Pesticides in Surface Waters of the Upper Colorado River Basin, Colorado, 1996–98

By Nancy J. Bauch and Norman E. Spahr

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FOREWORD

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

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

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

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

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

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

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

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

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
acre	4,047	square meter (m^2)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
inch	25.4	millimeter (mm)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
kilogram (kg)	2.2046	pound (lb)
liter (L)	0.2642	gallon (gal)
square mile (mi^2)	2.590	square kilometer (km^2)

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = 5/9 (°F - 32)$$

ADDITIONAL ABBREVIATIONS

E	estimated
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
µg/L	micrograms per liter
µm	micrometer
mm	millimeter
MRL	method reporting limit
NAWQA	National Water-Quality Assessment
NWQL	National Water Quality Laboratory
UCOL	Upper Colorado River Basin study unit
USEPA	U.S. Environmental Protection Agency
WY	water year

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Abstract

Forty-four river, stream, and drain sites in the Upper Colorado River Basin in Colorado were sampled during 1996–98 to determine the occurrence and distribution of pesticides in the basin. In a fixed-station study, 57 surface-water samples were collected from October 1996 through January 1998 at four sites. Each site was sampled approximately monthly for up to a year, with more frequent sampling during the spring and summer growing season. In a synoptic study, surface-water samples were collected at 43 sites in the agricultural areas of the Grand Valley and the Uncompahgre River Valley in May 1998. Each site was sampled once.

Pesticide concentrations generally were low and varied seasonally and across land uses. Thirty-five pesticides were detected at least once in the two studies, and 11 pesticides accounted for almost 82 percent of the detections. Herbicides were more commonly detected than insecticides, and only the herbicides alachlor and atrazine were detected in more than 50 percent of the samples. Carbofuran was the most commonly detected insecticide and was detected in 19 percent of the samples. Pesticide detections increased and were measured at higher concentrations in the summer months and at the agriculture sites. All pesticide concentrations were less than drinking-water standards, and most complied with human-health advisories and criteria for the protection of freshwater aquatic life. Pesticides in the Upper Colorado River Basin in Colorado were detected slightly less frequently and generally at lower concentrations than in 20 National Water-Quality Assessment Program study-unit basins that collected water-quality data from 1992 through 1996. Results from surface-water sampling conducted during 1996–98 in the Upper Colorado River Basin in Colorado indicate that beneficial uses of water were not being impaired by the presence of pesticides in surface waters in the basin.

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water-Quality Assessment (NAWQA) Program. The goals of the NAWQA Program are to (1) describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers; (2) describe how water quality is changing over time; and (3) improve understanding of the primary natural and human factors that affect water-quality conditions (Leahy and others, 1990). Many of the Nation's most important river basins and aquifers, represented as study units, are being investigated through the NAWQA Program. The Upper Colorado River Basin (UCOL) study unit (fig. 1), located primarily in western Colorado, is one of the NAWQA study units. As part of the NAWQA Program, investigations of the hydrology and water quality of the UCOL began in 1994. The occurrence and distribution of pesticides in surface water are two of the main topics of interest in the NAWQA Program. Issues of concern include the types and concentrations of pesticides in the Nation's rivers and streams, seasonal distribution of pesticides, relation of pesticide occurrences and concentrations to land use, and potential of pesticide concentrations to

Figure 1. Location of the Upper Colorado River Basin study unit, physiographic provinces, and fixed-station sites for pesticide sampling.

affect human health and aquatic ecosystems. In the UCOL, water samples were collected at four sites (fig. 1) during 1996–98 to determine temporal and spatial variations in the occurrence and concentrations of pesticides. A synoptic study of 43 sites (fig. 2) was completed in 1998 to determine the spatial distribution of pesticide concentrations within agricultural areas of the UCOL.

Purpose and Scope

The purposes of this report are to (1) describe pesticide concentrations in rivers, streams, and drains in the UCOL study unit during 1996–98 and (2) determine the distribution of pesticide detections and concentrations among different land uses, site types, and agricultural subbasins in the study unit. Surface-water sites in the UCOL basin were sampled, and samples were analyzed for a series of pesticide compounds to temporally and spatially describe pesticide concentrations. Four river and stream sites in the study unit were sampled frequently for up to one year. Forty-three river, stream, and drain sites in agricultural areas of the study unit were sampled once during a synoptic study.

