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Pesticides in Surface Water of the Yakima River Basin, Washington, 1999–2000—Their Occurrence and an Assessment of Factors Affecting Concentrations and Loads

By JAMES C. EBBERT and SANDRA S. EMBREY

Water-Resources Investigations Report 01–4211

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

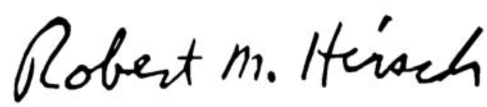
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)
micrograms per liter (µg/L)	1	parts per billion (ppb)
milligrams per liter (mg/L)	1	parts per million (ppm)
cubic feet per second (ft^3/s)	0.02832	cubic meter per second

ABBREVIATIONS

GC/MS gas chromatography/mass spectrometry

DDD dichlorodiphenyldichloroethane

DDE dichlorodiphenyldichloroethylene

DDT dichlorodiphenyltrichloroethane

MDL method detection limit

NAWQA National Water-Quality Assessment Program

USGS U.S. Geological Survey

Pesticides in Surface Water of the Yakima River Basin, Washington, 1999–2000—Their Occurrence and an Assessment of Factors Affecting Concentrations and Loads

By James C. Ebbert *and* Sandra S. Embrey

Abstract

The occurrence, distribution, and transport of pesticides in surface water of the Yakima River Basin were assessed using data collected during 1999–2000 as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. Samples were collected at 34 sites located throughout the basin in August 1999 using a Lagrangian sampling design. Samples also were collected weekly and monthly from May 1999 through January 2000 at three of the sites. This report includes data for 47 pesticide compounds from the analysis of filtered water using ocadecyl (C-18) solid-phase extraction and gas chromatography/mass spectrometry.

A total of 25 pesticide compounds were detected in samples collected during the study. Detection frequencies ranged from about 1 percent for ethalfluralin, ethoprophos, and lindane to 82 percent for atrazine. Maximum concentrations of azinphos-methyl, carbaryl, diazinon, *para,para*'-dichlorodiphenyldichloroethylene (*p,p*'-DDE), and lindane exceeded chronic-toxicity guidelines for the protection of freshwater aquatic life. Twenty pesticide compounds were detected during sampling in August 1999. Atrazine was the most widely detected herbicide, and azinphos-methyl was the most widely detected insecticide. The median number of sites at which a particular pesticide compound was detected was six. Pesticide compounds detected at more than six sites include atrazine, simazine, terbacil, trifluralin, deethylatrazine, azinphos-methyl, carbaryl, diazinon, malathion, and *p,p'*-DDE.

Because many factors affect the transport of pesticides from areas of application to surface water, there was not a simple correspondence between pesticide occurrence and use in the Yakima River Basin. For example, the high detection rates of atrazine, simazine, deethylatrazine, and *p,p'*-DDE are probably related more to their mobility and wide distribution in the hydrologic system than to their usage. Likewise, higher detection frequencies of the insecticides azinphos-methyl and carbaryl compared with chlorpyrifos appear to be related more to differences in their physical and chemical properties than to usage.

The highest detection frequencies and concentrations of pesticides generally occurred during irrigation season, which is from mid-March to mid-October. Pesticides are applied during irrigation season, and runoff of excess irrigation water from fields transports them to surface water.

Ground-water discharges also transport some pesticides to surface water. Atrazine, deethylatrazine, and simazine were frequently detected in samples collected after the irrigation season when there was little or no surface runoff and most of the flow in irrigation drains was derived from ground water.

Daily loads of atrazine, terbacil, azinphos-methyl, and carbaryl discharged to the Yakima

River from inflows between river mile 103.7 and river mile 72 varied widely between sites. For example, East Toppenish Drain discharged over 50 percent of the total load of terbacil to this reach of the Yakima River, but none of the total load of carbaryl and only about 4 percent of the total load of atrazine. Pesticide loads from the wastewater treatment plants were relatively small compared with loads from other inflows because their discharges were small.

Pesticide losses, defined as the ratio of the amount discharged from a basin from May 1999 through January 2000 divided by the amount applied during 1999, were estimated for Moxee and Granger Drains and the Yakima River at Kiona. Losses ranged from less than 0.01 to 1.5 percent of pesticides applied and are comparable to those observed (0.01 to 2.2 percent) in irrigated agricultural basins in the Central Columbia Plateau of Washington State.

INTRODUCTION

In 1986, the Yakima River Basin was selected as one of four surface-water pilot studies as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. Full implementation of the NAWQA Program began in 1991 with the intent to study 60 river basins throughout the Nation on a rotating schedule, with 20 studies beginning in each of the years 1991, 1994, and 1997. Full implementation of the NAWQA study in the Yakima River Basin, which was scheduled to start in 1997, was delayed until 1999. Starting in 1999, surface water throughout the Yakima River Basin was sampled for pesticides and other constituents. Although samples were analyzed for pesticides using up to three different laboratory methods, this report includes only the data from samples collected May 1999 through January 2000 and analyzed for 47 pesticide compounds (table 1) using C-18 solid-phase extraction and gas chromatography/mass spectrometry. A report including all of the pesticide data is planned.

Pesticides are applied in apple orchards to control insects like the coddling moth.

Purpose and Scope

This report describes the occurrence, concentrations, and transport of pesticide compounds in surface water of the Yakima River Basin using results from (1) a basinwide sampling of surface-water sites and wastewater discharges during August 1999, and (2) weekly and monthly sampling of three surface-water sites from May 1999 through January 2000. Specifically, the report discusses the occurrence of pesticides in relation to their usage; the relation between

Pesticide application using drip irrigation.

concentrations and chronic-toxicity criteria for the protection of freshwater aquatic life; the transport of pesticides from tributaries to the Yakima River and then in the river, following a parcel of water as it moved downstream in August 1999; ground water as a source of some pesticides based on seasonal variations in their concentrations; and the amounts of applied pesticides that are transported from drainage basins.

Table 1. Pesticides and pesticide breakdown products analyzed for in surface-water samples collected in the Yakima River Basin, Washington, 1999–2000, using ocadecyl (C-18) solid-phase extraction and gas chromatography/mass spectrometry

[μg/L, micrograms per liter; H, herbicide; I, insecticide; B, breakdown or degradation product]

Pesticide	Trade or common name(s)	Type of pesticide	Chemical Abstract Services registry number	Method detection limit (μg/L)	Chemical class
Acetochlor	Guardian	H	34256-82-1	0.002	acetanilide
Alachlor	Lasso	H	15972-60-8	.002	acetanilide
Atrazine	AAtrex	H	1912-24-9	.001	triazine
Azinphos-methyl[1]	Guthion	I	86-50-0	.001	organophosphorus
Benfluralin	Balan, Benefin	H	1861-40-1	.002	dinitroaniline
Butylate	Sutan +, Genate Plus	H	2008-41-5	.002	thiocarbamate
Carbaryl[1]	Sevin, Savit	I	63-25-2	.003	carbamate
Carbofuran[1]	Furadan	I	1563-66-2	.003	carbamate
Chlorpyrifos	Lorsban, Dursban	I	2921-88-2	.004	organophosphorus
Cyanazine	Bladex	H	21725-46-2	.004	triazine
DCPA	Dacthal	H	1861-32-1	.002	chlorobenzoic acid
p,p'-DDE	none	B	72-55-9	.006	DDT degradate
Deethylatrazine[1] (DEA)	none	B	6190-65-4	.002	atrazine degradate
Diazinon	Diazinon	I	333-41-5	.002	organophosphorus
Dieldrin	Panoram D-31	I	60-57-1	.001	organochlorine
2,6-Diethylanaline	none	B	579-66-8	.003	alachlor degradate
Disulfoton	Di-Syston	I	298-04-4	.017	organophosphorus
EPTC	Eptam, Eradicane	H	759-94-4	.002	thiocarbamate
Ethalfluralin	Sonalan, Curbit EC	H	55283-68-6	.004	dinitroaniline
Ethoprophos	Mocap	I	13194-48-4	.003	organophosphorus
Fonofos	Dyfonate	I	944-22-9	.003	organophosphorus
alpha-HCH	none	I	319-84-6	.002	organochlorine
gamma-HCH	Lindane	I	58-89-9	.004	organochlorine
Linuron	Lorox, Linex	H	330-55-2	.002	urea
Malathion	malathion	I	121-75-5	.005	organophosphorus
Methyl parathion	Penncap-M	I	298-00-0	.006	organophosphorus
Metolachlor	Dual, Pennant	H	51218-45-2	.002	acetanilide
Metribuzin	Lexone, Sencor	H	21087-64-9	.004	triazine
Molinate	Ordram	H	2212-67-1	.004	thiocarbamate
Napropamide	Devrinol	H	15299-99-7	.003	amide
Parathion	several	I	56-38-2	.004	organophosphorus
Pebulate	Tillam	H	1114-71-2	.004	thiocarbamate
Pendimethalin	Prowl, Stomp	H	40487-42-1	.004	dinitroaniline
cis-Permethrin	Ambush, Pounce	I	54774-45-7	.005	pyrethroid
Phorate	Thimet, Rampart	I	298-02-2	.002	organophosphorus
Prometon	Pramitol	H	1610-18-0	.018	triazine
Propyzamide	Kerb	H	23950-58-5	.003	amide
Propachlor	Ramrod	H	1918-16-7	.007	acetanilide
Propanil	Stampede	H	709-98-8	.004	amide
Propargite	Comite, Omite	I	2312-35-8	.013	sulfite ester
Simazine	Aquazine, Princep	H	122-34-9	.005	triazine
Tebuthiuron	Spike	H	34014-18-1	.01	urea
Terbacil[1]	Sinbar	H	5902-51-2	.007	uracil
Terbufos	Counter	I	13071-79-9	.013	organophosphorus
Thiobencarb	Bolero	H	28249-77-6	.002	thiocarbamate
Triallate	Far-Go	H	2303-17-5	.001	thiocarbamate
Trifluralin	Treflan, Trilin	H	1582-09-8	.002	dinitroaniline

[1]Concentrations of these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

Availability of Data Used in This Report

Data used in this report can be obtained from the Yakima River Basin NAWQA Web site at the URL <http://oregon.usgs.gov/yakima>.

Acknowledgments

The authors gratefully acknowledge the individuals and agencies who provided support and assistance to this project. Chris Coffin and Ryan Anderson, Washington State Department of Ecology, provided technical advice and assistance in the field during sample collection. Moses Squeochs and James Thomas, Yakama Indian Nation, worked with the Yakama Indian Nation Council to grant us access to sampling sites and accompanied us during site visits. Bill Rice, Roza Sunnyside Board of Joint Control, helped with selection of sampling sites, installed water-quality monitors, gaged streams, collected samples, and made turbidity measurements. Steve Fanciullo, Bureau of Reclamation, allowed us access to their stream gages and provided streamflow data and advice on the mass balance of water discharges needed for computing constituent loads. Bob Stevens, soil scientist with Washington State University, provided helpful advice on sampling design and provided land-use maps of the Granger Basin, which were used to compute pesticide application rates. Scott Manley, Director of Benton Conservation District, provided water-quality data for Spring and Snipes Creeks and maps showing crops in Benton County, which were used to compute pesticide application rates. Assistance during sample collection was provided by Jennifer Key, student at Central Washington University; Paivikki “Vickie” Pihl, student at Tampere University of Technology,

Clockwise from upper left: reuse of irrigation water by pumping from waterway; and application of irrigation water by wheel-line sprinkler, rill, drip, center-pivot sprinkler, and buried drip line.

Finland; and Brent Morace, USGS volunteer. Wastewater treatment plant operators in Cle Elum, Ellensburg, Granger, Prosser, Selah, Sunnyside, Yakima, and Zillah collected effluent samples during the basinwide sampling. Appreciation is also given to the agencies and individuals listed in Appendix 2 who provided information and helped review the pesticide application data.

The Yakima River near Cle Elum near the headwaters.

YAKIMA RIVER BASIN DESCRIPTION

The Yakima River flows 214.5 miles from the outlet of Keechelus Lake in the central Washington Cascades to the Columbia River, draining an area of 6,155 square miles (fig. 1). Altitude in the basin ranges from 8,184 feet in the Cascade Range to about 340 feet at the Columbia River. The basin contains a variety of landforms, including the glaciated peaks and deep valleys of the Cascade Range, broad river valleys, and the lowlands of the Columbia Plateau. Mean annual precipitation ranges from 140 inches in the Cascade Range to less than 10 inches near the mouth of the basin.

Because the lower valleys are arid during summer, most agricultural land in the basin (fig. 2) is irrigated. Reservoirs in the upper Yakima and Naches River Basins (fig. 1) are used to augment flows for irrigation and instream uses, and reservoir releases provide most of the water used for irrigation during the July-October period, when natural streamflows are lowest and irrigation demand is highest. About 450,000 acres of cropland in the Yakima River Basin are irrigated, and annual surface-water diversions from the Yakima River system for irrigation are equivalent to about 60 percent of the mean annual streamflow leaving the basin. During summer, the quality of agricultural return flows determines the quality of water in the lower Yakima

Yakima River at Umtanum.

Agricultural fields in the Moxee subbasin.

River downstream from the city of Yakima because they contribute as much as 80 to 90 percent of the flow in the lower main stem during irrigation season (Rinella and others, 1999). Additional information about the Yakima River Basin is presented in Rinella and others (1992 and 1999).

PREVIOUS FINDINGS

The Yakima NAWQA pilot study produced a comprehensive assessment of pesticides in surface water, suspended sediment, streambed sediment, soils, and aquatic biota in the Yakima River Basin for the period 1987–91 (Rinella and others, 1999; summarized by Morace and others, 1999). The pilot study showed that the quality of surface water in the Yakima River Basin varied with the gradation in land use and cover from the forested headwaters to agriculture and rangeland in

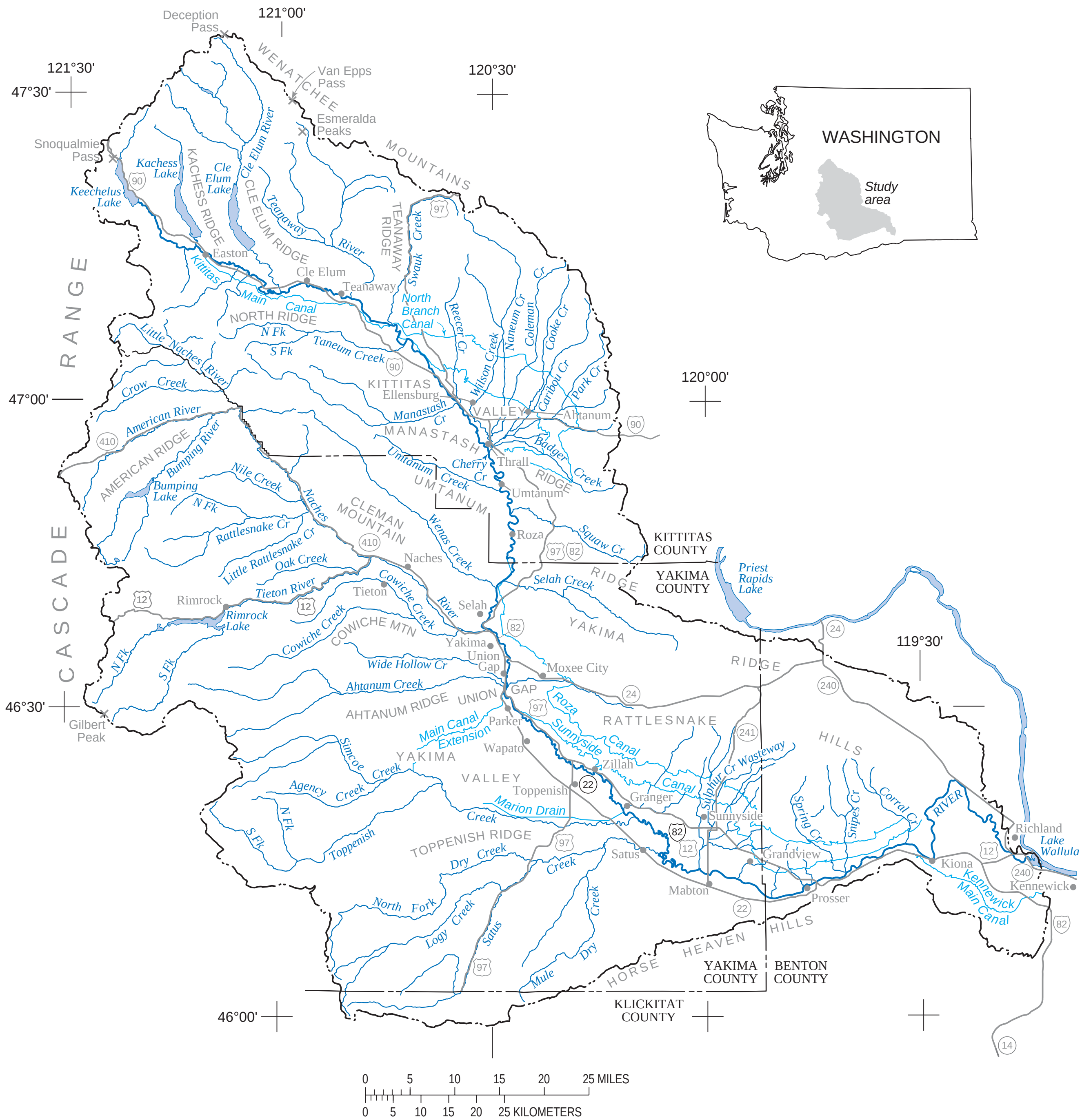


Figure 1. The Yakima River Basin, Washington.

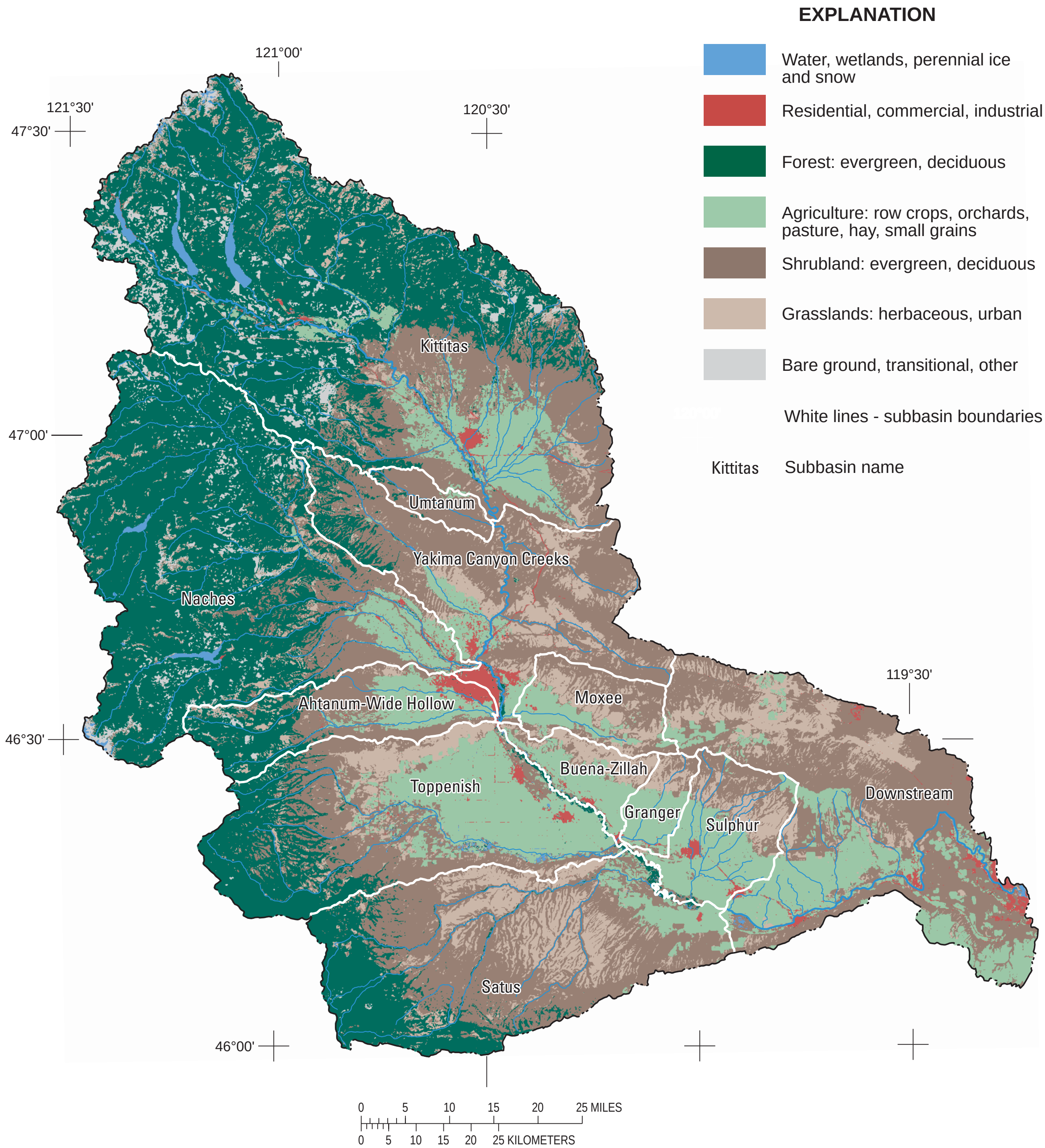


Figure 2. Land use and land cover in the Yakima River Basin, Washington, 1999.

the lower basin (fig. 2). The pilot study divided the Yakima River into three reaches based on changes in water quality influenced by differences in geology and land use. Water quality in the upper reach (fig. 1), which extends from the foot of Keechelus Dam (river mile [RM] 214.5) to just upstream of Umtanum (RM 140.5), was better than water quality in the lower reaches. Compared with lower reaches, few pesticides were detected in the upper reach, concentrations were low, and loads were small.

