyzed. Most of the pesticide concentrations in surface water were less than laboratory reporting levels. Of the 13 selected pesticides examined in surface water, atrazine, picloram, and 2,4-D were the most commonly detected. The percentage of detections was highest for mixed agricultural and urban land use; slightly lower for urban, built-up, and agricultural areas; and zero for forest areas (Dennehy and others, 1995).

As part of the South Platte NAWQA project, studies were designed and conducted during 1993–95 to collect additional pesticide data within the basin; these studies focused on agricultural and urban land-use areas because agriculture and urbanization have been identified as some of the primary factors that affect water quality in the basin (Dennehy and others, 1993). Two approaches were taken in designing the pesticide studies. The first approach was a sampling of surface water to determine the extent of pesticide occurrence over a large part of the South Platte River Basin. Using this approach, a study was conducted to determine the occurrence and distribution of pesticides in streams draining most of the irrigated agricultural area in the South Platte River Basin. The second approach focused on intensive sampling of surface water in small basins to identify the major factors and processes that affect pesticide occurrence in streams. Two studies were conducted using this approach. One of the studies involved intensive surface-water sampling for pesticides in a small agricultural and a small urban basin in the South Platte River Basin (Kimbrough and Litke, 1996). The other study involved intensive surface-water sampling for pesticides in two urban basins.

Purpose and Scope

This report presents results from two studies. The "Agricultural Study" section presents results of pesticide data collected at surface-water sites in agricultural areas along the South Platte River from Henderson, Colorado, to North Platte, Nebraska. This section summarizes pesticide detections and concentrations in the agricultural study area, describes the spatial and temporal distribution of pesticides between sampling rounds, and presents calculations of pesticide loads along the South Platte River. The occurrence and distribution of selected pesticides are examined in greater detail, and a discussion on ground-water transport of pesticides to streams is presented. Samples were collected at 16 to 20 sites along the main-stem South Platte River and at the mouths of major tributaries on three occasions from May through August 1994 and at 2 sites (1 main-stem and 1 tributary site) approximately biweekly during the same period.

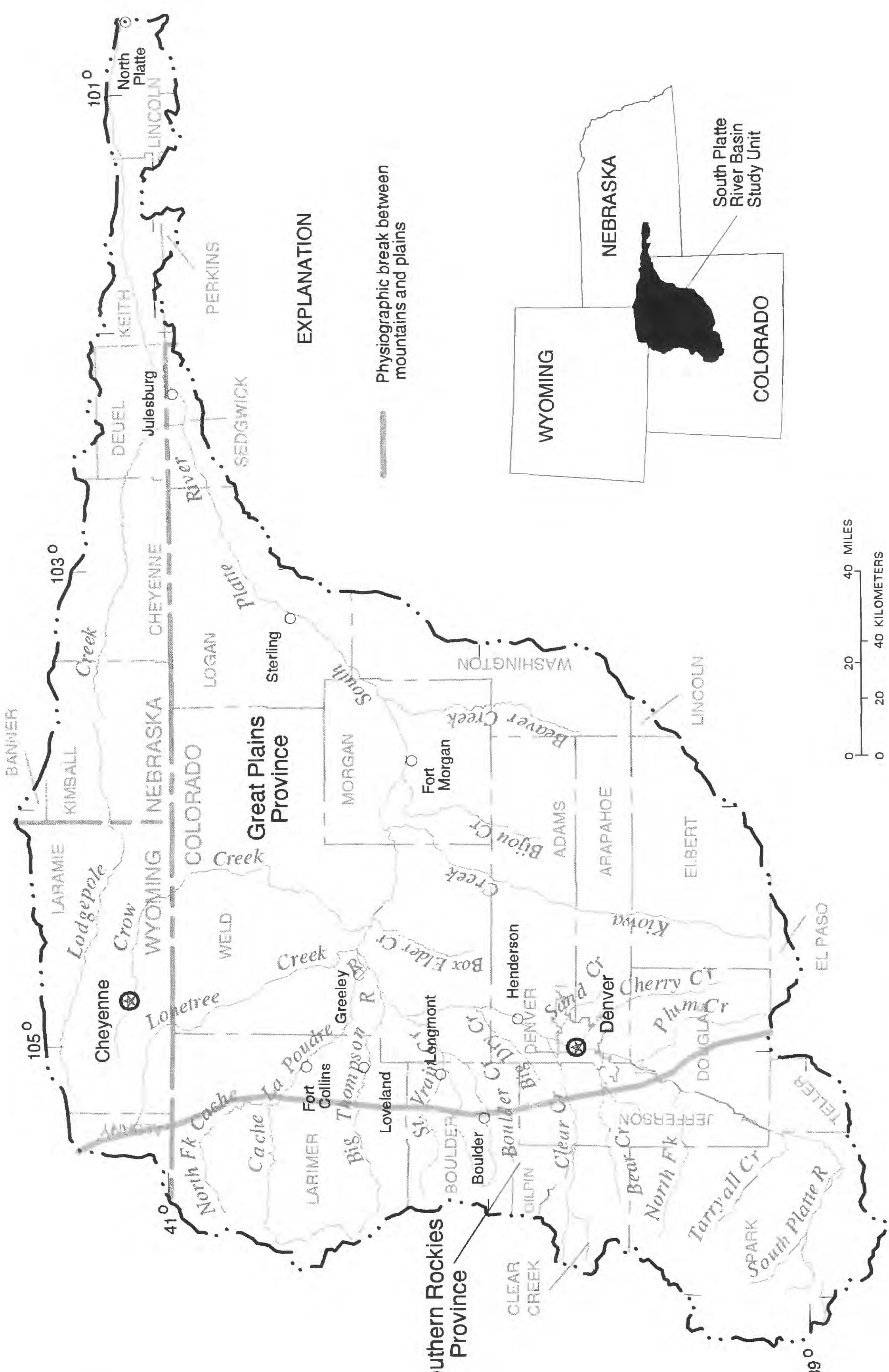


Figure 1. Location of the study unit and physiographic provinces in the South Platte River Basin.

The "Urban Study" section presents results of pesticide data collected at two surface-water sites in the Denver metropolitan area. One site was located on the main-stem South Platte River in Denver, whereas the second site was located on Cherry Creek at its confluence with the South Platte River, 0.4 mi upstream from the main-stem site. This section summarizes pesticide detections and concentrations at the urban sites, describes the occurrence and temporal variability of pesticides in storm-runoff and dry-weather samples, and compares pesticide loadings between the small urban basin (Cherry Creek) and the larger urban basin (South Platte River). Eighteen samples were collected at each site from December 1993 through November 1994.

Sampling and laboratory protocols and results of a combined quality-control program are summarized. A description of each study area and a discussion of study designs are included in the respective sections.

Acknowledgments

The authors wish to thank the staff of the Greeley Office of the Colorado Division of Water Resources for providing streamflow and diversion information during this study and the staff of the Urban Drainage and Flood Control District for providing real-time stage and precipitation data for the Denver metropolitan area. We also would like to thank Jerry Alldredge, Weld County Extension Agent, for providing information on agricultural pesticide use in the study area. Special thanks are given to Dennis Smits, USGS, who assisted in all of the sample collection.

METHODS

Equipment Preparation, Sample Collection, and Analysis

To prevent sample contamination from plasticizers and to minimize analyte losses through adsorption, sample-collection and -processing equipment used was made from Teflon, glass, or stainless steel. All sampling equipment was cleaned prior to use with a nonphosphate laboratory detergent and rinsed first with organic-free water followed by high-purity methanol. The equipment was rinsed with copious amounts of native water at the sampling sites before sample collection. Glass sample bottles and glass fiber filters were cleaned by baking at 450°C for 8 hours and were not field rinsed.

Depth- and width-integrated water samples were collected from streams in each study area by using the equal-width-increment method (Edwards and Glysson, 1988) and processed onsite using methods described by Shelton (1994). Samples were filtered onsite using glass fiber filters with a nominal-pore-diameter of 0.7 µm. Filtered samples were immediately chilled to 4°C before delivery to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado, for analysis.

Pesticides were extracted and analyzed from 1-L water samples at the NWQL using methods described by Zaugg and others (1995) and by Werner and others (1996). Analyses for as many as 83 pesticides (including 7 pesticide metabolites, referred to herein as pesticides) were done for individual samples (table 1). Concentrations for 46 pesticides were determined by C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry (GC/MS). Concentrations for 37 pesticides were determined by Carbopak-B SPE and high performance liquid chromatography (HPLC). Several pesticides (azinphos-methyl, carbaryl, carbofuran, chlorothalonil, desethylatrazine, dichlobenil, DNOC, esvenvalerate, 1-napthol, and terbacil) demonstrated variable performance during SPE or during analysis by GC/MS or HPLC (Zaugg and others, 1995; Werner and others, 1996). As a result, the concentrations for these analytes are qualitatively reported. A change in SPE column types following method-performance evaluations in 1992 (prior to this study) resulted in improved performance for carbaryl and carbofuran; however, the concentrations for these two compounds are still qualitatively reported because of the potential for variable performance (Zaugg and others, 1995). Pesticides and pesticide metabolites analyzed for the studies had individual method detection limits (MDL's) varying from 0.001 to 0.050 µg/L (table 1). A total of 127 1-L water samples were analyzed by GC/MS, and 102 samples were analyzed by HPLC.

Table 1. Pesticides and pesticide metabolites analyzed for during agricultural and urban land-use studies in the South Platte River Basin, December 1993 through November 1994

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; --, no standard or guideline]

Pesticide	Trade name(s)	Analysis method	Method detection limit	Standard or guideline for drinking water (MCL or HA)	Guideline for aquatic life
		Herbicides			
Acifluorfen	Blazer, Tackle	HPLC	0.035	--	--
Alachlor	Lasso	GC/MS	0.002	[1]2	--
Atrazine	AAtrex	GC/MS	0.001	[1]3	[2]2
Benfluralin	Balan, Benefin	GC/MS	0.002	--	--
Bentazon	Basagran	HPLC	0.014	20	--
Bromacil	Bromax 90, Urox B	HPLC	0.035	90	--
Bromoxynil	Buctril, Brominal	HPLC	0.035	--	[2]5
Butylate	Sutan +	GC/MS	0.002	350	--
Chloramben	Amiben	HPLC	0.011	100	--
Clopyralid	Lontrel	HPLC	0.050	--	--
Cyanazine	Bladex	GC/MS	0.004	1	[2]2
2,4-D	2,4-D and many other names	HPLC	0.035	[1]70	[3]3
2,4-DB	Butoxone	HPLC	0.035	--	--
DCPA	Dacthal	GC/MS	0.002	4,000	--
Desethylatrazine	metabolite of atrazine	GC/MS	0.002	--	--
Dicamba	Banvel	HPLC	0.035	200	[3]200
Dichlobenil	Casoron	HPLC	0.020	--	[3]37
Dichlorprop	2,4-DP	HPLC	0.032	--	--
2,6-Diethylanaline	metabolite of alachlor	GC/MS	0.003	--	--
Dinoseb	Basanite and many other names	HPLC	0.035	[1]7	
Diuron	Diurex and many other names	HPLC	0.020	10	[3]1.6
EPTC	Eptam	GC/MS	0.002	--	--
Ethalfluralin	Sonalan	GC/MS	0.004	--	--
Fenuron	Beet-Kleen	HPLC	0.013	--	--
Fluometuron	Cotoran	HPLC	0.035	90	--
Linuron	Lorox	GC/MS	0.002	--	--
MCPA	MCPA and many other names	HPLC	0.050	10	--
MCPB	Thistrol	HPLC	0.035	--	--
Metolachlor	Dual	GC/MS	0.002	100	[2]8
Metribuzin	Lexone, Sencor	GC/MS	0.004	200	[2]1
Molinate	Ordram	GC/MS	0.004	--	--
Napropamide	Devrinol	GC/MS	0.003	--	--
Neburon	Neburex, Neburon	HPLC	0.015	--	--
Norflurazon	Evital, Zorial	HPLC	0.024	--	--
Oryzalin	Surflan	HPLC	0.019	--	--
Pebulate	Tillam	GC/MS	0.004	--	--
Pendimethalin	Prowl	GC/MS	0.004	--	--
Picloram	Tordon	HPLC	0.050	[1]500	--

Table 1. Pesticides and pesticide metabolites analyzed for during agricultural and urban land-use studies in the South Platte River Basin, December 1993 through November 1994—Continued

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; --, no standard or guideline]

Pesticide	Trade name(s)	Analysis method	Method detection limit	Standard or guideline for drinking water (MCL or HA)	Guideline for aquatic life
		Herbicides—Continued			
Prometon	Pramitol	GC/MS	0.018	100	--
Pronamide	Kerb	GC/MS	0.003	50	--
Propachlor	Ramrod	GC/MS	0.007	90	--
Propanil	Stampede	GC/MS	0.004	--	--
Propham	IPC	HPLC	0.035	100	--
Simazine	Princep, Aquazine	GC/MS	0.005	[1]4	[3]10
2,4,5-T	Line Rider and many other names	HPLC	0.035	70	--
2,4,5-TP	Silvex	HPLC	0.021	[1]50	[3]1.4
Tebuthiuron	Spike, Graslan	GC/MS	0.010	500	--
Terbacil	Sinbar	GC/MS	0.007	90	--
Thiobencarb	Bolero	GC/MS	0.002	--	--
Triallate	Far-Go	GC/MS	0.001	--	[2]0.24
Triclopyr	Garlon	HPLC	0.050	--	--
Trifluralin	Treflan and several other names	GC/MS	0.002	5	[2]0.10
		Insecticides			
Aldicarb	Temik	HPLC	0.016	[1]3	--
Aldicarb sulfone	metabolite of aldicarb	HPLC	0.016	[1]2	--
Aldicarb sulfoxide	metabolite of aldicarb	HPLC	0.021	[1]4	--
Azinphos-methyl	Guthion	GC/MS	0.001	--	[4]0.01
Carbaryl	Sevin	GC/MS	0.003	700	[3]0.02
Carbofuran	Furadan	GC/MS	0.003	[1]40	[2]1.75
Chlorpyrifos	Dursban, Lorsban	GC/MS	0.004	20	[5]0.08
p,p'-DDE	metabolite of DDT	GC/MS	0.006	--	--
Diazinon	Diazinon and many other names	GC/MS	0.002	0.6	[3]0.009
Dieldrin	Panoram D-31	GC/MS	0.001	--	[5]0.36
Disulfoton	Disyston and several other names	GC/MS	0.017	0.3	[3]0.05
DNOC	Sinox and several other names	HPLC	0.035	--	--
Esfenvalerate	Asana	HPLC	0.019	--	--
Ethoprop	Mocap	GC/MS	0.003	--	--
Fonofos	Dyfonate	GC/MS	0.003	10	--
alpha-HCH	Lindane (impurity)	GC/MS	0.002	--	--
gamma-HCH	Lindane	GC/MS	0.011	[1]0.2	[5]2.0
Malathion	Malathion and many other names	GC/MS	0.005	200	[4]0.1
Methiocarb	Mesurol	HPLC	0.026	--	--
Methomyl	Lannate and several other names	HPLC	0.017	200	--
Methyl parathion	Penncap-M	GC/MS	0.006	2	--
1-Naphthol	metabolite of carbaryl	HPLC	0.007	--	--
3-OH-carbofuran	metabolite of carbofuran	HPLC	0.014	--	--
Oxamyl	Vydate	HPLC	0.018	[1]200	--
Parathion	Alkron and many other names	GC/MS	0.004	--	[5]0.065

Table 1. Pesticides and pesticide metabolites analyzed for during agricultural and urban land-use studies in the South Platte River Basin, December 1993 through November 1994—Continued

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; --, no standard or guideline]

Pesticide	Trade name(s)	Analysis method	Method detection limit	Standard or guideline for drinking water (MCL or HA)	Guideline for aquatic life
		Insecticides—Continued			
cis-Permethrin	Ambush, Pounce	GC/MS	0.005	--	--
Phorate	Thimet and several other names	GC/MS	0.002	--	--
Propargite	Comite, Omite	GC/MS	0.013	--	--
Propoxur	Baygon	HPLC	0.035	3	--
Terbufos	Counter	GC/MS	0.013	0.9	--
		Fungicide			
Chlorothalonil	Bravo	HPLC	0.035	--	--

[1]Value is the U.S. Environmental Protection Agency (USEPA) maximum contaminant level for drinking water; other values are USEPA lifetime health advisories for a 70-kilogram adult (Nowell and Resek, 1994).

[2]Canadian Government aquatic-life guidelines (Canadian Council of Resource and Environment Ministers, 1987; updates 1989-91, 1993).

[3]National Academy of Sciences and National Academy of Engineering aquatic-life guidelines, 1973 (Nowell and Resek, 1994).

[4]U.S. Environmental Protection Agency chronic aquatic-life guidelines (Nowell and Resek, 1994).

[5]U.S. Environmental Protection Agency acute aquatic-life guidelines (Nowell and Resek, 1994).

Quality Control

Twenty-four of the 127 samples analyzed by GC/MS and 16 of the 102 samples analyzed by HPLC were for quality-control purposes. Field blanks were prepared with organic-free water and processed onsite using the same equipment and handling techniques as were used for the environmental samples. No pesticides were detected in the eight equipment blanks analyzed by using GC/MS or in the six equipment blanks analyzed by using HPLC. Duplicate samples were collected to evaluate the combined effect of sampling and analytical procedures on the precision of measured concentrations. There were 55 occurrences of pesticides detected in duplicate sample sets (six sets of duplicate samples were analyzed by GC/MS, and five sets were analyzed by HPLC). The relative percent difference for 47 sets of duplicate concentrations ranged from 0 to 120 percent with a median of 22 percent (table 15 in the "Supplemental Data" section at the back of this report). Relative percent differences were only computed for 47 of the 55 duplicate concentrations because some duplicates sets had one value less than the MDL (table 15). Field-spiked samples were collected to address analyte recovery in sample matrices. Pesticides analyzed by GC/MS were spiked into 1-L environmental samples at a concentration of 0.1 μg/L. Mean recoveries for pesticides in four field-spiked samples analyzed by GC/MS ranged from 20 to 262 percent with a median of 112 percent (table 16 in the "Supplemental Data" section). Field-spiked samples were not collected for HPLC analysis, although the NWQL processed laboratory control spikes throughout the period of study. Laboratory control spikes were prepared by adding pesticides analyzed by HPLC to reagent-grade water at a concentration of 0.05 μg/L. Mean recoveries in 350 laboratory control spikes collected between April 1993 and April 1995 ranged from 11 to 100 percent with a median of 64 percent (table 17 in the "Supplemental Data" section).

Concentrations Related to Standards

Pesticide concentrations in discrete samples were compared to the U.S. Environmental Protection Agency's (USEPA) maximum contaminant levels (MCL's) and health advisories (HA's) for finished drinking water (Nowell and Resek, 1994) (table 1). Pesticide MCL's and HA's are based on chronic long-term exposure; therefore, pesticide concentrations in individual samples that exceed these criteria may not necessarily indicate a violation of a standard. Streams within the study areas generally are not used as sources of drinking water. If stream water is used for drinking, it is treated prior to consumption; however, conventional treatment plants do not always remove all the pesticides that are dissolved in water. Comparisons between pesticide concentrations and drinking-water standards are offered only as a point of reference for the pesticide concentrations measured in the study areas.

Water-quality guidelines also have been established by the USEPA and the National Academy of Sciences and National Academy of Engineering (NAS/NAE) for the protection of aquatic life (Nowell and Resek, 1994) (table 1). The USEPA guidelines include acute and chronic criteria. Acute criteria are based on exposure levels of as much as 1 hour, and chronic criteria are based on an exposure time of 1 to 4 days (Nowell and Resek, 1994). Table 1 also includes aquatic-life guidelines set by the Canadian Government (Canadian Council of Resource and Environment Ministers, 1987) for pesticides that have not yet been assigned criteria by the USEPA or NAS/NAE.

AGRICULTURAL STUDY—PESTICIDES IN THE SOUTH PLATTE RIVER FROM HENDERSON, COLORADO, TO NORTH PLATTE, NEBRASKA, DURING THE 1994 GROWING SEASON

Description of the Agricultural Study Area

Most agricultural lands in the South Platte River Basin are distributed throughout the Great Plains province (fig. 2). Almost all of the agricultural lands are cropland and pasture (99.6 percent of the total agricultural land-use class). Cropland and pasture compose about 5.7 million acres of land (Dennehy and others, 1993). Of this amount, about 3 million acres are fallow or nonirrigated pastureland, 1.6 million acres are in dryland farming (primarily dryland wheat), and 1.1 million acres are irrigated cropland and pasture.

Irrigated lands are predominantly located on alluvium adjacent to the South Platte River from Henderson, Colorado (just downstream from Denver), to North Platte, Nebraska, and along the principal mountain and plains tributary streams (fig. 2). The extent of irrigated lands in figure 2 is for Colorado only because digital coverages of irrigated lands in Nebraska and Wyoming are not presently (1996) available. Most of the irrigated land downstream from Henderson is in 10 counties (in a downstream direction, Adams, Boulder, Larimer, Weld, Morgan, Logan, and Sedgwick Counties in Colorado, and Deuel, Keith, and Lincoln Counties in Nebraska). The agricultural study considered the irrigated lands along the South Platte River and its tributaries downstream from Henderson as the study area (referred to herein as the 10-county study area).

Surface water and ground water are used to irrigate lands in the South Platte River Basin. Surface water provides most of the irrigation water, and it is delivered immediately to fields through a series of ditches and canals or stored in reservoirs for late irrigation-season use. An estimated 250,000 acres of land in the South Platte River Basin or about 23 percent of the irrigated lands presently are irrigated by ground water (Dennehy and others, 1993).

Irrigated farming (compared to nonirrigated farming) may have a greater potential to affect stream-water quality because of its close proximity to receiving waters and for its generation of surface- and ground-water irrigation return flows to the river. Return flows (primarily ground-water return flows) generated by irrigation are substantial. Of the 3.1 million acre-ft of water used for irrigation in the South Platte River Basin annually, about 1.3 million acre-ft returns to streams (Dennehy and others, 1993).

Pesticides can be transported from irrigated fields to receiving waters in surface-water and ground-water return flows. In surface-water return flows, pesticides are transported in the dissolved phase after being leached from the soil or in the suspended phase while attached to soil particles (Larson and others, 1997). In ground-water return flows, pesticides primarily are transported in the dissolved phase after leaching to the alluvial aquifer in applied irrigation water or in infiltrating precipitation (Larson and others, 1997).

The alluvial aquifers underlying irrigated fields in the study area have relatively shallow water tables and are hydraulically connected to the South Platte River and its tributaries. Depth to water in the alluvium usually is from 0 to 40 ft, and hydraulic conductivities are high, ranging from 100 to 2,000 ft/d (Dennehy and others, 1993). Several gain-and-loss investigations conducted on the main-stem South

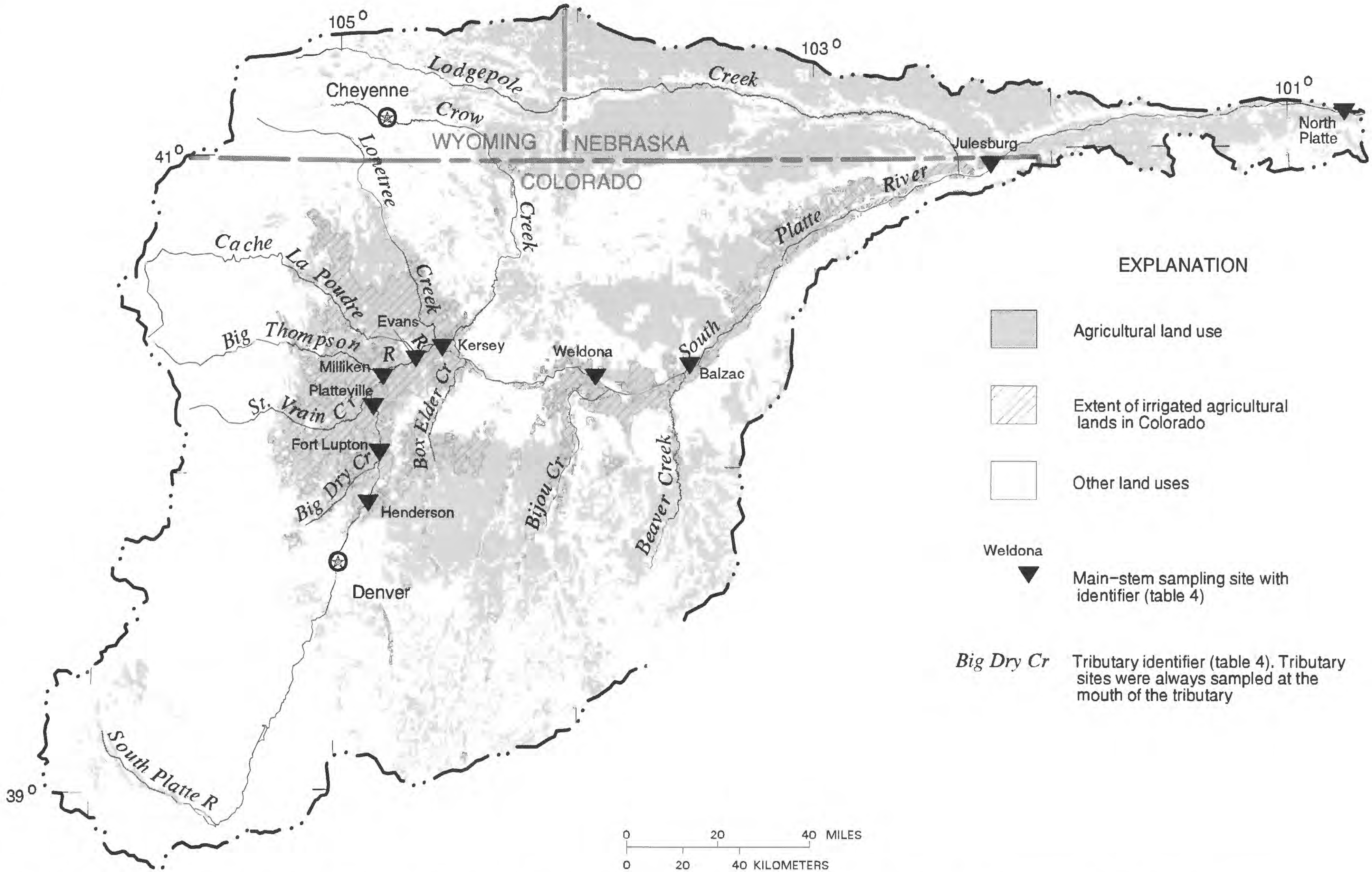


Figure 2. Location of agricultural land-use areas and pesticide sampling sites in the South Platte River Basin (data from Fegeas and others, 1983, and Eros Data Center, 1983).

Platte River have documented streamflow gains that result largely from ground-water discharging from adjacent alluvial aquifers. Two investigations on the South Platte River from Henderson to Julesburg (fig. 1) in March and November 1968 measured gains in almost all subreaches (gains for 23 of 25 subreach calculations) that ranged from 0.6 to 10 (ft^3/s)/mi (Hurr and others, 1975). Numerous investigations in 1977–79 along a 26-mi reach of the South Platte River near Fort Morgan documented an average gain in discharge of 143 ft^3/s (Minges, 1983). A second study conducted in 1982 along the same reach reported an average increase of 150 ft^3/s during the irrigation season (Ruddy, 1984). A median increase of 4.6 (ft^3/s)/mi was determined for three subreaches located within a 25-mi segment of the main-stem South Platte River just downstream from Denver (lengths of the subreaches were equal to 3.5, 8.0, and 8.4 mi) (McMahon and others, 1995).

Although agriculture is the predominant land use in the 10-county study area, pesticide use in urban areas within or adjacent to the study area may have contributed to pesticide detections in this study. Major urban centers are the Denver metropolitan area, which is just upstream from the study area; the cities of Boulder and Longmont in the St. Vrain Creek Basin; and the cities of Fort Collins and Greeley in the Cache La Poudre River Basin (fig. 1).

Major Irrigated Crops

Corn is the primary irrigated crop grown in the 10-county study area, and with the exception of Boulder and Larimer Counties, corn is the primary irrigated crop grown in each of the individual counties (table 2). In 1992, about 54 percent of the irrigated land in the 10 counties was harvested for corn (U.S. Department of Commerce, 1994a, b). Hay (21 percent), dry beans (6 percent), sugar beets (4 percent), wheat (4 percent), and barley (2 percent) were the other major irrigated crops. Vegetables, onions, potatoes, sunflowers, soybeans, sod, sorghum, oats, and other miscellaneous irrigated crops also were grown but in smaller amounts.