Description of the Upper Colorado River Basin study unit

The UCOL study unit has a drainage area of about 17,800 mi^2 (fig. 1), all located in western Colorado except for about 100 mi^2 in eastern Utah (Driver, 1994). The study unit is divided almost equally into two physiographic provinces—the Southern Rocky Mountains in the east and the Colorado Plateau in the west (fig. 1). The environmental setting of the UCOL study unit and its physiographic provinces has been described by Apodaca and others (1996).

Land uses in the UCOL study unit include rangeland or forest, mining, urban, and agriculture. Rangeland or forests make up about 85 percent of the study unit area and are used for recreation, wildlife habitat, livestock grazing, and logging. Tourism and recreation are the major land-use activities in the Southern Rocky Mountains province, and agriculture is the predominant land-use activity in Delta, Mesa, and Montrose Counties in the Colorado Plateau. Tourism, recreation, and agriculture are all important land-use activities in Gunnison County, located mostly in the Southern Rocky Mountains physiographic province. Because of the semiarid climate (generally, less than 10 in/yr of precipitation in the western valleys), little agricultural production is possible without irrigation. Irrigation takes place mainly in river valleys and in low-altitude areas of the Colorado Plateau. In the Grand and Uncompahgre River Valleys (fig. 2), agricultural areas are supported by an extensive system of canals and ditches. About 97 percent of the off-stream water use in the study unit is for irrigation (Apodaca and others, 1996).

The major crops produced in the study unit are alfalfa and other hay, corn (grain and silage), dry beans, grains, vegetables (primarily sweet corn and onions), fruit (apples, tart cherries, peaches, and pears), melons (cantaloupe and watermelon), and grapes for wine production. Acreage and production data for Colorado in 1997 are available by county for alfalfa, other hay, corn (grain and silage), dry beans, winter and spring wheat, barley, and oats (Colorado Department of Agriculture, 1998) and are shown in table 1 for 10 counties in the study unit. Alfalfa and other hay together were the major crops produced in each county in 1997 and were the only crops tallied for Eagle, Grand, Gunnison, Ouray, Pitkin, and Summit Counties. Dry beans and corn also were commonly harvested in Delta and Montrose Counties, while corn and winter wheat were commonly produced in Mesa County in 1997. Most (97.6 percent) of the harvested acreage was irrigated. Alfalfa, other hay, and winter wheat were produced on the nonirrigated land. Acreage and production data for individual counties were not available for vegetables, fruit, melons, and grapes.

Pesticide-use data for the 1996–98 sampling period were not available for the study unit. Pesticide use by crop type in Colorado was estimated by Bohmont (1991, 1993) for seven regions in the State for 1989 and statewide for 1992. In the 1989 survey, four counties (Garfield, Mesa, Delta, and Montrose) of the UCOL study unit were represented as the West Central agricultural region. Ouray County was included in the Four Corners region, and no pesticide-use data were reported for Eagle, Grand, Gunnison, Pitkin, and Summit Counties. The six most common pesticides applied to irrigated crops in the West Central agricultural region in 1989 were (1) EPTC, (2) alachlor, (3) 2,4-D, (4) parathion-ethyl [parathion], (5) metolachlor, and (6) atrazine, as measured by