Water-quality conditions in the middle reach, which extends from RM 140.5 near Umtanum Creek to RM 107.2 just downstream from Union Gap (fig. 1), were similar to those in the lower reach, which extends from RM 107.2 to the mouth of the Yakima River. Water quality in both reaches was degraded by the effects of irrigated agriculture (Morace and others, 1999). Numerous pesticides were found in water of both reaches; however, concentrations of many pesticides increase substantially in the lower reach because irrigation return flows make up a larger percentage of the total flow in the river (Rinella and others, 1999). Although pesticides applied to cropland were a major source of pesticides in surface water in the Yakima River Basin, other sources included applications of pesticides in urban areas, along road rights-of-way, and along channel banks of canals (Rinella and others, 1999).

STUDY DESIGN, METHODS, AND DATA SOURCES

Surface-water sites and wastewater treatment plant discharges throughout the Yakima River Basin (fig. 3, table 2) were sampled August 2–6, 1999 during dry weather at the peak of the irrigation season. Sampling of the Yakima River extended from Cle Elum (RM 182.5) to Kiona (RM 29.9). Other surface-water sites and wastewater treatment plant discharges sampled were distributed along the reach of the Yakima River extending from RM 179.6 near Cle Elum to about RM 42 (fig. 3), but not all of them discharge directly to the Yakima River; some discharge to tributaries of the Yakima River.

To the extent possible, basinwide sampling was timed according to the velocity of water as it moved downstream in the Yakima River. This is sometimes referred to as Lagrangian sampling, which can be visualized as sampling a distinct unit or "parcel" of water

USGS hydrologists cleaning and preparing sampling equipment.

as it moves downstream. The advantage of this design is that it is possible to account for additions and losses of water and pesticide compounds, or any constituent, as the unit moves downstream. Some sites (table 2) were sampled more than once during the basinwide sampling to assess daily variations in concentrations of pesticides and to bracket target sampling times if they were at night.

In addition to the basinwide sampling, the Yakima River at Kiona, Moxee Drain, and Granger Drain (fig. 3, table 2), were sampled at fixed intervals (monthly or more frequently) from May 1999 through January 2000 to assess changes in concentrations of pesticides over a longer time period. Data from these samples also were used to compute loads of pesticides transported during the sampling period.

Field Procedures

Samples representative of the flow in the stream cross section were obtained by collecting depth-integrated subsamples at equally spaced verticals across the stream using either the US DH-81 or US D-77TM sampler as described by Edwards and Glysson (1999) and Shelton (1994). Both samplers hold a 3-liter Teflon sample bottle and all parts of the sampler coming into contact with sample water are constructed of Teflon. Samples of the effluent from wastewater treatment plants were collected directly into 3-liter Teflon bottles. All equipment used to collect and process samples was cleaned with a 0.2-percent nonphosphate,

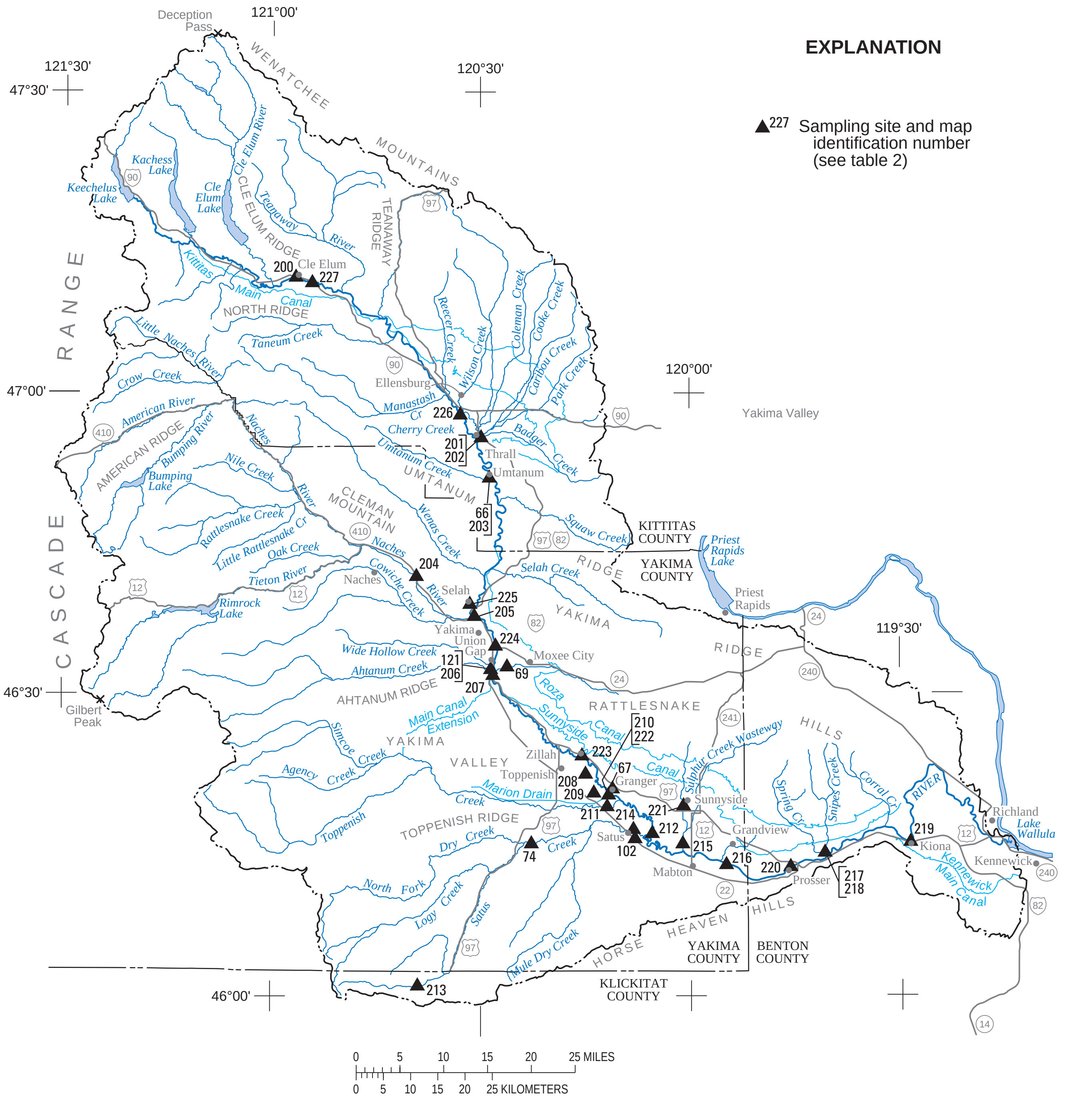


Figure 3. Location of surface-water sites and wastewater treatment plants sampled in the Yakima River Basin, Washington, 1999–2000.

Table 2. Surface-water sites and wastewater treatment plants sampled in the Yakima River Basin, Washington, 1999–2000
[USGS, U.S. Geological Survey; RM, river mile; --, not applicable; WWTP, wastewater treatment plant; abv, above; Cr, creek; WW, wasteway; nr, near; Rd, road; DID, Drainage Improvement District]

Map identi-fication number	USGS site identification number	Sampling site	RM[1]	RM sampled on tributary	Number of samples collected during basinwide sampling August 1999	Number of samples collected May 1999 through January 2000 at fixed sites
200	12479500	Yakima River at Cle Elum	182.5	--	1	--
227	471121120543400	Cle Elum WWTP	179.6	--	1	--
226	465748120325200	Ellensburg WWTP	151.6	--	1	--
201	12484100	Wilson Cr above Cherry Cr at Thrall	147	1.1	1	--
202	12484480	Cherry Cr at Thrall[2]	147	.1	1	--
203	12484500	Yakima River at Umtanum	140.4	--	1	--
66	12484550	Umtanum Cr near mouth at Umtanum	139.8	.1	1	--
225	463856120313000	Selah WWTP	117	--	1	--
204	12496510	Pacific Power and Light Wasteway[3]	116.3	.1	1	--
205	12499000	Naches River nr North Yakima	116.3	.6	1	--
224	463447120275200	Yakima WWTP	111	--	1	--
206	12500445	Wide Hollow Cr near mouth at Union Gap	107.4	.8	1	--
69	12500420	Moxee Drain at Birchfield Road near Union Gap	107.3	1.4	2	25
207	12500450	Yakima River above Ahtanum Creek at Union Gap	107.3	--	1	--
121	12502500	Ahtanum Cr at Union Gap	106.9	.8	1	--
223	462357120153200	Zillah WWTP	89.5	--	1	--
208	12505350	East Toppenish Drain at Wilson Road near Toppenish	86	1.3	1	--
209	12505410	Sub 35 Drain at Parton Road near Granger	83.2	1.7	1	--
222	462013120113700	Granger WWTP	82.8	--	1	--
67	12505450	Granger Drain at Granger	82.8	.8	2	24
210	12505510	Marion Drain at Indian Church Road at Granger	82.6	1.4	1	--
211	12507508	Toppenish Cr at Indian Church Road near Granger	80.4	2.4	1	--
212	12507585	Yakima River at RM 72 above Satus Cr near Sunnyside	72	--	1	--
213	12507595	Satus Cr abv Shinando Cr near Toppenish	69.6	41.3	1	--
74	12508500	Satus Cr below Dry Cr near Toppenish	69.6	15	1	--
214	12508620	Satus Cr at gage at Satus	69.6	2.7	1	--
102	12508630	South Drain near Satus	69.3	1.8	2	--
221	461850120005800	Sunnyside WWTP[4]	61	--	1	--
215	12508850	Sulphur Cr Wasteway nr Sunnyside	61	.8	2	--
216	12509050	Yakima River at Euclid Bridge at RM 55 near Grandview	55	--	1	--
220	461246119454700	Prosser WWTP	47	--	1	--
217	461404119410400	Spring Cr at Hess Road near Prosser	41.8	.4	1	--
218	461414119404200	Snipes Cr below Chandler Canal near Prosser	41.8	.4	1	--
219	12510500	Yakima River at Kiona	29.9	--	3	16

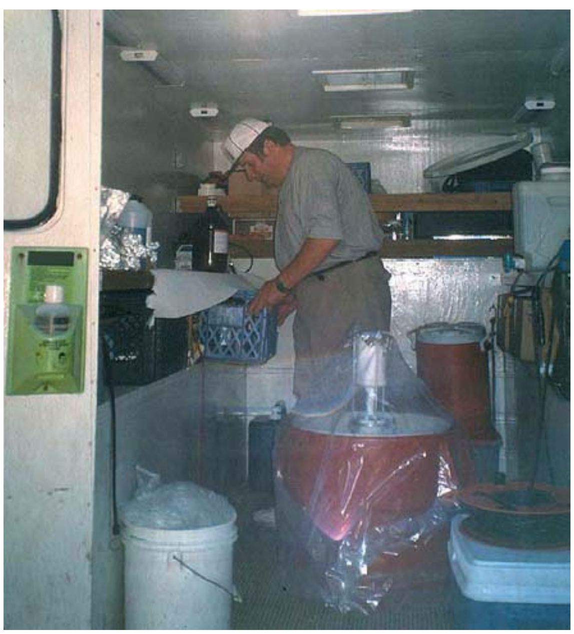
[1]River mile sampled on the Yakima River or where tributary or WWTP discharges to the Yakima River.
[2]Cherry Creek discharges to Wilson Creek at RM 1.1.
[3]Pacific Power & Light Wasteway discharges to the Naches River at RM 0.1.
[4] Sunnyside WWTP discharges to DID 3, which discharges to Sulphur Creek.

detergent, rinsed with deionized water, rinsed with pesticide-grade methanol, wrapped in aluminum foil, and stored in a dust-free environment prior to sample collection (Shelton, 1994).

Because more than 3 liters of water was needed for all types of analyses performed, several Teflon sample bottles were filled at each site. Water from all of the sample bottles was composited and split into aliquots for the various laboratory procedures using a Teflon cone splitter, as described by Shelton (1994). Water required for the pesticide analytes listed in table 1 was filtered through a 0.7 µm (micrometer) pore diameter glass-fiber filter into an amber glass sample bottle, which was shipped on ice to the USGS National Water Quality Laboratory for extraction and analysis.

Laboratory Procedures

Pesticide compounds were extracted from the sample water by pumping it through a polypropylene solid-phase extraction (SPE) cartridge containing porous silica coated with ocadecyl (C-18) phase that is chemically bonded to the surface of the silica (Sandstrom and others, 1992). The adsorbed pesticide compounds then were removed from the SPE cartridge by elution with a mixture of hexane and isopropanol. The extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) (Zaugg and others, 1995; Lindley and others, 1996). Several of the analytes (deethylatrazine, carbofuran, carbaryl, terbacil, and azinphos-methyl) have variable precision and recoveries or variable performance because of limitations in the procedure (Zaugg and others, 1995). The concentrations of these analytes are reported as estimated values because they do not have the statistical accuracy as those of the other target analytes.



Water samples are processed in the field for shipment to the laboratory.

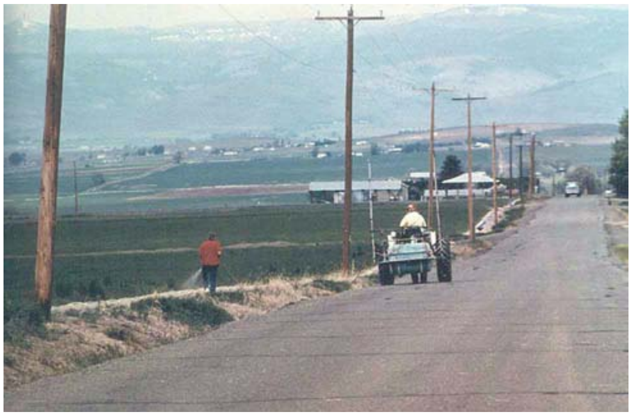
A Teflon cone is used to split water into separate containers for various chemical analyses.

Quality Control

About 23 percent of all samples submitted to the laboratory were quality-control samples, which included field blanks to measure contamination and bias, duplicate samples and duplicate spiked samples to measure variability, and field and laboratory spiked samples to measure recovery of analytes. For a definition of these quality-control techniques, see Shelton (1994). Additionally, quality-control samples were routinely analyzed as part of the laboratory quality-assurance plan described by Pritt and Raese (1995). See Appendix 1 for an evaluation of the quality-control sample results.

Method Used to Compute Pesticide Application Rates

Pesticide application rates, crop data, and other information were used to estimate amounts of pesticides applied during 1999 in the Kittitas Valley, the areas draining to Moxee and Granger Drains, and the Yakima River Basin. These data are presented in a subsequent section of the report assessing pesticide occurrence in relation to use. Although numerous pesticides are used in the Yakima River Basin, this report presents usage data only for the pesticides listed in table 1. All reported uses of these pesticides in the Yakima River Basin were for agricultural purposes, but some are probably used for other purposes. For example, diazinon is used in urban areas and prometon is used in urban areas and along road rights-of-way (U.S. Geological Survey, 1999a).



Herbicide application along a concrete-lined ditch.

Herbicide application by a commercial sprayer prior to planting.

The amount of a pesticide applied during 1999 in the Kittitas Valley or in the three drainage basins was computed as the product of its application rate to a particular crop (in pounds of active ingredient per acre per year), the total acreage of the crop in the valley or drainage basin, and the percentage of the total acreage treated with the pesticide. If the pesticide was applied to more than one crop, then application amounts were summed to obtain the total mass of the pesticide applied in the valley or drainage basin. Sources of data on crop acreages, pesticide application rates, and treatment percentages are listed in Appendix 2.

Insecticide application to an orchard using a fan-spray unit pulled behind a tractor.

Sources of Streamflow and Precipitation Data

Daily streamflow data were available from gaging stations at the three sites sampled at fixed intervals. The gaging station on the Yakima River at Kiona (station 12510500) is operated by the USGS. Data for Moxee Drain at Birchfield Road near Union Gap (station 12500420) were collected in cooperation with the North Yakima Conservation District and the Bureau of Reclamation. Discharge records for the station on Granger Drain at Granger (station 12505450) were provided by the Sunnyside Valley Irrigation District and reviewed by the USGS.

Daily precipitation data from National Weather Service data-collection sites were obtained from monthly publications of climatological data by the National Oceanic and Atmospheric Administration (NOAA)/National Climatic Data Center (National Oceanic and Atmospheric Administration, 1999 and 2000). For Yakima River at Kiona, the weather site at Richland was the primary source of precipitation data, with data from weather sites Prosser or Smyrna used for estimating brief periods of missing data at the Richland site. For Granger Drain, the weather site at Sunnyside was the primary source of precipitation data, with data from Wapato and Yakima Airport used for missing data at the Sunnyside site. For Moxee Drain, the weather site at Moxee City was the primary source of data, with precipitation data from Yakima Airport used for estimating missing data at Moxee City.

PESTICIDE OCCURRENCE AND DISTRIBUTION

Twenty-five pesticide compounds were detected during basinwide and fixed-interval sampling (table 3). Detection frequencies ranged from about 1 percent for ethalfluralin, ethoprophos, and lindane to 82 percent for atrazine. Numbers of detections shown in table 3 are based on the method detection limit (MDL) for each compound (table 1) and are not standardized to a common reporting level. (An MDL is the minimum concentration of a substance that can be identified, measured, and reported with a 99-percent confidence that the compound concentration is greater than zero.) Detection frequencies based on MDLs provide optimum information for each compound, but can introduce bias when comparing detection frequencies of compounds with different MDLs.