There is some geographic variability of crop production in the study area. The variety of crops grown in the five most upstream counties is greater than the variety of crops grown in the five most downstream counties (table 2). Sugar beets, barley, vegetables, onions, potatoes, and sod predominantly are grown in the five most upstream counties. Irrigated crops grown from Sedgwick County downstream to Lincoln County are predominated by corn.

The crop estimates cited in this report are for 1992, but they also are considered to be representative of crop production in 1994 because cropping patterns do not vary substantially within individual counties in the study area from year to year. During 1989–94, the proportion of harvested irrigated acreage for major irrigated crops grown in the seven Colorado counties in the study area remained fairly constant (fig. 29 in the "Supplemental Data" section of this report). As part of the South Platte NAWQA study, crop types for 1991 and 1993 were determined for the lower Lonetree Creek Basin in Weld County, Colorado, using satellite imagery (Wagner and Hoffer, 1994). The results indicate that the proportions of the principal crop acreages did not change substantially between the 2 years (table 18 in the "Supplemental Data" section).

Pesticide Use in the Agricultural Area

Pesticide-use data for the entire study area are not directly available, although pesticide use in a section of the study area recently has been compiled. In a 1992–93 study, 19 farmers within a 20-mi radius of Greeley (fig. 1) were asked to compile crop and pesticide-use data for two consecutive growing seasons (North Front Range Water Quality Planning Association, written commun., 1993). Corn (18 farms), dry beans (5 farms), and potatoes (5 farms) were the most common crops grown. Three pesticides used on corn—propargite (11 farms), terbufos (10 farms), and dicamba (10 farms)—were the three most commonly applied pesticides. The herbicides EPTC (nine farms) and trifluralin (eight farms), which commonly were applied to beans or potatoes in the study area, were ranked four and five in pesticide use.

Pesticide use by crop type for the State of Colorado for 1989 and 1992 was estimated by Bohmont (1991, 1993). The 1989 estimates are broken down into seven regions of the State, whereas the 1992 estimates are for the entire State. In the 1989 survey, six of the seven counties in the "northeast" region also are part of this study's 10-county study area. The five most common pesticides applied to irrigated crops in the "northeast" region in 1989 were (1) EPTC, (2) alachlor, (3) terbufos, (4) atrazine, and (5) butylate. The five pesticides primarily were applied to corn.

Table 2. Harvested acreage for irrigated crops and acreage of irrigated pasture and other irrigated lands in the agricultural study area, 1992

[Data from U.S. Department of Commerce, 1994a, b; --, no acreage]

Irrigated Crop	Counties										Total
	Adams	Boulder	Larimer	Weld	Morgan	Logan	Sedgwick	Deuel	Keith	Lincoln	
Corn	9,000	9,800	25,100	182,400	90,500	55,800	33,500	11,500	52,500	147,200	617,300
Hay	7,300	19,600	28,600	98,400	21,200	31,100	4,500	920	10,100	19,500	241,220
Dry beans	540	2,100	4,400	29,800	7,700	6,700	3,800	1,400	8,800	1,400	66,640
Sugar beets	700	950	2,700	21,800	11,500	5,500	--	--	--	--	43,150
Wheat	2,900	1,300	2,100	13,700	8,900	3,700	2,000	1,000	3,800	2,800	42,200
Barley	910	2,300	5,200	13,600	790	--	--	--	--	--	22,800
Vegetables	3,000	460	1,100	7,900	1,500	60	--	--	--	10	14,030
Onions	920	--	--	8,300	--	--	--	--	--	--	9,220
Potatoes	--	--	--	4,900	--	--	--	--	--	--	4,900
Sunflower seed	520	--	--	440	820	100	280	260	600	1,000	4,020
Soy beans	--	--	--	--	--	--	--	--	680	3,300	3,980
Sod	1,100	--	610	1,600	--	--	----	--	--	--	3,310
Sorghum	--	--	--	660	1,100	80	340	--	320	240	2,740
Oats	--	90	320	620	30	190	--	--	--	--	1,250
Millet	--	--	--	--	--	--	130	--	540	--	670
Triticale	--	--	--	--	--	110	--	--	--	--	110
Field seed	--	--	--	100	--	--	--	--	--	--	100
Berries	--	10	10	--	--	--	--	--	--	--	20
Total harvested irrigated acres	**26,890**	**36,610**	**70,140**	**384,220**	**144,040**	**103,340**	**44,550**	**15,080**	**77,340**	**175,450**	**1,077,660**
Irrigated pasture and other irrigated lands	**1,700**	**8,100**	**12,600**	**23,100**	**1,800**	**1,300**	**1,000**	**1,300**	**540**	**3,400**	**54,840**
Total irrigated acres	**28,590**	**44,710**	**82,740**	**407,320**	**145,840**	**104,640**	**45,550**	**16,380**	**77,880**	**178,850**	**1,132,500**

Agricultural pesticide use has been estimated for the irrigated acreage in the 10-county study area using 1992 county crop acreages, estimates of the percentage of acres treated, and typical pesticide-application rates for each crop (Bohmont, 1993; Gianessi and Puffer, 1992a, b, c; U.S. Department of Commerce, 1994a, b). The estimates represent an upper limit of pesticide applications in the study area because the estimates are the sum of county applications even though some parts of a county may not be completely within the South Platte River Basin. In 1992, about 90 pesticides were applied to irrigated acreage in the 10-county study area with a combined application amount of about 2.8 million pounds of active ingredients. The 20 most common pesticides applied to irrigated land in the study area are listed in table 3. The 20 pesticides (primarily herbicides) accounted for about 80 percent of total pesticide usage on irrigated land in 1992, and the top 5 pesticides accounted for about 50 percent of total usage. Most pesticides are applied to corn because corn is the primary irrigated crop grown. Other primary crops to which the top 20 pesticides were applied also are listed in table 3.

Study Design

The agricultural study included two principal components to assess the occurrence, distribution, and transport of pesticides in the South Platte River during the growing season—synoptic sampling along the length of the South Platte River and weekly to biweekly sampling at two sites, which are referred to as anchor sites. Three pesticide synoptic rounds were conducted during 1994. Twenty sites (10 main-stem sites and 10 tributary sites) (fig. 2 and table 4) were sampled as part of the synoptics. Three of the ten tributaries are perennial streams that originate in the Rocky Mountains (St. Vrain Creek, Big Thompson

Table 3. Estimated pesticide-application data for irrigated land in the 10-county agricultural study area, 1992

[lbs, pounds; H, herbicide; I, insecticide; %, percent; values estimated using data from Bohmont, 1993; Gianessi and Puffer, 1992a, b, c; U.S. Department of Commerce, 1994a, b]

Use ranking	Pesticide	Type	Amount of active ingredient applied (lbs)	Primary crop(s) and percentage of total amount applied
1	Atrazine	H	386,700	Corn (99%)
2	Alachlor	H	378,900	Corn (90%), dry beans (7%)
3	Terbufos	I	274,600	Corn (95%), sugar beets (5%)
4	EPTC	H	203,700	Dry beans (50%), corn (43%), potatoes (4%)
5	Metolachlor	H	194,200	Corn (94%), dry beans (4%)
6	Cyanazine	H	118,800	Corn (97%)
7	Dicamba	H	96,200	Corn (99%)
8	Pendimethalin	H	68,500	Corn (83%), sunflowers (13%), dry beans (2%)
9	DCPA	H	51,000	Onions (96%)
10	2,4-D	H	49,000	Corn (75%), barley (11%), sod (6%), hay (4%)
11	Carbofuran	I	45,900	Corn (60%), alfalfa (35%)
12	Chlorpyrifos	I	44,400	Corn (66%), alfalfa (29%)
13	Ethofumesate	H	44,400	Sugar beets (100%)
14	Propargite	I	44,100	Corn (100%)
15	Phorate	I	39,000	Corn (97%)
16	Trifluralin	H	35,900	Dry beans (45%), alfalfa (19%), corn (18%), sunflowers (7%)
17	Cycloate	H	34,500	Sugar beets (98%)
18	Dimethoate	I	24,500	Corn (90%), dry beans (7%)
19	Butylate	H	21,100	Corn (100%)
20	Methyl parathion	I	19,200	Corn (87%), alfalfa (5%), barley (3%),

Table 4. Sites sampled during synoptic sampling for pesticides, South Platte River Basin, 1994

[River mile for main-stem sites is measured downstream from the reference location of the confluence of the North Fork of the South Platte River with the South Platte River. River mile for tributary sites is the main-stem location of the confluence of the tributary with the South Platte River; @, at; --, no sample collected]

Map identifier in figure 2	River mile	Station number	Station name	Sampling dates and times		
				May synoptic	June synoptic	August synoptic
			Main-stem sites			
Henderson	48.7	06720500	South Platte River at Henderson, Colo.	05/09/94@0830	05/31/94@0950	08/29/94@0845
Fort Lupton	62.3	06721000	South Platte River at Fort Lupton, Colo.	05/09/94@1845	05/31/94@1830	08/29/94@1830
Platteville	75.9	401330104505800	South Platte River near Platteville, Colo.	05/10/94@0930	06/01/94@1025	08/30/94@0850
Milliken	85.9	401910104483900	South Platte River at Highway 60 near Milliken, Colo.	05/10/94@1700	06/01/94@1755	08/30/94@1700
Evans	95.3	402238104402500	South Platte River at Road 54 near Evans, Colo.	05/11/94@0745	06/02/94@0845	08/31/94@0715
Kersey	104.2	06754000	South Platte River near Kersey, Colo.[1]	05/11/94@1620	06/02/94@1600	08/31/94@1520
Weldona	144.6	06758500	South Platte River near Weldona, Colo.	05/10/94@0945	06/01/94@1145	08/30/94@1305
Balzac	178.2	06759910	South Platte River at Cooper Bridge near Balzac, Colo.	05/10/94@1230	06/02/94@0830	08/31/94@0905
Julesburg	266.2	06764000	South Platte River at Julesburg, Colo.	05/11/94@1100	06/02/94@1230	08/31/94@1345
North Platte	350.0	06765500	South Platte River at North Platte, Nebr.	05/11/94@0740	06/01/94@1000	08/30/94@1130
			Tributary sites			
Big Dry Cr.	61.8	06720990	Big Dry Creek at mouth near Fort Lupton, Colo.	--	05/31/94@1730	08/29/94@1630
St. Vrain Cr.	80.6	06731000	St. Vrain Creek at mouth near Platteville, Colo.	05/10/94@1100	06/01/94@1215	08/30/94@1020
Big Thompson R.	90.4	06744000	Big Thompson River at mouth near La Salle, Colo.	05/10/94@1500	06/01/94@1540	08/30/94@1315
Cache La Poudre R.	101.9	06752500	Cache La Poudre River near Greeley, Colo.	05/11/94@1150	06/02/94@1255	08/31/94@1025
Lonetree Cr.	103.0	06753990	Lonetree Creek near Greeley, Colo.[2]	05/11/94@1355	06/02/94@1435	08/31/94@1315
Crow Cr.	109.0	402331104292401	Crow Creek at mouth near Kuner, Colo.	05/11/94@0950	06/02/94@1045	08/31/94@0850
Box Elder Cr.	111.0	402024104302700	Box Elder Creek near Kuner, Colo.	--	06/01/94@0900	08/30/94@0950
Bijou Cr.	152.0	401648103523500	Bijou Creek near Log Lane Village, Colo.	--	06/01/94@1410	08/30/94@1445
Beaver Cr.	170.0	401913103324401	Beaver Creek at Hillrose, Colo.	--	06/01/94@1540	08/30/94@1635
Lodgepole Cr.	257.4	405733102230201	Lodgepole Creek near Ovid, Nebr.	05/11/94@1300	06/02/94@1400	08/31/94@1510

[1]This site was an anchor site also sampled on the following dates: 05/05/94, 05/18/94, 05/25/94, 06/15/94, 06/22/94, 06/29/94, 07/12/94, 07/28/94, and 08/10/94.
[2]This site was an anchor site also sampled on the following dates: 05/06/94, 05/18/94, 05/25/94, 06/15/94, 06/29/94, 07/12/94, 07/28/94, and 8/10/94.

River, and Cache La Poudre River). The remaining tributaries are plains streams. Main-stem sites are referred to in this report by naming only the city part of the site name; for example, the South Platte River at Henderson, Colorado, is referred to as Henderson. Tributary sites are referred to in this report by stream name; for example, Big Dry Creek at the mouth near Fort Lupton, Colorado, is referred to as Big Dry Creek.

Sites along the main stem were spaced fairly close together between Henderson and Kersey because major tributaries enter the river in this reach. From Kersey to North Platte, Nebraska, sites were spaced farther apart. Tributaries were sampled close to their confluence with the South Platte River. Samples were collected over 3-day periods to ensure that data from the study were comparable. From Henderson to Kersey, sampling was designed to follow the same parcel of water as it moved downstream in the main stem. For the Henderson to Kersey reach, the timing of sampling was approximate because detailed information about traveltime was not available. Samples were collected concurrently in the lower reach of the main stem from Kersey to North Platte. The May synoptic (May 9, 1994, through May 11, 1994) and the June synoptic (May 31, 1994, through June 2, 1994) were timed to sample high-pesticide-flux conditions when it was believed pesticide concentrations might be large due to early season pesticide applications and early season irrigation runoff. The August synoptic (August 29, 1994, through August 31, 1994) was timed to sample low-pesticide-flux conditions near the end of the growing season.

Two of the synoptic sites, Kersey and Lonetree Creek (fig. 2 and table 4), were designated as anchor sites. These two sites were sampled weekly or biweekly from May through August to provide finer temporal resolution to changes in pesticide concentrations and to provide a context within which to compare results from the synoptic sampling.

Sixteen of the 20 synoptic sites were sampled during all three synoptic rounds and are referred to in this report as the 16 base sites. Four tributaries were added to the synoptics after the first round and were only sampled during the second and third synoptic rounds (table 4). Samples were collected for analysis by GC/MS during all synoptic rounds, whereas samples for HPLC analysis were collected only during the second and third synoptic rounds.

Hydrologic Conditions During the Agricultural Study

During water year 1994 (October 1993–September 1994), annual mean streamflow in the South Platte River in the study area ranged from about 40 to 50 percent of the 20-year (1976–95) mean (U.S. Geological Survey, 1995). From May through August 1994, precipitation in the South Platte River Basin in Colorado was 65 percent of the long-term (1961–90) mean (National Oceanic and Atmospheric Administration, 1995), and spring snowmelt in May and June was mostly diverted out of the river to meet irrigation water demand. Snowmelt runoff measured in the South Platte River at Kersey was short-lived, and the peak (1,740 ft^3/s) occurred on June 4, 1994 (fig. 3). Precipitation was small, and air temperatures were high throughout the summer so that irrigation water demand remained high. The large offstream reservoirs were emptied by midsummer to provide irrigation water. Therefore, during the 1994 growing season, irrigation was active, river flows were relatively small, and irrigation return flows contributed substantially to river flow.

Streamflow at synoptic main-stem sites generally was highest during the June synoptic round, second highest in May, and lowest in August (fig. 4). During all three synoptics, streamflow in the main stem generally increased from Henderson to Kersey, mainly because of inflows from perennial tributaries (St. Vrain Creek, Big Thompson River, and Cache La Poudre River). Diversions for irrigation caused main-stem flows to decrease steadily from Kersey to Julesburg in May and resulted in large reductions in flow between Kersey and Weldona and between Balzac and Julesburg in June. In August, streamflow was fairly consistent between Kersey and Balzac as ground-water inflow offset diversions for irrigation. During all three synoptics, streamflow increased from Julesburg to North Platte owing to ground-water inflow.

Similar to the main stem, streamflows at tributary sites also generally were highest in June (fig. 4). Whereas snowmelt in the mountainous part of the watershed was the primary source of high flows in the main stem and perennial tributaries, high flows in June in several plains streams were from stormwater runoff. The hydrograph for the anchor site Lonetree Creek shows that a runoff event occurred in the watershed just prior to the June synoptic (fig. 3). The runoff

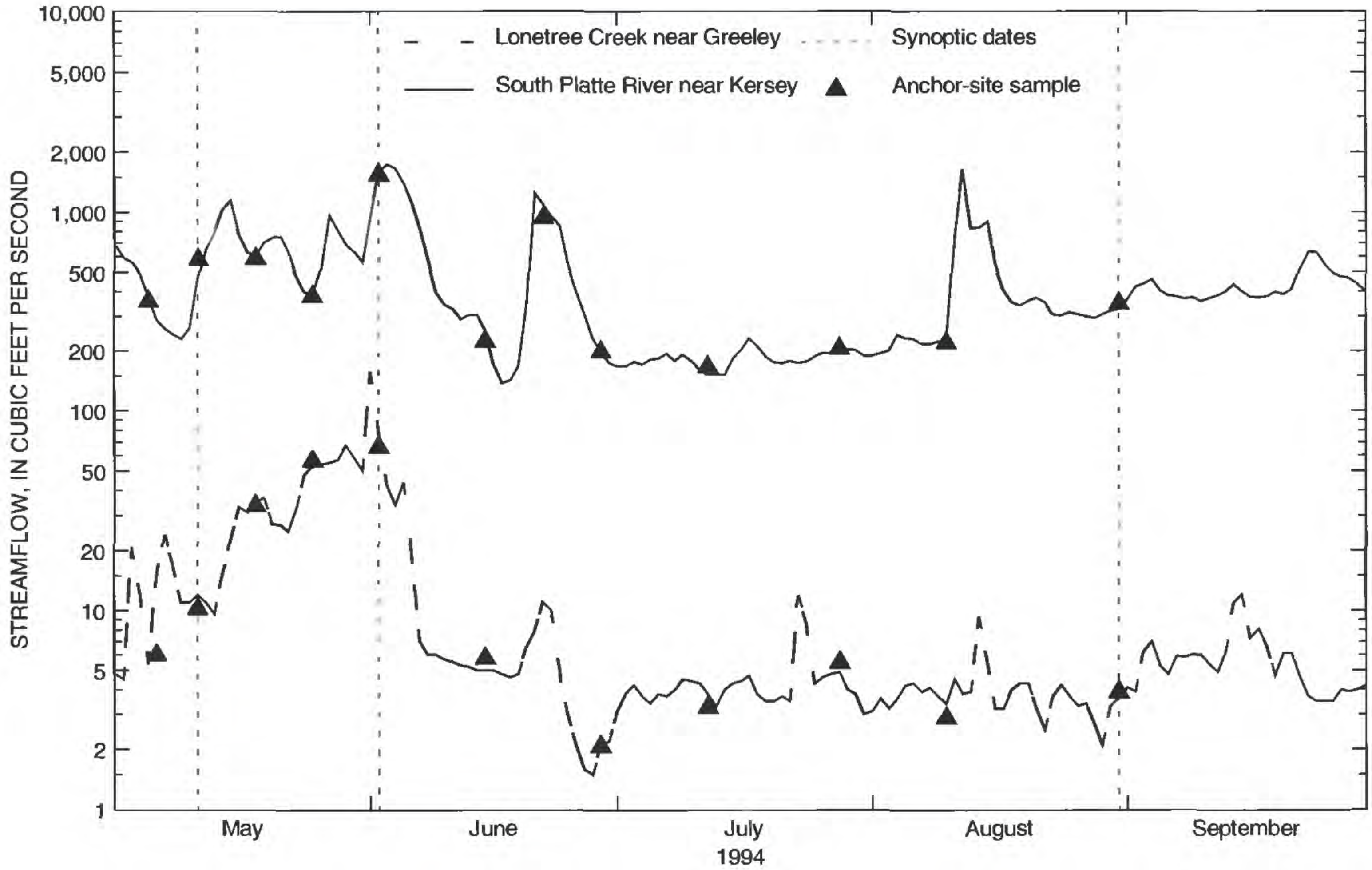


Figure 3. Streamflow and sampling dates at anchor sites, May–September 1994.

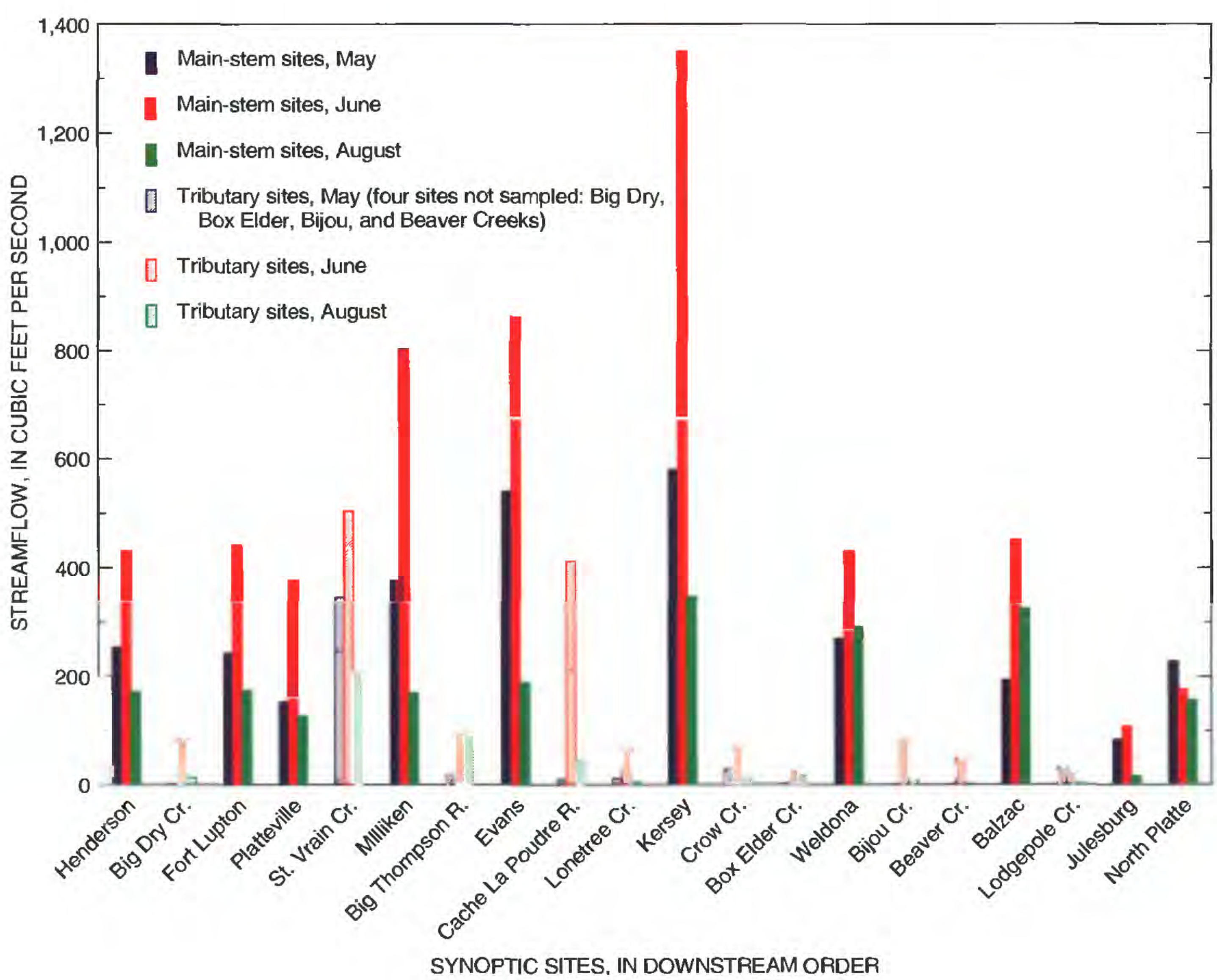


Figure 4. Instantaneous streamflow during synoptic sampling.

event occurred from a localized thunderstorm that tracked eastward off the mountains from Fort Collins, Colorado, to Deuel County in Nebraska (fig. 1). Flow in the Lonetree, Crow, and Lodgepole Creeks and, to a lesser extent, Box Elder Creek probably was affected by the storm. Streamflow at main-stem sites downstream from Kersey was not affected by the storm because of the relatively large amounts of snowmelt water present.

Pesticide Occurrence

During analysis, thirty-nine of the 83 pesticide compounds were detected at least once during the agricultural study (a detection for this study is defined as a measurable concentration that is greater than or equal to the pesticide's MDL) (table 5). Thirty-two compounds were detected at least once during the three synoptic rounds, whereas 29 compounds were detected in additional anchor-site samples. Twenty-two of the 39 compounds were detected at synoptic and at anchor sites.

Out of a total of 4,056 individual pesticide analyses performed on samples collected during the three synoptic rounds, there were 450 detections, or about 11 percent of the total possible. Ten pesticides accounted for about 80 percent of the synoptic detections. Of the 10 pesticides, 6 are some of the more commonly used pesticides for irrigated agriculture in the 10-county study area, including atrazine, metolachlor, DCPA, cyanazine, EPTC, and carbofuran. A seventh compound, desethylatrazine, is a metabolite of atrazine. The remaining three pesticides—prometon, diazinon, and simazine—are used to a varying extent in the study area. Prometon and simazine primarily are used for long-term, nonselective weed control in nonagricultural areas and are not applied to crops in the study area, whereas diazinon is used around households and commercially on some vegetable crops.

Out of a total of 1,411 individual pesticide analyses performed on anchor-site samples, there were 235 detections, or about 17 percent of the total possible. Most of the pesticides that commonly were detected at the anchor sites also were the commonly detected pesticides during the synoptic sampling; in fact, the seven most frequently detected pesticides in anchor-site and synoptic samples were the same pesticides (table 5). The detection of similar pesticides in anchor-site and synoptic samples could indicate that anchor sites were representative of other main-stem and tributary sites in the basin with regard to pesticide occurrence in streams.

Pesticide Concentrations

Pesticide concentrations measured in synoptic and anchor-site samples generally were low. Of the 39 pesticides detected, only 8 had median (50th percentile in table 5) concentrations greater than their respective MDL's (table 5). The herbicide DCPA was the only pesticide that had a concentration greater than 0.5 μg/L at the 90th percentile. The 90th-percentile concentration of 1.9 μg/L for DCPA largely was affected by several detections of the herbicide in anchor-site samples collected from Lonetree Creek. Seven detections of DCPA were measured at greater than 1.0 μg/L in Lonetree Creek, with a maximum concentration of 30 μg/L. Collectively, there were 22 detections of 10 pesticides that were measured at concentrations greater than 1.0 μg/L, including atrazine, alachlor, bromoxynil, cyanazine, 2,4-D, DCPA, EPTC, metolachlor, pendimethalin, and propargite. Twelve of the detections greater than 1.0 μg/L were in synoptic samples, and 10 of the detections were in anchor-site samples.

Median concentrations of individual pesticides for the period of study were less than any established drinking-water criteria, although the HA for cyanazine equal to 1.0 μg/L was exceeded in two synoptic samples at concentrations of 1.2 and 1.3 μg/L. Carbaryl, diazinon, and bromoxynil were the only pesticides to exceed aquatic-life criteria. Thirteen of 22 carbaryl detections (ranging from 0.022 to 0.20 μg/L) exceeded the NAS/NAE aquatic-life guideline of 0.02 μg/L. Thirty-one out of 34 diazinon detections (ranging from 0.010 to 0.083 μg/L) exceeded the NAS/NAE aquatic-life guideline of 0.009 μg/L. The Canadian aquatic-life guideline for bromoxynil equal to 5 μg/L was exceeded once in Lonetree Creek at a concentration of 6.1 μg/L.

Spatial Distribution of Pesticides in Streams

The spatial distribution of pesticide detections during the May, June, and August 1994 synoptic rounds is provided in table 6 (see fig. 2 for synoptic site locations). Atrazine, desethylatrazine, and prometon were detected at every site in the study area. The herbicides cyanazine, DCPA, metolachlor, EPTC, and simazine and the insecticides carbofuran and diazinon were detected at more than one-half of the sites.