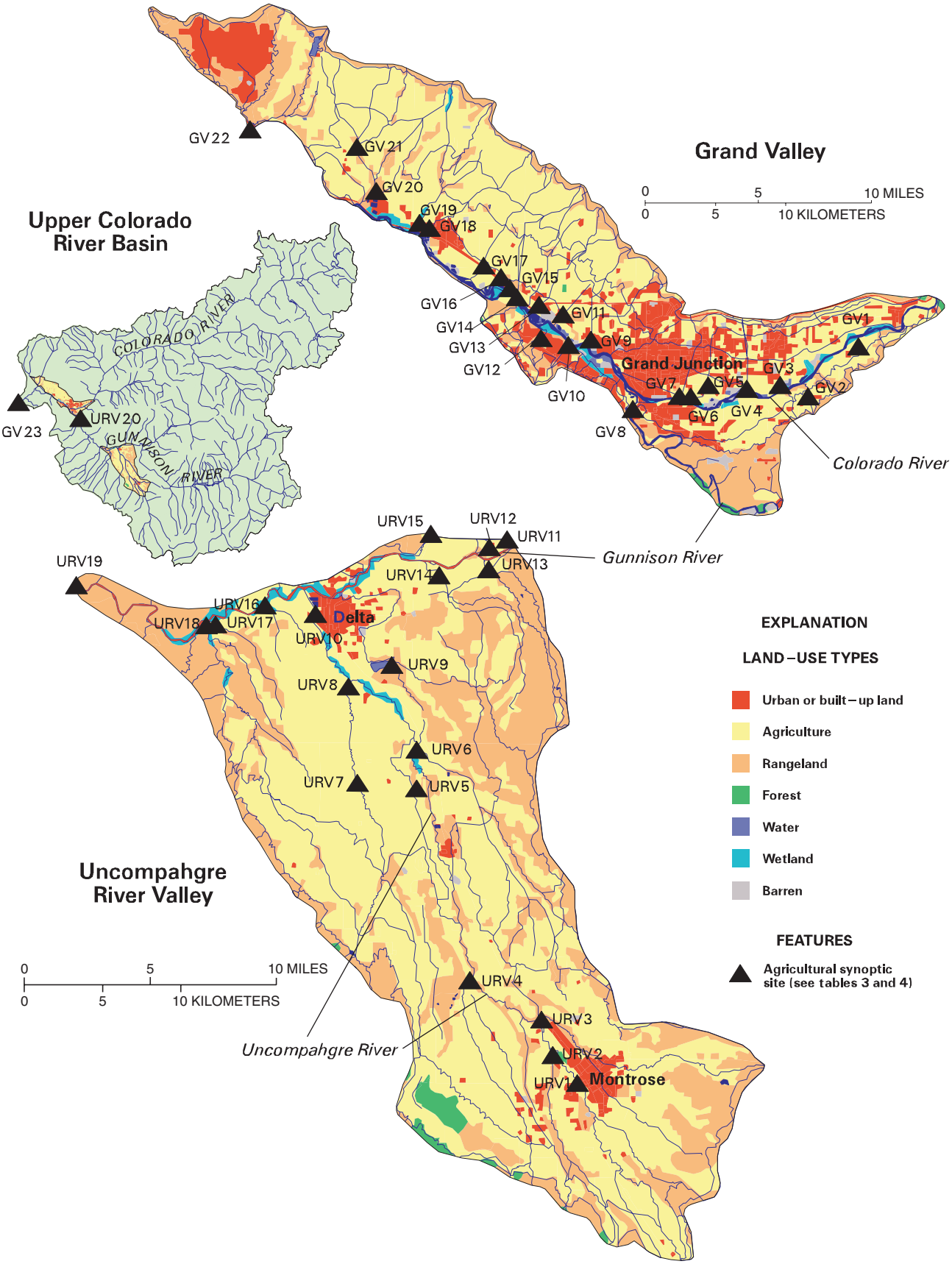

Figure 2. Location of agricultural synoptic sites in the Grand Valley and Uncompahgre River Valley, Upper Colorado River Basin.

Table 1. Harvested acreage for crops and percentage of harvested acreage irrigated in 10 counties in the Upper Colorado River Basin study unit, Colorado, 1997

[Data from Colorado Department of Agriculture, 1998; --, no data]