Maximum concentrations of azinphos-methyl, carbaryl, diazinon, lindane, and *p,p*'-DDE exceeded U.S. Environmental Protection Agency chronic-toxicity guidelines for the protection of aquatic life. The guideline for *p,p*'-DDE was exceeded in 90 percent of samples, but it should be noted that most of the reported concentrations of *p,p*'-DDE were below the MDL, and

Table 3. Summary statistics of concentrations and comparisons of concentrations to chronic-toxicity guidelines for the protection of aquatic life for pesticides detected during basinwide and fixed-interval sampling, Yakima River Basin, Washington, May 1999 through January 2000

[All concentrations are in micrograms per liter; H, herbicide; D, degradation product; I, insecticide; <, less than; E, estimated; bolded if concentration exceeds chronic aquatic-life criterion; MDL, method detection limit]

Pesticide	Type of pesticide	MDL	Number of samples	Number of detections	Minimum concen-tration	Concentration at indicated percentile[1] 10	25	50	75	90	Maximum concen-tration	Chronic-toxicity aquatic-life guideline[2]
Atrazine	H	0.001	98	80	<0.001	0.002	0.005	0.009	0.016	0.034	0.154	1.8
Deethylatrazine[3]	D	.002	98	70	<.002	.002	.003	.006	.011	.016	.037	None
Carbaryl[3]	I	.003	98	66	<.003	<.003	<.003	.008	.034	.097	**E 4.8**	.2
Azinphos-methyl[3]	I	.001	98	64	<.001	.003	.006	**.014**	**.037**	**.078**	**.523**	.01
Simazine	H	.005	98	53	<.005	<.005	<.005	.005	.008	.015	.226	10
p,p'-DDE[4]	D	.006	98	48	<.006	**E .001**	**E .002**	**E .002**	**E .003**	**E .004**	**.009**	.001
Terbacil [3]	H	.007	98	40	<.007	<.007	<.007	.007	.017	.046	.448	None
Trifluralin	H	.002	98	33	<.002	<.002	<.002	.002	.004	.014	.086	.2
Malathion	I	.005	98	26	<.005	<.005	<.005	<.005	.006	.008	.037	.1
Diazinon	I	.002	98	16	<.002	<.002	<.002	<.002	<.002	.013	**.169**	.08
EPTC	H	.002	98	16	<.002	<.002	<.002	<.002	<.002	.005	.026	None
Prometon	H	.018	98	15	<.018	<.018	<.018	<.018	<.018	<.018	.05	None
Acetochlor	H	.002	98	13	<.002	<.002	<.002	<.002	.002	.012	.13	None
Metolachlor	H	.002	98	13	<.002	<.002	<.002	.002	.002	.003	.009	7.8
Chlorpyrifos	I	.004	98	11	<.004	<.004	<.004	<.004	<.004	.004	.007	.041
Alachlor	H	.002	98	9	<.002	<.002	<.002	<.002	<.002	.002	.044	None
Tebuthiuron	H	.01	98	5	<.01	<.01	<.01	<.01	<.01	.01	.014	1.6
Disulfoton	I	.017	98	4	<.017	<.017	<.017	<.017	<.017	<.017	E 3.3	None
Propargite	I	.013	98	3	<.013	<.013	<.013	<.013	<.013	<.013	E .04	None
Cyanazine	H	.004	98	2	<.004	<.004	<.004	<.004	<.004	<.004	E .004	2
Dieldrin	I	.001	98	2	<.001	<.001	<.001	<.001	<.001	<.001	.004	.056
Pendimethalin	H	.004	98	2	<.004	<.004	<.004	<.004	<.004	<.004	.011	None
Ethalfluralin	H	.004	98	1	<.004	<.004	<.004	<.004	<.004	<.004	E .004	None
Ethoprophos	I	.003	98	1	<.003	<.003	<.003	<.003	<.003	<.003	.017	None
Lindane	I	.004	98	1	<.004	<.004	<.004	<.004	<.004	<.004	**.029**	.01

[1]Estimated concentrations below the MDL were counted as detections for computing percentiles.

[2]U.S. Geological Survey (1999b); State of Washington (1997) for *p,p*'-DDE.

[3]Concentrations of these pesticides are qualitatively identified and reported as estimated values (Zaugg and others, 1995).

[4]Estimated concentrations of *p,p*'-DDE below the MDL are listed because the aquatic-life guideline is below the MDL. The true minimum concentration of *p,p*'-DDE is unknown, so it is reported as less than the MDL.

therefore are estimated values (table 3). Also, there may be a positive bias in concentrations of *p,p*'-DDE as indicated by detections in blank samples (see Appendix 1). Because DDE was the only DDT-related compound included in GC/MS laboratory method, it should not be assumed that reported DDE concentrations represent the sum of concentrations of all DDT-related compounds.

Concentrations of azinphos-methyl exceeded its chronic-toxicity guideline for the protection of aquatic life in 50 percent of samples, and the concentration of lindane, detected in one sample of wastewater treatment plant effluent, exceeded its chronic-toxicity guideline. Because the summary statistics are based on concentrations in samples collected during both basinwide and fixed-interval sampling, they are more indicative of conditions in the middle and lower reaches of the river where the fixed-interval sampling sites were located. Results from the basinwide sampling, presented in the next section, provide a less biased comparison of detection frequencies along all reaches of the river.

Cherry Creek at Thrall looking downstream.

Pesticides Detected during Basinwide Sampling, August 1999

Twenty pesticide compounds were detected during basinwide sampling at 34 sites in August 1999 (table 4). Disulfoton, propargite, pendimethalin, ethalfluralin, and ethoprophos, which were detected at fixed-interval sampling sites (table 3), were not detected during basinwide sampling. The number of basinwide sampling sites at which a particular pesticide compound was detected ranged from 1 to 21, or from about 3 to 62 percent of the sites (table 4). Detection frequencies of individual compounds were lower in samples collected during basinwide sampling compared with fixed-interval sampling because some of the sampling sites were not in agricultural areas.

Atrazine was the most widely detected herbicide, and azinphos-methyl was the most widely detected insecticide. The median number of sites at which a particular pesticide compound was detected was six. Pesticide compounds detected at more than six sites include the herbicides atrazine, simazine, terbacil, and trifluralin; deethylatrazine, a breakdown product of atrazine; the insecticides azinphos-methyl, carbaryl, diazinon, and malathion; and *p,p*'-DDE, a breakdown product of DDT.

Five sites were sampled more than one time during basinwide sampling to assess variations in concentrations of pesticides on a time scale of 1 day or less. Because concentrations were often close to MDLs, small variations in concentrations can cause reported values to cross detection thresholds (table 5). For example, of the pesticides detected in three samples collected August 5–6 from the Yakima River at Kiona, none was detected in the sample collected closest to the time-of-travel target time as determined by the Lagrangian sampling design (see Methods).

Granger Drain at Granger looking upstream.

Pesticide Occurrence in Relation to Use

As shown in tables 6–9, there is not a general correspondence between pesticide occurrence and use at locations in the Yakima River Basin. Except for the Kittitas Valley (table 6) where detections are based on one sample each from Cherry Creek, Wilson Creek, and Yakima River at Umtanum, detections at other

Table 4. Pesticides detected during basinwide sampling, Yakima River Basin, Washington, August 1999
[RM, river mile: --, not detected; WWTP, wastewater treatment plant; X, pesticide detected; Cr, Creek; DID, Drainage Improvement District]

					Herbicides and breakdown products												Insecticides and breakdown products							
Sampling site	**RM[1]**	**RM sampled on tributary**	**Number of samples**	**Number of pesticides detected**	**Atrazine**	**Deethylatrazine**	**Simazine**	**Terbacil**	**Trifluralin**	**EPTC**	**Prometon**	**Metolachlor**	**Acetochlor**	**Alachlor**	**Cyanazine**	**Tebuthiuron**	**Carbaryl**	**Azinphos-methyl**	***p,p'*-DDE**	**Malathion**	**Diazinon**	**Chlorpyrifos**	**Dieldrin**	**Lindane**
Yakima River at Cle Elum	182.5	--	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Cle Elum WWTP	179.6	--	1	3	--	--	--	--	--	--	X	--	-	--	--	X	--	--	--	--	X	--	--	--
Ellensburg WWTP	151.6	--	1	6	X	--	X	--	--	--	X	X	--	--	--	--	X	--	--	--	X	--	--	--
Cherry Creek[2]	147	0.1	1	7	X	X	X	X	--	X	--	--	--	--	--	--	X	X	--	--	--	--	--	--
Wilson Creek	147	1.1	1	5	X	X	--	X	--	--	X	--	--	--	--	--	X	--	--	--	--	--	--	--
Yakima River at Umtanum	140.4	--	1	3	X	X	--	X	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Umtanum Creek at Umtanum	139.8	.1	1	1	--	--	--	--	--	X	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Selah WWTP	117	--	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Pacific Power & Light[3]	116.3	.1	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Naches River	116.3	.6	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Yakima WWTP	111	--	1	3	--	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	X	--	--	--
Wide Hollow Cr at Union Gap	107.4	.8	1	6	X	X	X	--	--	--	X	--	--	--	--	--	--	X	X	--	--	--	--	--
Moxee Drain	107.3	1.4	2	7	X	X	X	X	X	--	--	--	--	--	--	--	--	X	X	--	--	--	--	--
Yakima River at Union Gap	107.3	--	1	2	X	--	--	--	--	--	--	--	--	--	--	--	--	X	--	--	--	--	--	--
Ahtanum Cr at Union Gap	106.9	.8	1	2	--	--	--	--	--	--	--	--	---	--	--	--	--	X	--	--	X	--	--	--
Zillah WWTP	89.5	--	1	5	X	--	X	--	--	--	--	--	--	--	--	--	X	X	--	--	X	--	--	--
East Toppenish Drain	86	1.3	1	4	X	X	--	X	--	--	--	--	--	--	--	--	--	X	--	--	--	--	--	--
Sub 35 Drain at Parton Road	83.2	1.7	1	12	X	X	--	X	X	X	X	X	--	--	--	--	X	X	X	X	--	X	--	--
Granger WWTP	82.8	--	1	8	X	X	--	--	--	--	--	--	--	X	--	--	X	X	--	X	X	--	--	X
Granger Drain at Granger	82.8	.8	2	12	X	X	X	X	X	--	--	--	X	--	--	--	X	X	X	X	X	--	X	--

Table 4. Pesticides detected during basinwide sampling, Yakima River Basin, Washington, August 1999—Continued
[RM, river mile: --, not detected; WWTP, wastewater treatment plant; X, pesticide detected; Cr, Creek; DID, Drainage Improvement District]

Sampling site	RM[1]	RM sampled on tributary	Number of samples	Number of pesticides detected	Herbicides and breakdown products												Insecticides and breakdown products							
					Atrazine	Deethylatrazine	Simazine	Terbacil	Trifluralin	EPTC	Prometon	Metolachlor	Acetochlor	Alachlor	Cyanazine	Tebuthiuron	Carbaryl	Azinphos-methyl	*p,p'*-DDE	Malathion	Diazinon	Chlorpyrifos	Dieldrin	Lindane
Marion Drain at Granger	82.6	1.4	1	9	X	X	X	X	X	--	--	X	--	--	--	--	X	X	--	X	--	--	--	--
Toppenish Creek near Granger	80.4	2.4	1	9	X	X	X	X	X	--	--	X	--	--	--	--	X	X	--	X	--	--	--	--
Yakima River at RM 72	72	--	1	1	--	--	--	--	--	--	--	--	--	--	--	--	X	--	--	--	--	--	--	--
Satus Cr above Shinando Creek	69.6	41.3	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Satus Cr below Dry Creek	69.6	15	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Satus Cr at Satus	69.6	2.7	1	11	X	X	X	X	X	X	--	X	--	X	--	--	X	X	--	X	--	--	--	--
South Drain near Satus	69.3	1.8	2	12	X	X	X	X	--	X	--	X	--	X	X	--	X	X	X	X	--	--	--	--
Sunnyside WWTP[4]	61	--	1	3	--	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	X	--	--	--
Sulphur Cr Wasteway	61	.8	2	12	X	X	X	X	X	X	--	--	--	--	--	--	X	X	X	X	--	X	X	--
Yakima River at Euclid Bridge	55	--	1	9	X	X	X	X	X	--	--	--	--	--	--	--	X	X	X	X	--	--	--	--
Prosser WWTP	47	--	1	3	--	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	X	--	--	--
Spring Creek at Hess Road	41.8	.4	1	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Snipes Creek below Chandler Canal	41.8	.4	1	1	--	--	--	--	--	--	--	--	--	--	--	--	--	X	--	--	--	--	--	--
Yakima River at Kiona	29.9	--	3	6	X	X	X	X	--	--	--	--	--	--	--	--	X	X	--	--	--	--	--	--
Percentage of sites where pesticide was detected					55.9	47.1	38.2	41.2	23.5	17.6	14.7	17.6	2.9	8.8	2.9	2.9	52.9	61.8	20.6	26.5	26.5	5.9	5.9	2.9

[1]River mile sampled on the Yakima River or where tributary or WWTP discharges to the Yakima River.
[2]Cherry Creek discharges to Wilson Creek at RM 1.1.
[3]Pacific Power & Light Wasteway discharges to the Naches River at RM 0.1.
[4]Sunnyside WWTP discharges to DID 3, which discharges to Sulphur Creek.

Table 5. Short-term variations in concentrations of pesticides detected during basinwide sampling, Yakima River Basin, Washington, August 1999
[All concentrations in micrograms per liter; bolded time is the time closest to time-of-travel target time; --, not detected; <, less than; E, estimated concentration]

Sampling site	Date sampled	Time sampled	Herbicides and breakdown products										Insecticides and breakdown products						
			Atrazine	Deethylatrazine	Simazine	Terbacil	Trifluralin	EPTC	Metolachlor	Acetochlor	Alachlor	Cyanazine	Carbaryl	Azinphos-methyl	*p,p'*-DDE	Malathion	Diazinon	Chlorpyrifos	Dieldrin
Moxee Drain	8/3/99	**7:40 AM**	0.008	E0.006	0.005	E0.017	E0.004	--	--	--	--	--	--	E0.034	E0.002	--	--	--	--
	8/3/99	7:40 PM	.007	E.005	<.005	<.007	<.002	--	--	--	--	--	--	E.063	E.003	--	--	--	--
Granger Drain	8/3/99	5:30 PM	.036	E.017	.008	E.035	.013	--	--	0.012	--	--	E0.375	E.034	E.005	0.013	0.004	--	0.004
	8/4/99	**7:40 AM**	.027	E.014	.006	E.024	.014	--	--	.006	--	--	E.192	E.013	E.003	.005	<.002	--	<.001
South Drain near Satus	8/499	**5:50 PM**	.030	E.021	.011	E.058	--	E0.002	E0.002	--	0.007	<0.004	E.037	E.009	0.009	<.005	--	--	--
	8/5/99	10:50 AM	.023	E.020	.010	E.1	--	<.002	E.004	--	.006	E.003	E.162	E.011	E.003	.005	--	--	--
Sulphur Creek Wasteway	8/4/99	**6:10 PM**	.016	E.011	.006	E.012	E.002	--	--	--	--	--	E.022	E.026	E.001	.007	--	E0.004	E.003
	8/5/99	2:20 PM	<.01	E.016	<.005	<.007	<.002	--	--	--	--	--	E.030	<.2	<.006	.015	--	<.004	<.002
Yakima River at Kiona	8/5/99	5:40 PM	.016	E.011	<.005	<.007	--	--	--	--	--	--	<.003	<.001	--	--	--	--	--
	8/6/99	**10:30 AM**	<.02	<.01	<.005	<.007	--	--	--	--	--	--	<.003	<.001	--	--	--	--	--
	8/6/99	3:10 PM	.013	E.010	.008	E.045	--	--	--	--	--	--	E.016	E.014	--	--	--	--	--

Table 6. Estimates of agricultural pesticide usage in the Kittitas Valley, Washington, during 1999 and detections in surface waters, August 1999

[Usage data are only for the pesticides listed in table 1; I, insecticide; H, herbicide; %, percent; detections are based on one sample each from Cherry Creek, Wilson Creek, and Yakima River at Umtanum; percentages for usage may not total to 100 because of rounding]

Pesticide	Type	Amount of active ingredient applied (pounds)	Detected in basin	Primary uses
Azinphos-methyl	I	6,700	yes	Apples 89%, other tree fruit 10%, potato 1%
Malathion	I	6,700	no	Timothy hay 78%, beef 14%, apples 3%, alfalfa 3%, other tree fruit 2%
EPTC	H	5,000	yes	Sweet corn 45%, alfalfa 39%, potato 16%
Metribuzin	H	3,200	no	Alfalfa 90%, potato 7%, other 3%
Chlorpyrifos	I	3,200	no	Apples 85%, other tree fruit 11%, cattle 3%, mint 1%
Carbaryl	I	2,800	yes	Apples 68%, other tree fruit 25%, cattle 6%, potato 1%
Terbacil	H	1,400	yes	Alfalfa 85%, mint 15%
Metolachlor	H	1,300	no	Sweet corn 98%, potato 2%
Alachlor	H	1,200	no	Sweet corn 100%
Atrazine	H	600	yes	Sweet corn 90%, pasture 10%
Ethoprophos	I	570	no	Potato 100%
Phorate	I	540	no	Potato 100%
Carbofuran	I	530	no	Potato 43%, other 32%, alfalfa 25%
Methyl parathion	I	290	no	Apples 62%, sweet corn 33%, alfalfa 3%, winter wheat 2%
Pendimethalin	H	270	no	Mint 100%
Diazinon	I	250	no	Cattle 80%, apples 12%, other tree fruit 6%
Trifluralin	H	100	no	Potato 90%, mint 10%
Cyanazine	H	46	no	Sweet corn 100%
Propargite	I	45	no	Mint 100%
Fonofos	I	38	no	Sweet corn 100%
Terbufos	I	34	no	Sweet corn 100%
Lindane	I	4	no	Cattle 100%
Disulfoton	I	1	no	Winter wheat 100%
Also detected: deethylatrazine, prometon, simazine				

locations (tables 7–9) are based on multiple samples collected from May 1999 through January 2000. For the sites with multiple samples, detection frequencies are shown in the tables.

The potential for transport of pesticides from areas of application to surface water is a combined function of the properties of the pesticide, soil properties, slope, climate, and management factors (Goss, 1992). Detection of a pesticide is also influenced by the relation between time of application and time of sample collection, but the probability of not detecting a pesticide because of incorrect sample timing is minimized when multiple samples are collected over time as was done at Moxee Drain, Granger Drain, and Yakima River at Kiona.

Although factors affecting the detection frequencies of all of the pesticides listed in tables 7–9 will not be examined in this report, it is of interest to consider some of them. For example, the high rates of detection

USGS hydrologists collect samples from a cableway across the Yakima River at Kiona.

of the triazine herbicides atrazine and simazine, which were used in relatively small amounts in 1999; deethylatrazine, a breakdown product of atrazine; and *p,p'*-DDE, a breakdown product of DDT, are related to their wide distribution in the hydrologic system, including ground water. The importance of ground water as a source of some of these compounds in surface water was demonstrated in irrigated areas of the Central

Sediment is transported from a field to a drain leading to Sulphur Creek Wasteway.

The Wapato Canal diversion on the Yakima River downstream from Union Gap.