At main-stem sites, the number of pesticides detected and the number of pesticide detections were greater in the reach from Henderson to Kersey than in the reach from Kersey to North Platte. The greater variety of pesticide detections in the Henderson to

Table 5. Summary of statistics for pesticides detected in synoptic and anchor-site samples, May–August 1994

[Concentrations in **bold** are greater than the method detection limit; conc., concentration; µg/L, micrograms per liter; <, less than]

Pesticide	Synoptic samples		Anchor-site samples		Total number of analyses	Total number of detections	Minimum conc. (µg/L)	Concentration at indicated percentile (µg/L)					Maximum conc. (µg/L)
	Number of analyses	Number of detections	Number of analyses	Number of detections				10	25	50	75	90	
Atrazine	56	55	17	17	73	72	<0.001	**0.035**	**0.062**	**0.15**	**0.25**	**0.38**	**1.1**
Desethylatrazine	56	52	17	17	73	69	<0.002	**0.007**	**0.018**	**0.049**	**0.086**	**0.14**	**0.30**
Prometon	56	50	17	16	73	66	<0.018	**0.018**	**0.038**	**0.052**	**0.072**	**0.11**	**0.26**
Metolachlor	56	44	17	17	73	61	<0.002	<0.002	**0.006**	**0.022**	**0.082**	**0.17**	**1.8**
DCPA	56	37	17	16	73	53	<0.002	<0.002	<0.002	**0.020**	**0.17**	**1.9**	**30**
Cyanazine	56	29	17	16	73	45	<0.004	<0.004	<0.004	**0.020**	**0.066**	**0.28**	**1.3**
EPTC	56	30	17	15	73	45	<0.002	<0.002	<0.002	**0.010**	**0.054**	**0.14**	**1.2**
Diazinon	56	26	17	11	73	37	<0.002	<0.002	<0.002	**0.004**	**0.023**	**0.048**	**0.083**
Simazine	56	19	17	14	73	33	<0.005	<0.005	<0.005	<0.005	**0.011**	**0.017**	**0.11**
Carbofuran	56	15	17	10	73	25	<0.003	<0.003	<0.003	<0.003	**0.037**	**0.13**	**0.38**
Alachlor	56	11	17	12	73	23	<0.002	<0.002	<0.002	<0.002	**0.008**	**0.065**	**1.5**
Carbaryl	56	16	17	6	73	22	<0.003	<0.003	<0.003	<0.003	**0.012**	**0.055**	**0.20**
Pendimethalin	56	7	17	12	73	19	<0.004	<0.004	<0.004	<0.004	**0.009**	**0.15**	**3.2**
Tebuthiuron	56	14	17	2	73	16	<0.010	<0.010	<0.010	<0.010	<0.010	**0.028**	**0.083**
2,4-D	40	8	17	6	57	14	<0.035	<0.035	<0.035	<0.035	**0.040**	**0.25**	**1.1**
Linuron	56	2	17	8	73	10	<0.002	<0.002	<0.002	<0.002	<0.002	**0.013**	**0.20**
Chlorpyrifos	56	7	17	2	73	9	<0.004	<0.004	<0.004	<0.004	<0.004	**0.007**	**0.035**
Propargite	56	2	17	7	73	9	<0.013	<0.013	<0.013	<0.013	<0.013	**0.024**	**2.3**
Trifluralin	56	2	17	7	73	9	<0.002	<0.002	<0.002	<0.002	<0.002	**0.005**	**0.019**
Malathion	56	5	17	0	73	5	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	**0.048**
Bromoxynil	40	2	17	3	57	4	<0.035	<0.035	<0.035	<0.035	<0.035	<0.035	**6.1**
Dieldrin	56	1	17	3	73	4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	**0.19**
Ethalfluralin	56	0	17	4	73	4	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.072**
Methyl parathion	56	0	17	4	73	4	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	**0.30**

Table 5. Summary of statistics for pesticides detected in synoptic and anchor-site samples, May–August 1994—Continued

[Concentrations in **bold** are greater than the method detection limit; conc., concentration; µg/L, micrograms per liter; <, less than]

Pesticide	Synoptic samples		Anchor-site samples		Total number of analyses	Total number of detections	Minimum conc. (µg/L)	Concentration at indicated percentile (µg/L)					Maximum conc. (µg/L)
	Number of analyses	Number of detections	Number of analyses	Number of detections				10	25	50	75	90	
Metribuzin	56	4	17	0	73	4	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.023**
Terbufos	56	1	17	3	73	4	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	**0.23**
gamma-HCH	56	3	17	0	73	3	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.048**
Bentazon	40	0	17	2	57	2	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	**0.050**
Chlorothalonil	40	0	17	2	57	2	<0.035	<0.035	<0.035	<0.035	<0.035	<0.035	**0.18**
Diuron	40	2	17	0	57	2	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	**0.48**
Aldicarb	40	0	17	1	57	1	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	**0.08**
Aldicarb sulfoxide	40	0	17	1	57	1	<0.021	<0.021	<0.021	<0.021	<0.021	<0.021	**0.98**
Butylate	56	1	17	0	73	1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.007**
Disulfoton	56	0	17	1	73	1	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	**0.041**
Ethoprop	56	1	17	0	73	1	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	**0.019**
Pebulate	56	1	17	0	73	1	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.20**
Pronamide	56	1	17	0	73	1	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	**0.045**
Propachlor	56	1	17	0	73	1	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	**0.091**
Terbacil	56	1	17	0	73	1	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	**0.085**

Table 6. Spatial distribution of pesticide detections in synoptic samples (detections in anchor-site samples are not included)

[Dark gray shading represents two to three detections at a site, light gray shading represents 1 detection; tributary sites and pesticides shaded medium gray were only sampled twice, all other sites and pesticides were sampled three times; main-stem and tributary site names and locations are shown in fig. 2]

Pesticide	Main-stem sites (arranged in downstream order)										Tributary sites (arranged in downstream order)										Number of sites where pesticide was detected
	Henderson	Fort Lupton	Platteville	Milliken	Evans	Kersey	Weldona	Balzac	Julesburg	North Platte	Big Dry Cr.	St. Vrain Cr.	Big Thompson R.	Cache La Poudre R.	Lonetree Cr.	Crow Cr.	Box Elder Cr.	Bijou Cr.	Beaver Cr.	Lodgepole Cr.	
HERBICIDES																					
Atrazine																					20
Desethylatrazine																					20
Prometon																					20
Cyanazine																					19
DCPA																					18
Metolachlor																					18
EPTC																					17
Simazine																					13
Tebuthiuron																					10
Alachlor																					8
2,4-D																					8
Metribuzin																					4
Pendimethalin																					4
Bromoxynil																					2
Diuron																					2
Linuron																					2
Trifluralin																					2
Butylate																					1
Pebulate																					1
Pronamide																					1
Propachlor																					1
Terbacil																					1
INSECTICIDES																					
Carbofuran																					14
Diazinon																					14
Carbaryl																					9
Chlorpyrifos																					6
Malathion																					3
gamma-HCH																					2
Propargite																					2
Dieldrin																					1
Ethoprop																					1
Terbufos																					1
Number of pesticides detected at a site	14	13	15	12	16	14	13	8	8	5	11	11	14	16	16	18	14	10	9	9	
Number of pesticide detections at a site	30	29	30	26	28	29	23	19	15	11	17	19	25	26	30	33	19	10	14	17	
Number of individual pesticide analyses at a site	212	212	212	212	212	212	212	212	212	212	166	212	212	212	212	212	166	166	166	212	

Kersey reach resulted from: (1) Several detections of pesticides that are generally associated with nonagricultural use in the basin (such as simazine and tebuthiuron); (2) detections of insecticides that are applied to crops in the 10-county study area, but also commonly are used in urban areas (diazinon, carbaryl, chlorpyrifos, and malathion); and (3) the miscellaneous detection of several pesticides (2,4-D, metribuzin, diuron, pebulate, propachlor, and *gamma*-HCH) due to the larger variety of crops grown in the upstream counties. The number of different pesticides detected in the main stem steadily declined from a maximum at Evans (16 pesticides) to a minimum at North Platte (5 pesticides). Insecticide detections generally declined in a downstream direction along the entire main stem, and no insecticides were detected at Julesburg and North Platte. With the exception of prometon, main-stem detections downstream from Kersey primarily were limited to the agricultural pesticides commonly used in the study area. At North Platte, pesticide detections were limited to prometon and to the corn herbicides atrazine, cyanazine, and metolachlor and to the metabolite desethylatrazine.

At tributary sites, the number of pesticides detected (and the number of pesticide detections) was highest in five tributaries that enter the main stem within a 20-mi radius of Kersey (Big Thompson and Cache La Poudre Rivers and Lonetree, Crow, and Box Elder Creeks). Several pesticides were detected only at these sites, including the herbicides bromoxynil, trifluralin, butylate, pronamide, and terbacil and the insecticides propargite, dieldrin ethoprop, and terbufos. The largest variety of pesticides detected was in Crow Creek (18 pesticides); however, 14 pesticides were detected in Box Elder Creek even though it was only sampled during two of the three synoptic rounds.

Pesticide concentrations measured in synoptic samples are shown for each site in figure 5. Figure 5 only includes measured concentrations; that is, the concentrations that were equal to or greater than the pesticide MDL's. Median pesticide concentrations (ranging from 0.02 to 0.031 μg/L) were lowest in the six most upstream sites from Henderson to Milliken and included main-stem and tributary sites (fig. 5). Median pesticide concentrations were highest in Crow (0.10 μg/L) and Lonetree Creeks (0.084 μg/L), which enter the South Platte River in the immediate vicinity of Kersey. The highest concentrations were most numerous in Lonetree, Crow, and Box Elder Creeks, as indicated by higher values for the 75th and 90th percentiles at these sites. Of the 12 pesticide measurements that exceeded 1.0 μg/L in synoptic samples, 10 were from these three tributaries. Higher pesticide concentrations in plains streams may occur for several reasons. Plains streams, compared to the main stem and to tributaries that drain from the mountains, contain smaller volumes of annual spring snowmelt that can help to dilute pesticide concentrations. During dry weather, streamflow in plains streams primarily is derived from irrigation return flows or water that was previously applied to crops. As an example, a detailed water balance for Lonetree Creek (Kimbrough and Litke, 1996) in August 1993 during the irrigation season indicated that Lonetree Creek was dry in the far upper reaches of the irrigated part of the watershed, yet streamflow increased by 3 (ft^3/s)/mi in a 5-mi reach farther downstream. The total increase in streamflow was attributed to surface-water and ground-water irrigation return flows.

The presence of stormwater in certain plains tributaries at the time of sampling also could have resulted in higher pesticide concentrations. Increases in pesticide concentrations in streams from storm runoff have been documented in several studies (Thurman and others, 1992; Goolsby and others, 1993; Kimbrough and Litke, 1996). As indicated in the "Hydrologic Conditions During the Agricultural Study" section of this report, some stormwater was present in Lonetree, Crow, and Box Elder Creeks during the June synoptic. Of the 10 pesticide measurements that exceeded 1.0 μg/L in the Lonetree, Crow, and Box Elder Creeks, 7 were from the June synoptic samples.

Temporal Distribution of Pesticides in Streams

A discussion of the temporal distribution of pesticides in streams is more valid if only the sites and pesticides that were sampled during all three synoptic rounds are considered. Therefore, comparisons in this section are limited to the 16 base sites that were sampled during each synoptic round (table 4) and to the pesticides that were analyzed during all synoptic rounds (the pesticides analyzed by GC/MS, table 1).

The timing of pesticide detections was related in part to the timing of application. The quantity of pesticide residue on fields that is available for transport to receiving streams is greatest following application and decreases with time as the pesticide breaks down in the environment or is assimilated by

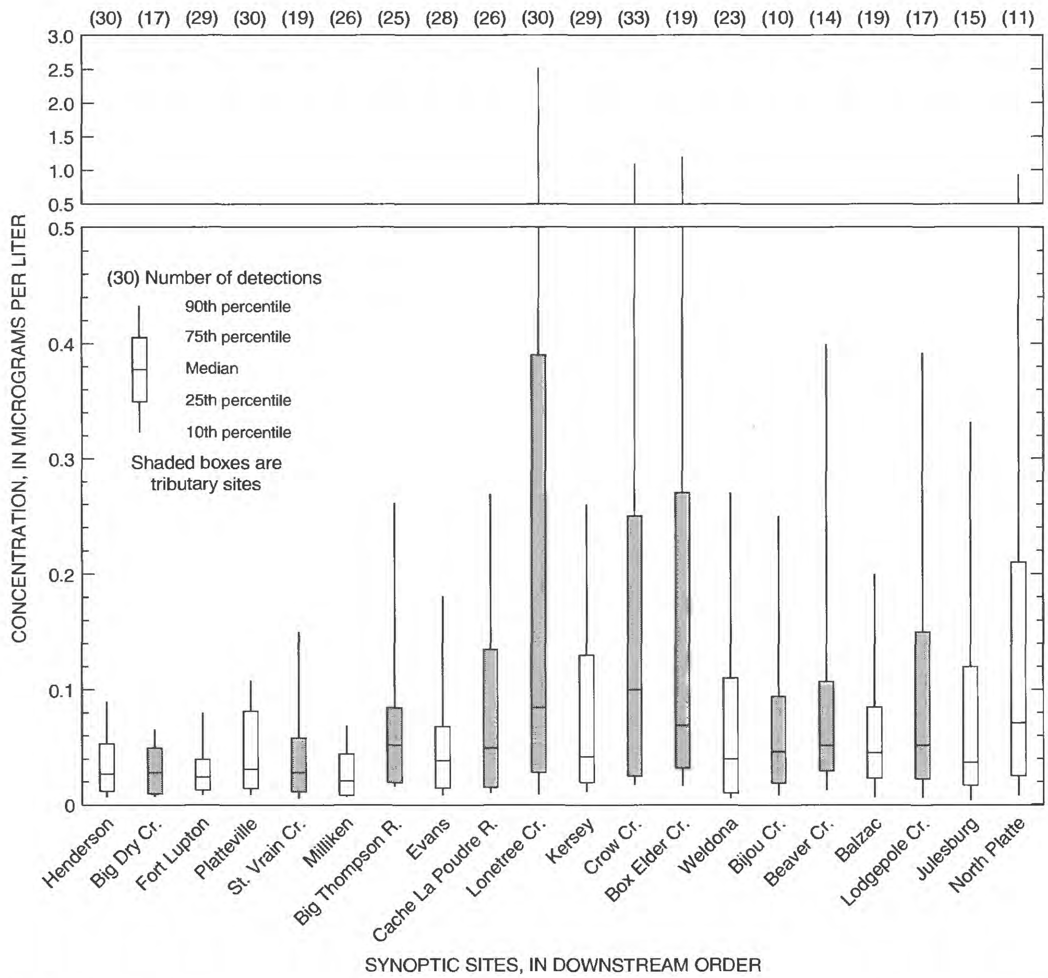


Figure 5. Pesticide concentrations (equal to or greater than the pesticide method detection limits) at synoptic sites (data are for all three synoptic rounds).

plants. Most herbicides are applied to fields during March through May before planting (preplant incorporated) or just after planting (preplant or early postplant emergent). Insecticides typically are applied in June and July after insects have been identified in established fields. Herbicide detections and the number of different herbicide compounds detected were more numerous in May and June as compared to August (fig. 6), correlating with early season application, and insecticide detections and the number of different insecticide compounds detected were most numerous in June, correlating with mid-growing-season application.

Measurable pesticide concentrations (concentrations equal to or greater than the pesticide MDL's) did not vary significantly between synoptic rounds (fig. 7). During each of the synoptics, measurable pesticide concentrations generally ranged between 0.01 and 0.10 µg/L, and median concentrations ranged from 0.03 µg/L in May to 0.05 µg/L in August. The highest pesticide concentrations were most numerous in June when 10 percent of the pesticide detections were greater than 0.35 µg/L. Stormwater in tributaries near Kersey during the June synoptic probably resulted in these higher concentrations.

Discussion of Selected Pesticides in Streams

Although measurable pesticide concentrations were similar between synoptic rounds on a collective basis, the concentrations of individual pesticides did vary with time. Concentration plots for some of the more frequently detected pesticides illustrate the variability of concentrations between synoptic rounds (fig. 8). As previously discussed, the timing of application (pesticide use) affects when pesticides are detected in streams; however, the duration of pesticide detection after application may indicate how persistent a pesticide is in the environment. Spatial variations in

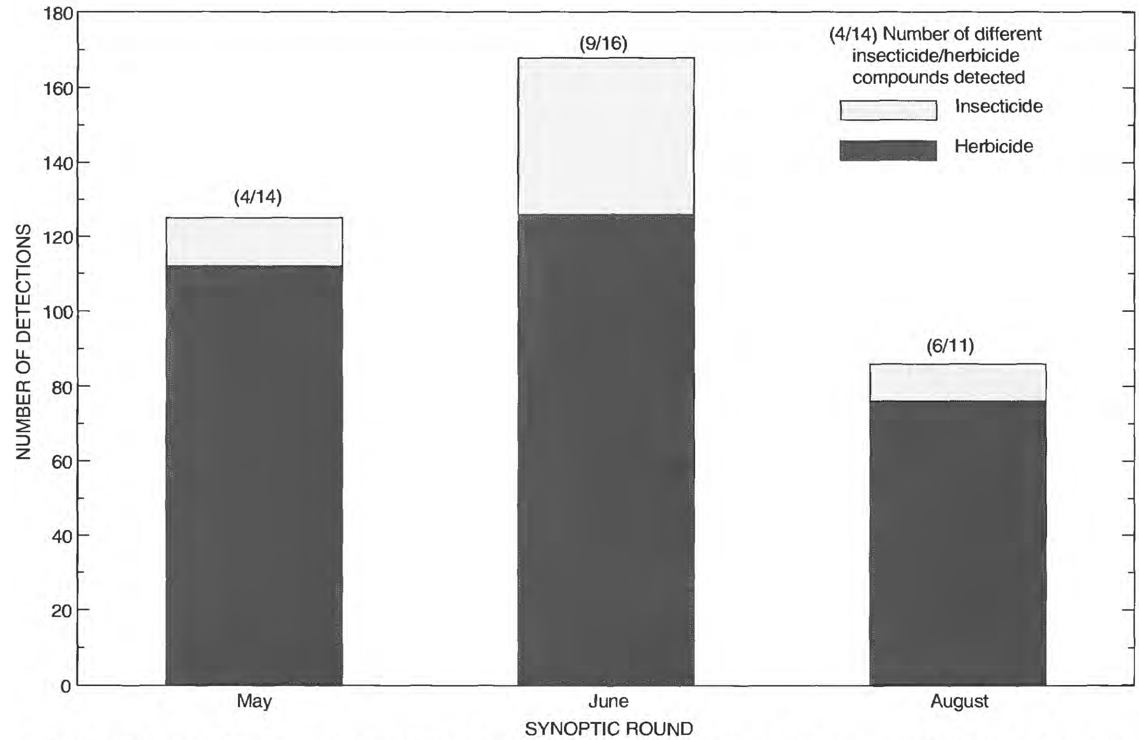


Figure 6. Number of insecticide and herbicide detections by synoptic round (data are for the 16 sites and pesticides sampled during all three synoptic rounds).

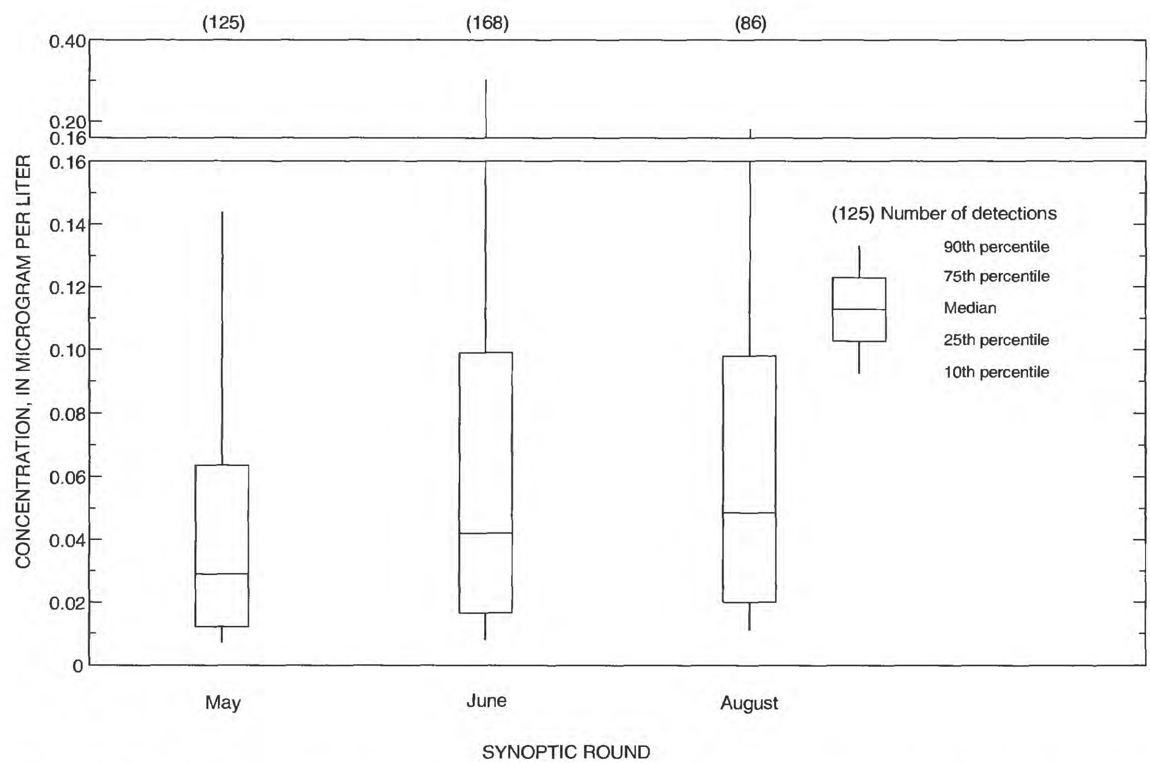


Figure 7. Pesticide concentrations (equal to or greater than the pesticide method detection limits) by synoptic round (data are for the 16 synoptic sites and pesticides sampled during all three synoptic rounds).

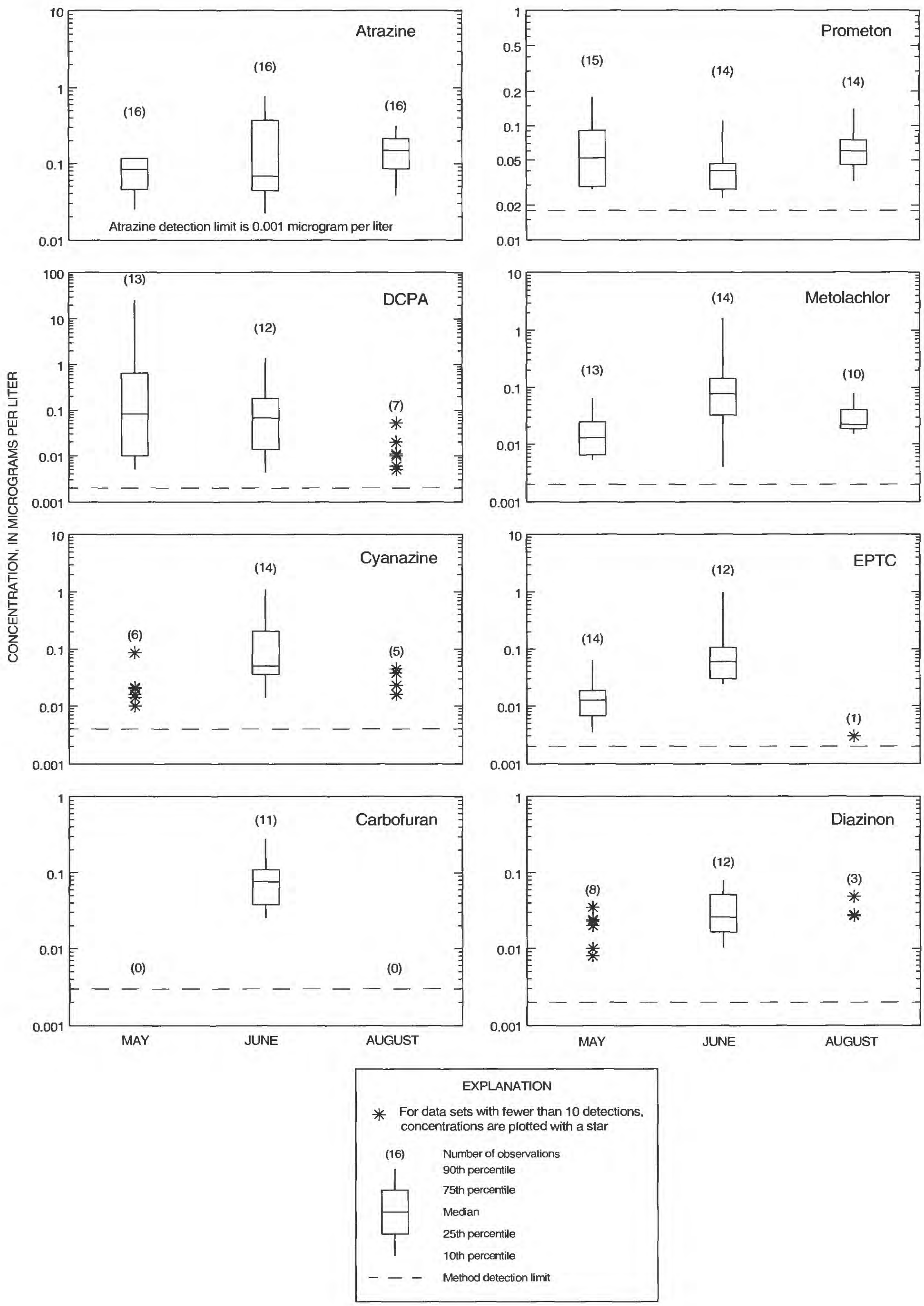


Figure 8. Concentrations of selected pesticides by synoptic round (data are for the 16 synoptic sites sampled during all three synoptic rounds). Graphs have different vertical scales.

detections also can be related to pesticide use because certain pesticides are applied more in certain parts of the study area.

The spatial and temporal distribution of selected pesticides can be examined using the data along the South Platte River and its tributaries for each of the three synoptic rounds and the weekly to bi-weekly data from the two anchor sites. Data for some of the more commonly detected pesticides are shown in figures 9–14. The horizontal scale for the synoptic plots is river mile; note that there is a scale change at river mile 120, which allows data from the more closely spaced sites on the upper river to be more easily seen. The anchor-site plots are time series plots with the horizontal axis in time (as opposed to synoptic plots, which are in distance). The vertical lines on the anchor-site plots denote the dates when the three synoptic rounds occurred. Note that figures 9–14 have different vertical scales.

Atrazine

Atrazine primarily is used as a preemergent or early postplant emergent herbicide on corn and is the most commonly used pesticide in the study area. Atrazine appears to persist in the environment throughout the growing season, as indicated by its detection in almost all samples collected for this study. Although typically applied early in the growing season, the median atrazine concentration at the 16 base sites was highest (0.15 µg/L) in August (fig. 8). During all three synoptic rounds, atrazine concentrations in the main-stem South Platte River increased from Henderson to Kersey (fig. 9). Downstream from Kersey, concentrations decreased from Kersey to North Platte (in May) and from Weldona to North Platte (in August). In June, main-stem concentrations steadily increased downstream from Kersey to a maximum at North Platte. The smallest atrazine concentrations measured in the main stem primarily occurred in the upper reaches of the study area from Henderson to Milliken. Ten of 12 main-stem samples collected from Henderson to Milliken had atrazine concentrations less than 0.06 µg/L. The lowest main-stem concentration was measured at Henderson at a concentration of 0.018 µg/L. The largest main-stem atrazine concentrations were measured in the reach from Kersey to North Platte where 9 of 14 samples had concentrations greater than or equal to 0.20 µg/L. The maximum main-stem atrazine concentration of 1.1 µg/L was at North Platte. At tributary sites, concentrations primarily were less than 0.1 µg/L at sites located upstream from Kersey. Downstream from Kersey, all tributary concentrations of atrazine (except for one nondetection in Bijou Creek) were greater than 0.1 µg/L. The highest concentration in tributaries occurred in June in Crow, Box Elder, Beaver, and Lodgepole Creeks where concentrations were between 0.5 and 0.7 µg/L.

Atrazine concentrations in anchor-site samples were between 0.05 and 0.4 µg/L. The smallest concentration measured at the main-stem anchor site (South Platte River near Kersey) was measured in early June and coincided with the highest streamflow. Dilution of instream atrazine levels by snowmelt water from the upper basin may have caused the decrease.