Crop	County										Total
	Delta	Eagle	Garfield[1]	Grand	Gunnison	Mesa[1]	Montrose[1]	Ouray	Pitkin	Summit	
Alfalfa	24,000	6,000	31,000	1,500	500	32,000	32,000	3,000	1,500	--	131,500
Hay[2]	5,500	5,500	10,000	41,000	22,500	12,000	9,000	8,000	4,000	3,500	121,000
Corn—grain and silage	8,600	--	--	--	--	10,000	11,800	--	--	--	30,400
Dry beans	3,500	--	--	--	--	500	13,000	--	--	--	17,000
Winter wheat	500	--	1,500	--	--	4,000	2,000	--	--	--	8,000
Oats	900	--	600	--	--	500	1,000	--	--	--	3,000
Barley	--	--	200	--	--	200	1,100	--	--	--	1,500
Spring wheat	--	--	--	--	--	--	500	--	--	--	500
Total harvested acres	**43,000**	**11,500**	**43,300**	**42,500**	**23,000**	**59,200**	**70,400**	**11,000**	**5,500**	**3,500**	**312,900**
Percentage harvested acres irrigated	**98.4**	**95.7**	**93.5**	**95.3**	**100**	**98.3**	**99.3**	**100**	**100**	**100**	**97.6**

[1] Includes those areas of the county outside the boundaries of the Upper Colorado River Basin study unit. Actual values for the study unit may be less.
[2] Includes wild, millet, sudan, clover and timothy, grain, and other miscellaneous tame hays.

pounds active ingredient applied. These pesticides were primarily applied to corn, dry beans, pasture, and alfalfa. Newer pesticides, such as acetochlor, were not included in the 1989 or 1992 pesticide-use surveys. Nationally, the most heavily used pesticides in agriculture in 1992 were the herbicides (1) atrazine, (2) metolachlor, (3) 2,4-D, (4) cyanazine, and (5) alachlor (U.S. Geological Survey, 1998a).

Study Design

The surface-water sampling for this study was designed to investigate the occurrence and temporal and spatial distribution of pesticides in the rivers, streams, and drains of the UCOL study unit. To accomplish this, two sampling networks were developed—the fixed-station network and the synoptic network.

The fixed-station network was developed out of the larger surface-water-monitoring network of the UCOL study unit (Spahr and others, 1996). Four stations were designated for pesticide collection, one in the Southern Rocky Mountains physiographic province and three in the Colorado Plateau physiographic province (fig. 1, table 2). Three of the stations —Gore Creek at mouth near Minturn, Dry Creek near Begonia Road, near Delta, and Reed Wash near Mack—were selected as "indicator" sites. These sites represent a particular land use and in this study represented either urban/forest or agriculture. The watershed for the Gore Creek station includes Vail, Colorado, a resort town with a permanent population of 4,353 in 1995 (Northwest Colorado Council of Governments, 1997) and substantial increases in summer and winter because of tourism. Most of the Gore Creek watershed is forest land that is included in the White River National Forest. Both Dry Creek near Begonia Road and Reed Wash near Mack are natural watercourses in the agricultural areas of the Uncompahgre River Valley and Grand Valley, respectively, and function as drains for irrigation return flows during parts of the year. The final station in the fixed-station network, the Colorado River near Colorado-Utah State Line, was selected as an "integrator" site. Located at the terminus of the study unit, this station represented the integration of water quality from all land uses in the Upper Colorado River Basin in Colorado, including agriculture, forest, mining, rangeland, and urban. Each station was sampled approximately monthly for a 6-month to 1-year time period; sampling occurred from October 1996 through January 1998. Samples were collected more frequently (weekly or biweekly) during the spring and summer growing season. The total number of samples collected at each site varied, depending on expected pesticide use, and was greater for the Dry Creek near Begonia Road and Reed Wash near Mack agriculture sites.

Table 2. Description of surface-water-sampling sites for pesticides in the Upper Colorado River Basin fixed-station network

[USGS, U.S. Geological Survey]

Site number (fig. 1)	Site name	USGS site number	Sampling period	Number of samples (excluding quality assurance)	Site type	Land use	Drainage area (square miles)
FS1	Gore Creek at mouth near Minturn	09066510	10/96–09/97	10	Indicator	Urban/Forest	102
FS2	Dry Creek near Begonia Road, near Delta	09149480	10/96–09/97	15	Indicator	Agriculture	175
FS3	Reed Wash near Mack	09153290	10/96–09/97	24	Indicator	Agriculture	16
FS4	Colorado River near Colorado-Utah State Line	09163500	04/97–01/98	8	Integrator	All[1]	17,843

[1]Includes agriculture, forest, mining, rangeland, and urban.