Columbia Plateau where median concentrations of atrazine, simazine, and deethylatrazine were similar in shallow ground water, samples from subsurface field drains, and base-flow samples collected from agricultural drains and wasteways (Williamson and others, 1998). Additional evidence that these compounds are transported from ground water to surface water is provided

Table 7. Estimates of agricultural pesticide usage in the Moxee Drainage Basin, Washington, during 1999 and pesticide detections in Moxee Drain, Washington, May 1999 through January 2000

[Usage data are only for the pesticides listed in table 1; I, insecticide; H, herbicide; %, percent; detection rates are based on 25 samples collected from Moxee Drain; percentages for usage may not total to 100 because of rounding]

Pesticide	Type	Amount of active ingredient applied (pounds)	Percent detections	Primary uses
Azinphos-methyl	I	18,500	72	Apples 100%
Propargite	I	13,600	8	Hops 100%
Chlorpyrifos	I	8,400	8	Apples 100%
Carbaryl	I	5,900	48	Apples 100%
Diazinon	I	1,900	4	Hops 94%, apples 6%
Malathion	I	750	8	Apples 95%, alfalfa 5%
Metribuzin	H	600	0	Alfalfa 100%
Methyl parathion	I	550	0	Apples 99%, sweet corn 1%
EPTC	H	480	8	Alfalfa 84%, sweet corn 16%
Trifluralin	H	260	12	Hops 96%, sweet corn 2%, peas and beans 2%
Simazine	H	260	40	Apples 94%, juice grapes 6%
Terbacil	H	240	20	Alfalfa 100%
Metolachlor	H	140	0	Peas and beans 68%, sweet corn 32%
Alachlor	H	67	0	Sweet corn 60%, peas and beans 40%
Atrazine	H	36	96	Sweet corn 58%, peas and beans 42%
Carbofuran	I	29	0	Alfalfa 94%, sweet corn 6%
Triallate	H	17	0	Peas and beans 100%
Pendimethalin	H	10	0	Peas and beans 100%
Ethalfluralin	H	4	0	Peas and beans 100%
Cyanazine	H	2	0	Sweet corn 100%
Fonofos	I	1	0	Sweet corn 100%
Also detected: deethylatrazine 72%, *p,p'*-DDE 64%, prometon 32%, tebuthiuron 4%				

Table 8. Estimates of agricultural pesticide usage in the Granger Drainage Basin, Washington, during 1999 and pesticide detections in Granger Drain, Washington, May 1999 through January 2000

[Usage data are only for pesticides listed in table 1; I, insecticide; H, herbicide; %, percent; detection rates are based on 24 samples collected from Granger Drain; percentages for usage may not total to 100 because of rounding]

Pesticide	Type	Amount of active ingredient applied (pounds)	Percent detections	Primary uses
Disulfoton	I	6,100	17	Asparagus 100%
Azinphos-methyl	I	4,900	79	Apples 100%
Chlorpyrifos	I	2,700	21	Apples 82%, corn silage 10%, juice grapes 8%
Carbaryl	I	2,200	100	Apples 69%,asparagus 30%, juice grapes 1%
EPTC	H	2,200	21	Corn silage 93%, alfalfa 7%
Metolachlor	H	1,400	4.2	Corn silage 81%, peas and beans 19%
Acetachlor	H	1,200	54	Corn silage 100%
Alachlor	H	1,100	13	Corn silage 93%, peas and beans 7%
Propargite	I	660	4.2	Hops 98%, mint 2%
Trifluralin	H	610	88	Asparagus 90%, juice grapes 5%, misc. 3%, hops 2%
Metribuzin	H	580	0	Asparagus 58%, alfalfa 42%
Malathion	I	570	38	Asparagus 49%, apples 33%, feedlot 15%, alfalfa 3%
Simazine	H	500	83	Asparagus 59%, juice grapes 28%, apples 13%
Atrazine	H	490	100	Corn silage 98%, pasture 2%
Linuron	H	320	0	Asparagus 100%
Butylate	H	170	0	Corn silage 100%
Methyl parathion	I	160	0	Apples 91%, corn silage 7%, winter wheat 2%
Terbacil	H	150	54	Alfalfa 65%, mint 35%
Diazinon	I	150	25	Hops 59%, apples 19%, feedlot 12%
Pendimethalin	H	92	8.3	Mint 71%, peas and beans 29%
Fonofos	I	68	0	Asparagus 64%, corn silage 36%
Triallate	H	48	0	Peas and beans 100%
Cyanazine	H	41	4.2	Corn silage 100%
Carbofuran	I	32	0	Corn silage 66%, alfalfa 34%
Phorate	I	20	0	Corn silage 100%
Ethalfluralin	H	10	4.2	Peas and beans 100%

Also detected: deethylatrazine 100%, dieldrin 4.2%, ethoprophos 4.2%, *p,p'*-DDE 96%, tebuthiuron 8.3%

in the next section of this report where variations of concentrations at fixed sampling sites are discussed.

Detection frequencies for the insecticides azinphos-methyl, carbaryl, and chlorpyrifos provide an example of how pesticide properties may affect detection frequencies. Although all three insecticides were used in relatively large amounts, chlorpyrifos was detected less frequently (tables 7–9). This may be because it has a lower dissolved runoff potential, which is based on the half-life of a compound, its solubility, and its affinity to sorb to soils and sediment (Goss, 1992; Larson and others, 1997). More soluble compounds with longer half-lives have a higher runoff potential than less soluble compounds with shorter half-lives.

Pump station near drain at Snipes Road.

Table 9. Estimates of agricultural pesticide usage in the Yakima River Basin, Washington, during 1999 and detection rates of the pesticides in Yakima River at Kiona, Washington, May 1999 through January 2000

[Usage data are only for pesticides listed in table 1; I, insecticide; H, herbicide; %, percent;detection rates are based on 16 samples collected from Yakima River at Kiona; percentages for usage may not total to 100 because of rounding]

Pesticide	Type	Amount of active ingredient applied (pounds)	Percent detections	Primary uses
Azinphos-methyl	I	294,600	50	Apples 88%, pears 7%, cherries 4%
Chlorpyrifos	I	162,900	12	Apples 73%, cherries 11%, pears 8%
Carbaryl	I	116,200	75	Apples 71%, cherries 19%, asparagus 4%, pears 3%
Propargite	I	49,900	0	Hops 95%, wine grapes 3%, mint 2%
Malathion	I	43,400	38	Cherries 48%, apples 23%, timothy hay 12%, cattle 6%, asparagus 4%
EPTC	H	39,900	19	Corn grain 30%, alfalfa 26%, sweet corn 23%, corn silage 12%
Disulfoton	I	39,000	0	Asparagus 100%
Metolachlor	H	20,200	31	Corn grain 32%, sweet silage 27%, sweet corn 25%, peas and beans 14%
Metribuzin	H	18,900	0	Alfalfa 84%, asparagus 11%, other nonorchard 9%, potatoes 5%
Alachlor	H	16,600	12	Corn grain 36%, corn silage 31%, sweet corn 28%, peas and beans 5%
Carbofuran	I	12,700	0	Wine grapes 83%, other nonorchard 22%, potatoes 8%, alfalfa 6%
Diazinon	I	12,000	6	Hops 52%, pears 17%, apples 12%, cherries 12%, cattle 5%
Terbacil	H	11,500	62	Alfalfa 55%, mint 45%
Simazine	H	8,400	69	Juice grapes 30%, asparagus 28%, pears 28%, wine grapes 13%
Methyl parathion	I	8,400	0	Apples 92%, sweet corn 5%
Atrazine	H	7,600	94	Corn grain 36%, corn silage 31%, sweet corn 29%, pasture 3%
Pendimethalin	H	7,000	0	Mint 96%, peas and beans 4%
Acetachlor	H	6,200	0	Corn silage 95%, corn grain 5%
Trifluralin	H	5,700	19	Asparagus 61%, hops 15%, juice grapes 9%, potatoes 7%, mint 4%
Phorate	I	2,500	0	Potatoes 92%, corn grain 5%, corn silage 4%
Ethoprophos	I	2,500	0	Potatoes 100%
Linuron	H	2,100	0	Asparagus 100%
Terbufos	I	2,000	0	Corn grain 50%, corn silage 43%, sweet corn 7%
Butylate	H	1,900	0	Corn grain 54%, corn silage 46%
Cyanazine	H	1,600	0	Corn silage 74%, corn grain 15%, sweet corn 11%
Fonofos	I	700	0	Asparagus 41%, sweet corn 22%, corn grain 20%, corn silage 17%
Triallate	H	520	0	Peas and beans 100%
Ethalfluralin	H	110	0	Peas and beans 100%
Lindane	I	10	0	Cattle 100%

Also detected: deethylatrazine 81%, *p,p'*-DDE 19%, prometon 6%, tebuthiuron 6%

As mentioned previously, MDLs probably affected observed detection frequencies. Disulfoton, for example, was used in relatively large amounts in the Granger and Yakima River Basins, but was not detected as frequently as some of the other compounds with similar usage rates (tables 8 and 9). The MDL for disulfoton (0.017 µg/L [microgram per liter]) is among the highest of the compounds analyzed for in samples collected during this study (table 1).

Variations in Concentrations of Pesticides at Fixed Sampling Sites

In samples collected from surface-water sites in the Yakima River Basin during 1987–91, Rinella and others (1999) observed that temporal variations in concentrations of atrazine, deethylatrazine, DDE, and simazine were similar. The highest concentrations generally occurred in June and July near or during the peak of the irrigation season, which is from about mid-March to mid-October, and during storm runoff from agricultural land. For atrazine, the temporal pattern was slightly offset from the June-July pattern, with highest concentrations occurring in March, May, and June. Variations in temporal patterns of pesticide concentrations were attributed to differences in the time and frequency of pesticide applications, hydrologic connection to streams, and other physical, chemical, and biological characteristics of the compounds and the soils (Rinella and others, 1999).

Similar to the 1987–91 study, the highest detection frequencies and concentrations of the nine most frequently detected pesticide compounds during 1999–2000 also generally occurred during peak irrigation season (figs. 4–12). During irrigation season, runoff of excess irrigation water from fields transports pesticides to surface water (drains, wasteways, and ultimately to streams) because of increased erosion of soils with sorbed pesticides or because of increased flushing of the more soluble compounds (Rinella and others, 1999; U.S. Geological Survey, 1999a). Storm runoff transports pesticides from fields in the same manner.

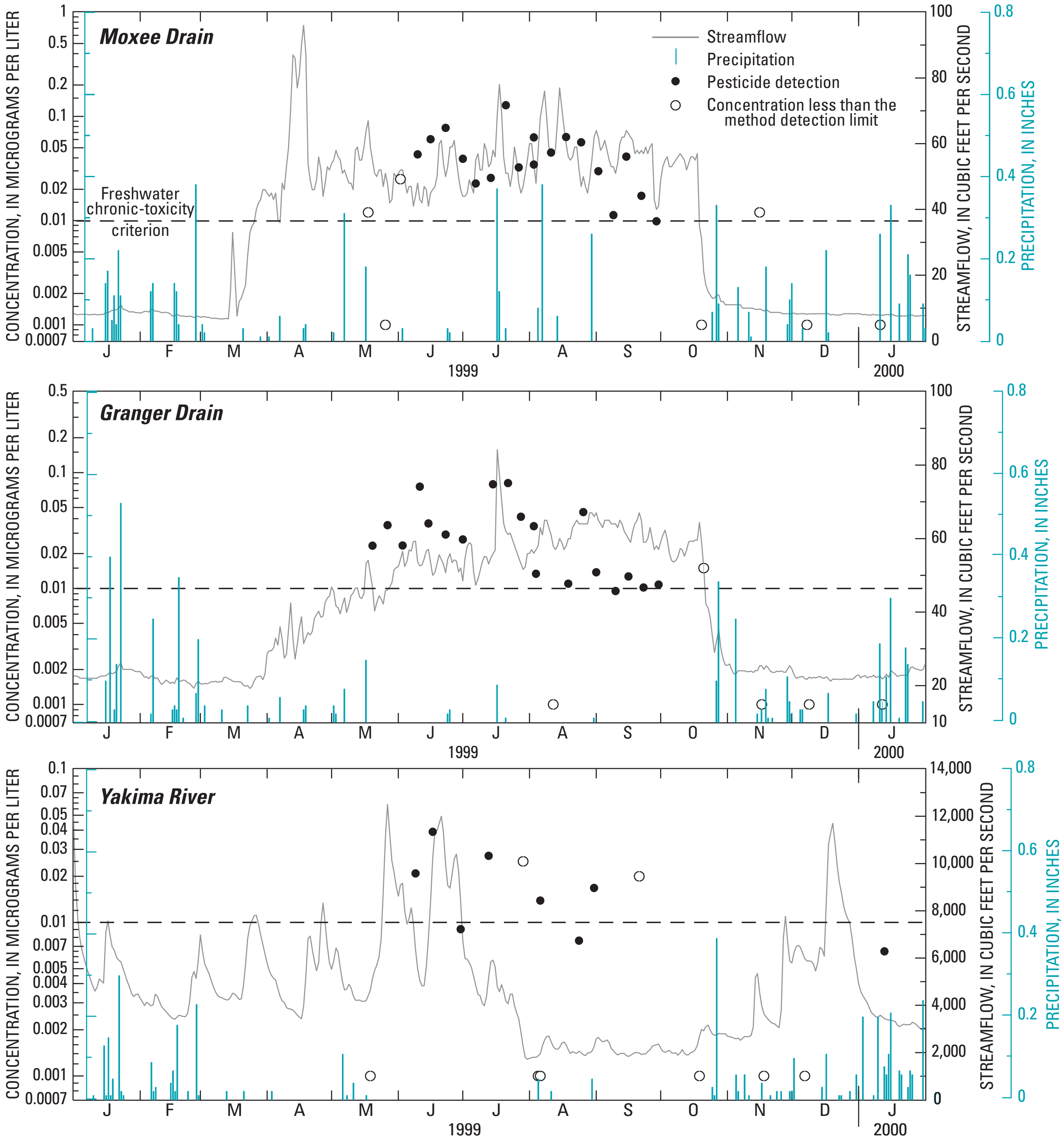


Figure 4. Concentrations of azinphos-methyl and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

Because surface runoff carries both sediment and pesticides from fields, an increase in the concentration of a pesticide with a corresponding increase in the concentration of suspended sediment in surface water suggests surface runoff as transport mechanism (Rinella and others, 1999). This is illustrated by the moderate correlation between concentrations of the insecticide azinphos-methyl and suspended-sediment (Kendall's rank correlation *tau* of 0.36, p-value of 0.01, for Moxee Drain and *tau* of 0.43, p-value of 0.003, for Granger Drain) (fig. 13), both of which peaked during June, mid-July, and early August of the 1999 irrigation season (fig. 4).

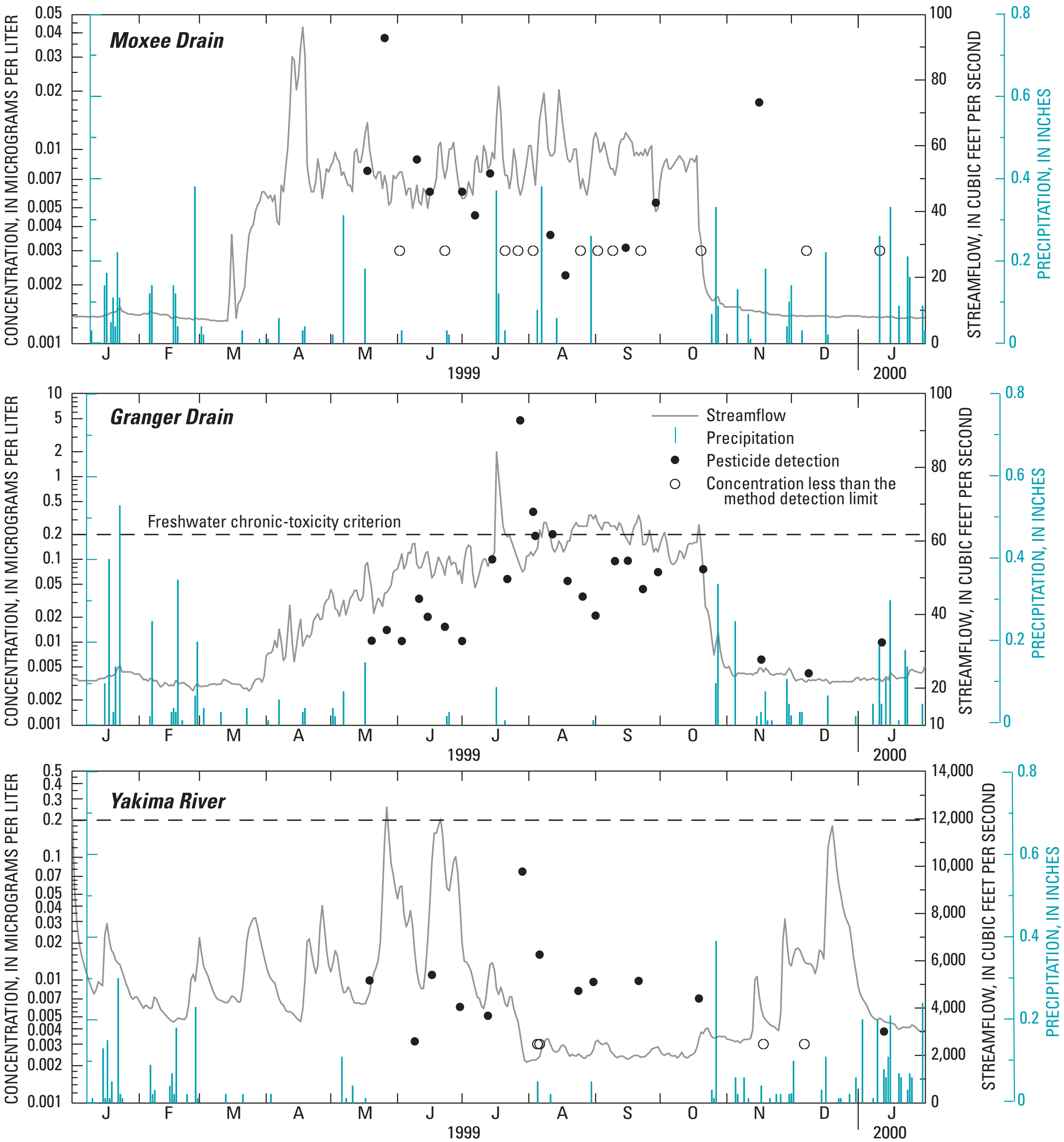


Figure 5. Concentration of carbaryl and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

Some pesticide compounds, especially atrazine, deethylatrazine, and simazine, can percolate to ground water and are frequently detected in ground water beneath both urban and agricultural land uses (Barbash and others, 1999). Ground-water discharges can then become a source of pesticides in surface water (Williamson and others, 1998).