Prometon

Prometon is not applied to crops in the study area; however, it is used as a nonselective, long-term soil sterilant in urban and agricultural land-use settings. Because it is not applied to crops, there is no defined application period for prometon, and it may be used at any time throughout the year. Prometon is recommended for bare-ground weed control on noncropped areas in agricultural settings, such as around buildings, storage areas, fences, and machinery (Chemical and Pharmaceutical Press, 1993, p. 397). The persistence of prometon in the environment may be evident by its detection at consistent concentrations in almost every sample collected during the agricultural study. Prometon concentrations were similar among synoptic rounds; median concentrations at the 16 base sites were 0.052 µg/L in May, 0.04 µg/L in June, and 0.06 µg/L in August (fig. 8). The variability in prometon concentrations at main-stem sites generally was less than 0.05 µg/L (fig. 10). Exceptions occurred at Kersey and North Platte, where concentrations varied by about 0.2 µg/L. The maximum concentration in the main stem was measured at Kersey (0.26 µg/L). The three main-stem samples in which prometon was not detected were collected in the most downstream section of the study area at Julesburg and North Platte. During all three synoptic rounds, prometon concentrations in the tributaries generally increased from St. Vrain Creek to maximum concentrations in tributaries near Kersey. Downstream from the Kersey area, prometon concentrations in tributaries decreased.The largest concentration in tributaries occurred in August in the Cache La Poudre River (0.17 µg/L).

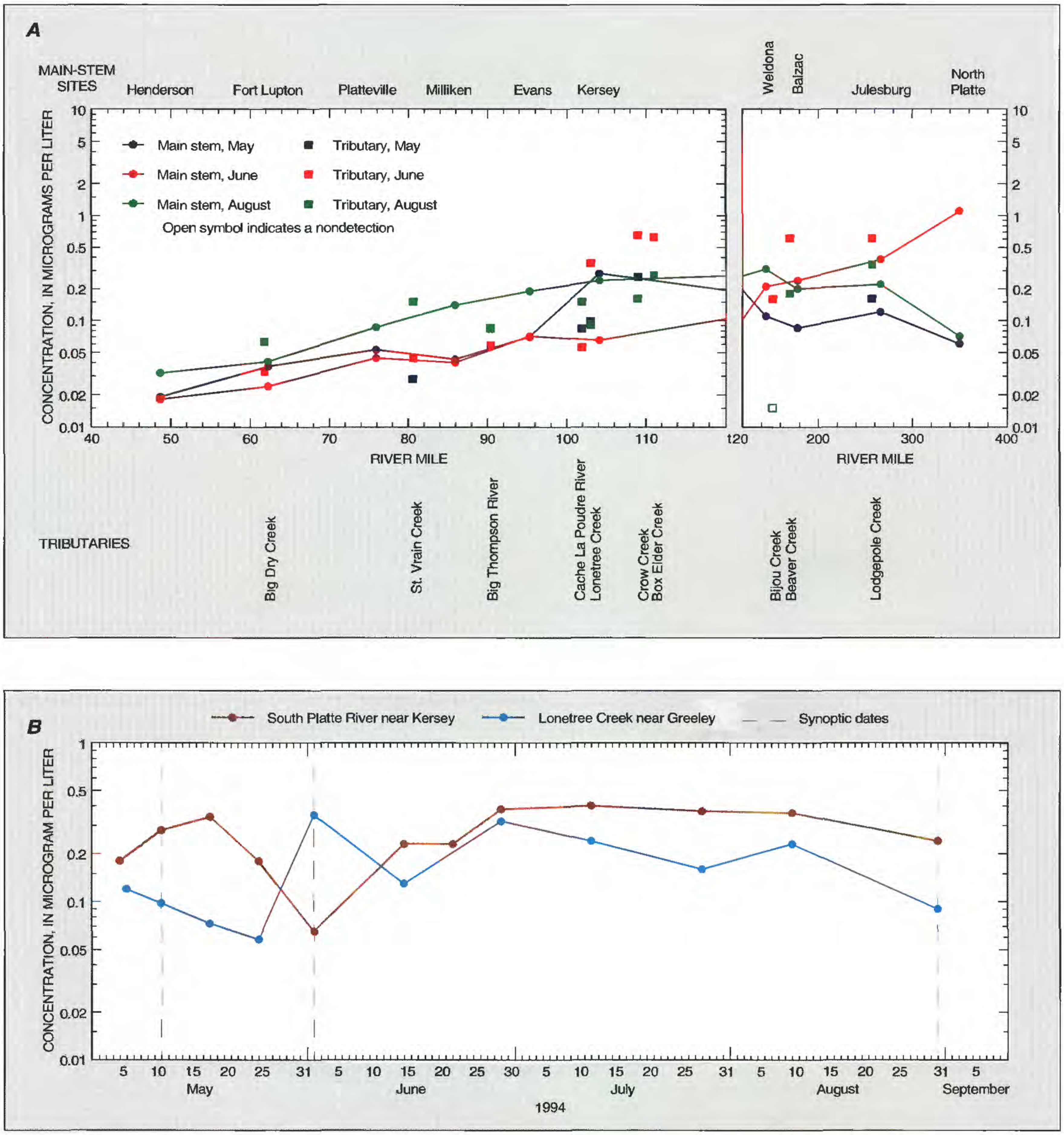
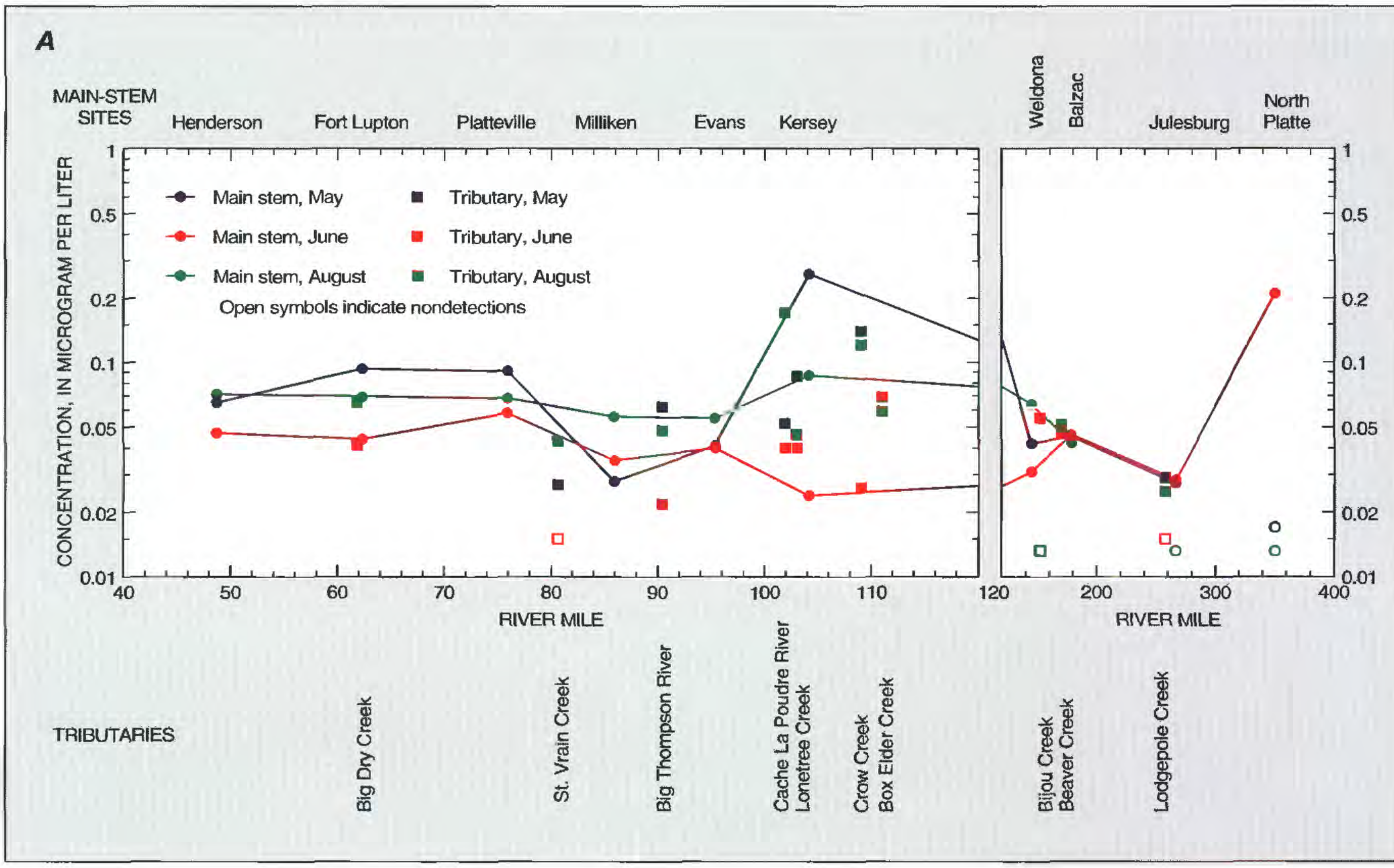


Figure 9. Atrazine concentrations *(A)* during the three synoptic rounds by river mile and (*B)* at the anchor sites by sampling date.



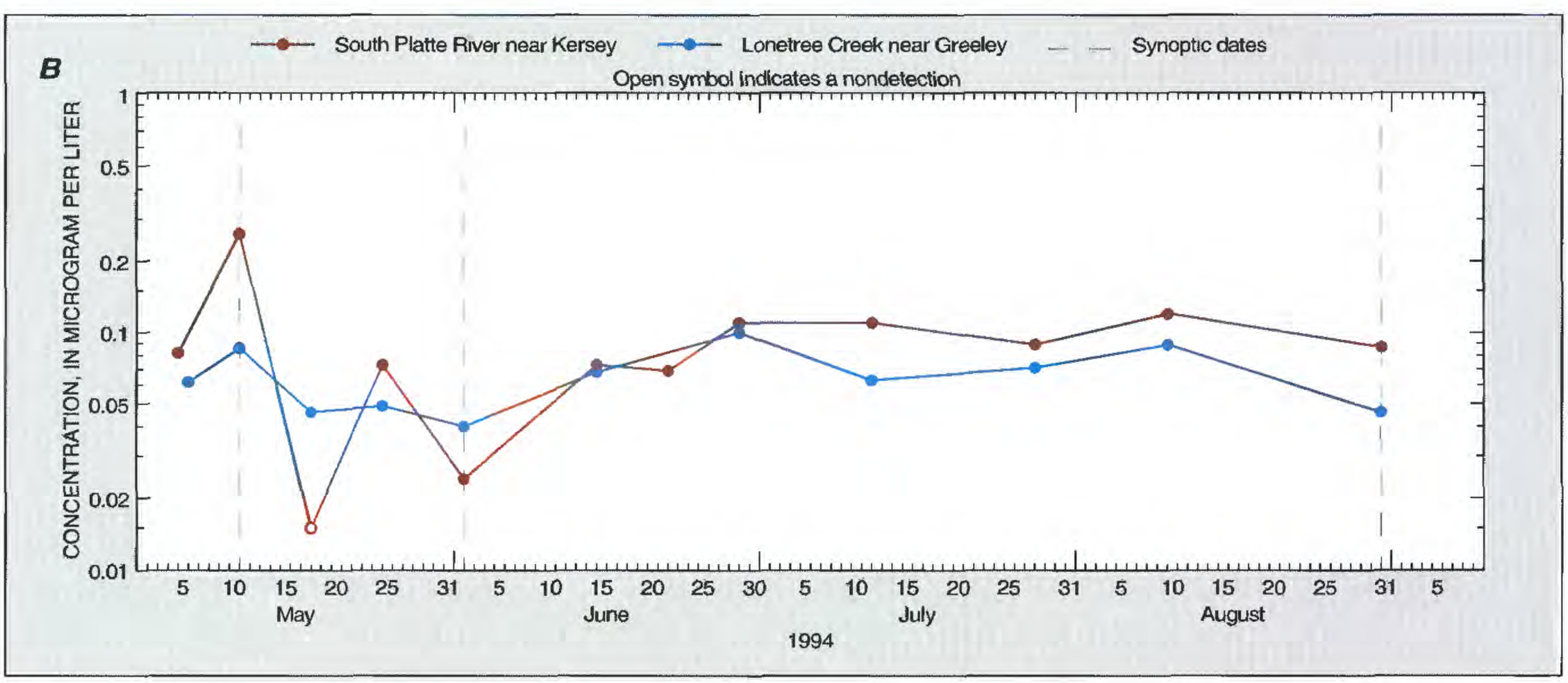


Figure 10. Prometon concentrations *(A)* during the three synoptic rounds by river mile and *(B)* at the anchor sites by sampling date.

Prometon was detected in almost all anchor-site samples. Prometon concentrations in Lonetree Creek were consistent throughout the study and varied from 0.04 to 0.10 µg/L. In the South Platte River near Kersey, the largest variability in concentrations was in May and early June. From mid-June through August, concentrations at Kersey were less variable and were similar to concentrations in Lonetree Creek.

DCPA

The herbicide DCPA is one of the 10 most commonly used pesticides on irrigated lands in the study area. It primarily is used on onions (96 percent of its use) but also is applied to commercially grown sod and some vegetables. Categorized as a selective preemergent herbicide, DCPA typically is applied to crops before or early in the growing season (March and April) before weed seeds have germinated. When used on onions, its most common form of application is surface spraying because preplant incorporation into the soil is not recommended (Chemical and Pharmaceutical Press, 1993, p. 1129). DCPA was detected more frequently in May and June as compared to August (fig. 8). DCPA concentrations were measured at a maximum in May following early season application. In May and June, DCPA consistently was detected in the main stem from Henderson to Balzac (fig. 11). In August, main-stem detections were limited to Henderson, Fort Lupton, and the reach from Kersey to Balzac. DCPA also was detected in most tributaries between Henderson and Balzac in May and June. In August, tributary detections were limited to 3 of the 10 tributaries sampled. DCPA was not detected at any site downstream from Balzac, except for one detection at Julesburg equal to 0.004 µg/L. The highest DCPA concentrations in the main stem and tributaries occurred in the Kersey area, where most of the onions in the study area are grown. The highest DCPA concentration in the main stem occurred in May at Kersey (0.85 µg/L). The highest tributary concentrations also were measured in May in Lonetree and Crow Creeks (30 and 20 µg/L, respectively).

DCPA was detected in almost every anchor-site sample. Similar to trends in the synoptic samples, the concentration of DCPA at the anchor sites generally decreased after peak concentrations were measured in early May following the application season. Although DCPA was detected in almost all anchor-site samples, the decreasing concentrations may indicate that DCPA does not persist above detectable levels in stream water past the growing season.

Metolachlor, Cyanazine, and EPTC

Metolachlor, cyanazine, and EPTC are preemergent herbicides primarily used on corn (all three herbicides) and dry beans (EPTC) and are among the five most commonly used herbicides in the study area. Metolachlor, cyanazine, and EPTC were ranked fourth, sixth, and seventh, respectively, in frequency of detection in the agricultural study (table 5). The temporal distribution of detections of these three herbicides was similar (fig. 8). All three herbicides were detected in May following early season application; however, maximum concentrations were measured in June. Compared to cyanazine and EPTC, metolachlor appears to persist longer in the environment as evidenced by its detection in 10 of 16 base-site samples collected in August. EPTC persistence appears to be shorter because it was detected at only one base site in August (fig. 8).

With the exception of one detection in Big Dry Creek, metolachlor detections were limited to synoptic sites from Platteville to North Platte (fig. 12) (although not shown in fig. 12, the detection patterns for cyanazine and EPTC were similar to the detection patterns of metolachlor). Detections of metolachlor upstream from Platteville may be limited because corn production is less upstream from Platteville as compared to areas downstream. In June, most detections downstream from Platteville were greater than 0.05 µg/L, and main-stem concentrations of about 0.1 µg/L were fairly consistent from Evans to North Platte. The maximum metolachlor concentrations occurred in June in Lonetree and Crow Creeks at concentrations of 1.8 and 1.5 µg/L, respectively. Although metolachlor also was detected at most synoptic sites between Platteville and North Platte in May and August, concentrations during May and August generally were less than 0.05 µg/L.

Similar to the synoptic sites, the maximum metolachlor concentrations at the anchor sites also were in June. It appears that the peak metolachlor concentration measured in Lonetree Creek during the June synoptic was short-lived. Metolachlor concentrations in Lonetree Creek rose abruptly in late May to the peak June synoptic concentration (1.8 µg/L) and then dropped to a level of about 0.1 µg/L for the remainder of the study. Higher concentrations in Crow Creek in June also may have been short-lived because Lonetree and Crow Creeks are very similar hydrologically and geographically. At Kersey, metolachlor concentrations continued to rise after the June

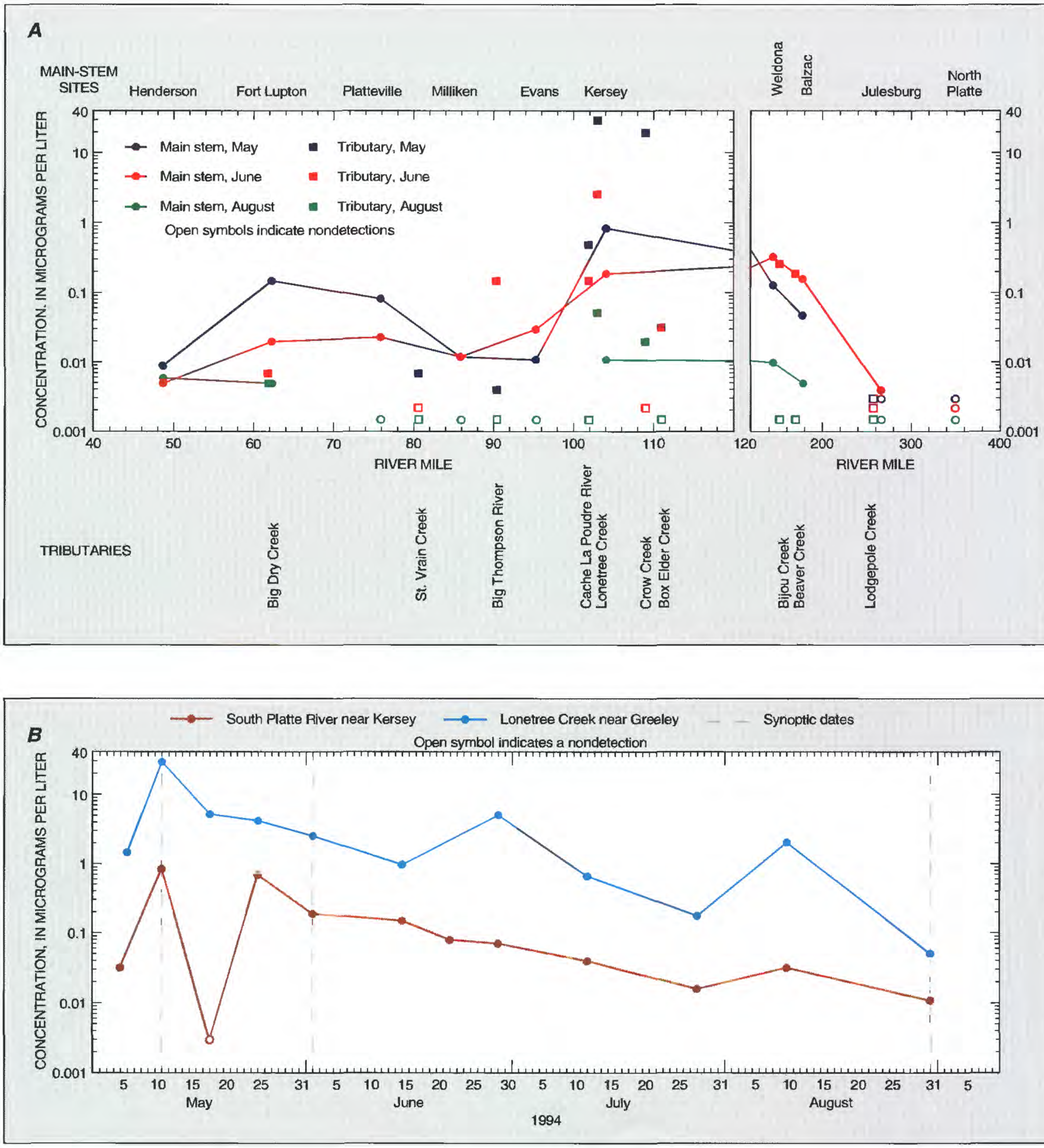


Figure 11. DCPA concentrations *(A)* during the three synoptic rounds by river mile and *(B)* at the anchor sites by sampling date.

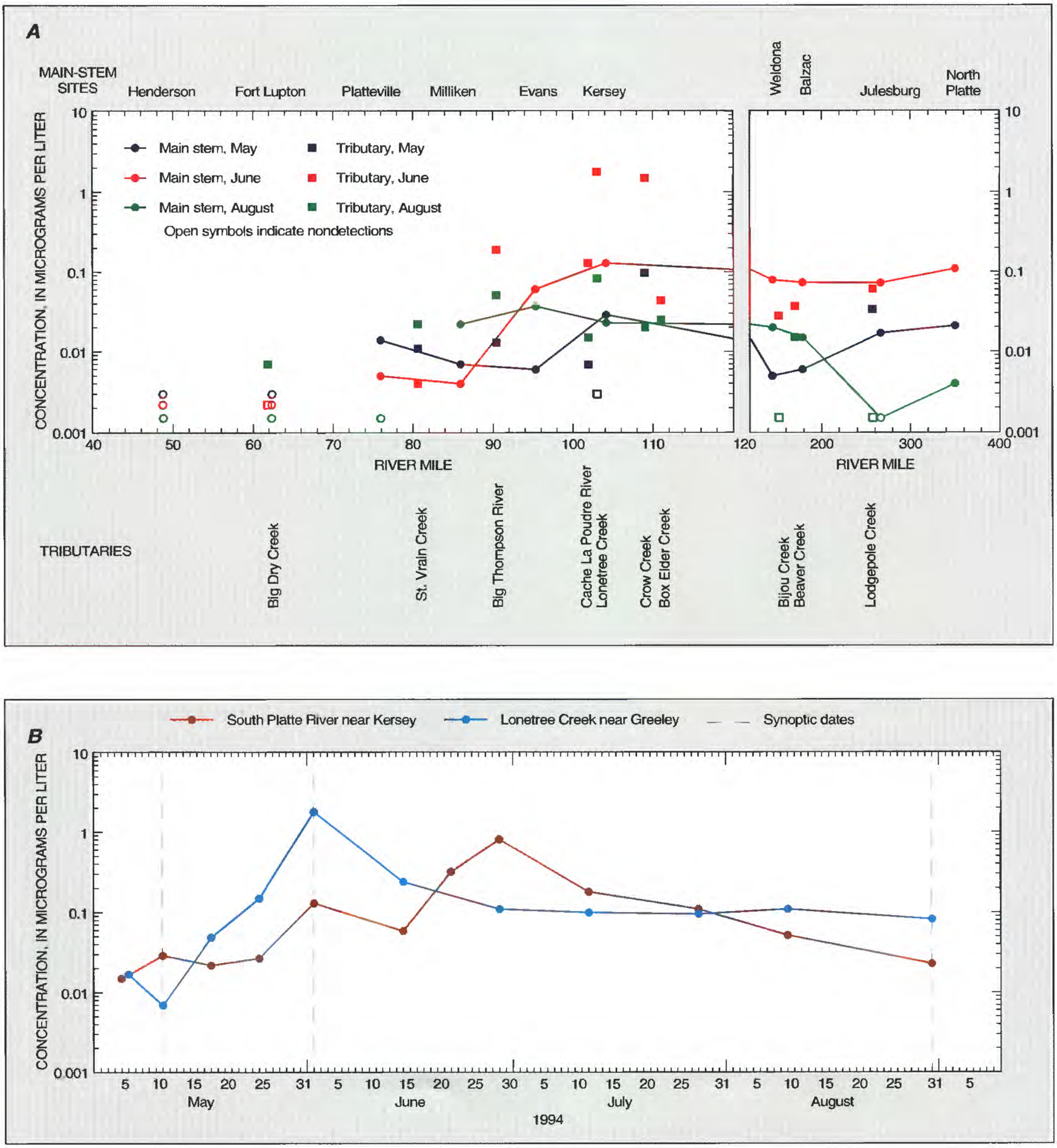


Figure 12. Metolachlor concentrations *(A)* during the three synoptic rounds by river mile and (*B)* at the anchor sites by sampling date.

synoptic to a peak concentration of 0.81 µg/L in late June. This pattern at Kersey could indicate that main-stem concentrations at other sites also were higher in late June compared to those concentrations measured in the June synoptic.

Carbofuran

The insecticide carbofuran primarily is used on corn (60 percent of its use in the study area) and alfalfa (35 percent of its use). It also is used to a lesser extent on sorghum, sugar beets, and potatoes. Carbofuran is applied to corn either at planting (April–May) or during postplant emergent. However, postplant-emergent application is more effective in Colorado if it occurs before June 15 (Peairs and others, 1993). Its application to alfalfa typically occurs in the latter part of May prior to the first harvest. Carbofuran was not detected in any synoptic samples collected in May or August (figs. 8 and 13). In the June synoptic, carbofuran was detected at every main-stem and tributary site from Platteville to Balzac (fig. 13). Additionally, carbofuran was detected in June in Big Dry Creek, just upstream from Fort Lupton. In the main-stem South Platte River, the maximum concentration of carbofuran was at Platteville (0.11 µg/L) and steadily decreased to a minimum at Balzac (0.023 µg/L). The concentrations at tributary sites were similar to main-stem concentrations, except in Lonetree, Crow, and Box Elder Creeks, where concentrations ranged from 0.24 to 0.32 µg/L.

Similar to synoptic samples, carbofuran was not detected in any anchor-site samples that were collected in the first part of May or all of August. The concentrations of carbofuran in anchor-site samples were at a maximum in late May and decreased to nondetectable levels by late July. The absence of carbofuran in all early May samples and its detection in late May anchor-site samples and June synoptic samples correlates with its primary application period. The nondetection of carbofuran in August at any site in the study area may indicate that carbofuran is not as persistent as atrazine or prometon in the environment.

Diazinon

The insecticide diazinon has agricultural and nonagricultural uses in the study area. In agriculture, it is primarily used on carrots and, to a lesser extent, corn, onions, potatoes, and sugar beets. Diazinon also is a common household insecticide. The pattern of diazinon detections indicates that agricultural and nonagricultural uses are probable sources of diazinon in streams. Its occurrence primarily was limited to the reach from Henderson to Kersey (fig. 14), which is the reach that drains the primary vegetable growing area and the major urban areas. Diazinon concentrations were consistently higher at Henderson, just downstream from Denver, as compared to most other synoptic sites. Concentrations at Henderson ranged from 0.035 to 0.074 µg/L. Other than a slight increase in June from Fort Lupton to Platteville, diazinon concentrations in the main stem generally decreased from Henderson to nondetectable levels downstream from Kersey (in May), Weldona (in June), and Platteville (in August). Detections of diazinon at any site downstream from Kersey were limited. In tributaries, the detection of diazinon mainly was limited to June, when it was detected in 7 of 10 tributaries sampled. The highest tributary concentration was in June in Big Dry Creek (0.058 µg/L). Big Dry Creek drains urban and agricultural areas. At anchor sites, diazinon detections were limited primarily to May and June. The highest concentrations of diazinon at the anchor sites were in mid-May between two of the synoptic rounds, indicating that diazinon concentrations might have been higher at other sites in the study area between the May and June synoptics.

Propargite

The insecticide propargite typically is applied to corn in mid-July by aerial spraying. The persistence of propargite in streams appears to be very short as indicated by its detection at the anchor sites only for several weeks following application (fig. 15). Although detections at the anchor sites were limited, propargite was measured at a relatively high concentration of 2.3 µg/L in Lonetree Creek in late July. The timing of application and its relatively short persistence in the environment could explain why propargite was detected in only two synoptic samples (samples collected from the Big Thompson River and Box Elder Creek in August).