In the UCOL study unit, areas of intensive agriculture are located in the Grand Valley and the Uncompahgre River Valley (fig. 2). Both areas have been used for agriculture since the 1880's. Extensive systems of canals and ditches provide the means for delivery of irrigation water, and many drains have been developed to carry the irrigation return flows to rivers and streams in the two areas. A synoptic study investigating the water quality of agricultural drains in the Grand and Uncompahgre River Valleys was conducted in May 1998. Water samples collected from a network of 43 river, stream, and drain sites were analyzed for physical properties and chemical constituents, nutrients, major ions, pesticides, and suspended sediment. This report focuses only on the pesticide data. May was chosen as the time period for the synoptic sampling because pesticides were frequently detected in this month in the fixed-station sampling during the previous year, and May is early in the growing season. Site selection for the synoptic study was based on the availability of historical pesticide-occurrence data (Butler and others, 1991, 1994) and on the spatial distribution of streams and drains. Twenty-three sites in the Grand Valley area (hereinafter Grand Valley), including two sites in the fixed-station network pesticide-sampling scheme, were sampled once in May 1998 (fig. 2, table 3). Twenty sites in the Uncompahgre River Valley area (hereinafter Uncompahgre River Valley), including one fixed-station pesticide-sampling site, were sampled once in May 1998 (fig. 2, table 4). The Gunnison River near Grand Junction site (URV20), located downstream from the Uncompahgre River Valley, is included in table 4 with the Uncompahgre River Valley sites because its streamflow includes all of the streamflow of the Uncompahgre River Basin.

Table 3. Agricultural synoptic surface-water-sampling sites, Grand Valley, Upper Colorado River Basin

[USGS, U.S. Geological Survey]

Site number (fig. 2)	Site name	USGS site number	Sampling date
GV1	Drain at 36 Road, East Orchard Mesa	390517108230501	05/05/98
GV2	Drain at C 1/2 and 33 3/4 Roads, Central Orchard Mesa	390322108253401	05/05/98
GV3	33 Road Drain at mouth near Clifton	390347108265800	05/05/98
GV4	Lewis Wash near Grand Junction	09106200	05/05/98
GV5	Drain at D and 29 3/4 Roads	390345108073301	05/06/98
GV6	Drain at C 1/2 and 28 1/2 Roads	390319108312501	05/06/98
GV7	Indian Wash at C 1/2 Road	390320108315901	05/06/98
GV8	Orchard Mesa Drain at Grand Junction	09152600	05/07/98
GV9	Leach Creek at Durham	09152650	05/06/98
GV10	Drain along Redlands Parkway, at mouth	390514108373201	05/07/98
GV11	Appleton Drain near mouth at G Road	390624108374900	05/07/98
GV12	Limekiln Gulch near mouth	390529108385401	05/07/98
GV13	Persigo Wash at River Road	390645108390101	05/11/98
GV14	Copeco Drain near mouth at Hwy 50	390723108400500	05/11/98
GV15	Hunter Wash at River Road	390717108400501	05/12/98
GV16	Goodwin Drain at Highway 50	390747108405600	05/12/98
GV17	Adobe Creek near Fruita	09152900	05/12/98
GV18	Little Salt Wash at Hwy 50	390938108443101	05/12/98
GV19	Big Salt Wash at Fruita	09153270	05/13/98
GV20	Reed Wash near Loma	09153300	05/13/98
GV21	Reed Wash near Mack	09153290	05/08/98
GV22	Salt Creek near Mack	09163490	05/13/98
GV23	Colorado River near Colorado-Utah State Line	09163500	05/20/98

Table 4. Agricultural synoptic surface-water-sampling sites, Uncompahgre River Valley, Upper Colorado River Basin

[USGS, U.S. Geological Survey]