Between Moxee Drain and Granger Drain, temporal patterns of concentrations varied for some pesticides during the irrigation season. For example, early

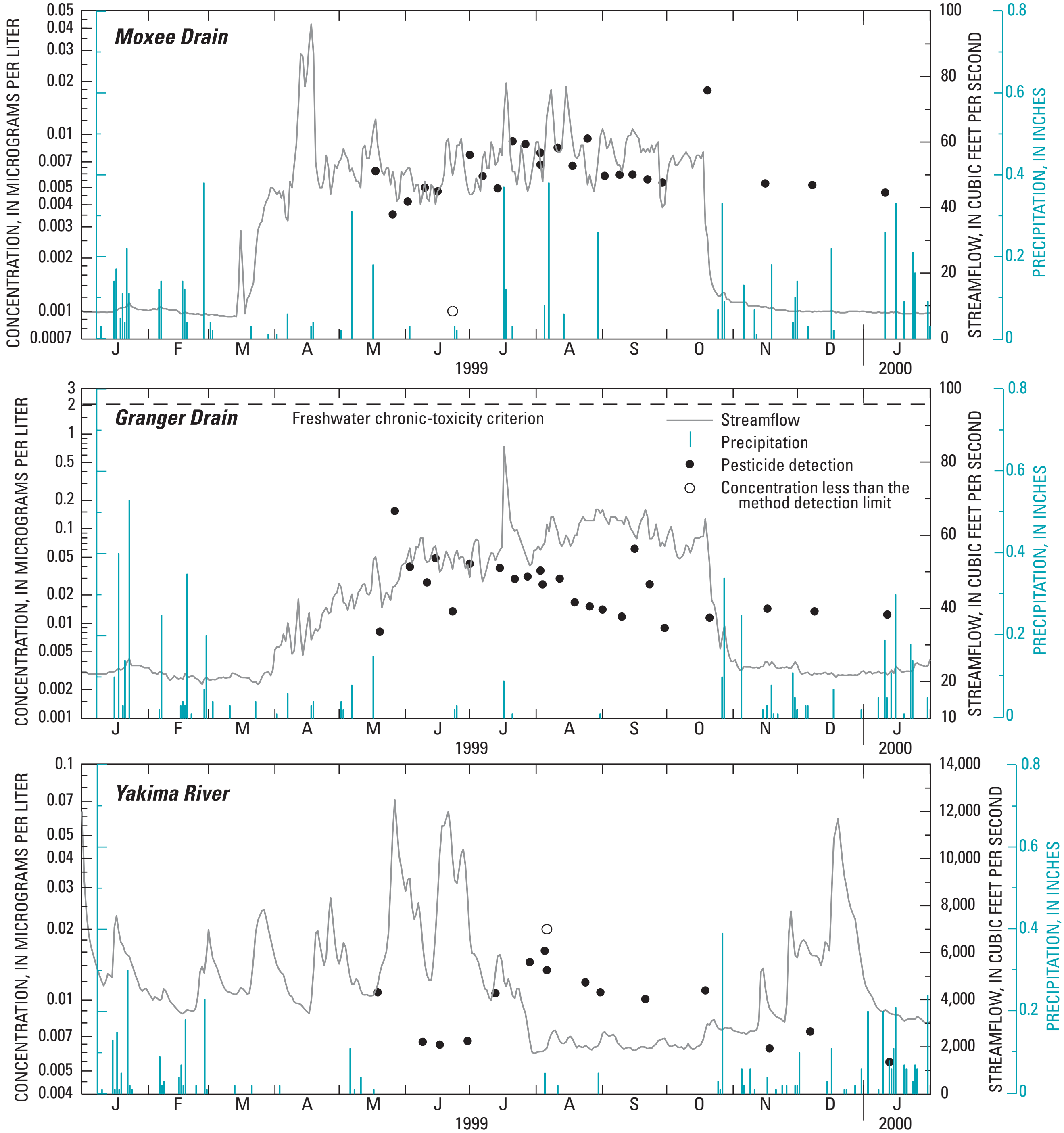


Figure 6. Concentrations of atrazine and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

in the irrigation season at Moxee Drain, carbaryl concentrations were at their highest, whereas early in the season at Granger Drain, carbaryl concentrations were low and peaked later during mid-irrigation season (fig. 5). Also, atrazine concentrations tended to be highest during July and August in Moxee Drain, but were highest during June and July in Granger Drain (fig. 6). In addition to the other factors causing temporal variability in concentrations as noted by Rinella and others (1999), the different patterns in peak concentrations of

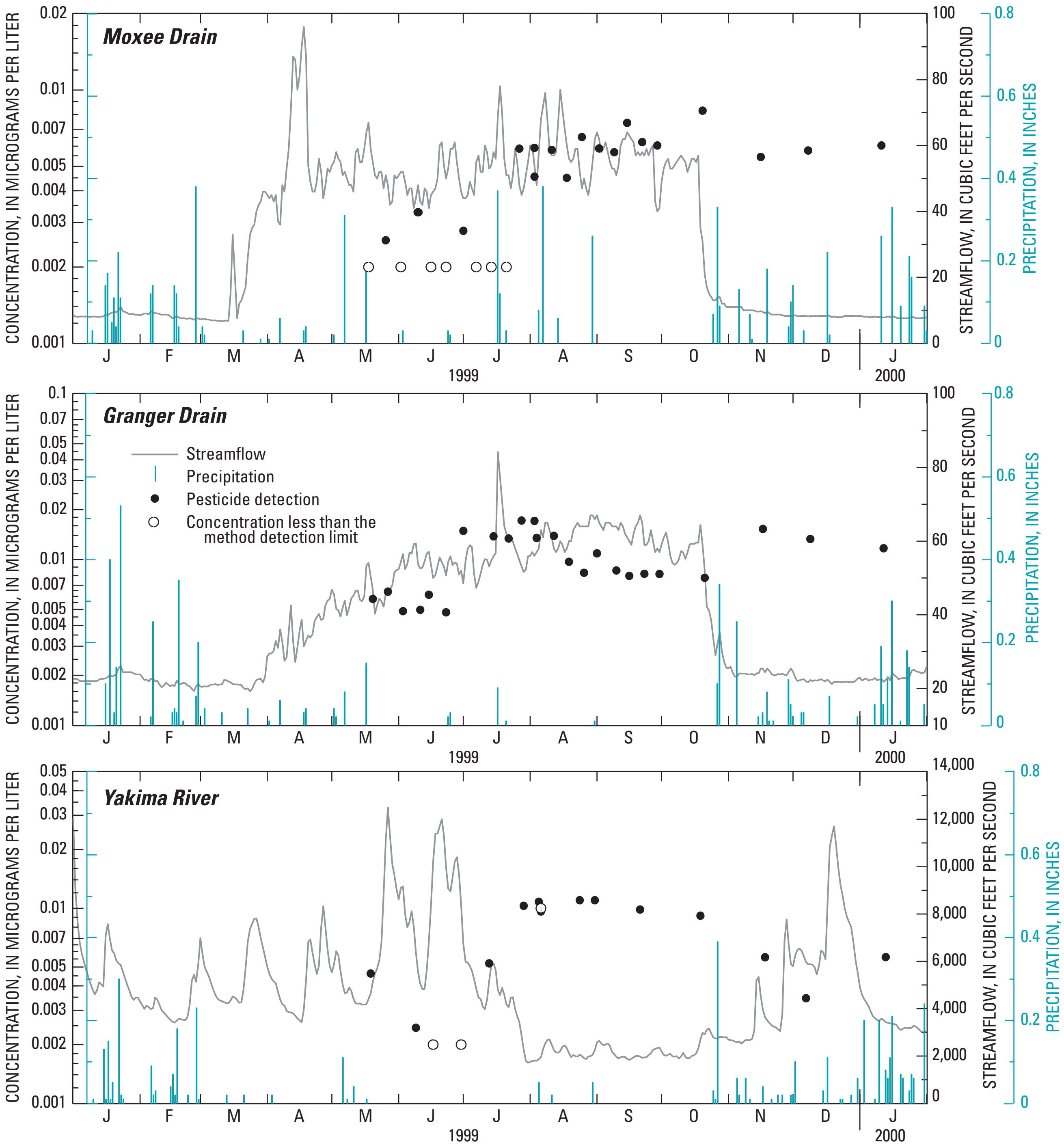


Figure 7. Concentrations of deethylatrazine and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

carbaryl and atrazine suggest different timings of pesticide applications, with carbaryl applied earlier in the season and atrazine applied later in the season in the Moxee Basin than in the Granger Basin.

Of the nine most frequently detected compounds, atrazine (fig. 6), deethylatrazine (fig. 7), and simazine (fig. 8) were detected in samples collected at all three sites after the irrigation season. Carbaryl (fig. 5) and *p,p'*-DDE, a breakdown product of DDT (fig. 9) also were detected in Granger Drain after the irrigation season. The detections of *p,p'*-DDE during the post-irrigation season might indicate a ground-water source,

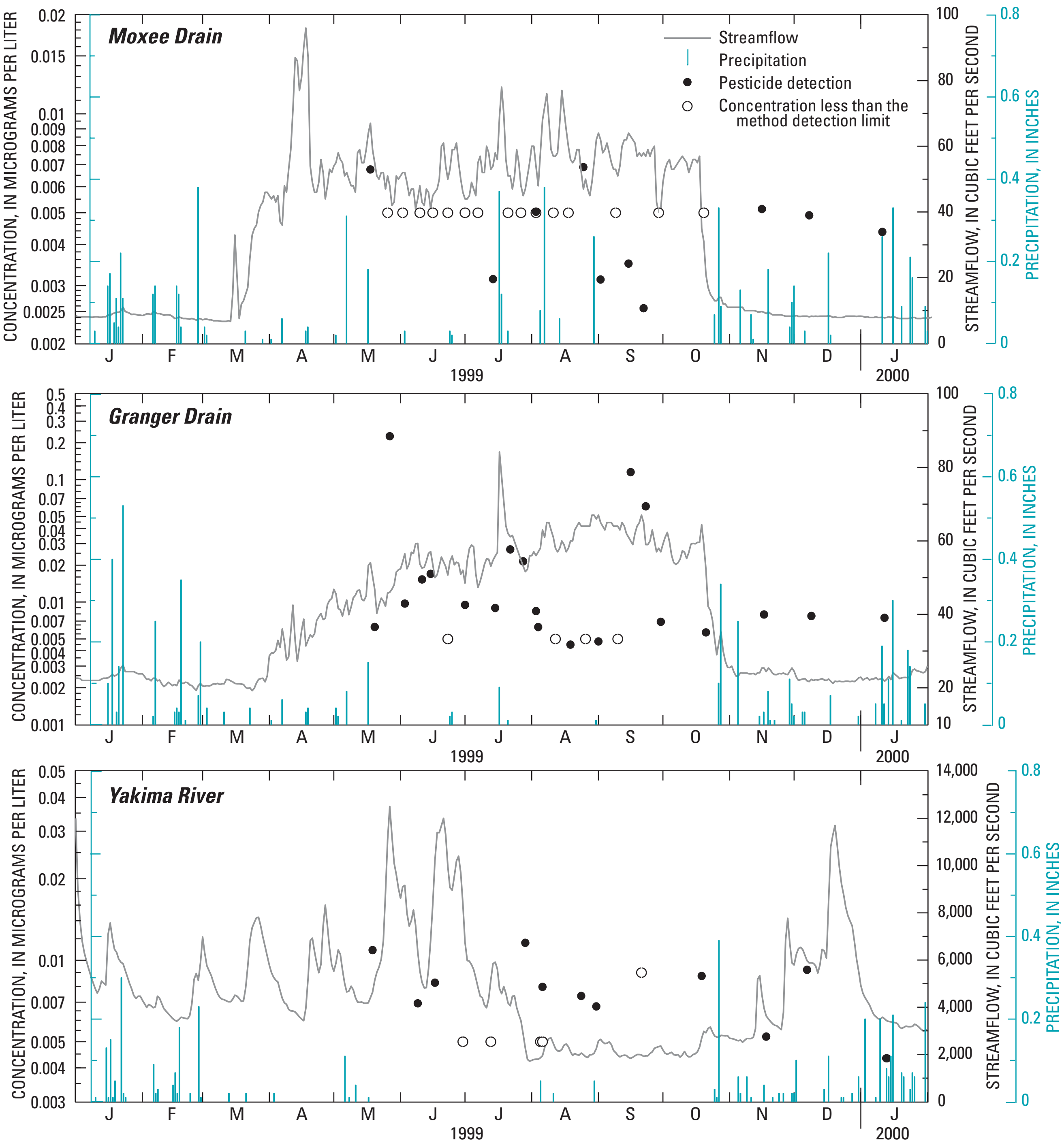


Figure 8. Concentrations of simazine and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

which is discussed below; however, Rinella and others (1999) also reported that some pesticides (carbamates such as carbaryl and organochlorines such as *p,p'*-DDE) that persist in soils, continued to be transported in the streams and drains throughout the year, especially during storm runoff or snowmelt from agricultural fields. Although detected throughout the 9-month study spanning both the irrigation and post-irrigation seasons, concentrations of all compounds, except for deethylatrazine, tended to be lower after the irrigation season. For example, concentrations of atrazine in Granger Drain averaged 0.013 µg/L during the post-irrigation

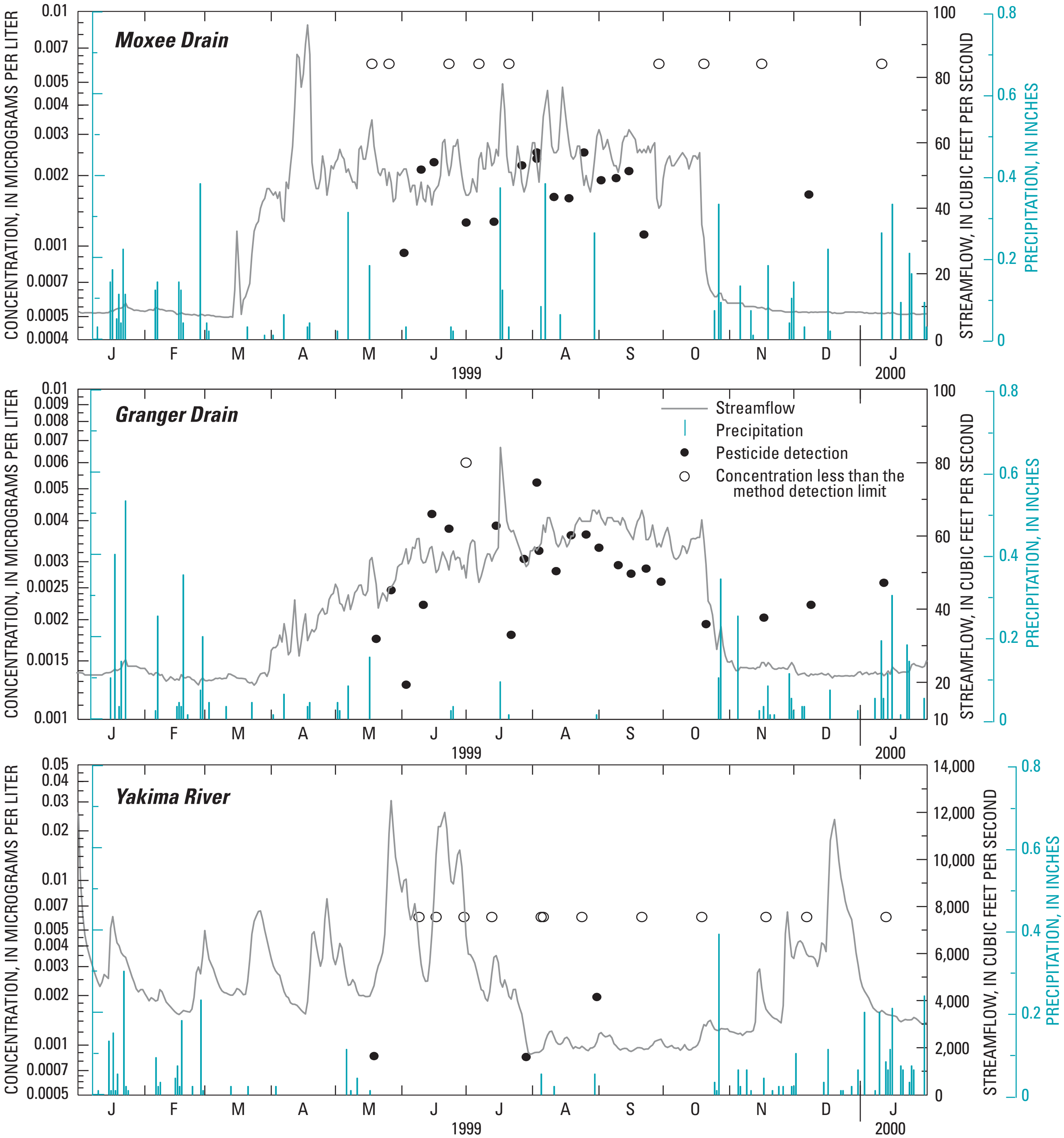


Figure 9. Concentrations of p,p'-DDE and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

season compared with 0.034 µg/L during the irrigation season.

Most of the post-irrigation season flow in Moxee and Granger Drains, when concentrations of deethylatrazine are at their highest (fig. 7), is derived from ground water (Rinella and others, 1999). The ratio of deethylatrazine-to-atrazine concentrations (DAR) has been used in some studies to indicate that ground water is a source of atrazine and deethylatrazine to surface waters (Kimbrough and Litke, 1998; Thurman and others, 1992). In a study in the Midwest United States, an increase in the median DAR values from the post-

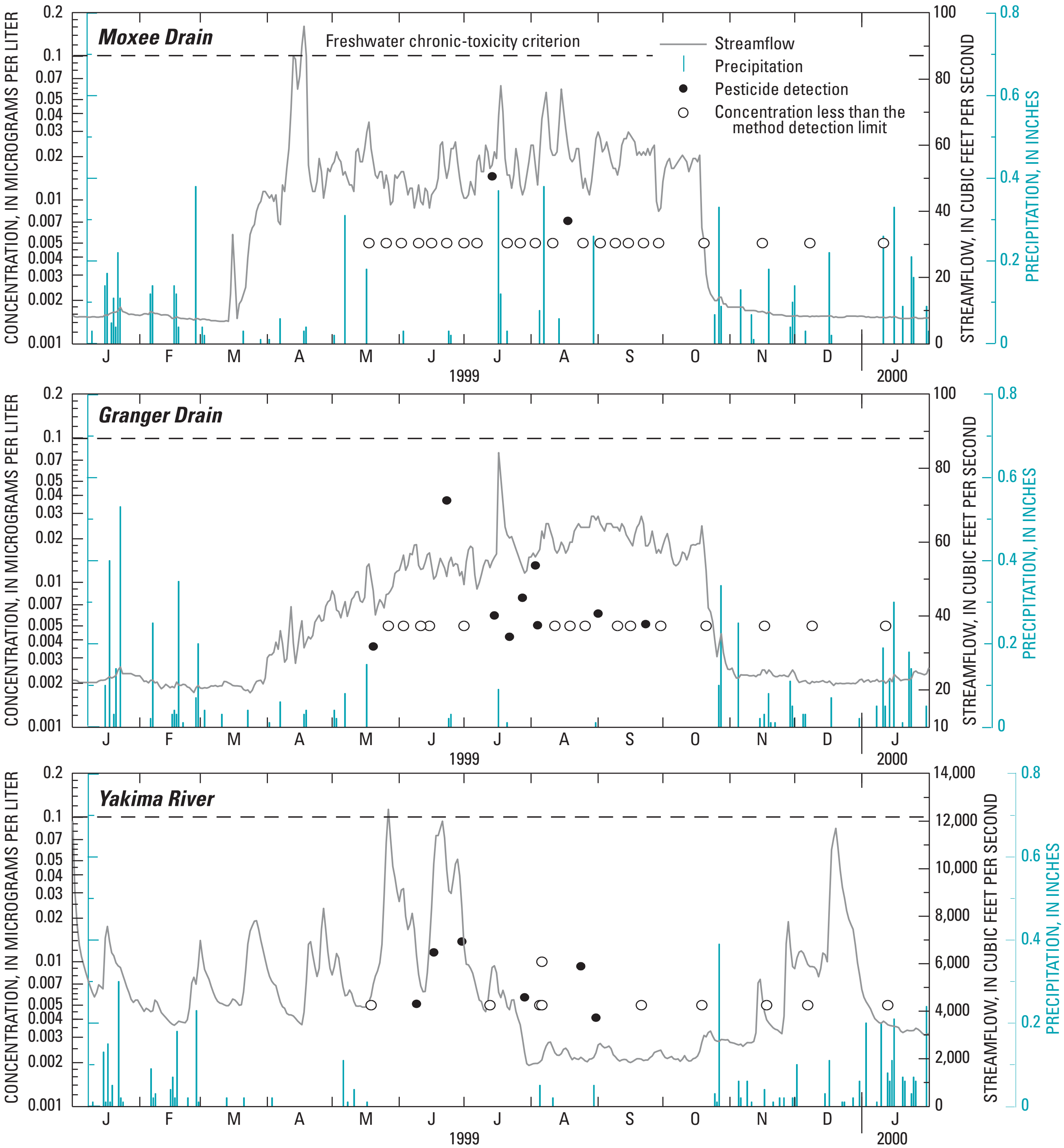


Figure 10. Concentrations of malathion and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

planting period when surface-water runoff dominated streamflows, to the harvesting period when ground-water was a larger component of the streamflow than runoff, indicated that ground water was transporting these compounds to the streams (Thurman and others, 1992). In Moxee Drain, an increase in the DAR from 0.7 during irrigation season, when streamflows were high due to irrigation-water runoff, to 1.1 during post-irrigation, when streamflows were low and mostly derived from ground water, and a similar increase in DAR from 0.5 to 1.0 in Granger Drain suggests that some of atrazine and deethylatrazine in the drains is