Pesticide Loads Along the South Platte River

Whereas concentrations indicate the amount of pesticides dissolved in stream water, loads indicate the

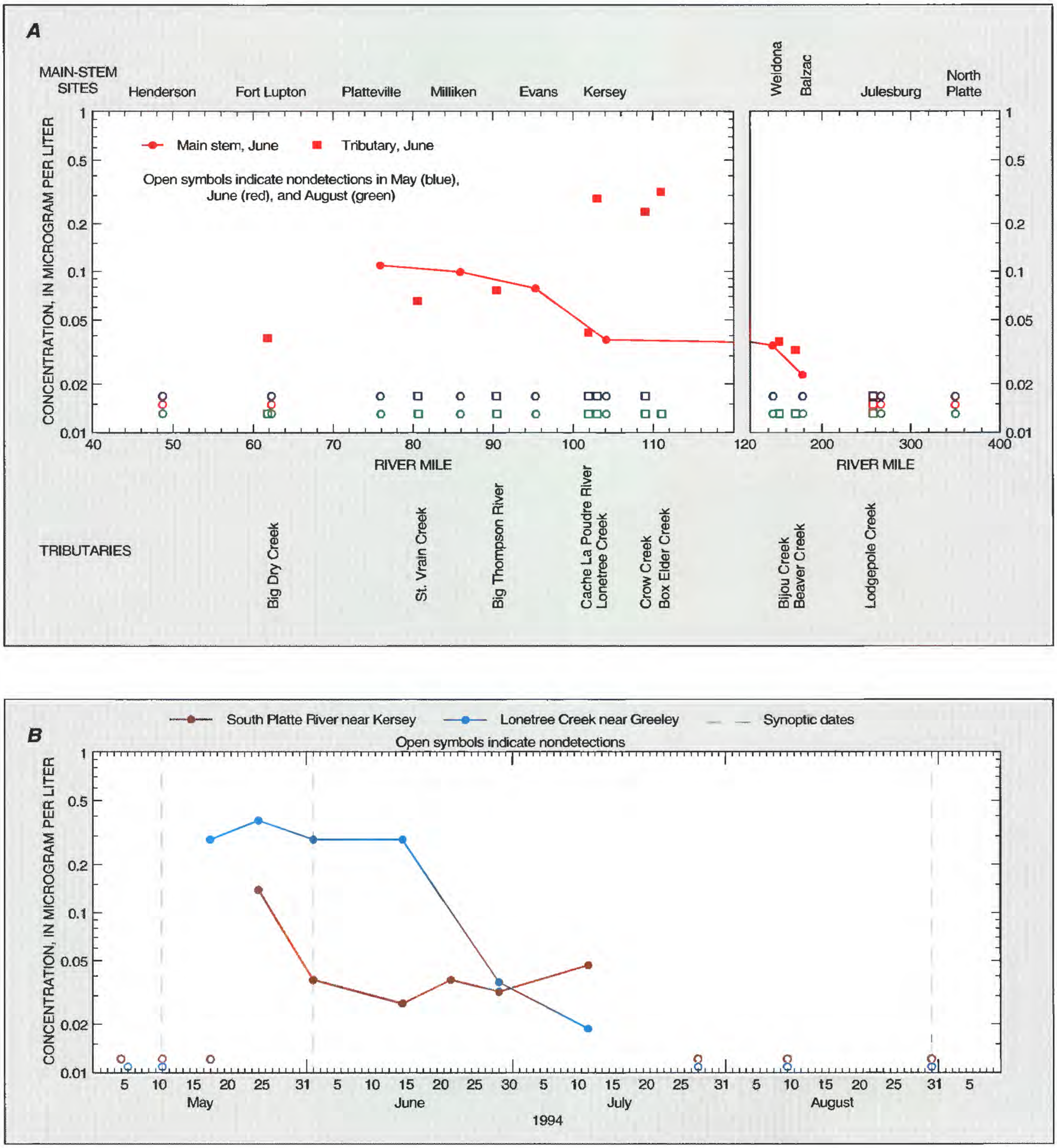


Figure 13. Carbofuran concentrations *(A)* during the three synoptic rounds by river mile and *(B)* at the anchor sites by sampling date.

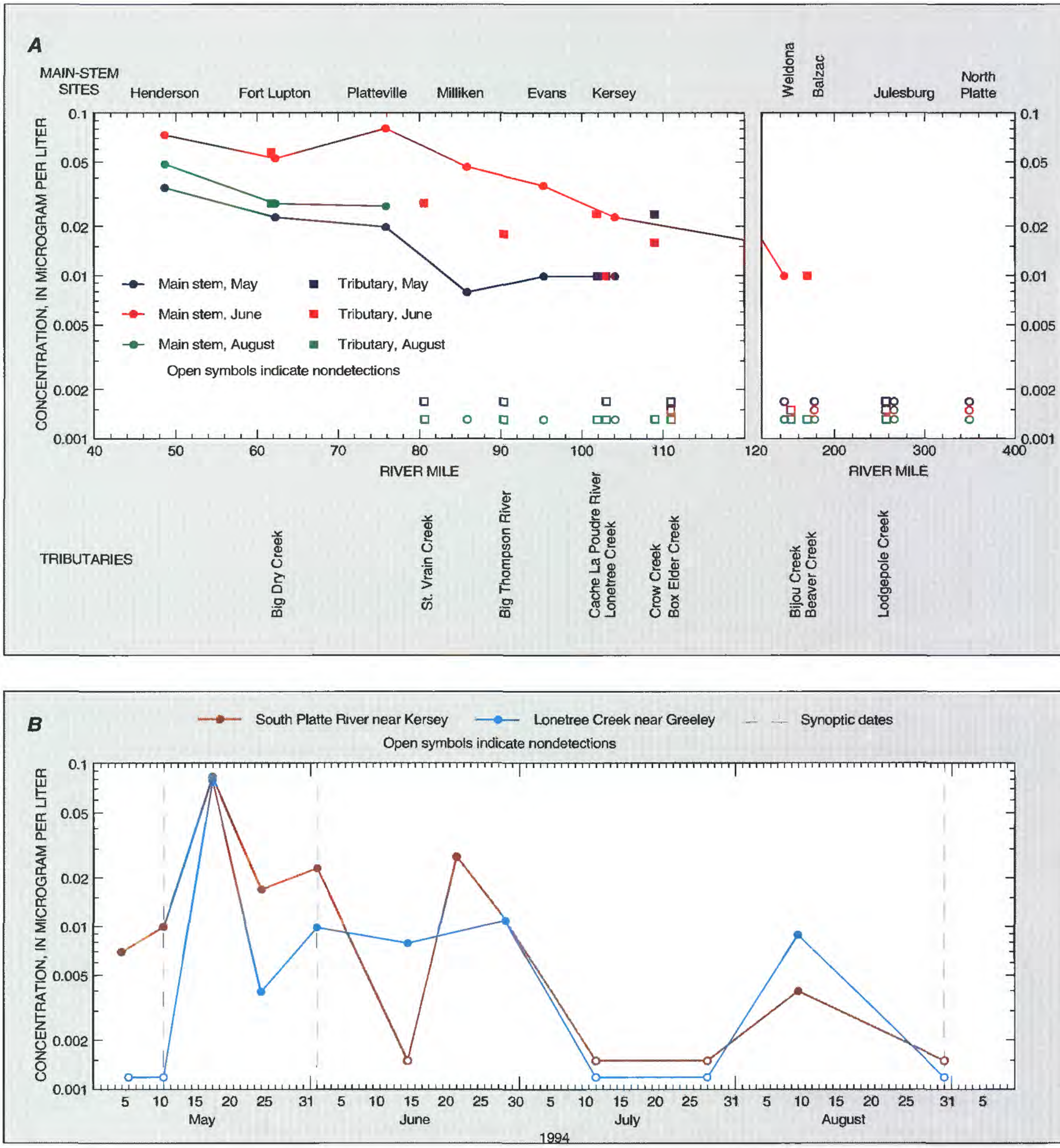


Figure 14. Diazinon concentrations *(A)* during the three synoptic rounds by river mile and (*B)* at the anchor sites by sampling date.

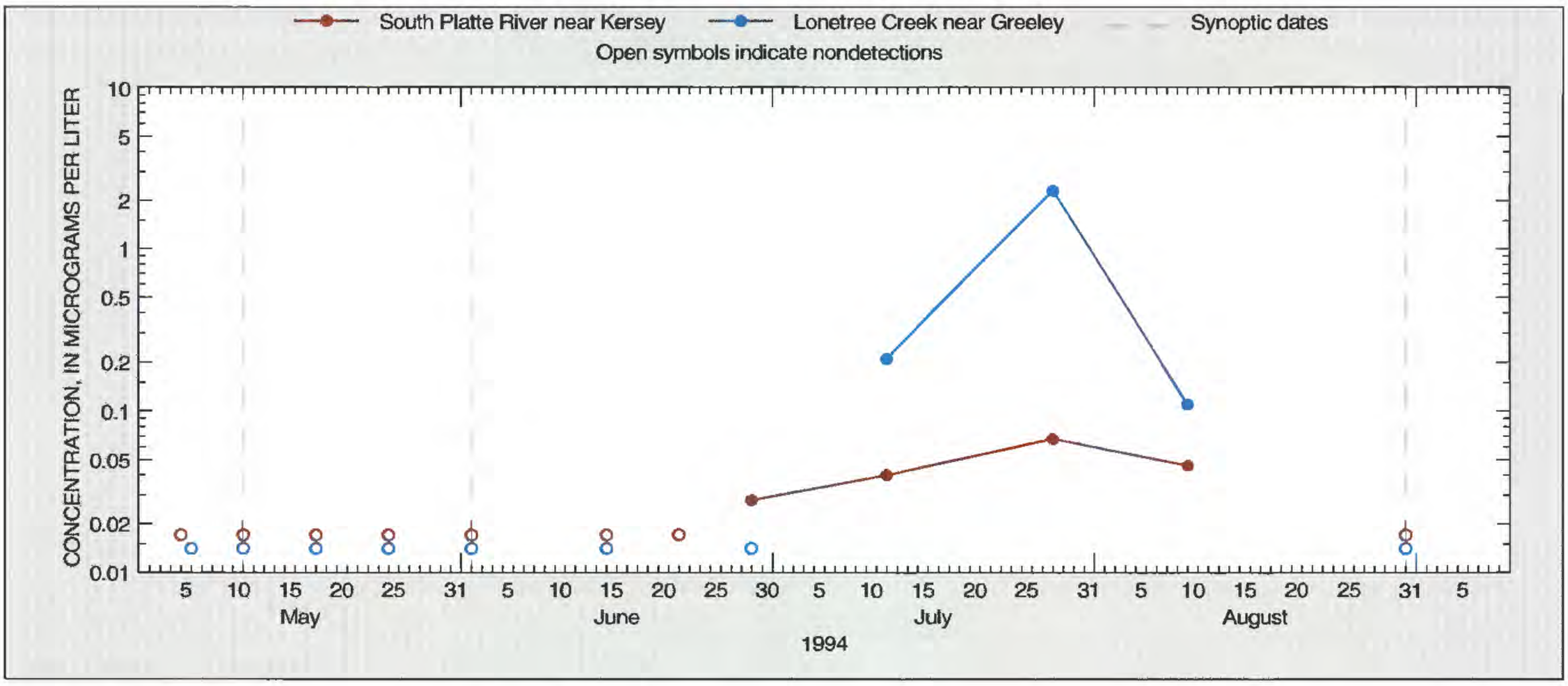


Figure 15. Propargite concentrations at the anchor sites by sampling date.

amount of pesticides transported in streamflow. Pesticide loads or transport rates are a function of pesticide concentrations and streamflow volume; therefore, loads increase with increasing concentration or streamflow. Pesticide loads for the synoptic samples are shown for each site in figure 16; loads are included only for the pesticides measured at concentrations equal to or greater than the pesticide MDL's. Although median pesticide concentrations tended to be higher at tributary sites compared to main-stem sites (fig. 5), higher streamflow resulted in higher pesticide loads at main-stem sites (fig. 16).

The variability of pesticide loads in the main-stem South Platte River (fig. 16) primarily is a function of varying streamflow because median pesticide concentrations were similar among main-stem sites (fig. 5). Maximum pesticide loads in the main stem primarily were at Kersey because that site had the highest streamflow of all main-stem synoptic sites (fig. 4). As flows decreased from Kersey to Julesburg as a result of water diversions for irrigation, loads also decreased. Pesticide loads increased from Julesburg to North Platte because of an increase in streamflow and concentrations.

The plot of atrazine load illustrates the effect of streamflow on load (fig. 17). Atrazine concentrations in tributaries were similar to surrounding main-stem concentrations and, in some cases, higher than main-stem concentrations (Cache La Poudre to Lodgepole, fig. 9). In contrast, atrazine loads in most of the tributaries were smaller than the loads at nearby main-stem sites because of less streamflow (fig. 17). An exception is the atrazine loads in St. Vrain Creek. St. Vrain Creek consistently had the highest streamflows of any tributary (fig. 4). Streamflow and atrazine concentrations in St. Vrain Creek during the synoptic rounds were similar to surrounding main-stem sites; as a result, atrazine loads in St. Vrain Creek were similar to loads in surrounding main-stem sites. During the synoptics, the highest atrazine loads occurred in the main stem at Kersey and North Platte (about 1 lb/d). The high load at Kersey in May primarily is a result of high streamflow, whereas the high load at North Platte in June is more a result of high atrazine concentration.

Atrazine loads at the main-stem anchor site (Kersey) were fairly consistent throughout the study and varied from about 0.5 to 1 lb/d. Atrazine loads at the tributary anchor site (Lonetree Creek) generally were two orders of magnitude less than at Kersey.

Although median pesticide loads generally were higher in the main stem as compared to tributaries, the highest load of any pesticide did occur in a tributary (fig. 18). The herbicide DCPA had a maximum load of about 2.9 lb/d in Crow Creek during the May synoptic round. The maximum DCPA load resulted from a relatively high concentration (20 μg/L) in a flow of 26.7 ft^3/s, whereas the second highest DCPA load of 2.6 lb/d (at Kersey) resulted from a much lower

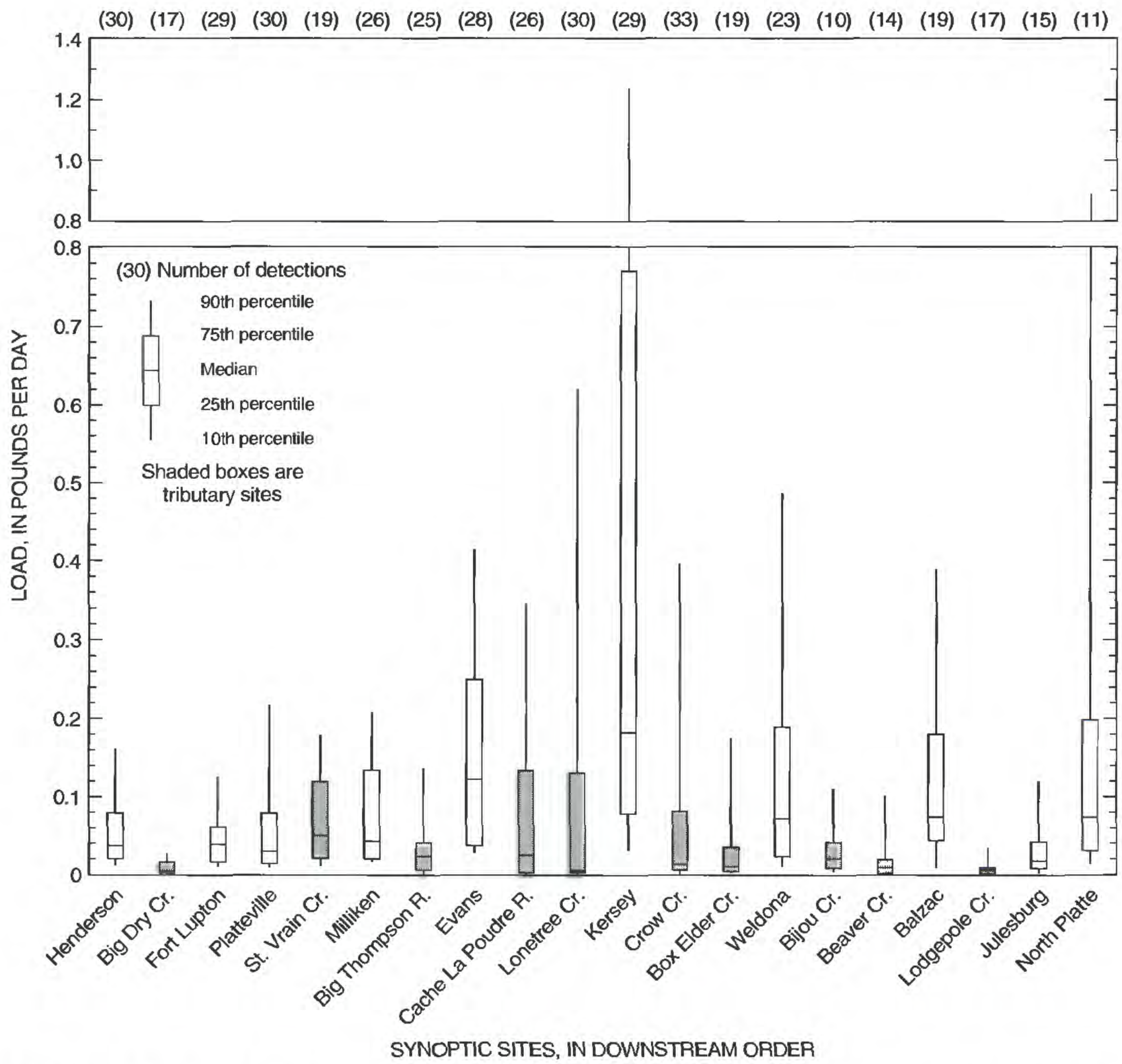


Figure 16. Pesticide loads (computed from concentrations equal to or greater than the pesticide method detection limits) at synoptic sites (data are for all three synoptic rounds).

concentration (0.85 µg/L) in a relatively higher streamflow of 579 ft^3/s. In contrast to atrazine, DCPA loads generally were of equivalent magnitude at both anchor sites. Additionally, high DCPA loads at the anchor sites were short-lived because DCPA concentrations and streamflow generally decreased throughout the study period.

Ground-Water Transport of Pesticides to Streams

Atrazine, desethylatrazine, and prometon were detected in almost all of the samples (table 5), and they were present throughout the study area (table 6). The presence of atrazine, desethylatrazine, and prometon in streams may result from their presence in ground water. In a study of pesticides in alluvial ground water in agricultural areas near the South Platte River (Bruce and McMahon, 1998), atrazine, desethylatrazine, and prometon were the three most commonly detected pesticides, and each was measured at concentrations similar to and often greater than concentrations measured in the South Platte River as part of this study. Pesticides that persist in the alluvial aquifer in the study area can be transported to streams with ground-water return flows or ground water that discharges from the alluvial aquifer to the stream.

Pesticide loads contained in ground-water return flows can be estimated using streamflow and pesticide-load balances. Streamflow balances and load balances for atrazine, desethylatrazine, and prometon were computed for reaches of the South Platte River in the study area for the August synoptic. The August synoptic was chosen because of its relatively low and stable streamflows throughout the study area, which enabled a more accurate computation of a surface-water mass budget. Streamflow balances for reaches

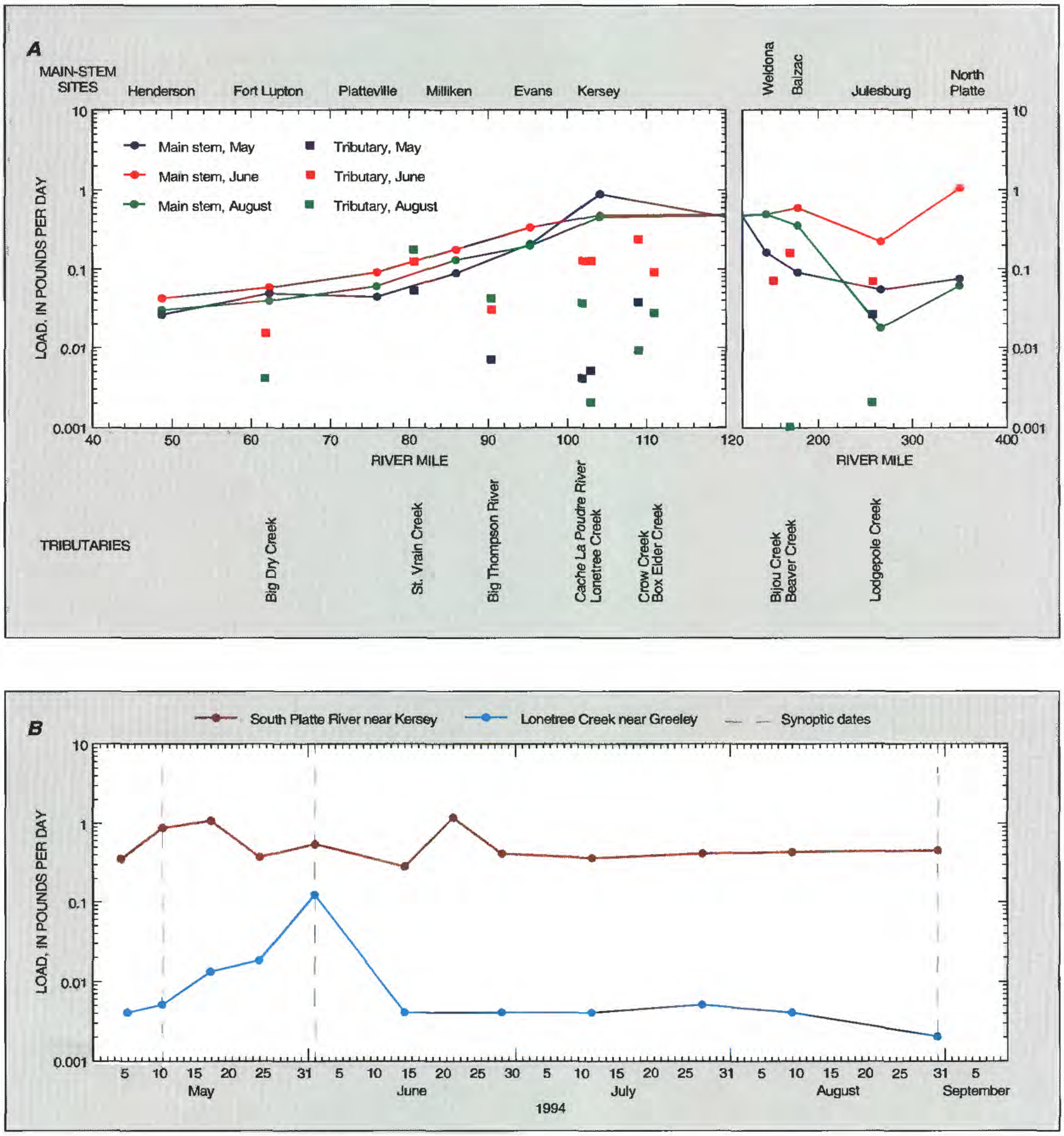


Figure 17. Atrazine loads *(A)* during the three synoptic rounds by river mile and (*B)* at the anchor sites by sampling date.

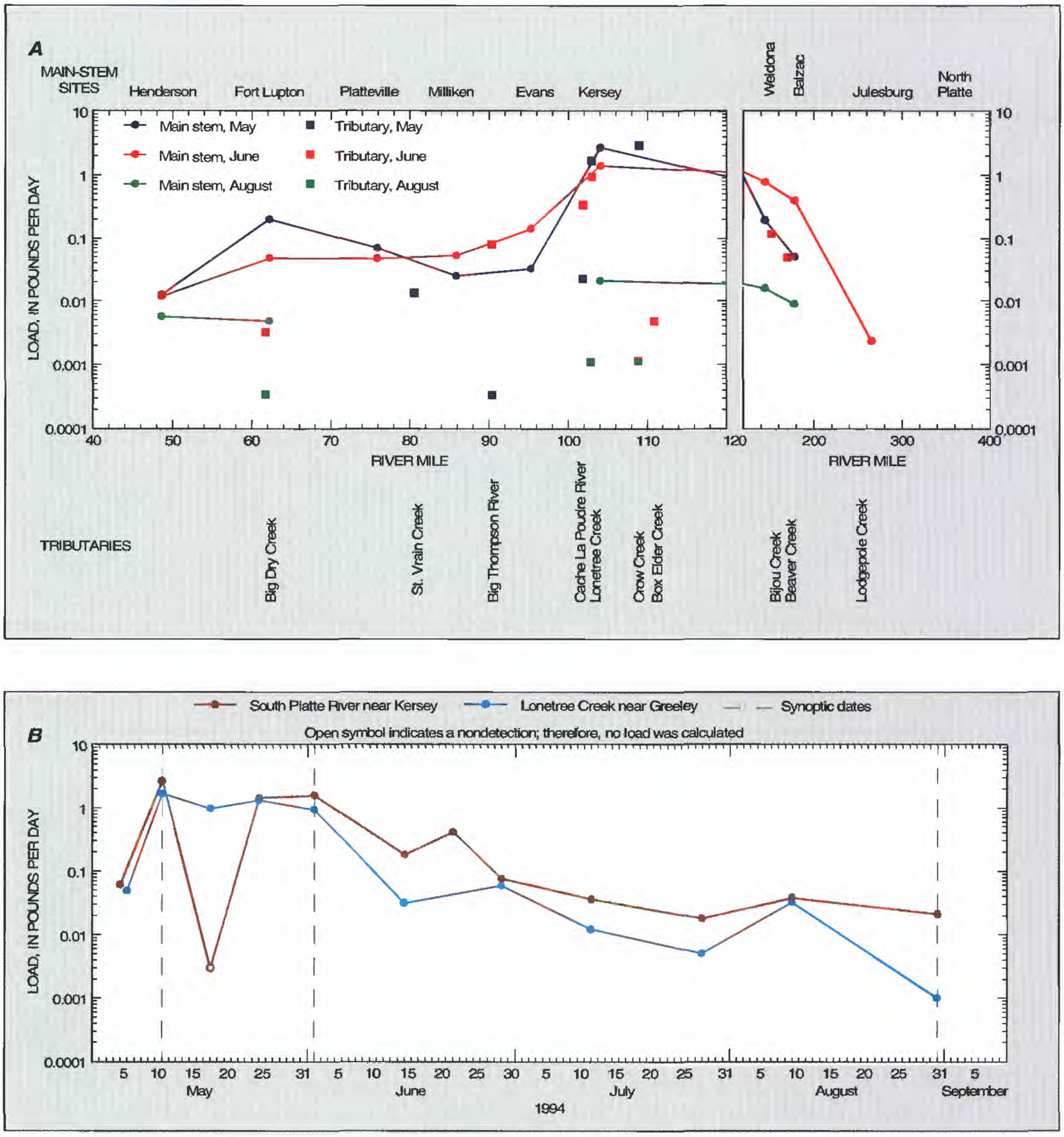


Figure 18. DCPA loads *(A)* during the three synoptic rounds by river mile and *(B)* at the anchor sites by sampling date.

along the South Platte River were calculated by summing surface-water outputs along a reach and subtracting surface-water inputs along that same reach. As an example, a residual streamflow equal to 175 ft^3/s [6.5 (ft^3/s)/mi] was calculated for the reach of the South Platte River from Henderson to Platteville using data in table 7. Positive streamflow residuals for all reaches (table 8) indicated that ground water is a probable source of streamflow in the South Platte River throughout the study area.

Residual pesticide loads also were calculated for reaches along the South Platte River by summing loads diverted out of the river along a reach and subtracting the load contained in inflows along that same reach. As an example, a residual atrazine load of 0.08 lb/d was calculated for the Henderson to Platteville reach using data listed in table 7. Pesticide loads removed by diversion ditches were calculated using the lowest main-stem concentration measured in the vicinity of the diversions. As an example, water diverted out of the river in the Brighton and Lupton Bottom Ditches was assumed to have an atrazine concentration of 0.032 μg/L (table 7), or the smaller of the two concentrations measured in the main stem at Henderson and Fort Lupton. Using the smallest main-stem concentration for computing loads diverted out of the river yields the most conservative estimate of residual loads. Positive pesticide-load residuals for most reaches (table 8) may indicate that ground water transports atrazine, desethylatrazine, and prometon to the South Platte River throughout the study area.

The ratio of desethylatrazine to atrazine (called the DAR) also may be used to signify that atrazine and desethylatrazine are transported to surface waters through ground water in the study area. After its incorporation into fields at the beginning of the growing

Table 7. Streamflow and atrazine data for sites along the South Platte River from Henderson to Platteville, Colorado, August 29–30, 1994

[ft^3/s, cubic feet per second; μg/L, microgram per liter; lb/d, pound per day; --, not applicable; mi, mile]

River mile	Site	Streamflow (ft^3/s)		Atrazine concentration (μg/L)	Atrazine load (lb/d)	
		Outflow from reach	Inflow to reach		Outflow from reach	Inflow to reach
48.7	South Platte River at Henderson, Colorado	--	173	[1]0.032	--	0.03
52.9	Brighton Ditch	22	--	[2]0.032	0.004	--
54.9	City of Brighton Wastewater Treatment Plant	--	2	[3]0	--	0
61.7	Lupton Bottom Ditch	59	--	[2]0.032	0.010	--
61.8	Big Dry Creek at mouth	--	12	[1]0.063	--	0.004
62.3	South Platte River at Fort Lupton, Colorado	--	--	[1]0.041	--	--
63.5	Platteville Ditch	48	--	[4]0.041	0.011	--
66.2	Meadow Island No. 1 Ditch	20	--	[4]0.041	0.004	--
66.8	Platte Valley/Evans No. 2 Ditch	0	--	--	0	--
70.8	Meadow Island No. 2 Ditch	23	--	[4]0.041	0.005	--
73.9	Farmers Independent Ditch	63	--	[4]0.041	0.014	--
75.9	South Platte River at Platteville, Colorado	128	--	[1]0.086	0.059	--
	Total (rounded)	**363**	**187**		**0.11**	**0.03**
	Residual	**175 [6.5 (ft^3/s)/mi]**			**0.08**	

[1]Measured concentration.

[2]Concentration measured in the South Platte River at Henderson.

[3]Assumed concentration.

[4]Concentration measured in the South Platte River at Fort Lupton.

Table 8. Residual streamflow and residual load for selected pesticides in reaches of the South Platte River, August 29–31, 1994

[(ft^3/s)/mi, cubic feet per second per mile; lb/d, pound per day]

Main-stem reach	Residual streamflow not accounted for by outflows and inflows [(ft^3/s)/mi]	Pesticide	Pesticide load (lb/d)		
			Total load in outflows from reach	Total load in inflows to reach	Residual load not accounted for by outflows and inflows
Henderson to Platteville	6.5	Atrazine	0.11	0.03	0.08
		Desethylatrazine	0.03	0	0.03
		Prometon	0.13	0.07	0.06
Platteville to Kersey	5.7	Atrazine	0.66	0.33	0.33
		Desethylatrazine	0.34	0.18	0.16
		Prometon	0.25	0.17	0.08
Kersey to Weldona	5.0	Atrazine	0.85	0.47	0.38
		Desethylatrazine	0.46	0.26	0.20
		Prometon	0.20	0.17	0.03
Weldona to Balzac	3.6	Atrazine	0.47	0.55	-0.08
		Desethylatrazine	0.26	0.30	-0.04
		Prometon	0.10	0.11	-0.01
Balzac to Julesburg	1.3	Atrazine	0.56	0.43	0.13
		Desethylatrazine	0.32	0.30	0.02
		Prometon	0	0.09	-0.09
Julesburg to North Platte	1.8	Atrazine	0.07	0.02	0.05
		Desethylatrazine	0.04	0.02	0.02
		Prometon	0.01	0	0.01

season, atrazine contained in water infiltrating through the aerobic unsaturated zone can be degraded to desethylatrazine.The longer atrazine resides in the unsaturated zone, the larger the DAR value can become. Adams and Thurman (1991) determined that atrazine transported through the unsaturated zone resulted in DAR values equal to or greater than 1.0 in the underlying aquifer (nonpoint-source contamination to the aquifer), whereas atrazine transported relatively quickly to the aquifer (point-source contamination) produced DAR values much less than 1.0. Acknowledging these results, Thurman and others (1992) hypothesized that the DAR also might be used as a tracer for the discharge of atrazine-laden ground water to streams. In a study of herbicides and their metabolites in streams of the Midwestern United States, Thurman and others (1992) reported a median DAR value of <0.1 in postplanting samples obtained when surface-water runoff from fields was a larger component of streamflow relative to ground-water inflow, and a median DAR value of 0.4 in harvest-time samples obtained when surface-water runoff was a smaller component of streamflow than ground-water inflow. The increase in the DAR from <0.1 to 0.4 indicated that ground water likely was the major method for transport of herbicides to streams at harvest time (Thurman and others, 1992).

The DAR values calculated for this study probably are not comparable to DAR values cited in the literature because the recovery rate for atrazine differed considerably from the recovery rate for desethylatrazine (table 16 in the "Supplemental Data" section). However, the DAR values for this study did show a relation to streamflow. The lowest median DAR of 0.22 occurred in June (fig. 19) when streamflow was high and probably was dominated by surface runoff from snowmelt and stormflow. Conversely, the highest median DAR of 0.54 occurred in August when streamflow was low, and ground-water discharge may have been a larger component of streamflow as compared to its contribution during the other synoptic rounds. These results may indicate that ground water transports atrazine and desethylatrazine to the South Platte River and tributaries in the study area.

URBAN STUDY—COMPARISON OF PESTICIDE OCCURRENCE AT TWO SURFACE-WATER SITES IN THE DENVER METROPOLITAN AREA, COLORADO

Analyses of water samples collected at two streamflow-gaging stations in the Denver metropolitan area—the South Platte River at Denver and Cherry Creek at Denver (fig. 20)—were used to examine the effects of urban land use on the occurrence and temporal variability of pesticides in streams and to compare pesticide loadings between a large and a small urban basin.

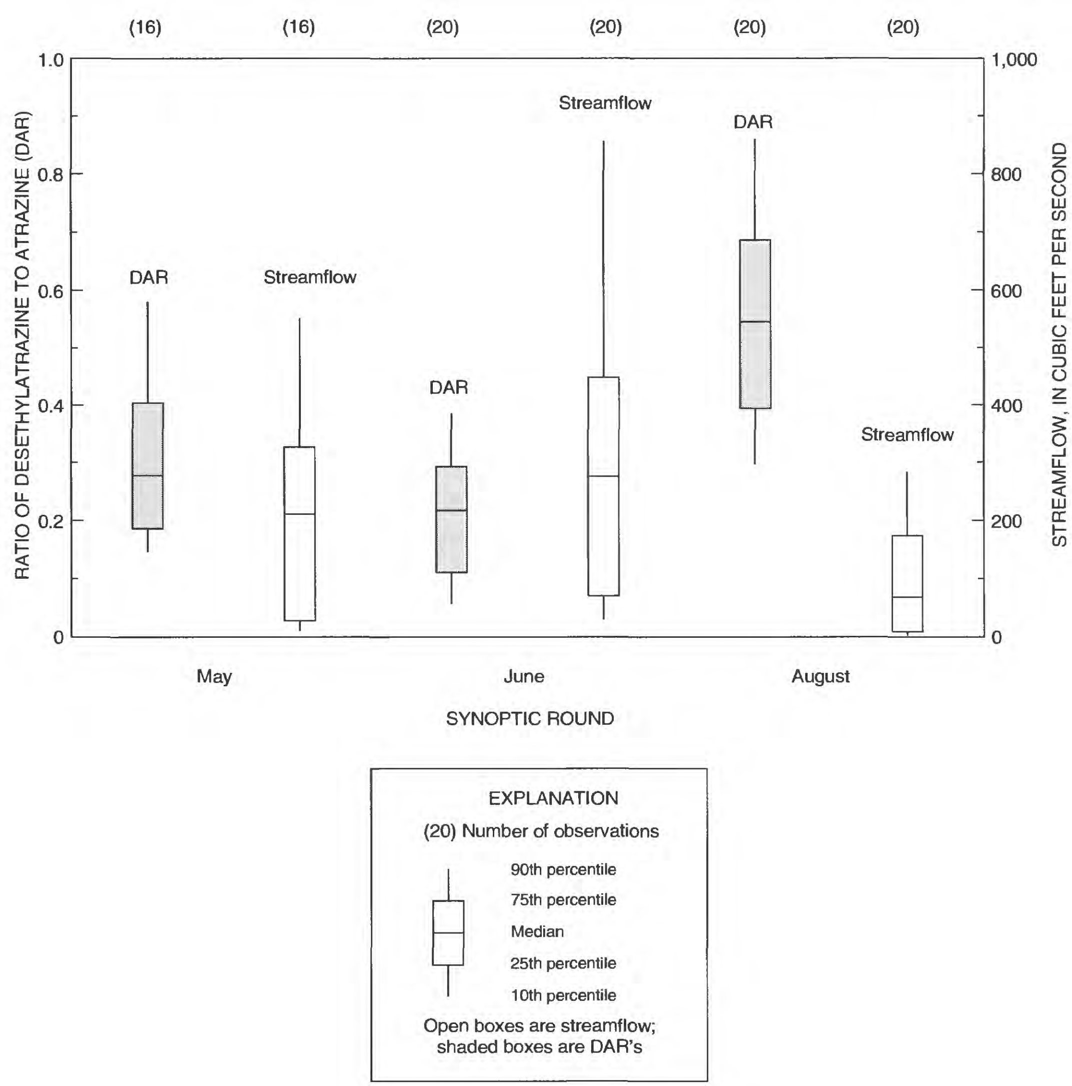


Figure 19. Distribution of desethylatrazine/atrazine (DAR) ratios and streamflow by synoptic round.

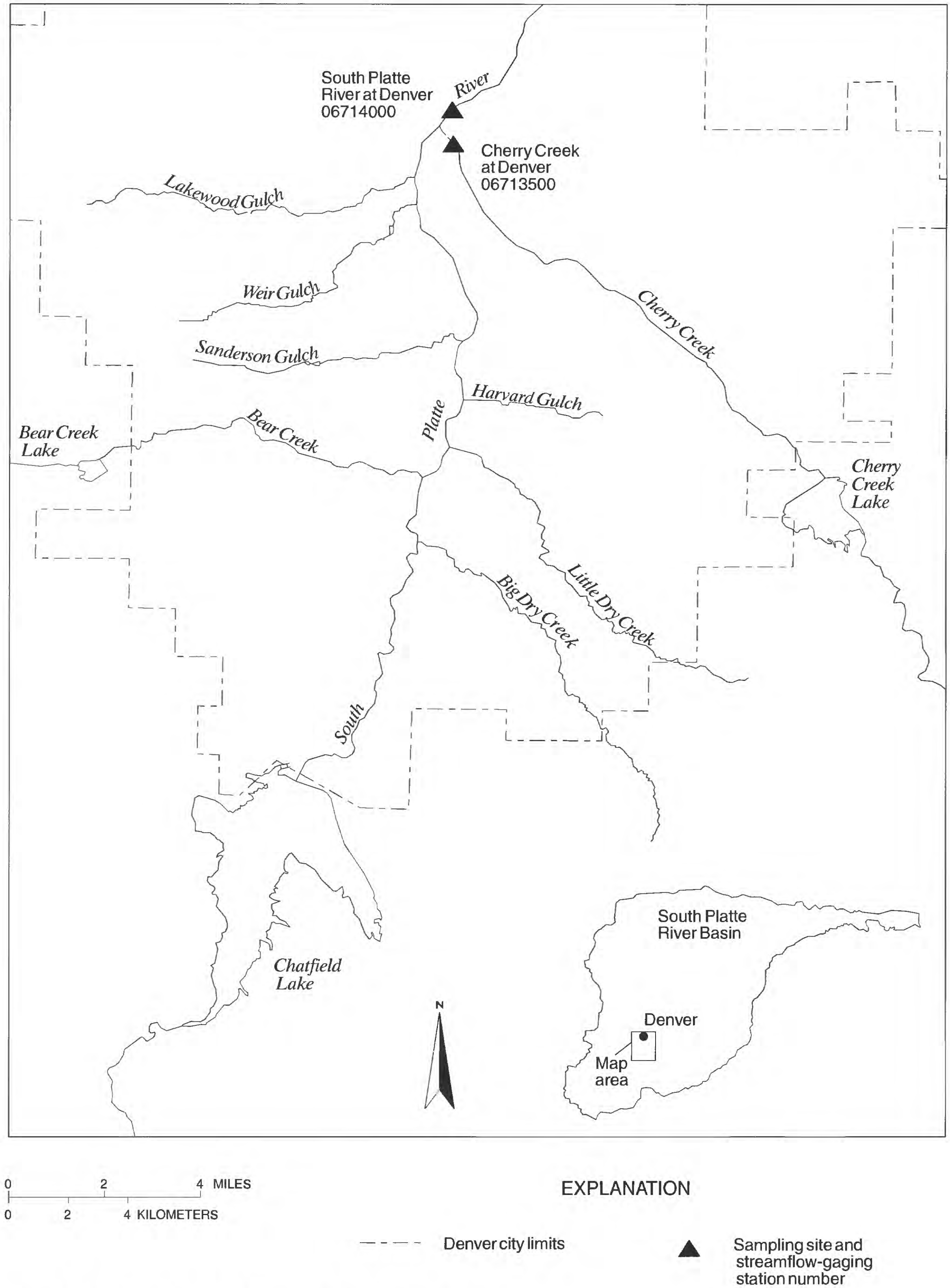


Figure 20. Location of urban study area and sampling sites.

Description of the Urban Study Area

South Platte River at Denver

The South Platte River originates in the Southern Rocky Mountains in the southwestern part of the basin (fig. 1) and flows east and northeast through forest and rangeland before entering Chatfield Lake, a reservoir, located on the southern edge of the Denver metropolitan area. Downstream from the lake, the South Platte River flows for 17 river miles through predominantly urban land to the South Platte River monitoring site in downtown Denver. The South Platte River at Denver monitoring site has a drainage area of 3,861 mi^2, of which only about 230 mi^2 is urban land located downstream from Chatfield Lake (fig. 20). Most of the water from the forested headwaters is used as municipal water supply for the Denver metropolitan area and is removed from the river upstream from Chatfield Lake. As a result, annual mean streamflow (December 1993–November 1994) during the study at the outflow from Chatfield Lake (68.6 ft^3/s) constituted only about 35 percent of the annual mean streamflow at the monitoring site (194 ft^3/s). Reservoirs also are located on the edge of the Denver metropolitan area on Bear and Cherry Creeks (fig. 20), which are the two largest tributaries draining into the urban study area. During the study, releases from Chatfield, Bear Creek, and Cherry Creek Lakes accounted for about 50 percent of the flow at the main-stem monitoring site.

The remaining 50 percent of the water at the main-stem monitoring site is derived from sources within the 230-mi^2 urban area. Effluent from a wastewater-treatment plant located on the main stem in the urban area constitutes about 18 percent of the flow at the South Platte River monitoring site. Streamflow generated within the Bear Creek and Cherry Creek Basins downstream from the lakes accounted for about 10 percent of the flow. Streamflow from several small creeks and gulches (fig. 20) that are almost entirely within the urban area and flow from numerous piped outfalls and ground-water inflow are the other sources of water measured at the South Platte River at Denver monitoring site. In four base-flow water budgets computed for the urban South Platte River corridor from late 1982 to early 1984, the sum of flows from the small tributaries (excluding Bear and Cherry Creeks) and piped outfalls upstream from the South Platte River at Denver gage ranged from 21 to 36 ft^3/s (Spahr and others, 1985), or about 11 to 18 percent of the total flow measured at the South Platte monitoring site during this study.

Cherry Creek at Denver

The Cherry Creek at Denver monitoring site is located near the mouth of Cherry Creek, which joins the South Platte River in downtown Denver, 0.4 mi upstream from the South Platte River at Denver monitoring site (fig. 20). As previously mentioned, Cherry Creek's headwaters also are impounded in an artificial lake situated on the edge of the Denver metropolitan area. Land use in the 386-mi^2 area of the basin upstream from Cherry Creek Lake predominantly is rangeland and nonirrigated farmland. Land use in the remaining 23 mi^2 of the basin located downstream from the lake primarily is urban and is categorized as 48 percent residential, 18 percent commercial and industrial, 18 percent other urban land, and 16 percent other (Rodrigo, 1994). During the urban study, annual mean streamflow at the outflow of the lake (4.4 ft^3/s) was only about 23 percent of the annual streamflow at the mouth of Cherry Creek (19 ft^3/s). Sources of additional water in the lower 23-mi^2 area of the Cherry Creek Basin are alluvial ground-water inflows and surface-water inflows from tributaries, urban storm runoff, and treated effluent from a small wastewater-treatment plant. A water balance computed for Cherry Creek through the urban study area during one nonstorm day in August 1993 when there was no reservoir outflow indicated that about 74 percent of the streamflow at the mouth was from ground-water inflow. Eighteen percent of the flow was attributed to tributary inflows, and 8 percent was from the wastewater-treatment plant (Kimbrough and Litke, 1996).

Hydrologic Conditions During the Urban Study

During dry weather, daily mean streamflow in the South Platte River typically ranged between 100 and 200 ft^3/s, except from April through mid-July when snowmelt runoff from the mountainous headwater areas and from the upper Bear Creek drainage contributed to higher streamflows (fig. 21). Daily mean streamflow in Cherry Creek was about 10 ft^3/s, except from mid-February through mid-June, when Cherry Creek Lake releases contributed to higher flows. The hydrographs for both sites display a

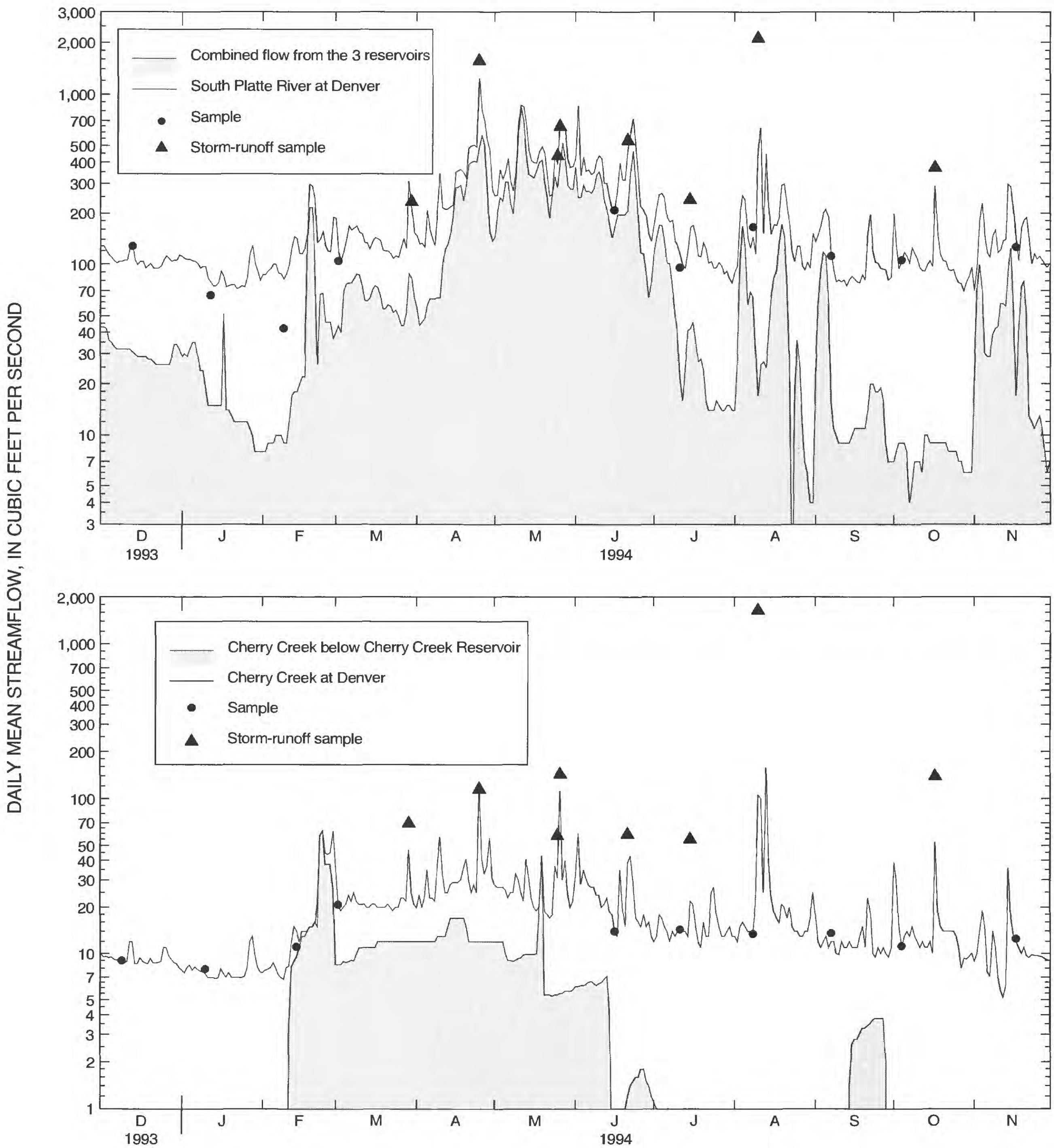


Figure 21. Daily mean streamflow and dates of sample collection for the South Platte River at Denver and Cherry Creek at Denver.

series of storm-runoff peaks, which are large in magnitude but short in duration because runoff moves quickly through the largely impervious urban areas. During storms, the streams at the monitoring sites turn brown or black and carry floating debris, such as plastic packaging materials and lawn clippings.

Annual mean streamflow during the study was only 52 percent of the long-term (1976–94) mean for the South Platte River but was 94 percent of the long-term (1942–94) mean for Cherry Creek. The shortfall of water in the South Platte River mostly was due to less than average mountain snowmelt runoff. Situated in the plains, Cherry Creek was not affected by the shortfall in mountain snowmelt runoff. During the study, about 10 percent of the mean streamflow in the South Platte River at Denver was attributed to Cherry Creek. However, on days when samples were collected, Cherry Creek contributed from 6 to 23 percent of the daily mean streamflow in the South Platte River.

Pesticide Use in the Urban Area

Although quantified estimates of urban pesticide usage in the South Platte River Basin are scarce, information on the predominant types of pesticides used has been compiled through a series of informal surveys. The pesticides that were most commonly applied outdoors by several large landowners and several commercial applicators in Fort Collins, Colorado (North Front Range Water Quality Planning Association, written commun., 1993), are listed in table 9. Included in the 1993 survey for Fort Collins were one large university, one golf course, two large manufacturing corporations, and four private lawn-care companies. The data in table 9 also are supplemented with pesticide-use information obtained by the authors in a 1994 telephone survey of several companies in the Denver metropolitan area. Included in the 1994 telephone survey were one pesticide distributor, one golf course, three commercial applicators, the City of Denver Grounds and Maintenance Department, and two highway maintenance offices (one State and one county office). Pesticide usage in the urban area also can be attributed to private homeowners. The pesticides commonly available in several lawn and garden stores that were visited by the authors in the Denver metropolitan area during 1994 are summarized in table 10. The surveys indicated that similar insecticides were used by commercial and private applicators, whereas a greater number of herbicides were used by commercial applicators and large landowners. State certification that is required to use certain herbicides, such as bromacil, diuron, picloram, prometon, and tebuthiuron, limits the number of herbicides available to the general public.

Table 9. Pesticides commonly used in urban areas of the South Platte River Basin by commercial applicators, golf courses, highway maintenance departments, or large urban landowners

[Pesticides in **bold** were analyzed for this study; source of data: North Front Range Water Quality Planning Association, written commun., 1993, and R.A. Kimbrough and D.W. Litke, unpublished data, 1994]

Herbicides			Insecticides
Bromacil	Imazapyr	**Prometon**	Bifenthrin
Clopyralid	**MCPA**	**Tebuthiuron**	**Carbaryl**
Dicamba	**Oryzalin**	**Triclopyr**	**Chlorpyrifos**
Diuron	**Picloram**	**Trifluralin**	**Diazinon**
Glyphosate	Prodiamine	**2,4-D**	Pyrethroids

Table 10. Pesticides commonly available at lawn and garden stores in the Denver metropolitan area

[Pesticides in **bold** were analyzed for this study; source of data: R.A. Kimbrough and D.W. Litke, unpublished data, 1994]

Herbicides	Insecticides
DCPA	**Carbaryl**
Glyphosate	**Chlorpyrifos**
Trifluralin	**Diazinon**
2,4-D	**Malathion**

A home pesticide-use survey compiled for the USEPA (Whitmore and others, 1992) provides a summary of pesticides commonly found in homes across the United States in 1990. In the survey of 2,447 homeowners across the Nation (including Denver), 312 active ingredients in pesticides were identified as being used outdoors around homes and in gardens. The most common herbicides and insecticides identified in the study, ranked by thousands of outdoor applications, are listed in table 11. The national survey revealed that the number of outdoor insecticide applications greatly outnumbered the number of outdoor herbicide applications. For

Table 11. Most common pesticides used around homes and gardens in the United States

[Pesticides in **bold** were analyzed for this study; source of data: Whitmore and others, 1992]

Herbicides		Insecticides	
Compound	Outdoor applications (x 1,000)	Compound	Outdoor applications (x 1,000)
2,4-D	44,054	**Diazinon**	56,758
MCPP	32,378	**Propoxur**	53,594
Glyphosate	25,618	Allethrin (total)	52,277
Acifluorfen	7,081	**Chlorpyrifos**	41,900
Dicamba	6,431	Pyrethrins	39,289
Mecoprop	3,266	Resmethrin	34,576
Oryzalin	1,766	Sumithrin	31,856
Prometon	1,281	**Carbaryl**	31,735
Chlorflurenol, methyl ester	1,067	Tetramethrin	31,464
Triclopyr	823	Metaldehyde	27,094
Oxyfluorfen	643	Acephate	19,167
Diquat dibromide	635	**Permethrin**	18,461
Trifluralin	547	**Malathion**	16,597
Atrazine	488	Diethyltoluamide	14,134
Fluazifop-butyl	426	Dichlorvos	13,043
DCPA	368	Hydramethylon	10,485
Pendimethalin	338	**Disulfoton**	6,464
MSMA	267	Cyfluthrin	5,654
Dichlobenil	124	Rotenone	4,510
Benefin	81	Dicofol	4,179

example, only the five top-ranked herbicides are applied more frequently than the insecticide ranked 20th in the survey. Pesticides common among all surveys cited in this section are the herbicides glyphosate, trifluralin, and 2,4-D and the insecticides carbaryl, chlorpyrifos, and diazinon.

Study Design

In order to compare pesticide occurrence at the two surface-water sites, each site was sampled 18 times during varying hydrologic conditions from December 1993 through November 1994 (fig. 21). On four occasions (December, January, February, and late March), the sites were sampled within a few days of each other. On 14 occasions, the sites were sampled on the same day. Eight of the 18 samples at each site were collected during storm-runoff events (one snowmelt-runoff event in March and seven rainfall-runoff events). The instantaneous discharges for storm-runoff samples plot above the daily mean streamflows because the runoff events last only for a few hours. Samples collected from the South Platte River in January and February plotted below the daily mean streamflow because samples were collected during the low-flow part of the day.

A total of 1,457 individual pesticide analyses were performed on the 18 samples collected from each site. Seventeen samples from each site were analyzed for the 83 pesticides listed in table 1. One sample at each site was only analyzed for the 46 pesticides determined by GC/MS (table 1).