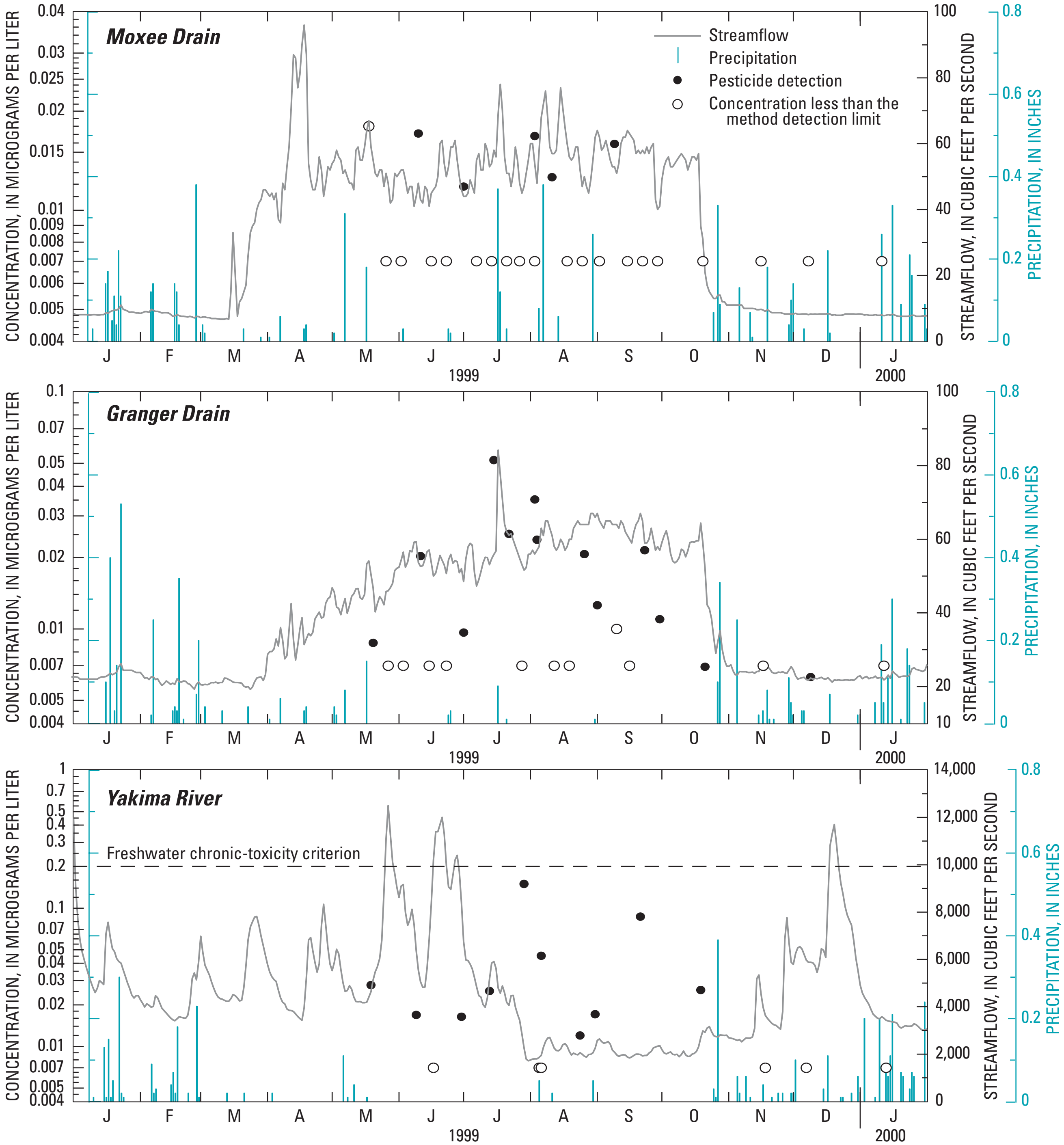


Figure 11. Concentrations of terbacil and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

derived from ground-water sources. DAR values, along with consistent detections of atrazine, deethylatrazine, and simazine in post-irrigation season samples, suggests that ground water is a source of these, and possibly other, compounds. In fact, atrazine and simazine, at concentrations as high as 0.006 µg/L, as well as total DDT (sum of concentrations of DDT, DDE, and DDD), EPTC, and malathion, were detected during the 1987–91 study in ground-water sampled from wells located within the Toppenish and the Sulphur subbasins (fig. 2) of the lower Yakima River Basin (Rinella and others, 1999).

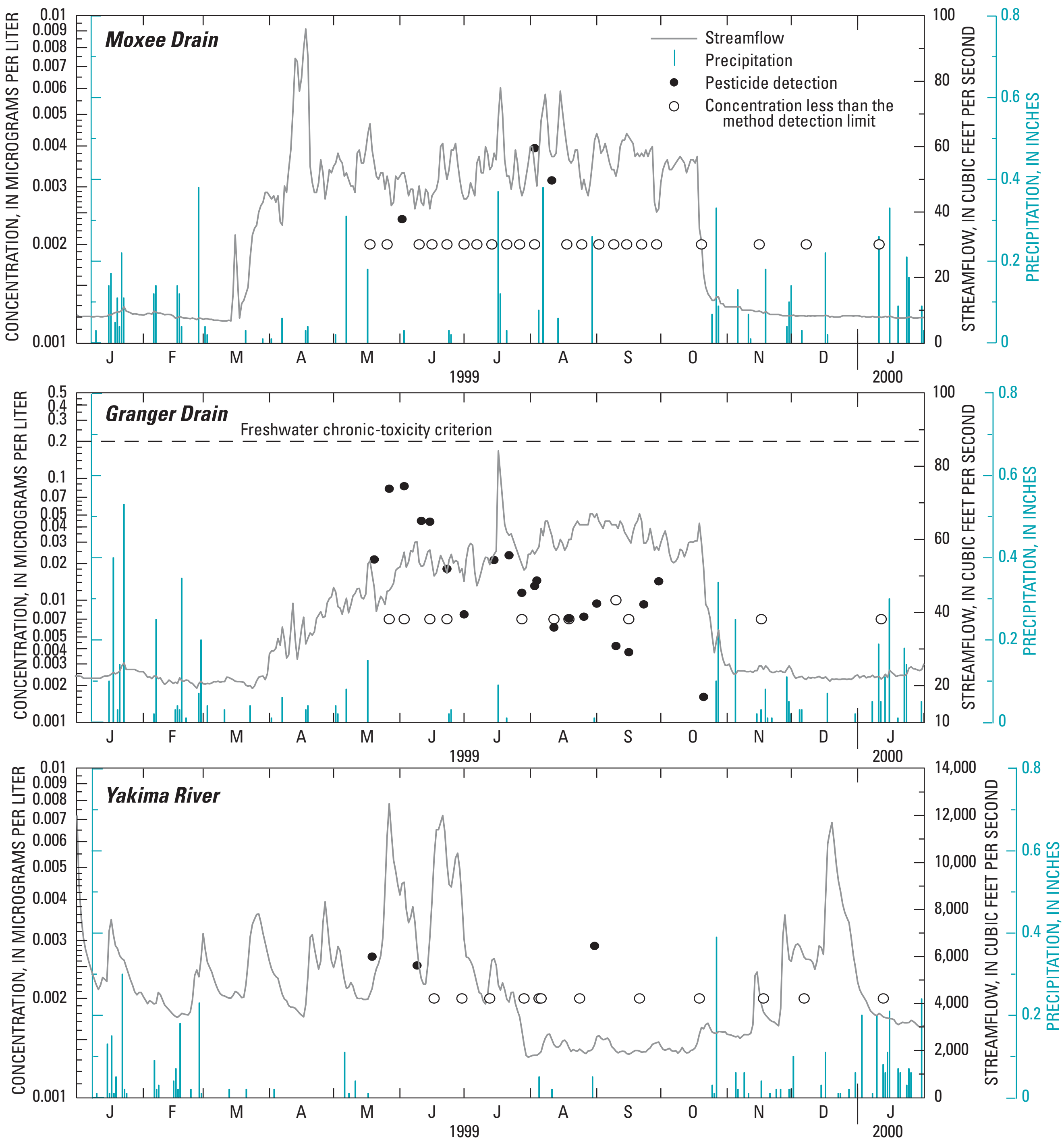


Figure 12. Concentrations of trifluralin and corresponding daily precipitation amounts and daily streamflows at Moxee Drain, Granger Drain, and Yakima River at Kiona, May 1999–January 2000.

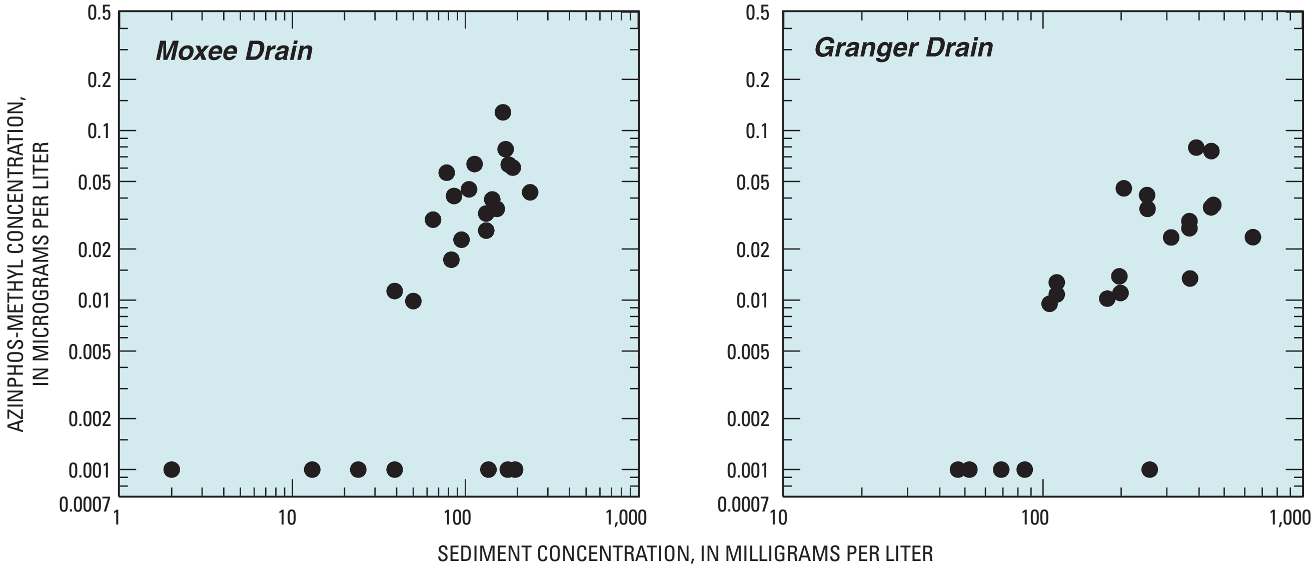


Figure 13. Relation between concentrations of azinphos-methyl and concentrations of suspended sediment in samples from Moxee Drain and Granger Drain, May 1999–January 2000.

Of the most frequently detected pesticides, the insecticides azinphos-methyl (fig. 4) and malathion (fig. 10), and the herbicides terbacil (except for one detection in a sample from Granger Drain) (fig. 11) and trifluralin (fig. 12) were detected only during the irrigation season. Concentrations of these pesticides were below detection levels during the post-irrigation season, which suggests that they were not in ground water or that their concentrations were below their MDLs.

Because of diversions, flow regulation in the headwaters, and dry summers, the Yakima River at Kiona differs hydrologically from Moxee and Granger Drains, with a low-flow period during late summer instead of during winter and with streamflows generally more variable in magnitude during the remainder of the year. In spite of hydrologic differences, pesticides and breakdown products were still detected more frequently and in higher concentrations during the irrigation season than during post-irrigation season. This is because the quality of water in the lower Yakima River during low-flow conditions is controlled by agricultural return flows, which contribute pesticides and pesticide breakdown products to the river during the irrigation season (Rinella and others, 1999).

PESTICIDE TRANSPORT, LOADS, AND YIELDS

Pesticide transport was assessed at two time scales. In the first, data from the basinwide sampling were used to account for masses (loads) of pesticides entering and leaving the Yakima River following a parcel of water as it moved from Cle Elum to Kiona in August 1999. In the second, data collected at the three sites sampled at fixed intervals were used to compute cumulative loads and yields of pesticides transported from May 1999 through January 2000—the time period these stations were in operation. These loads and yields were then compared with estimates of pesticide usage in the contributing drainage basins.

Pesticide Transport During Basinwide Sampling, August 2–6, 1999

Concentrations and loads of pesticides at sites sampled on the Yakima River were computed using a mass-balance method that accounted for pesticide loads transported into and out of the upstream reach. Concentrations and loads computed using the mass-balance method are compared with observed loads, which were computed as the product of measured concentrations and water discharge. Surface-water discharges to the Yakima River and diversions (outflows) from the river that were needed for mass-balance computations are listed in table 10. Several assumptions were made in computing pesticide loads and concentrations.

1. Loads, computed as the product of a concentration in a single sample and either a mean daily or instantaneous discharge, are expressed as daily loads.

Table 10. Surface-water discharges to and outflows from the Yakima River, Washington, August 2–6, 1999

[RM, river mile; --, not applicable; Rd, road; No., number; WWTP, wastewater treatment plant; discharge is in cubic feet per second; computed discharge equals inflows to a reach minus outflows]

Site name	RM	Sampled for pesticides	Yakima River			Inflows and diversions	
			Measured	Computed	Difference	Inflow	Outflow
Yakima River at Cle Elum	182.5	yes	2,565	--	--	--	--
Cle Elum WWTP	179.6	yes	--	--	--	1.0	--
Teanaway River Below Lambert Rd	176.1	no	--	--	--	9	--
Kittitas Main Canal Wasteway	173.9	no	--	--	--	0	--
Morrison Canyon Creek (Kittitas Main Canal Wasteway)	172.1	no	--	--	--	0	--
Swauk Creek	169.9	no	--	--	--	10	--
Taneum Creek	166.1	no	--	--	--	20	--
West Side Canal / Ellison-Bruton Ditch	166.1	no	--	--	--	--	107
Town Canal (Ellensburg Town Canal)	161.3	no	--	--	--	--	129
Cascade Canal Headworks (Lower)	160.3	no	--	--	--	--	110
Yakima River at Ellensburg	155.9	no	2,640	2,259	381	--	--
Manastash Creek	154.5	no	--	--	--	40	--
Ellensburg WWTP	151.6	yes	--	--	--	5.6	--
Wilson Creek above Cherry Creek at Thrall	147	yes	--	--	--	132	--
Cherry Creek at Thrall	147	yes	--	--	--	125	--
Yakima River at Umtanum	140.4	yes	2,730	2,943	-213	--	--
Umtanum Creek near mouth at Umtanum	139.8	yes	--	--	--	.52	--
Roza Canal Diversion	127.9	no	--	--	--	--	1,875
Yakima River below Roza Dam	123.9	no	916	856	60	--	--
Selah/Moxee Canal diversion	123.6	no	--	--	--	--	65
Wenas Creek	122.4	no	--	--	--	20	--
Selah WWTP	117	yes	--	--	--	1.5	
Naches River near North Yakima	116.3	yes	--	--	--	2,085	--
Moxee Canal diversion	115.9	no	--	--	--	--	40
Roza Wasteway No. 2 (mostly return flow from power plant)	113.3	no	--	--	--	775	--
City of Yakima WWTP discharge	111	yes	--	--	--	16	--
Wide Hollow Creek near Mouth at Union Gap	107.4	yes	--	--	--	19	--
Moxee Drain at Birchfield Road	107.3	yes	--	--	--	59	--
Yakima River at Union Gap	107.3	yes	3,560	3,787	-227	--	--
Ahtanum Creek at Union Gap	106.9	yes	--	--	--	27	--
New Reservation Canal Headworks (Wapato Canal)	106.7	no	--	--	--	--	1,905
Sunnyside Canal	103.8	no	--	--	--	--	1,287
Pumpage from the Sunnyside fish bypass into Sunnyside Canal	103.8	no	--	--	--	--	80
Yakima River near Parker	103.7	no	685	315	370	--	--
Return from the Sunnyside fish bypass	103.6	no	--	--	--	40	--
Roza Canal Wasteway No. 3	98.6	no	--	--	--	0	--
Zillah WWTP	89.5	yes	--	--	--	.3	--
Sunnyside Canal - Zillah Wasteway	89.1	no	--	--	--	0	--
Roza Canal Wasteway No. 4	87.6	no	--	--	--	0	--
East Toppenish Drain at Wilson near Toppenish	86	yes	--	--	--	27.5	--
Sub-Drain No. 35 at Parton Road	83.2	yes	--	--	--	62.5	--
Granger Drain at Granger	82.8	yes	--	--	--	62	--
Granger WWTP	82.8	yes	--	--	--	.4	--
Marion Drain at Indian Church Rd	82.6	yes	--	--	--	66.8	--
Toppenish Creek near Granger	80.4	yes	--	--	--	117	--
Coulee Drain	77	no	--	--	--	30	--

Table 10. Surface-water discharges to and outflows from the Yakima River, Washington, August 2–6, 1999—Continued
[RM, river mile; --, not applicable; Rd, road; No., number; WWTP, wastewater treatment plant; discharge is in cubic feet per second; computed discharge equals inflows to a reach minus outflows]

Site name	RM	Sampled for pesticides	Yakima River			Inflows and diversions	
			Measured	Computed	Difference	Inflow	Outflow
Yakima River at RM 72 above Satus	72	yes	1,270	1,092	178	--	--
Satus Creek at gage at Satus	69.6	yes	--	--	--	128	--
South Drain near Satus	69.3	yes	--	--	--	33	--
Drainage Improvement District (DID) No. 7	65.1	no	--	--	--	25	--
Sulphur Creek Wasteway	61	yes	--	--	--	260	--
Satus Drain 303	60.2	no	--	--	--	22	--
Yakima River at Euclid Rd Bridge at RM 55 near Grandview	55	yes	2,050	1,738	312	--	--
Chandler Canal at Bunn Road at Prosser	47.1	no	--	--	--	--	1,209
Prosser WWTP	47	yes	--	--	--	1.2	--
Yakima River near Prosser	46.3	no	773	842	-69	--	--
Spring Creek at Hess Road	41.8	yes	--	--	--	46.4	--
Snipes Creek below Chandler Canal	41.8	yes	--	--	--	12.5	--
Chandler Power Return	35.8	no	--	--	--	900	--
Kiona Canal	34.9	no	--	--	--	--	20
Corral Canyon Creek at mouth near Benton	33.5	no	--	--	--	20	--
Yakima River at Kiona	29.9	yes	1,950	1,732	218	--	--

2. Pesticide concentrations in inflows to the Yakima River that were not sampled (table 10) were set to zero, which is equivalent to assuming the inflows discharged no pesticides to the river.
3. Pesticide concentrations reported as less than the MDL were set to zero.
4. The load of a pesticide in an outflow from the Yakima River was computed as the product of the observed concentration at the sampled site immediately upstream on the Yakima River and the water discharge in the outflow.
5. Computed concentrations of pesticides at sites on the Yakima River were calculated by dividing net loading to the reach upstream from a site by water discharge at the site. The net loading of a pesticide to a reach was computed as the sum of the load contributed from the upstream sampled site on the river plus the loads from inflows to the reach minus the loads leaving the reach. Inputs and losses to and from ground water were not estimated.
6. Once in the river, pesticides were treated as conservative (no degradation).
7. For sites on the Yakima River sampled more than one time (table 5), observed concentrations were those at time-of-travel target times, except for the Yakima River at Kiona where the sample collected August 6, 1999, at 3:10 p.m. was used instead. The pesticides atrazine, terbacil, azinphos-methyl, and carbaryl were not detected in the time-of-travel sample, and these pesticides were usually detected in the Yakima River at Kiona during August (figs. 4–6, fig. 11).