Pesticide Occurrence

During analysis, twenty-eight of the 83 pesticides were detected during the urban study (table 12). Twenty-one of the pesticides (14 herbicides and 7 insecticides) were detected in the South Platte River, whereas 25 pesticides (16 herbicides and

Table 12. Summary of statistics for pesticides detected in urban samples, December 1993–November 1994 (36 samples were collected, 18 samples per site)

[Concentrations are in micrograms per liter; concentrations in **bold** are above the method detection limit; --, not detected; conc., concentration; <, less than]

Compound	Number of detections		South Platte River at Denver, Colorado							Cherry Creek at Denver, Colorado						
	South Platte River	Cherry Creek	Minimum conc.	Concentration at indicated percentile					Maximum conc.	Minimum conc.	Concentration at indicated percentile					Maximum conc.
				10	25	50	75	90			10	25	50	75	90	
Carbaryl	18	17	**0.014**	**0.018**	**0.032**	**0.32**	**0.69**	**4.8**	5.2	<0.003	**0.008**	**0.062**	**0.34**	1.6	4.9	5.5
Atrazine	16	15	<0.001	<0.001	**0.006**	**0.010**	**0.020**	**0.13**	**0.20**	<0.001	<0.001	**0.011**	**0.014**	**0.035**	**0.16**	**0.34**
Prometon	16	15	<0.018	<0.018	**0.031**	**0.042**	**0.065**	**0.096**	**0.16**	<0.018	<0.018	**0.035**	**0.064**	**0.089**	**0.13**	**0.43**
Diazinon	14	11	<0.002	<0.002	**0.008**	**0.039**	**0.13**	**0.22**	**0.24**	<0.002	<0.002	<0.002	**0.021**	**0.14**	**0.37**	**0.63**
Simazine	9	14	<0.005	<0.005	<0.005	**0.006**	**0.020**	**0.045**	**0.048**	<0.005	<0.005	**0.009**	**0.023**	**0.036**	**0.12**	**0.12**
DCPA	12	10	<0.002	<0.002	<0.002	**0.003**	**0.012**	**0.020**	**0.029**	<0.002	<0.002	<0.002	**0.003**	**0.016**	**0.029**	**0.029**
Tebuthiuron	10	9	<0.010	<0.010	<0.010	**0.015**	**0.036**	**0.12**	**0.17**	<0.010	<0.010	<0.010	**0.012**	**0.034**	**0.060**	**0.061**
Chlorpyrifos	5	6	<0.004	<0.004	<0.004	<0.004	**0.010**	**0.051**	**0.11**	<0.004	<0.004	<0.004	<0.004	**0.031**	**0.11**	**0.34**
Malathion	5	4	<0.005	<0.005	<0.005	<0.005	**0.017**	**0.057**	**0.089**	<0.005	<0.005	<0.005	<0.005	**0.008**	**0.055**	**0.063**
Desethylatrazine	3	5	<0.002	<0.002	<0.002	<0.002	<0.002	**0.011**	**0.016**	<0.002	<0.002	<0.002	<0.002	**0.002**	**0.018**	**0.024**
2,4-D	2	3	<0.035	<0.035	<0.035	<0.035	<0.035	**0.35**	**0.76**	<0.035	<0.035	<0.035	<0.035	<0.035	**0.33**	**1.5**
Trifluralin	1	3	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.005**	<0.002	<0.002	<0.002	<0.002	<0.002	**0.007**	**0.008**
Benfluralin	2	1	<0.002	<0.002	<0.002	<0.002	<0.002	**0.004**	**0.009**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.010**
EPTC	2	1	<0.002	<0.002	<0.002	<0.002	<0.002	**0.015**	**0.021**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.026**
Carbofuran	1	1	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	**0.031**	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	**0.059**
gamma-HCH	1	1	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.008**	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.11**
Metolachlor	1	1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.009**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	**0.009**
Propargite	1	1	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	**0.042**	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	**0.057**
Dichlobenil	2	0	<0.020	<0.020	<0.020	<0.020	<0.020	**0.050**	**0.32**	--	--	--	--	--	--	--
Metribuzin	2	0	<0.004	<0.004	<0.004	<0.004	<0.004	**0.10**	**0.13**	--	--	--	--	--	--	--
Pebulate	1	0	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.023**	--	--	--	--	--	--	--
Dichlorprop	0	1	--	--	--	--	--	--	--	<0.032	<0.032	<0.032	<0.032	<0.032	<0.032	**0.060**
Diuron	0	1	--	--	--	--	--	--	--	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	**0.10**
1-Naphthol	0	1	--	--	--	--	--	--	--	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	**0.12**
Pendimethalin	0	1	--	--	--	--	--	--	--	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	**0.028**
cis-Permethrin	0	1	--	--	--	--	--	--	--	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	**0.005**
Propham	0	1	--	--	--	--	--	--	--	<0.035	<0.035	<0.035	<0.035	<0.035	<0.035	**0.070**
Terbacil	0	1	--	--	--	--	--	--	--	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	**0.035**

9 insecticides) were detected in Cherry Creek. Eighteen pesticides (11 herbicides and 7 insecticides) were detected in both drainage basins. The greater number of individual pesticides detected in Cherry Creek compared to the South Platte River resulted from single detections of several compounds, including dichlorprop, diuron, 1-naphthol, pendimethalin, *cis*-permethrin, propham, and terbacil. The pesticides dichlobenil, metribuzin, and pebulate were detected in the South Platte River but not in Cherry Creek. The total number of pesticide detections was similar for each site. Of the 1,457 individual pesticide analyses performed on samples from each site, there were 124 detections for the South Platte River and 125 detections for Cherry Creek, or about 8.5 percent of the total possible for each site.

Nine pesticides accounted for about 80 percent of the detections in each drainage basin (table 12), indicating that pesticide use is similar in each basin. Five of the nine most frequently detected pesticides (carbaryl, chlorpyrifos, DCPA, diazinon, and malathion) have been identified as being commonly used by homeowners or commercial applicators in urban areas of the South Platte River Basin (tables 9 and 10) and throughout the Nation (table 11). Three of the nine pesticides (prometon, simazine, and tebuthiuron) are herbicides generally associated with nonagricultural uses in Colorado and are used for long-term, nonselective weed control. Although prometon and tebuthiuron became unavailable to Colorado homeowners in 1991 (Colorado Department of Agriculture, 1989), they still are available for use in urban areas by certified applicators. Prior to 1991, a mixture of simazine and prometon was available to the general public under the trade name Pramitol 5PS for total vegetation control, but because of the prometon content, Pramitol 5PS also became a restricted-use product in Colorado in 1991. Used alone, simazine was available to the general public until 1993 as an algicide for ponds and swimming pools. The herbicide atrazine completes the list of the nine most frequently detected pesticides in each basin. Nonagricultural use of atrazine in Colorado has been limited to roadside and turf application since 1992 when the USEPA accepted voluntary label revisions for many atrazine-containing products.

Pesticide Concentrations

Pesticide concentrations in the urban streams were small. Seventy-eight percent of all pesticide detections were less than 0.1 µg/L, and about 94 percent of all detections were less than 0.5 µg/L. Only seven pesticides (table 12) at each site had median concentrations greater than the MDL's (carbaryl, atrazine, prometon, diazinon, simazine, DCPA, and tebuthiuron). Carbaryl (10 detections) and the herbicide 2,4-D (1 detection) were the only pesticides detected in concentrations greater than 1 µg/L (table 12). Carbaryl was detected at the highest concentration of any pesticide at 5.2 µg/L in the South Platte River and 5.5 µg/L in Cherry Creek. Additionally, carbaryl concentrations generally were an order of magnitude higher than the concentration of other pesticides at almost every percentile. Overall, the distribution in concentration of all pesticides detected was similar between sites (fig. 22). Similar concentrations in the small and the large basin could indicate that pesticide concentrations in streams throughout the

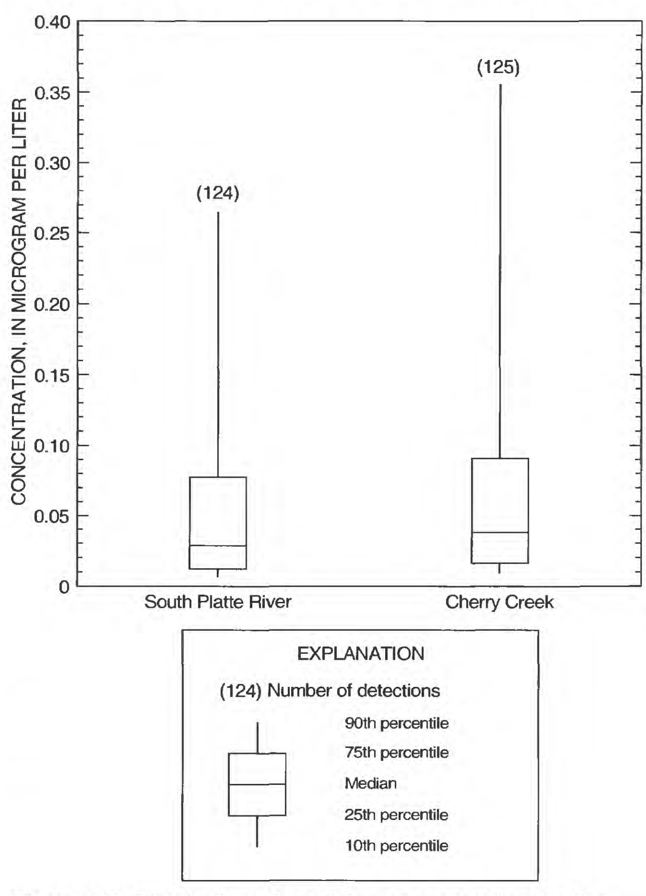


Figure 22. Distribution of pesticide concentrations in the South Platte River at Denver and Cherry Creek at Denver.

Denver metropolitan area may not vary substantially from what was measured in this study.

Although average concentrations of individual pesticides during the study were less than any established MCL or HA, the HA for diazinon, 0.6 µg/L, was exceeded in one Cherry Creek storm-runoff sample at a concentration of 0.63 µg/L. A total of 31 samples (16 from the South Platte River, 15 from Cherry Creek) exceeded the NAS/NAE aquatic-life guideline for carbaryl of 0.02 µg/L. A total of 24 samples (14 from the South Platte River, 10 from Cherry Creek) exceeded the NAS/NAE aquatic-life guideline for diazinon of 0.009 µg/L. Two samples from Cherry Creek and one sample from the South Platte River exceeded the USEPA acute aquatic-life guideline for chlorpyrifos of 0.08 µg/L.

Multiple pesticides were detected in all of the samples, and the number of compounds per sample ranged from 3 to 14 (fig. 23). The effects of long-term exposure to low concentrations of multiple pesticides on human health and aquatic life are not well understood. Currently (1997), human health and aquatic life standards are set only for individual compounds. The USEPA is considering establishing health standards for combinations of triazine herbicides and their metabolites (U.S. Environmental Protection Agency, 1994).

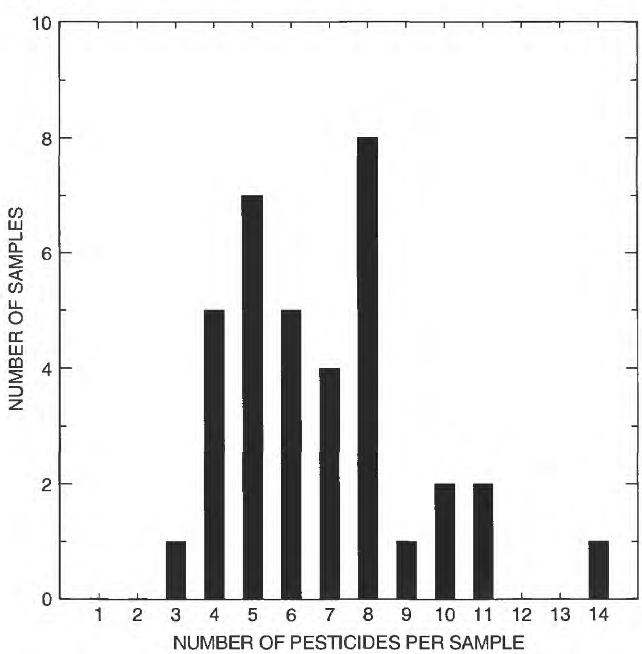


Figure 23. Histogram showing the number of pesticides detected per sample.

Pesticide Detections in Storm-Runoff Samples

There has been extensive documentation that pesticide concentrations increase in streams as a result of storm runoff (Thurman and others, 1992; Goolsby and others, 1993; Kimbrough and Litke, 1996). During storms, pesticides are removed from land surfaces by precipitation and transported to the streams in surface runoff in the dissolved phase or in the suspended phase attached to soil particles. In urban areas, the large expanses of impervious surfaces provide a continuous pathway along which surface runoff can be transported to streams. In this study, pesticide detections were more frequent in storm-runoff samples as compared to nonstorm samples. Out of a total of 1,254 individual storm analyses, there were 131 detections, or about 10 percent of the total possible. Out of a total of 1,660 individual nonstorm analyses, there were 118 detections, or about 8 percent of the total possible. Ten of the 28 pesticides detected during the study only were present in storm-runoff samples (carbofuran, dichlobenil, EPTC, metolachlor, 1-naphthol, pebulate, pendimethalin, *cis*-permethrin, propargite, and trifluralin). In the South Platte River at Denver, 20 of the 21 pesticides detected were measured at peak concentrations in storm-runoff samples. In Cherry Creek, 21 of the 25 pesticides detected were measured at peak concentrations in storm-runoff samples.

The storm-runoff samples were collected from a variety of hydrologic conditions with flows ranging from 234 to 5,460 ft^3/s in the South Platte River and from 55.1 to 1,650 ft^3/s in Cherry Creek (table 13, fig. 24). Most of the storm-runoff events were the result of convective thunderstorms, which move over the Denver metropolitan area very quickly (May, June, July, and August); however, one snowmelt-runoff event was sampled in March and two frontal storms, which tend to move through the metropolitan area more slowly, were sampled in April and October. All storm-runoff samples were collected sequentially on the same day, with samples being collected from Cherry Creek first, except during the snowmelt-runoff event. During the snowmelt event, samples were collected from Cherry Creek on the peak of snowmelt on the first day following the spring snowstorm. The South Platte River was sampled on the second day, on a smaller snowmelt peak (fig. 24). Three storms were sampled on the rising limb of the storm hydrograph (April, June, October), one storm was sampled at the

Table 13. Selected data for storm-runoff samples, March — October 1994

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; g/min, gram per minute]

Date	Type of storm	Streamflow sampled (ft^3/s)	Number of pesticides detected	Number of pesticides detected in peak concentration	Total pesticide concentration (µg/L)	Total pesticide load (g/min)	Dominant pesticide(s)	Concentration of dominant pesticide(s) (µg/L)	Load of dominant pesticide(s) (g/min)	Percentage of total load from dominant pesticide(s)
South Platte River at Denver, Colorado										
03/30/94	snowmelt	234	6	0	0.11	0.04	Prometon	0.033	0.01	25
04/25/94	frontal	1,560	4	3	1.3	3.4	2,4-D	0.76	2.0	59
05/25/94	convective	436	9	2	1.0	0.74	Carbaryl	0.31	0.23	31
05/26/94	convective	647	11	3	1.8	2.0	Carbaryl	1.1	1.2	60
06/21/94	convective	536	11	3	5.9	5.4	Carbaryl	5.2	4.7	87
07/15/94	convective	241	8	2	2.6	1.1	Carbaryl	2.0	0.82	75
08/10/94	convective	5,460	10	5	5.3	49	Carbaryl	4.8	45	92
10/17/94	frontal	364	5	1	0.72	0.45	Carbaryl	0.55	0.34	76
Cherry Creek at Denver, Colorado										
03/29/94	snowmelt	69.6	7	2	2.3	0.27	Carbaryl	2.1	0.25	93
04/25/94	frontal	115	5	3	1.9	0.37	2,4-D	1.5	0.29	78
05/25/94	convective	57.9	10	5	1.6	0.16	Diazinon Carbaryl	0.63 0.60	0.06 0.06	38 38
05/26/94	convective	143	14	5	2.6	0.63	Carbaryl	1.7	0.41	65
06/21/94	convective	59.3	8	2	6.0	0.60	Carbaryl	5.5	0.55	92
07/15/94	convective	55.1	6	3	6.0	0.56	Carbaryl	4.8	0.45	80
08/10/94	convective	1,650	8	2	2.1	5.9	Carbaryl	1.6	4.5	76
10/17/94	frontal	139	8	0	1.6	0.38	Carbaryl	1.3	0.31	82

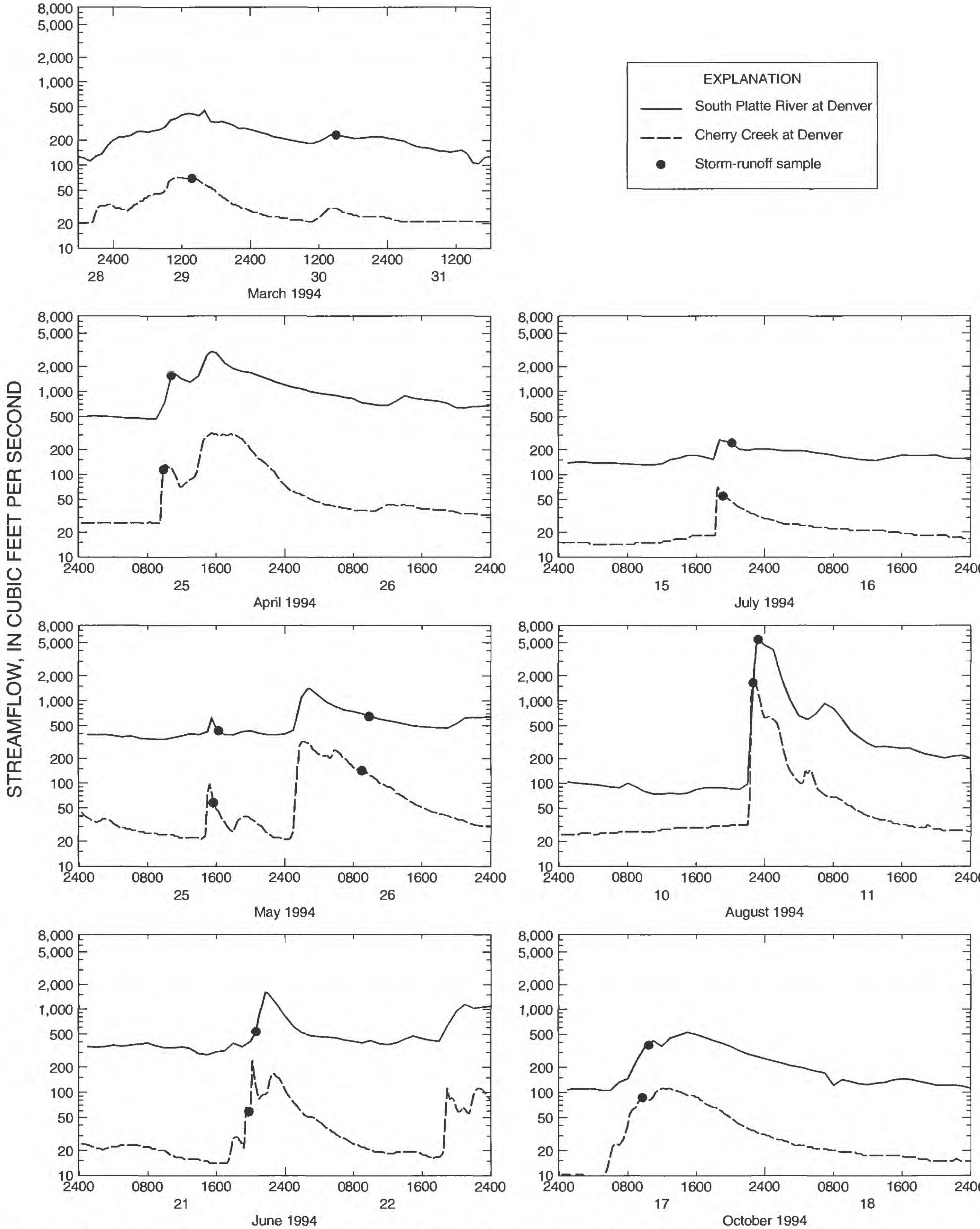


Figure 24. Hydrographs showing the South Platte River at Denver and Cherry Creek at Denver on days when storm-runoff samples were collected.

peak of runoff (August), and three storms were sampled on the falling limb of the hydrograph (two in May and one in July).

In the South Platte River, pesticide detections were most frequent in storm-runoff samples collected from May through August. The number of pesticides detected at peak concentration was fairly well distributed among the storms, which may indicate that there is no single time period in the urban area when most of the pesticides are applied. In Cherry Creek, the number of pesticides detected in a storm-runoff sample primarily ranged from 5 to 8 compounds (table 13); however, the two storms in May had the highest frequency of detections (10 and 14 detections).

Carbaryl was measured in highest concentration of any compound in 12 of the 16 storm-runoff samples. In an additional sample, carbaryl and the insecticide diazinon were measured in highest concentration (table 13). Carbaryl concentrations in storm-runoff samples generally were 1 to 2 orders of magnitude higher than other pesticide concentrations, and as a result, carbaryl accounted for about 30 to 90 percent of the total pesticide load in most of the samples. The herbicide 2,4-D was the dominant pesticide in both storm-runoff samples collected on April 25. The presence of 2,4-D in these storm samples accounted for two of five of its detections throughout the entire study. The snowmelt-runoff sample collected from the South Platte River on March 30 was obtained near the end of the snowmelt recession curve (fig. 24) and could indicate why the total pesticide concentration was small compared to other storm-runoff samples. Prometon was the dominant pesticide in this sample; however, the prometon load constituted only 25 percent of the total pesticide load.

Pesticide transport, or pesticide loads, are the product of pesticide concentration and streamflow (storm pesticide loads are expressed in grams per minute because concentrations and streamflow may vary substantially over a storm hydrograph). The variability of pesticide loads listed in table 13 indicate the effect of streamflow on this calculation. For example, although the total measured pesticide concentration for the June and August samples are similar for the South Platte River, the pesticide load in the August sample is an order of magnitude higher as a result of the larger volume of streamflow (or storm runoff).

Concentration plots for several pesticides (fig. 25) illustrate the effect of storm runoff on pesticide occurrence in streams. The detection of DCPA, chlorpyrifos, and malathion almost exclusively in storm samples indicates that storm runoff is the predominant mechanism for transporting these pesticides to Cherry Creek and the South Platte River at Denver. The detection of DCPA in all of the storm-runoff samples could indicate that DCPA was present on land surfaces from late March through October and that it was available for transport to the streams through surface runoff. Conversely, the absence of chlorpyrifos and malathion in the late March and April (spring) storm samples could indicate that a surface source of these pesticides did not exist because the pesticides had not yet been applied in the urban area.

Pesticide Detections in Dry-Weather Samples

In addition to detections in many storm samples, the detection of certain pesticides, such as atrazine, carbaryl, diazinon, prometon, and simazine, during dry weather was substantial (fig. 26). Detections during dry weather indicate that storm runoff is not the sole source for transporting pesticides to streams. Although not quantified for this study, other sources might include surface runoff from urban irrigation, wet and dry atmospheric deposition, direct application from spray drift, pesticides sorbed to streambed sediments, and ground water discharging from the adjacent alluvial aquifer.

Prometon and simazine most likely are being transported with ground water in the Cherry Creek Basin. Evidence of this is provided by the consistent detection of prometon and simazine in dry-weather samples that were collected when the outflow from Cherry Creek Lake was shut off (fig. 21) or when ground water was the predominant source of water in the lower Cherry Creek Basin (dry-weather samples in December, January, June, July, August, September, October, and November) (fig. 26). In 1993, during a separate study, prometon and simazine were the two most frequently detected pesticides in alluvial ground water in the lower 23-mi^2 area of the Cherry Creek Basin (B.W. Bruce, U.S. Geological Survey, written commun., 1995). Although the contribution of ground water to streamflow in the urbanized corridor of the South Platte River Basin has not been calculated, prometon concentrations in the South Platte River were consistent and similar to concentrations in Cherry Creek. This may indicate that prometon is most likely transported with ground water in the urban part of the South Platte River Basin.

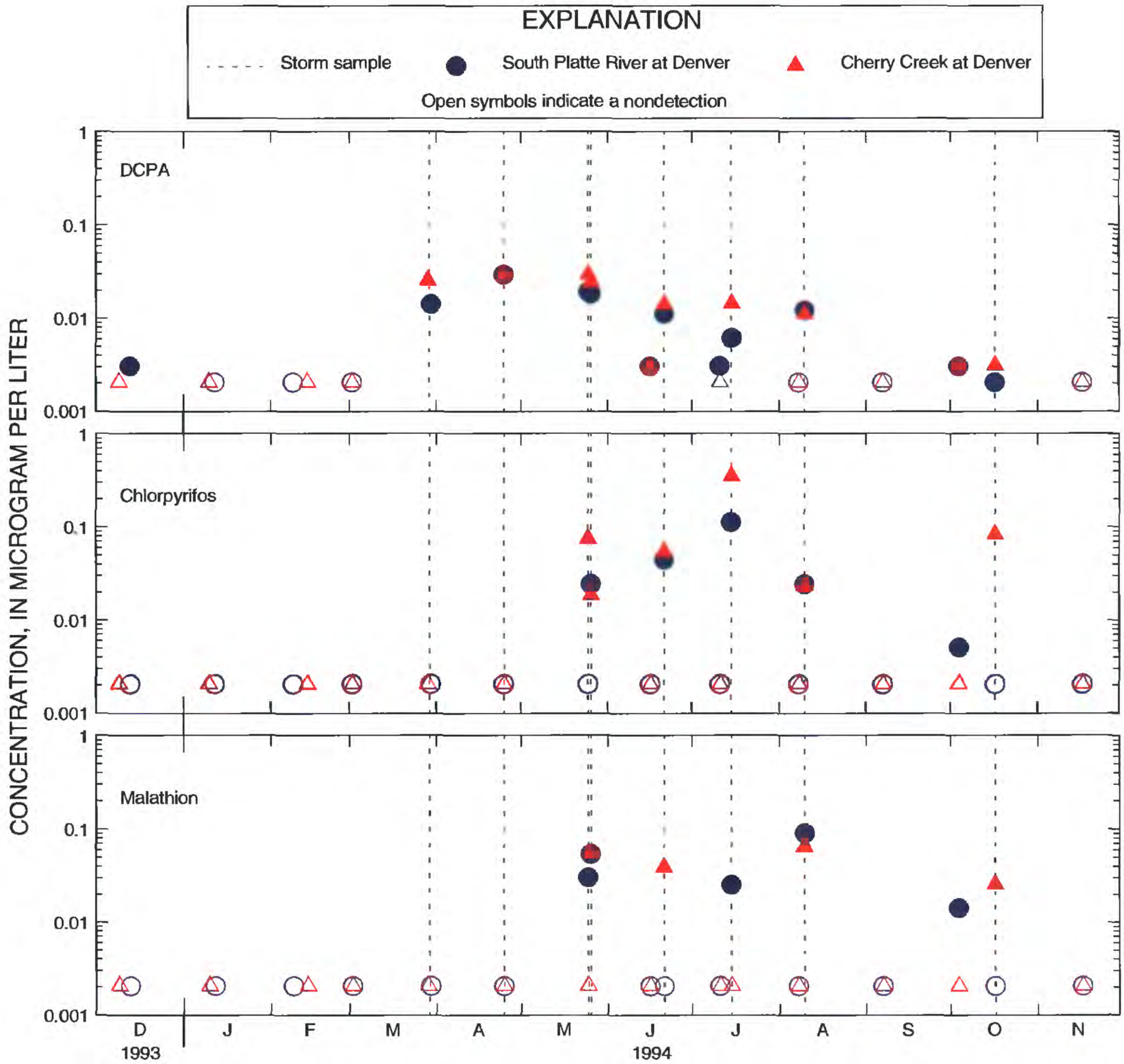


Figure 25. Concentrations of DCPA, chlorpyrifos, and malathion in the South Platte River at Denver and Cherry Creek at Denver by sampling date.