Comparisons between observed and computed concentrations of pesticides in the Yakima River are shown for the herbicides atrazine and terbacil and the insecticides azinphos-methyl and carbaryl (fig. 14), all of which were frequently detected during basinwide sampling (table 4). The closest agreement between observed and computed concentrations was for carbaryl (fig. 14). Carbaryl was not detected in the Yakima River at Umtanum (RM 140.4) and Ahtanum (RM 107.3), and computed concentrations, which were well below the MDL of 0.003 µg/L, were consistent with the no detections. Discharge of carbaryl to the Yakima River from inflows downstream from RM 89.5 were sufficient to account for observed concentrations at RM 72, RM 55, and Yakima River at Kiona.

Differences between observed and computed concentrations of atrazine, terbacil, and azinphos-methyl were relatively large at RM 55. This is partly because these three pesticides were not detected at RM 72, and the computed concentration of a pesticide at RM 55 is a function of its concentration at RM 72 as well as in inflows to the river between RM 72 and RM 55.

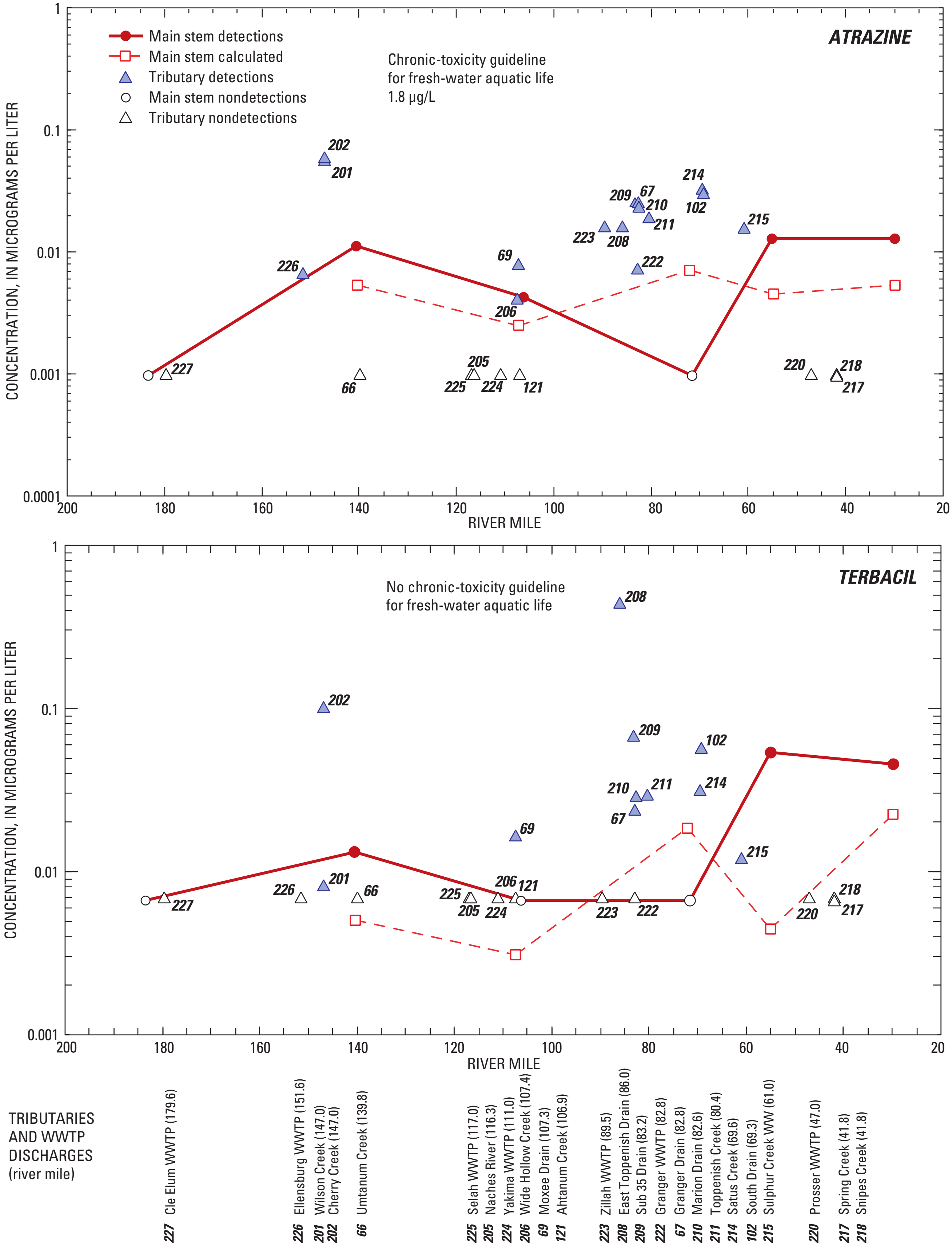
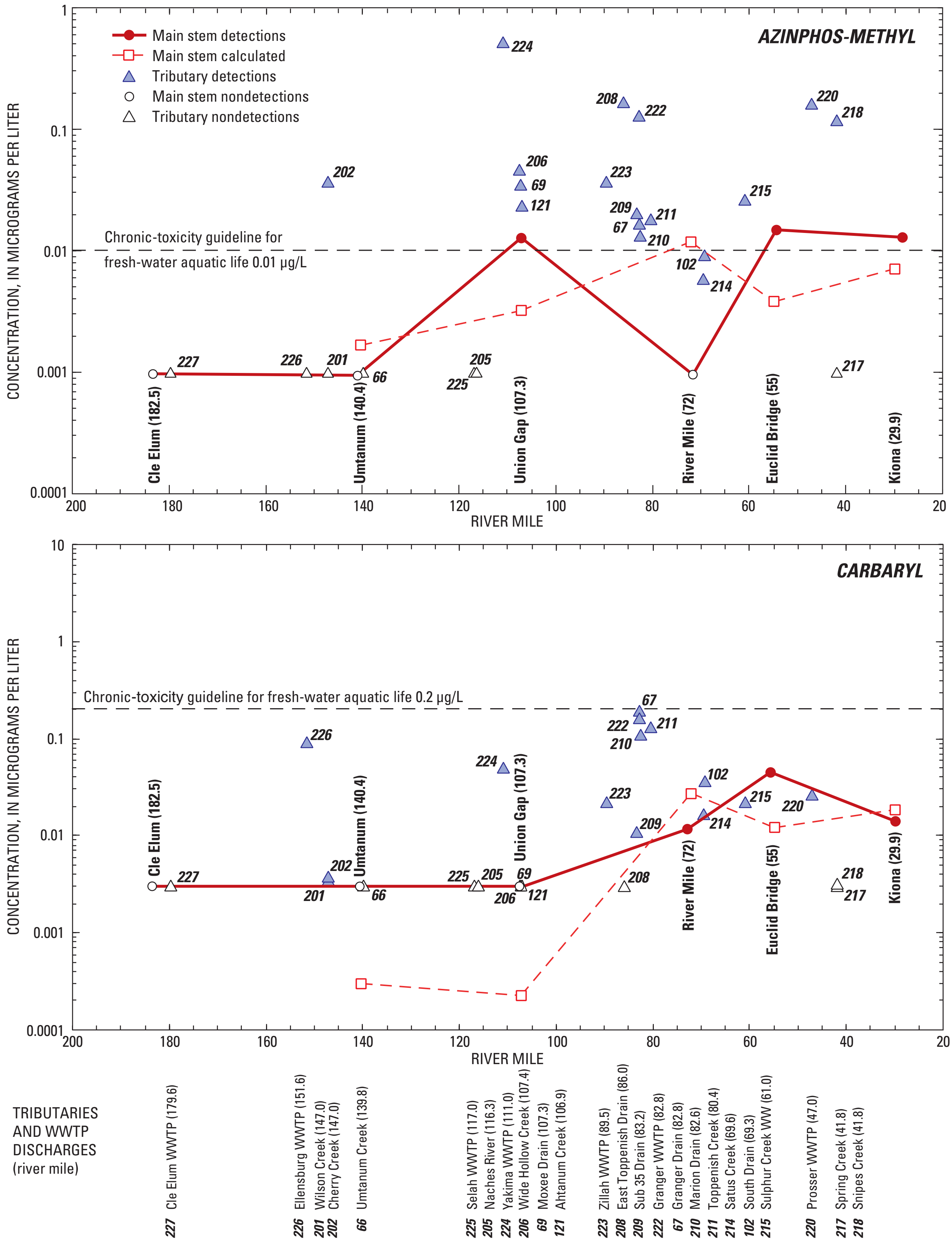


Figure 14. Observed and computed concentration of atrazine, terbacil, azinphos-methyl, and carbaryl in the Yakima River and observed August 1999. (Map identification numbers [see table 2 and figure 3] are shown for tributaries and wastewater treatment plants.)



concentrations of terbacil, azinphos-methyl, and carbaryl in tributaries and wastewater treatment plant discharges to the Yakima River, Like carbaryl, atrazine, terbacil, and azinphos-methyl should have been detected at RM 72 (fig. 14) based on loads discharged to the reach of the river extending upstream to RM 103.7 near Parker (table 11). Although some degradation or loss of these compounds during transport to RM 72 is likely, the half-lives of atrazine (59 days) and azinphos-methyl (8 days) compared with the 9-day half-life of carbaryl suggest that all or none of the compounds should have been detected. The data on half-lives, which were measured in river water exposed to sunlight (Lartiges and Garrigues, 1995), did not include terbacil. However, other data on rates of hydrolysis and photolysis (U.S. Department of Agriculture, 1995) indicate that terbacil is relatively persistent compared with the other three compounds. Additionally, the travel time for a parcel of water moving from RM 103.7 to RM 72, which was estimated to be about 36 hours during basinwide sampling, is short compared with the half-lives of these compounds. Volatilization, another loss mechanism, is unlikely because these compounds have low vapor pressures (U.S. Department of Agriculture, 1995).

Yakima River at river mile 72 looking upstream.

One explanation for not detecting atrazine, terbacil, and azinphos-methyl at RM 72 is short-term temporal variability of their concentrations in the river, as indicated by data from other sampling sites (table 5). High variability suggests that one sample does not provide a representative concentration upon which to base load computations.

Daily loads of atrazine, terbacil, azinphos-methyl, and carbaryl discharged to the Yakima River between Parker and river mile 72 were highly variable (table 11). For example, East Toppenish Drain discharged over 50 percent of the total load of terbacil to this reach of the Yakima River, but none of the total load of carbaryl and only about 4 percent of the total load of atrazine. Pesticide loads from the wastewater treatment plants were relatively small compared with loads from other inflows because their discharges were small. When comparing loads it should be emphasized that they represent a time period of less than 2 days, and if the basinwide sampling had been conducted at another time, the results would likely be different.

Granger Drain discharging to the Yakima River. (Granger wastewater treatment plant in background).

Pesticide Loads and Yields

Pesticide loads, in pounds of active ingredient, were computed for the fixed sampling sites for the time period over which samples were collected (May 1999 through January 2000). Loads for this time period were obtained by summing daily loads, which were computed as the product of a daily concentration, either measured or interpolated, and the daily mean water discharge. Although the use of linear interpolation to estimate pesticide concentrations on days when no samples were collected is relatively simple compared with some other methods, it has been used when samples are closely spaced in time (Larson and others, 1995), and it was used for fixed-site data collected from rivers and irrigation wasteways in the central Columbia Plateau of Washington State (Ebbert and Kim, 1998).

Other methods used to compute constituent loads use a rating-curve method to estimate concentrations on days when no samples were collected (Cohn and others, 1989; Crawford, 1991). This method uses multiple regression relations between logarithms of measured concentrations and logarithms of daily mean water discharges and other explanatory variables to estimate concentrations on days when no samples were

Table 11. Daily loads of atrazine, terbacil, azinphos-methyl, and carbaryl measured in the Yakima River at river mile 72 and discharged to the reach of the Yakima River extending from Parker to river mile 72, Washington, August 1999

[ft^3/s, cubic feet per second; µg/L, micrograms per liter; WWTP, wastewater treatment plant; <, less than; pesticide concentrations reported as less than the method detection limit were set to zero for all load computations except those at river mile 72]

Source	River mile	Water discharge (ft^3/s)	Concentration (µg/L)	Daily load (pounds)	Cumulative loading to river (pounds per day)	Fraction of total loading to river (percent)
Atrazine						
Yakima River near Parker[1,2]	103.7	685	0.004	0.0158	0.016	27.8
Return from Sunnyside fish bypass[2]	103.6	40	.004	.0009	.017	1.6
Zillah WWTP	89.5	.3	.016	.00003	.017	.05
East Toppenish Drain	86	27.5	.016	.0024	.019	4.3
Sub-Drain 35	83.2	62.5	.025	.0085	.028	15.0
Granger Drain	82.8	62	.026	.0086	.036	15.2
Granger WWTP	82.8	.4	.007	.00002	.036	.03
Marion Drain	82.6	66.8	.024	.0085	.045	14.9
Toppenish Creek	80.4	117	.019	.0120	.057	21.1
Yakima River at river mile 72	72	1,270	<.001	<.007		
Terbacil						
Yakima River near Parker[1,2]	103.7	685	<.007	.000	.000	.00
Return from Sunnyside fish bypass[2]	103.6	40	<.007	.000	.000	.00
Zillah WWTP	89.5	.3	<.007	.000	.000	.00
East Toppenish Drain	86	27.5	.448	.0665	.066	52.4
Sub-Drain 35	83.2	62.5	.068	.0230	.089	18.1
Granger Drain	82.8	62	.024	.0080	.097	6.3
Granger WWTP	82.8	.4	<.007	.000	.097	.00
Marion Drain	82.6	66.8	.029	.0106	.108	8.3
Toppenish Creek	80.4	117	.030	.0188	.127	14.8
Yakima River at river mile 72	72	1,270	<.007	<.048		
Azinphos-methyl						
Yakima River near Parker[1,2]	103.7	685	.012	.0455	.045	44.4
Return from Sunnyside fish bypass[2]	103.6	40	.012	.0027	.048	2.6
Zillah WWTP	89.5	.3	.037	.0001	.048	.06
East Toppenish Drain	86	27.5	.169	.0251	.073	24.5
Sub-Drain 35	83.2	62.5	.020	.0068	.080	6.7
Granger Drain	82.8	62	.013	.0045	.085	4.4
Granger WWTP	82.8	.4	.129	.0003	.085	.27
Marion Drain	82.6	66.8	.017	.0060	.091	5.8
Toppenish Creek	80.4	117	.018	.0115	.102	11.2
Yakima River at river mile 72	72	1,270	<.001	<.007		
Carbaryl						
Yakima River near Parker[1,2]	103.7	685	<.003	.0000	.000	.00
Return from Sunnyside fish bypass[2]	103.6	40	<0.003	0.0000	0.000	.00
Zillah WWTP	89.5	0.3	.022	<.0001	<.001	<.02
East Toppenish Drain	86	27.5	<.003	.0000	.000	.00
Sub-Drain 35	83.2	62.5	.011	.0037	.004	2.0
Granger Drain	82.8	62	.192	.0642	.068	33.8
Granger WWTP	82.8	.4	.160	.0003	.068	.18
Marion Drain	82.6	66.8	.111	.0400	.108	21.1
Toppenish Creek	80.4	117	.129	.0814	.190	42.9
Yakima River at river mile 72	72	1,270	.0123	.084		

[1]Yakima River near Parker is used as upstream end of reach ending at river mile 72 because of large diversions between Ahtanum Creek (river-mile 107.3) and Parker.

[2]Site was not sampled, so the concentration measured at Yakima River above Ahtanum Creek was used to compute load.

collected. This method works well if there is a good correlation between concentrations and water discharges, as is often the case for suspended sediment and total phosphorus, but it works poorly if concentrations and discharges do not correlate. The rating-curve method was not used for this report because of poor correlation between pesticide concentrations and water discharges.

One disadvantage of using linear interpolation to estimate concentrations is the need to assign values to analytical results reported as less than the MDL. A high percentage of "less-than" values in a sample record is a source of error in the interpolated values, and for this reason, it was decided to compute loads (table 12) only for pesticides that were detected in 50 percent or more of samples collected at a site. Following guidelines provided by Capel and others (1996), loads were computed using two computational schemes. In the first, zero is substituted for concentrations reported as less than the MDL, and in the second, one-half the MDL is substituted. In most instances, there was very little difference between loads computed by substituting the two different values (table 12).

Because loads are a function of both water discharge and concentration, pesticide loads in Yakima River at Kiona are much larger than corresponding loads in Moxee and Granger Drains (table 12) even though concentrations in the drains are often higher (figs. 4–12). A better comparison among basins is found in table 13, which lists pesticide losses and yields from the basins. Pesticide loss, defined here as the ratio of the load divided by the estimate of the amount applied during 1999, is not a true measure of how much of a pesticide applied during 1999 was exported from a basin. This is because (1) the time period for which loads were computed was less than 1 year, and (2) previous applications of some pesticides make up part of the load exported from a basin during subsequent years. Examples are atrazine and deethylatrazine (figs. 6 and 7), which are transported via ground water to Moxee and Granger Drains throughout the year. Instead, pesticide loss can be considered as an indicator of pesticide mobility or usage practices that affect the movement of a pesticide to surface water. Pesticide losses ranged from less than 0.01 to 1.5 percent of pesticides applied (table 13) and are comparable to those observed (0.01 to 2.2 percent) in irrigated agricultural basins in the central Columbia Plateau of Washington State (Ebbert and Kim, 1998).

Pesticide yields, which are loads per unit area of agricultural land, are another indicator of pesticide mobility or usage practices that affect the movement of pesticides to surface water. For example, the loss and yield of carbaryl from the Granger Basin are two orders of magnitude larger than those from the Moxee Basin (table 13). Because these basins are of similar size, the large differences in losses and yields suggest different usage or management practices. This is probable as indicated by the use of carbaryl on asparagus in the Granger Basin, but not in the Moxee Basin (tables 7 and 8). Also asparagus is irrigated by rill, which usually produces more surface runoff than sprinkler or drip irrigation.

Table 12. Pesticide loads in Moxee Drain, Granger Drain, and Yakima River at Kiona, Washington, May 1999 through January 2000
[MDL, method detection limit; nc, not computed]

Pesticide	Moxee Drain			Granger Drain			Yakima River at Kiona		
		Load, in pounds, computed with concentrations of nondetects set to:			Load, in pounds, computed with concentrations of nondetects set to:			Load, in pounds, computed with concentrations of nondetects set to:	
	Detection frequency, in percent[1]	Zero	0.5 MDL	Detection frequency, in percent[1]	Zero	0.5 MDL	Detection frequency, in percent[1]	Zero	0.5 MDL
Atrazine	96	0.34	0.34	100	1.6	1.6	100	49	49
Deethylatrazine	71	.21	.22	100	.61	.61	87	28	29
Carbaryl	50	.21	.25	100	12	12	80	46	48
Azinphos-methyl	71	1.6	1.6	79	1.3	1.4	53	58	59
Simazine	42	nc	nc	83	1.2	1.2	73	37	40
p,p'-DDE	62	.05	.11	96	.16	.16	20	nc	nc
Terbacil	21	nc	nc	54	.61	.7	67	120	130
Trifluralin	12	nc	nc	88	.94	.95	20	nc	nc

[1]Percentages are slightly different from those listed in tables 7–9 because only one sample was used for load computations on days when more than one sample was collected (see table 5).