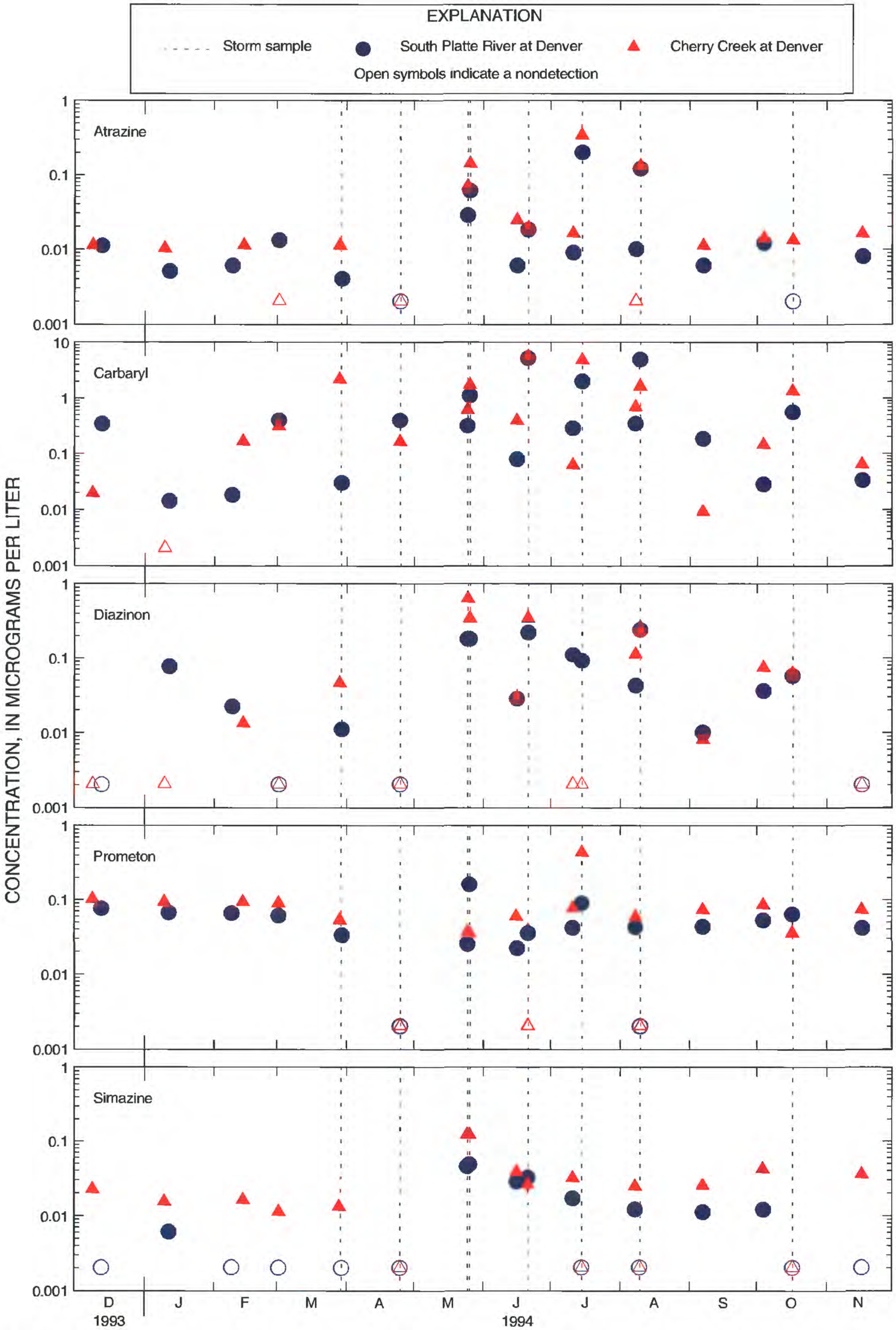


Figure 26. Concentrations of atrazine, carbaryl, diazinon, prometon, and simazine in the South Platte River at Denver and Cherry Creek at Denver by sampling date.

Further evidence that prometon and simazine persist in the alluvial ground water is provided by their nondetection in some storm-runoff samples; in fact, all of the nondetections of prometon (at both sites) and simazine (at Cherry Creek) occurred in storm-runoff samples (fig. 26). Although simazine was not detected in the South Platte River as frequently as in Cherry Creek, it was detected in five dry-weather samples and in only three of eight storm-runoff samples collected from the South Platte River. Decreases in stream pesticide concentrations during storms could result from the dilution caused by the large percentage of surface runoff sampled during storms.

Comparison of Pesticide Loads in the South Platte River and Cherry Creek

A comparison of pesticide loads in the South Platte River and Cherry Creek can be used to determine whether pesticide loads in urban streams of the South Platte River Basin are proportionate based on land-use area. Prior to load comparisons, the physical attributes of each basin can be compared using various measures (table 14). The similarity in ratios of drainage area, urban area, lawn area, and mean streamflow for the period of study indicates that the Cherry Creek Basin is physiograpically representative of the larger South Platte River Basin. Because Cherry Creek is a plains stream and the South Platte River is a mixed plains/mountain stream, one might expect a smaller value for the ratio of mean streamflow due to larger flows in the South Platte River from mountain snowmelt. However, as previously stated, annual mean streamflow during the study was only 52 percent of average in the South Platte River but 94 percent of average in Cherry Creek.

Table 14. Comparison of areas and mean streamflow for the South Platte River at Denver and Cherry Creek at Denver

[mi^2, square miles; ft^3/s, cubic feet per second; source of data: U.S. Geological Survey, 1990, 1995, 1996; Rodrigo, 1994; Colorado Division of Water Resources, 1995; Dennehy and others, 1995]

Feature	Cherry Creek at Denver	South Platte River at Denver	Feature ratio
Drainage area (mi^2)	409	3,861	0.11
Urban area (mi^2)	23	230	0.10
Lawn area (mi^2)	7	94	0.07
Mean streamflow for period of study (ft^3/s)	19	194	0.10

A comparison of pesticide loads at the two sites is made easier by only considering the 14 of 18 sample sets that were collected on the same day and by limiting the comparison to the occurrences when pesticides were detected at both sites on the same day. In the 14 sample sets, there were 80 occurrences (160 detections) when pesticides were detected at both sites; however, there also were 34 occurrences (34 detections) when a pesticide was only detected at one site.

The percentage of pesticide load in the South Platte River at Denver attributed to Cherry Creek was not consistent. For example, the percentage of carbaryl load from Cherry Creek varied from 1 to 57 percent and correlated poorly with the percentage of streamflow from Cherry Creek (fig. 27).

Overall, for the pesticides detected at both sites on the same day, the distribution of pesticide loads in the South Platte River at Denver that was attributed to Cherry Creek primarily ranged from 7 to 50 percent with a median value of 21 percent (fig. 28). Compared to the median contribution of streamflow to the South Platte River in the 14 sample sets (12.5 percent), it appears that Cherry Creek contributes proportionally more pesticide loading than streamflow to the main stem.

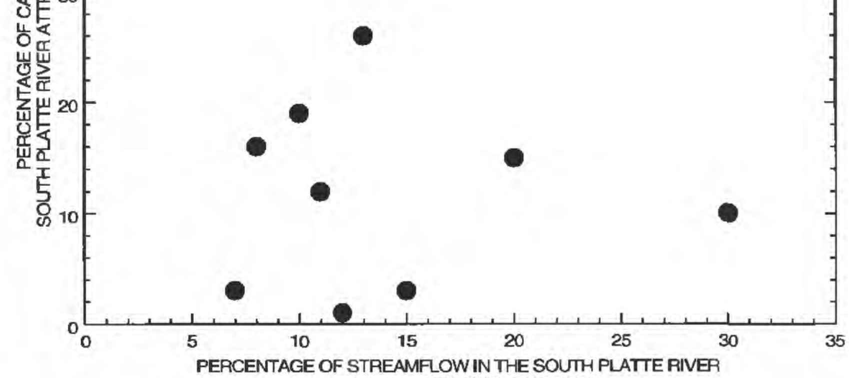


Figure 27. Percentage of carbaryl load and streamflow in the South Platte River at Denver attributed to Cherry Creek.

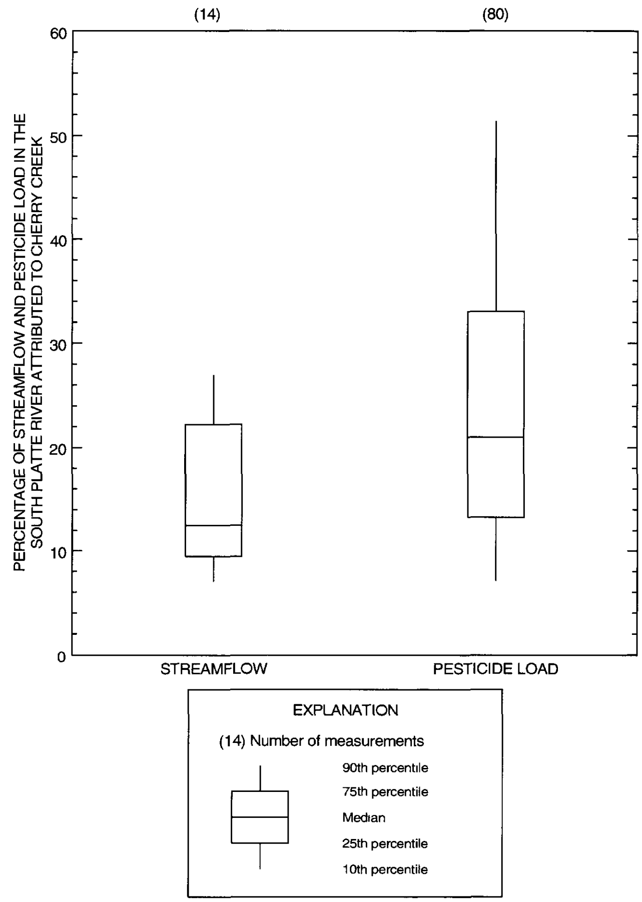


Figure 28. Distribution of streamflow and pesticide loads in the South Platte River at Denver attributed to Cherry Creek (data are only for streamflows sampled and pesticides detected at both sites on the same day).

The variability in the percentage of pesticide loads from Cherry Creek is affected by several factors, such as pesticide use, the timing of application, and the hydrologic conditions at the time of sampling. Hydrologic conditions varied between samples with the variability in releases from upstream reservoirs and from the spatial variability in rainfall and the amount of subsequent runoff sampled.

SUMMARY

Historical data for pesticides in surface water in the South Platte River Basin are scarce. As part of the South Platte River NAWQA project, surface-water samples were collected primarily during 1994 from agricultural and urban areas to provide more data on pesticides in streams of the basin. The following sections summarize the pesticide data collected in the agricultural area ("Agricultural Study" section) and in the urban area ("Urban Study" section).

Agricultural Study

The first section of this report describes results of pesticide data collected at surface-water sites in the irrigated agricultural areas along the South Platte River from Henderson, Colorado, to North Platte, Nebraska. The purpose of this study was to document the occurrence and spatial distribution of pesticides in surface water in the South Platte River Basin during the 1994 growing season. Water samples were collected during May, June, and August 1994 at 16 to 20 sites along the main-stem South Platte River and at the mouths of major tributaries. Pesticide data also were collected approximately biweekly throughout the growing season at two anchor sites.

The principal irrigated crops grown in the 10-county study area (in order of amount harvested) are corn, hay, dry beans, sugar beets, wheat, and barley. Corn is the primary crop grown in most counties of the study area, and corn predominates in counties in the downstream part of the study area. A larger variety of crops are grown in counties in the upstream part of the study area where, in addition to the major crops listed above, minor crops such as vegetables, onions, potatoes, and sod also are grown. About 2.8 million pounds of pesticides (active ingredients) are applied annually to irrigated acreage in the 10-county study area. The principal pesticides used (in order of use) are atrazine, alachlor, terbufos, EPTC, metol-achlor, and cyanazine. These pesticides primarily are used on corn.

During water year 1994, streamflow in the South Platte River in the agricultural study area ranged from about 40 to 50 percent of the 20-year (1976–95) mean. Irrigation water demand was high throughout the growing season, and irrigation ditches diverted much of the water from the river; large offstream reservoirs also were emptied by midsummer to help meet the irrigation water demand. Streamflow at synoptic main-stem sites was highest during the June synoptic round, second highest in May, and lowest in August.

Thirty-nine pesticides were detected at least once during the agricultural study. Ten pesticides accounted for about 80 percent of the synoptic detections. Of the 10 pesticides, 6 commonly are used for irrigated agriculture in the study area (atrazine, metol-achlor, DCPA, cyanazine, EPTC, and carbofuran); one (desethylatrazine) is a metabolite of atrazine; two (prometon and simazine) primarily are used for long-term weed control in noncropped areas; and one (diazinon) is an insecticide used around households and commercially on some vegetable crops.

Pesticide concentrations generally were less than standards and guidelines for drinking water or aquatic life. Average concentrations of individual pesticides for the study period were less than MCL's and HA's; however, the HA for cyanazine was exceeded in two synoptic samples. Carbaryl, diazinon, and bromoxynil were the only pesticides to exceed aquatic-life criteria.

Atrazine, desethylatrazine, and prometon were detected at every site in the agricultural study area. The herbicides cyanazine, DCPA, metolachlor, EPTC, and simazine and the insecticides carbofuran and diazinon were detected at more than one-half of the sites. Along the main-stem South Platte River, the number of different pesticides detected and the total number of detections were greater in the upstream reach from Henderson to Kersey than in the downstream reach from Kersey to North Platte. A greater variety of pesticide detections in the upstream reach resulted from (1) several detections of pesticides that are generally associated with nonagricultural use in the basin; (2) detections of insecticides that are applied to crops, but also commonly are used in urban areas; and (3) the miscellaneous detection of several pesticides due to the larger variety of crops grown in the upstream counties. The number of different pesticides detected in the main stem steadily declined from a maximum at Evans (16 pesticides) to a minimum at North Platte (5 pesticides). At North Platte, pesticide detections primarily were limited to common corn herbicides.

Pesticide concentrations (equal to or greater than the pesticide MDL's) generally were higher in plains streams. Plains streams, compared to the main stem and to tributaries that drain from the mountains, contain smaller volumes of annual spring snowmelt that dilute instream pesticide concentrations. Additionally, streamflow in plains streams primarily is derived from irrigation return flows.

The timing of pesticide detections was related, in part, to the timing of application. Herbicide detections were more numerous in May and June, correlating with early season application. Insecticide detections were most frequent in June, correlating with mid-growing-season application.

The detection of individual compounds varied spatially and temporally, indicating that differences exist among pesticide use. For example, detections of metolachlor, which commonly is applied to corn, primarily were limited to sites downstream from Platteville where most of the corn is grown. Detections of diazinon, which is used in urban areas and on vegetables, primarily were limited to sites in the upper one-half of the study area. The timing of application also resulted in variations of detections. DCPA concentrations were highest in May, following early season application, and steadily declined throughout the growing season, whereas propargite was detected for only several weeks following its application to corn in July. Temporal and spatial variability in detections is also affected by a pesticide's persistence in the environment. For example, the detection of atrazine and prometon at every site in almost all samples indicates that these compounds are resistant to breakdown in the environment. Conversely, carbofuran does not appear to be as persistent in the environment because it was not detected at any sites in August after being detected at several sites in June.

Higher streamflows resulted in generally higher pesticide loads at main-stem sites compared to tributary sites. In the South Platte River at Kersey, Colorado, atrazine loads persisted throughout the study and varied between about 0.5 to 1 pound per day. The maximum pesticide load (about 2.9 pounds per day of DCPA) occurred in Crow Creek during the May synoptic round. Large DCPA loads probably did not persist throughout the growing season because DCPA loads at anchor sites steadily decreased throughout the study period.

Ground-water discharge may transport atrazine, desethylatrazine, and prometon to surface waters in the study area. Residual streamflows in the main-stem for the August synoptic round were positive, signifying that ground water is a probable source of streamflow. Most residual loads for the three pesticides also were positive, indicating that ground-water discharge to the river may transport atrazine, desethylatrazine, and prometon to the river. An increase in the desethylatrazine to atrazine ratio (called the DAR) throughout the study also may signify that ground water transports atrazine and desethylatrazine to surface waters in the study area.

Urban Study

Pesticide data were collected from the South Platte River at Denver, Colorado, and Cherry Creek at

Denver, Colorado, primarily during 1994 in order to characterize urban pesticide occurrence across varying hydrologic conditions and to compare pesticide loadings between a small and a large urban basin. Each site was sampled 18 times; 8 of the samples at each site were collected during storm-runoff conditions.

Although both sampling sites have headwaters outside the urban area, upstream reservoirs or diversions limit the volume of upstream water that passes the sites. During the study period, water from outside the urban area constituted about 50 percent of the annual mean flow in the South Platte River at Denver; water from upstream rangeland and rural areas constituted about 23 percent of the annual mean flow at Cherry Creek at Denver. Urban sources of water to the streams include wastewater-treatment-plant discharges, inflows from urban tributaries, urban base flow from the surrounding alluvial aquifer, and urban stormwater runoff. Annual mean streamflow during the study was only 52 percent of average in the South Platte River but was 94 percent of average in Cherry Creek.

Quantitative pesticide-use data are not available for the Denver metropolitan area. Local surveys indicate that 4 herbicides and 4 insecticides commonly are available at lawn and garden stores, and 15 herbicides and 5 insecticides commonly are used by commercial applicators and managers of large urban tracts. Pesticides common among all surveys were the herbicides glyphosate, trifluralin, and 2,4-D and the insecticides carbaryl, chlorpyrifos, and diazinon.

Twenty-eight pesticides were detected during the urban study. Twenty-one of the pesticides were detected in the South Platte River, whereas 25 of the pesticides were detected in Cherry Creek. Nine pesticides accounted for about 80 percent of the detections in each drainage basin, indicating that pesticide use is similar in each basin. Of the nine most commonly detected pesticides, five (carbaryl, chlorpyrifos, DCPA, diazinon, and malathion) commonly are used by homeowners or commercial applicators in urban areas of the South Platte River Basin; three (prometon, simazine, and tebuthiuron) are herbicides generally associated with nonagricultural uses in Colorado and are used for long-term, nonselective weed control; and one (atrazine) has had nonagricultural uses in Colorado limited to roadside and turf application since 1992 when the USEPA accepted voluntary label revisions for many atrazine-containing products.

Pesticide concentrations generally were less than standards and guidelines for drinking water and aquatic life, although the HA for diazinon was exceeded in one sample from Cherry Creek. Aquatic-life criteria were exceeded for carbaryl, diazinon, and chlorpyrifos. Multiple pesticides were detected in all of the samples. The effects of long-term exposure to low concentrations of multiple pesticides on human health and aquatic life are not well understood. Currently, human health and aquatic-life standards are set only for individual compounds. The USEPA is considering establishing health standards for combinations of triazine herbicides and their metabolites.

During the urban study, individual pesticide concentrations were higher in storm-runoff samples than in nonstorm-runoff samples. In the South Platte River, 20 of the 21 pesticides detected had peak concentrations in storm-runoff samples. In Cherry Creek, 21 of the 25 pesticides detected had peak concentrations in storm-runoff samples. The insecticide carbaryl was the dominant pesticide in most of the storm-runoff samples. Carbaryl concentrations in storm-runoff samples generally were 1 to 2 orders of magnitude higher than other pesticide concentrations. DCPA, chlorpyrifos, and malathion generally were detected only during storm-runoff events, indicating that storm runoff is the predominant mechanism for transporting these pesticides to Cherry Creek and the South Platte River at Denver.

The detection of certain pesticides, such as atrazine, carbaryl, diazinon, prometon, and simazine, during dry weather was substantial. Detections during dry weather indicate that mechanisms other than storm runoff transport pesticides to streams. Prometon and simazine most likely are being transported with ground water in the Cherry Creek Basin. Prometon and simazine consistently were detected in dry-weather samples when the outfall from Cherry Creek Lake was dry or when ground water was the predominant source of water in the lower Cherry Creek Basin. Additionally, all of the nondetections of prometon (at both sites) and simazine (at Cherry Creek) occurred in storm-runoff samples. Decreases in stream pesticide concentrations during storms could result from dilution caused by the large percentage of surface runoff sampled during storms.

The percentage of a particular pesticide load in the South Platte River at Denver attributed to Cherry Creek was not consistent. For example, the percentage of carbaryl load at Denver from Cherry Creek on days when carbaryl was detected at both sites on the same day ranged from 1 to 57 percent and correlated poorly with the contribution of streamflow from Cherry Creek. Overall, when detected at both sites on the same day, the distribution of pesticide loads in the South Platte River at Denver that was attributed to Cherry Creek primarily ranged from 7 to 50 percent, with a median value of 21 percent. Compared to the median contribution of streamflow to the South Platte River (12.5 percent), it appears that Cherry Creek contributes proportionally more pesticides than streamflow to the main stem.

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SUPPLEMENTAL DATA

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Table 15. Concentrations and relative percent differences for pesticides detected in duplicate samples

[μg/L, microgram per liter; --, no data; <, less than]

Pesticide	Concentration in duplicates (μg/L)	Relative percent difference	Pesticide	Concentration in duplicates (μg/L)	Relative percent difference	Pesticide	Concentration in duplicates (μg/L)	Relative percent difference	Pesticide	Concentration in duplicates (μg/L)	Relative percent difference
Alachlor	0.008 <0.002	--	Chlorpyrifos	0.007 0.007	0	Diazinon (continued)	0.042 0.035	18	Pendimethalin	<0.004 0.052	--
Atrazine	<0.001 0.014	--		0.035 0.047	29		0.049 0.043	13		0.22 0.39	56
	0.01 0.008	22	Cyanazine	<0.004 0.015	--		0.11 0.12	8.7	Prometon	0.022 0.048	74
	0.032 0.029	9.8		0.37 0.78	71	Diuron	<0.02 0.14	--		0.042 0.039	7.4
	0.058 0.099	52	2,4-D	0.77 0.71	8.1	EPTC	0.003 0.012	120		0.046 0.061	28
	0.053 0.047	12	DCPA	0.006 0.004	40		0.018 0.019	5.4		0.058 0.062	6.7
	0.09 0.14	43		0.052 0.069	28		0.052 0.050	3.9		0.071 0.057	22
Bromoxynil	0.14 0.13	7.4		0.083 0.078	6.2	*gamma*-HCH	<0.004 0.018	--		0.091 0.080	13
Carbaryl	0.022 <0.003	--		0.15 0.16	6.5		0.022 0.021	4.7	Propachlor	0.091 0.079	14
	0.18 0.15	18	Desethyl-atrazine	0.011 0.007	44	Malathion	0.020 0.026	26	Simazine	0.012 0.013	8
	0.34 0.24	34		0.018 0.009	67	Metolachlor	0.014 0.011	24		0.024 0.031	25
	0.68 0.94	32		0.064 0.084	27		0.083 0.13	44		0.033 0.029	13
Carbofuran	0.077 0.14	58	Diazinon	0.018 0.026	36		0.19 0.38	67	Tebuthiuron	0.037 0.026	35
				0.020 0.022	9.5	Metribuzin	<0.004 0.01	--		0.083 0.073	13

Table 16. Mean and standard deviation of pesticide recovery in four field-spiked samples determined by gas chromatography/mass spectrometry

Pesticide	Mean recovery (percent)	Standard deviation (percent)	Pesticide	Mean recovery (percent)	Standard deviation (percent)
Alachlor	126	5.5	Malathion	130	15
Atrazine	113	7.1	Methyl parathion	262	60
Azinphos-methyl	141	7.4	Metolachlor	132	7.2
Benfluralin	113	6.6	Metribuzin	105	10
Butylate	109	9.4	Molinate	102	3.3
Carbaryl	132	7.4	Napropamide	91	3.6
Carbofuran	128	12	Parathion	255	28
Chlorpyrifos	107	13	Pebulate	96	4.5
Cyanazine	136	8.7	Pendimethalin	190	7.2
DCPA	113	6.6	*cis*-Permethrin	27	19
p,p'-DDE	58	3.5	Phorate	33	4.9
Desethylatrazine	44	4.0	Prometon	123	12
Diazinon	104	13	Pronamide	111	9.7
Dieldrin	86	5.4	Propachlor	109	4.2
2,6-Diethylaniline	87	4.4	Propanil	145	3.9
Disulfoton	20	2.7	Propargite	77	19
EPTC	96	4.5	Simazine	113	8.5
Ethalfluralin	136	5.2	Tebuthiuron	101	9.4
Ethoprop	115	5.0	Terbacil	97	14
Fonofos	119	8.7	Terbufos	72	9.1
alpha-HCH	106	8.0	Thiobencarb	128	8.4
gamma-HCH	132	7.8	Triallate	96	4.5
Linuron	147	0.7	Trifluralin	113	5.2

Table 17. Mean and standard deviation of pesticide recovery in 350 laboratory control spike samples determined by high performance liquid chromatography

[Data from Werner and others, 1996]

Pesticide	Mean recovery (percent)	Standard deviation (percent)	Pesticide	Mean recovery (percent)	Standard deviation (percent)
Acifluorfen	83	24	Esfenvalerate	17	21
Aldicarb	61	31	Fenuron	66	29
Aldicarb sulfone	53	22	Fluometuron	78	23
Aldicarb sulfoxide	100	35	MCPA	66	22
Bentazon	75	24	MCPB	39	26
Bromacil	82	23	Methiocarb	59	29
Bromoxynil	74	22	Methomyl	79	26
3-OH-carbofuran	64	30	1-Naphthol	22	26
Chloramben	60	21	Neburon	69	21
Chlorothalonil	11	22	Norflurazon	78	22
Clopyralid	60	29	Oxamyl	56	28
2,4-D	71	22	Oryzalin	68	22
2,4-DB	44	25	Picloram	55	23
Dicamba	64	23	Propham	64	28
Dichlobenil	34	29	Propoxur	76	26
Dichlorprop	73	21	Silvex	73	19
Dinoseb	69	19	2,4,5-T	77	28
Diuron	61	23	Triclopyr	63	24
DNOC	35	25			

Table 18. Comparison of crop acreages in the lower Lonetree Creek Basin, 1991 and 1993

[Source of data: Wagner and Hoffer, 1994]

Crop	1991 acreage	1993 acreage
Alfalfa	14,249	10,925
Corn	22,322	22,532
Sugar beets	4,719	3,735
Pinto beans	4,632	4,042
Onions	1,657	1,514
Winter wheat	11,090	11,847

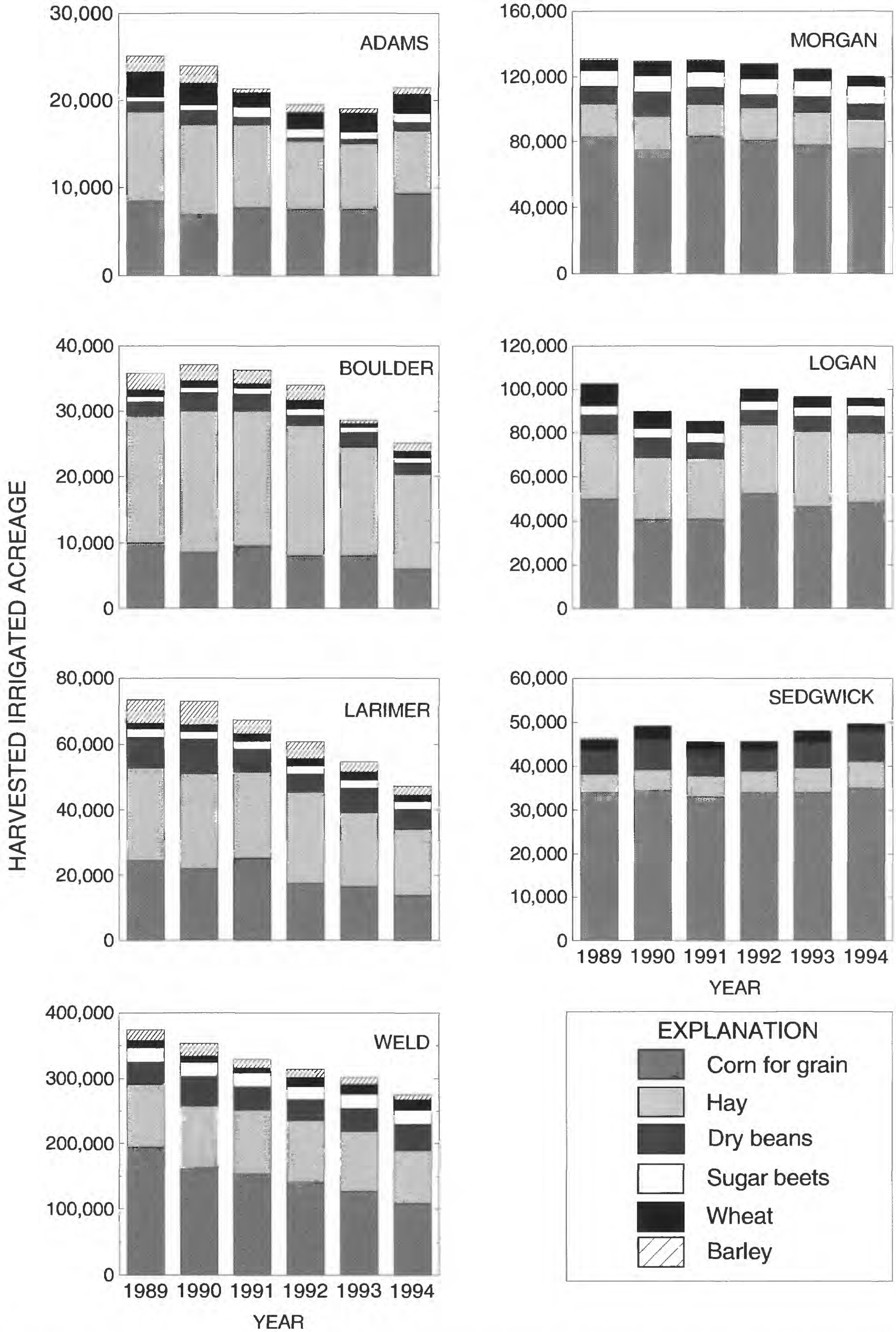

Figure 29. Harvested irrigated acreage for major crops grown in Colorado counties in the South Platte River Basin, 1989–94 (data from Colorado Agricultural Statistics Service, 1995).

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