Table 13. Amounts of pesticides applied for agricultural purposes during 1999 in the Moxee and Granger subbasins, and the Yakima River Basin, Washington, and loads, losses, and yields of pesticides transported in surface-water discharges from each, May 1999 through January 2000

[Loads and yields computed by setting concentrations of nondetections to zero; yields are in pounds per square mile of agricultural land shown in parentheses after the basin name; agricultural land areas are based on data used to estimate pesticide application rates, see Appendix 2; nc, not computed]

	Moxee Drain (29.3)				Granger Drain (19.8)				Yakima River at Kiona (616)			
Pesticide	Applied (pounds)	Load (pounds)	Loss (load/applied, in percent)	Yield (pounds per square mile)	Applied (pounds)	Load (pounds)	Loss (load/applied, in percent)	Yield (pounds per square mile)	Applied (pounds)	Load (pounds)	Loss (load/applied, in percent)	Yield (pounds per square mile)
Atrazine[1]	36	0.55	1.5	0.019	490	2.2	0.45	0.11	7,600	77	1.0	0.13
Carbaryl	5,900	.21	.0036	.0072	2,200	12	.55	.6	116,200	46	.040	.074
Azinphos-methyl	18,500	1.6	.0086	.053	4,900	1.3	.03	.068	294,600	58	.020	.094
Simazine	260	nc	nc	nc	500	1.2	.24	.061	8,400	37	.44	.06
Terbacil	240	nc	nc	nc	150	.61	.41	.031	11,500	120	1.0	.19
Trifluralin	260	nc	nc	nc	610	.94	.15	.048	5,700	nc	nc	nc

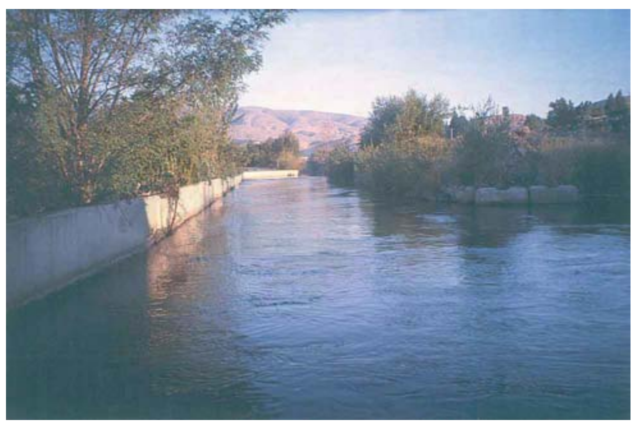
[1]Loads and yields include both atrazine and deethylatrazine.

SUMMARY

The occurrence, distribution, and transport of pesticides in surface water of the Yakima River Basin were assessed using data collected during 1999–2000 as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. Samples were collected at 34 sites located throughout the basin in August 1999 using a Lagrangian sampling design. Samples also were collected weekly and monthly from May 1999 through January 2000 at three of the sites (Granger Drain, Moxee Drain, and Yakima River at Kiona). This report includes data for 47 pesticide compounds from the analysis of filtered water using C-18 solid-phase extraction and gas chromatography/mass spectrometry.

Twenty-five pesticide compounds were detected in samples collected during both basinwide and fixed-interval sampling. Detection frequencies ranged from about 1 percent for ethalfluralin, ethoprophos, and lindane to 82 percent for atrazine. Maximum concentrations of azinphos-methyl, carbaryl, diazinon, and *p,p'*-DDE, a breakdown product of DDT, exceeded chronic-toxicity guidelines for the protection of aquatic life. The concentration of lindane, which was detected in one sample of wastewater treatment plant effluent, also exceeded the chronic-toxicity guideline for the protection of aquatic life.

Twenty pesticide compounds were detected during basinwide sampling of 34 sites. Atrazine was the most widely detected herbicide, and azinphos-methyl was the most widely detected insecticide. The median number of sites at which a particular pesticide compound was detected was six. Pesticide compounds detected at more than six sites include the herbicides atrazine, simazine, terbacil, and trifluralin; deethylatrazine, a breakdown product of atrazine; the insecticides azinphos-methyl, carbaryl, diazinon, and malathion; and *p,p'*-DDE.



Diversion of water from the Naches River near Yakima for public supply.

Because the potential for transport of pesticides from areas of application to surface water is a combined function of the chemical and physical properties of the pesticide, soil properties, slope, climate, application rate, and management factors, there was not a simple correspondence between pesticide occurrence and use in the Yakima River Basin. For example, the high

detection rates of atrazine, simazine, deethylatrazine, and *p,p'*-DDE are probably related more to their mobility and wide distribution in the hydrologic system than usage. Likewise, higher detection frequencies of the insecticides azinphos-methyl and carbaryl compared with chlorpyrifos appear to be related more to differences in their physical and chemical properties than usage.

The highest detection frequencies and concentrations of pesticides generally occurred during irrigation season, which is from mid-March to mid-October. Pesticides are applied during irrigation season, and runoff of excess irrigation water from fields transports them to surface water.

Ground-water discharges also transport some pesticides to surface water. Atrazine, deethylatrazine, and simazine were frequently detected in samples collected in Moxee and Granger Drains after the irrigation season when there was little or no surface runoff and most of the flow in the drains was derived from ground water. Carbaryl and *p,p'*-DDE also were detected in Granger Drain after the irrigation season.

Daily loads of atrazine, terbacil, azinphos-methyl, and carbaryl transported by the Yakima River at river mile 103.7 near Parker and discharged to the Yakima River between river mile 103.7 and river mile 72 varied widely between sites. For example, East Toppenish Drain discharged over 50 percent of the total load of terbacil to this reach of the Yakima River, but none of the total load of carbaryl and only about 4 percent of the total load of atrazine. Pesticide loads from the wastewater treatment plants were relatively small compared with loads from other inflows because their discharges were small.

Pesticide losses, defined as the ratio of the amount discharged from a basin from May 1999 through January 2000 divided by the amount applied during 1999, were estimated for Moxee and Granger Drains and the Yakima River at Kiona. Losses ranged from less than 0.01 to 1.5 percent of pesticides applied and are comparable to those observed (0.01 to 2.2 percent) in irrigated agricultural basins in the Central Columbia Plateau of Washington State.

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APPENDIXES

APPENDIX 1. EVALUATION OF QUALITY-CONTROL DATA

No pesticides were detected in field blanks, except for *p,p'*-DDE, which was detected in one of nine, or 11 percent of field blanks. The estimated concentration of p,p'-DDE in the one blank sample was 0.002 µg/L (microgram per liter), which is at the 25th percentile of concentrations of *p,p'*-DDE in all surface-water samples (table 3). Although laboratory quality control data for 1999 were not available, the detection rate of *p,p'*-DDE in 91 laboratory blank samples analyzed during 1998 was 14 percent. Detection of *p,p'*-DDE in more than 10 percent of field and laboratory blank samples indicates that a positive bias in the detection frequency of this compound is probable. Because it is not possible to determine which samples might be affected, no adjustments to concentrations and detection frequencies of *p,p'*-DDE in surface-water samples were made.

Mean relative percent differences in concentrations of pesticides detected in six pairs of surface-water samples ranged from 6.2 percent for atrazine to 15 percent for carbaryl (table A–1). Mean relative percent differences in concentrations of pesticides in pairs of spiked surface-water samples ranged from 2.7 for carbaryl to 16.3 for propargite (table A–2). The percent differences for the spiked sample pairs were generally smaller than those for the unspiked sample pairs because concentrations in the spiked samples were usually higher (about 0.1 µg/L). This is because for a fixed difference between concentrations in sample pairs, the relative percent difference increases as concentrations in samples decrease.

Recovery of analytes was determined for spiked surface-water samples and spiked pesticide-grade blank water (table A–3). Spike solution is usually added to surface-water samples in the field, but because of a shortage of spike mixture from the manufacturer, the spike mixture was added to all but 3 of 13 surface-water samples in the laboratory. Laboratory-reagent spikes, prepared with reagent (pesticide-free) water, are done routinely as part of laboratory quality control. In general, recoveries were poorest (as measured by the difference in the mean percent recovery from 100 percent) for the compounds azinphos-methyl, carbaryl, carbofuran, deethylatrazine, and terbacil. The concentrations of all these compounds are reported as estimated, which is consistent with the acknowledged difficulties in analyzing for them (Zaugg and others, 1995).

Martin (1999) discusses aspects of adjusting concentrations in samples based on recovery of analytes in field and laboratory spiked samples. For example, one might use the mean or median recovery to adjust concentrations in samples. If the recovery were 80 percent, then concentrations in samples would be multiplied by 100/80, or 1.25, to adjust for bias and other factors affecting recovery. Conversely, if the recovery were 120 percent, then concentrations in samples would be multiplied by factor of 100/120, or 0.83.

Because there are no definitive guidelines for adjusting concentrations based on recovery data, concentration data in this report were not adjusted. Some support for this decision could be inferred from Rose and Schroeder (1995), who suggested a mean recovery of 60 percent for volatile organic compounds as an acceptable lower limit. Applying this standard to the pesticides, only *p,p'*-DDE with a mean recovery of 56 percent for spiked surface-water samples and 55 percent for spiked reagent water had recoveries lower than this limit (table A–3). If one were to apply the difference between the 100 and 60 percent to the upper limit, then 140 percent would be an acceptable upper limit. Mean recoveries of azinphos-methyl, carbaryl, and carbofuran exceeded this limit in spiked surface-water samples, but not in spiked reagent water (table A–3).

APPENDIX 1. EVALUATION OF QUALITY-CONTROL DATA

Table A–1. Concentration and precision data for pesticides detected in more than one member of duplicate surface-water samples, Yakima River Basin, Washington, 1999–2000

[Concentrations are in micrograms per liter; <, less than; estimated (E) values were used in computations; nc, not calculated; relative percent difference = $\frac{|R1 - R2|}{\left(\frac{R1 + R2}{2}\right)} \times 100$, where $R1$ = sample 1 result and $R2$ = sample 2 result]

Site number	Sample date	Acetochlor	Atrazine	Azinphos-methyl	Carbaryl	Deethyl-atrazine	Malathion	*p,p'*-DDE	Simazine	Terbacil	Trifluralin
12500420	July 14, 1999	<0.002	0.00496	E0.0257	E0.00752	<0.002	0.0146	E0.00127	E0.00314	<0.007	<0.002
		<.002	.00524	E.0299	E.00826	<.002	.0140	E.00128	E.00323	<.007	<.002
	Relative percent difference	nc	5.5	15.1	9.4	nc	4.2	.78	2.8	nc	nc
12505450	July 15, 1999	.0208	.0385	E.0793	E.100	E.0138	.0059	E.00386	.00894	E.0516	.0214
		.0188	.0368	E.0839	E.117	E.0133	<.01	E.00420	.00758	E.0456	.0206
	Relative percent difference	10.1	4.5	5.6	15.7	3.7	nc	8.4	16.5	12.3	3.8
12505450	July 22, 1999	.0132	.0295	E.0812	E.0578	E.0134	E.0042	E.0018	.00269	E.0252	.0234
		.0155	.0294	<.08	E.0575	E.0117	<.01	E.00242	.00246	E.031	.0195
	Relative percent difference	16.0	.34	nc	.52	13.5	nc	29.4	8.9	20.6	18.2
12505450	Sept. 30, 1999	<.002	.00894	E.0108	E.07	E.00818	<.005	E.00261	.00690	E.011	.0143
		<.002	.00858	E.009	E.0541	E.00771	<.005	E.00264	.00772	E.0103	.0135
	Relative percent difference	nc	4.1	18.2	25.6	5.9	nc	1.1	11.2	6.6	5.8
12510500	July 29, 1999	<.002	.0145	<.0250	E.0765	E.0103	.00567	E.00847	.0116	E.15	<.002
		<.002	.0120	E.0242	E.0601	E.0097	E.00497	E.00912	E.00998	E.144	E.00252
	Relative percent difference	nc	18.9	nc	nc	6.0	13.2	7.4	15.0	4.1	nc
12510500	Nov. 11, 1999	<.002	.00624	<.001	<.003	E.00561	<.005	<.006	.00522	<.007	<.002
		<.002	.00647	<.001	<.003	E.00583	<.005	<.006	.00564	<.007	<.002
	Relative percent difference	nc	3.6	nc	nc	3.8	nc	nc	7.7	nc	nc
Summary:											
	Minimum percent difference	10.1	.34	5.6	0.52	3.7	4.2	.78	2.8	4.1	3.8
	Maximum percent difference	16.0	18.9	18.2	25.6	13.5	13.2	29.4	16.5	20.6	18.2
	Mean percent difference	13.1	6.2	13.0	15.0	6.6	8.7	9.4	10.4	10.9	9.2

Table A–2. Precision data for pairs of spiked surface-water samples, Yakima River Basin, Washington, 1999–2000

[Relative percent difference = $\frac{|R1 - R2|}{\left(\frac{R1 + R2}{2}\right)}$ X 100, where *R1* = sample 1 result and *R2* = sample 2 result; estimated values were used in computations]

Pesticide	Trade or common name(s)	Number of pairs	Minimum relative percent difference	Maximum relative percent difference	Mean relative percent difference
Acetochlor	Guardian	4	0.0	8.9	3.0
Alachlor	Lasso	4	2.5	8.7	5.8
Atrazine	AAtrex	4	3.3	7.9	5.0
Azinphos-methyl	Guthion	4	2.2	4.6	3.7
Benfluralin	Balan, Benefin	4	4.3	10.2	6.6
Butylate	Sutan +, Genate Plus	4	1.8	17.5	6.7
Carbaryl	Sevin, Savit	4	2.2	3.0	2.7
Carbofuran	Furadan	4	2.3	4.4	3.1
Chlorpyrifos	Lorsban, Dursban	4	.5	9.5	5.8
Cyanazine	Bladex	4	3.9	15.9	8.8
p,p'-DDE	none	4	1.9	7.2	4.6
Deethylatrazine (DEA)	none	4	5.0	7.5	6.3
Diazinon	Diazinon	4	.9	5.7	3.9
Dieldrin	Panoram D-31	4	2.0	6.7	3.7
2,6-Diethylanaline	none	4	1.8	5.2	3.7
Disulfoton	Di-Syston	4	3.9	11.7	8.5
EPTC	Eptam, Eradicane	4	1.9	6.6	4.3
Ethalfluralin	Sonalan, Curbit EC	4	1.9	11.7	5.4
Ethoprophos	Mocap	4	4.4	8.9	6.2
Fonofos	Dyfonate	4	2.7	9.7	6.5
alpha-HCH	none	4	3.5	11.3	5.8
gamma-HCH	Lindane	4	1.9	23.3	9.4
Linuron	Lorox, Linex	4	3.2	11.7	7.3
Malathion	malathion	4	3.2	15.9	9.7
Methyl parathion	Penncap-M	4	3.3	7.8	6.0
Metolachlor	Dual, Pennant	4	1.9	11.1	4.8
Metribuzin	Lexone, Sencor	4	5.7	9.3	7.9
Molinate	Ordram	4	4.3	14.3	7.4
Napropamide	Devrinol	4	3.3	9.4	5.7
Parathion	several	4	3.3	14.4	7.9
Pebulate	Tillam	4	2.8	5.8	4.4
Pendimethalin	Prowl, Stomp	4	5.1	10.5	8.5
cis-Permethrin	Ambush, Pounce	4	2.3	10.9	6.9
Phorate	Thimet, Rampart	4	2.8	10.9	7.1
Prometon	Pramitol	4	2.3	14.5	8.3
Propachlor	Ramrod	4	5.0	14.9	7.8
Propanil	Stampede	4	3.9	14.1	8.1
Propargite	Comite, Omite	4	.9	38.1	16.3
Simazine	Aquazine, Princep	4	3.6	10.1	5.4
Tebuthiuron	Spike	4	1.8	9.7	4.8
Terbacil	Sinbar	4	.8	10.3	5.6
Terbufos	Counter	4	5.1	6.5	5.8
Thiobencarb	Bolero	4	2.5	10.9	6.6
Triallate	Far-Go	4	2.8	15.5	6.7
Trifluralin	Treflan, Trilin	4	1.8	10.7	5.8

Table A–3. Summary of recoveries from field-matrix- and laboratory-reagent-spike pesticide analyses

[SD, standard deviation of the mean recovery; --, no data; laboratory-reagent spikes were analyzed at the National Water Quality Laboratory during calendar year 1999]

Pesticide target analyte	Field-matrix spikes			Laboratory-reagent spikes		
	Mean recovery (percent)	SD recovery (percent)	Number of samples	Mean recovery (percent)	SD recovery (percent)	Number of samples
Acetochlor	105	11	13	99	12	422
Alachlor	106	11	13	102	13	422
Atrazine	100	11	13	97	10	422
Azinphos-methyl	153	44	13	86	34	422
Benfluralin	77	7.8	13	64	13	422
Butylate	97	5.8	13	88	9.8	422
Carbaryl	151	84	13	125	60	422
Carbofuran	175	102	13	133	57	422
Chlorpyrifos	86	10	13	90	9.8	422
Cyanazine	115	19	13	100	13	422
DCPA	--	--	--	97	11	422
p,p'-DDE	56	6.1	13	55	8.4	422
Desethylatrazine	71	9.8	13	61	17	422
Diazinon	95	11	13	93	11	422
Dieldrin	92	16	13	87	13	422
2,6-Diethylanaline	93	4.7	13	86	11	422
Disulfoton	69	21	13	76	14	422
EPTC	99	11	13	91	9.2	422
Ethalfluralin	90	12	13	77	15	422
Ethoprophos	93	9.6	13	86	13	422
Fonofos	96	15	13	93	12	422
alpha-HCH	92	16	13	94	12	422
gamma-HCH	98	15	13	96	12	422
Linuron	135	25	13	114	46	422
Malathion	99	24	13	92	14	422
Methyl parathion	109	20	13	95	27	422
Metolachlor	103	9.5	13	97	12	422
Metribuzin	106	17	13	91	14	422
Molinate	97	6.2	13	93	9.2	422
Napropamide	105	13	13	89	14	422
Parathion	105	21	13	92	32	422
Pebulate	96	5.7	13	90	8.8	422
Pendimethalin	85	13	13	71	17	422
cis-Permethrin	--	--	--	38	9.8	422
Phorate	68	20	13	81	14	422
Prometon	101	11	13	95	12	422
Propyzamide	99	10	13	94	11	422
Propachlor	112	9.3	13	101	12	422
Propanil	109	16	13	106	15	422
Propargite	128	68	13	74	22	422
Simazine	115	11	13	108	14	422
Tebuthiuron	129	11	13	119	21	422
Terbacil	140	67	13	113	46	422
Terbufos	82	11	13	82	10	422
Thiobencarb	97	11	13	97	11	422
Triallate	92	14	13	90	12	422
Trifluralin	82	11	13	68	14	422

APPENDIX 2. SOURCES OF DATA USED TO ESTIMATE PESTICIDE USAGE

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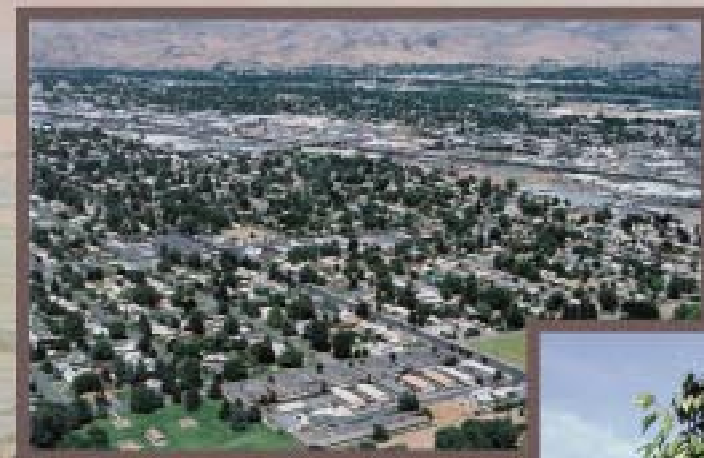

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