Site number (fig. 2)	Site name	USGS site number	Sampling date
URV1	Uncompahgre River at Montrose at Hwy 90	382831107530601	05/21/98
URV2	Happy Canyon Creek at Marine Road, near mouth	382928107541101	05/22/98
URV3	Cedar Creek near mouth	383041107544201	05/21/98
URV4	Spring Creek at Jay-Jay Road	383201107575301	05/20/98
URV5	Drain at Blossom Road, near Chipeta	383834108001701	05/19/98
URV6	Loutsenhizer Arroyo below Garnet Canal, at mouth	383953108001701	05/19/98
URV7	Dry Creek near Begonia Road, near Delta	09149480	05/21/98
URV8	Dry Creek at mouth, near Delta	384202108032001	05/21/98
URV9	Garnet Canal above Sweitzer Lake diversion	384247108012401	05/19/98
URV10	Uncompahgre River at Delta	09149500	05/14/98
URV11	Currant Creek near Read	09137050	05/15/98
URV12	Alfalfa Run at Austin	384649107570501	05/15/98
URV13	Peach Valley Arroyo near mouth	384604107570701	05/19/98
URV14	Unnamed drainage at Highway 92 near Read	384551107591901	05/14/98
URV15	Tongue Creek at Cory	09144200	05/18/98
URV16	Cummings Gulch at mouth	384448108070301	05/14/98
URV17	Seep Creek at G Road, near mouth	384408108091501	05/14/98
URV18	Roubideau Creek at mouth, near Delta	09150500	05/18/98
URV19	Gunnison River above Escalante Creek, near Delta	384527108152701	05/20/98
URV20	Gunnison River near Grand Junction	09152500	05/04/98

Sampling and Laboratory Methods

Water-quality samples for pesticide analysis were collected by equal-width-increment sampling and processed onsite using techniques described by Shelton (1994). Pesticide samples were filtered in the field through a 142-mm-diameter, 0.7-µm baked glass-fiber filter and stored on ice for shipment or delivery to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado.

The dissolved pesticide samples were extracted and analyzed at the NWQL using methods described by Zaugg and others (1995) and Werner and others (1996). The concentrations of 83 pesticides and pesticide degradation products (hereinafter known as pesticides) were determined either by gas chromatography with mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC) with ultraviolet spectroscopy. Forty-seven pesticides were analyzed by GC/MS and 39 by HPLC (table 5). Both methods analyzed for carbaryl, carbofuran, and linuron. Water samples from both the fixed-station network and the synoptic network were analyzed for the same pesticides. A total of 155 (86 fixed-station, 69 synoptic) water samples, including quality-assurance samples, were analyzed for pesticides at the NWQL for this UCOL pesticide study.

Pesticide concentrations are reported in terms of method reporting limits (MRLs). The MRL is the minimum concentration of a pesticide that can be reliably reported for an analytical method (Timme, 1995). For this study, MRLs ranged from 0.001 to 1.2 µg/L (table 5). Some MRLs for pesticides analyzed with the HPLC method were adjusted upwards on December 15, 1997 (table 5). Pesticide concentrations less than the MRL are reported with a "<" symbol. Concentrations for some pesticides are reported as estimated (E) concentrations because of variable analytical performance, or a measured concentration was greater than the maximum method calibration value for the particular pesticide. For a pesticide with an estimated concentration, the pesticide has passed all qualitative

Table 5. Pesticide target analytes, method reporting limits, drinking-water standards, and aquatic-life criteria

[µg/L, micrograms per liter; H, herbicide; I, insecticide; D, pesticide degradate; F, fungicide; --, no drinking-water standard, guideline, or criteria for aquatic-life protection established; drinking-water standards are U.S. Environmental Protection Agency primary drinking-water standards; drinking-water standards and guidelines are from U.S. Environmental Protection Agency (1999a), unless otherwise noted; criteria for aquatic-life protection are chronic criteria from U.S. Environmental Protection Agency (1999b), unless otherwise noted]

Pesticide	Trade or common name	Type of pesti-cide	Chemical Abstract Service registry number	Method reporting limit (µg/L)	Drinking-water standard or health-advisory guideline (µg/L)	Freshwater-chronic criterion for protection of aquatic life (µg/L)
Gas Chromatography/Mass Spectrometry analysis method						
Acetochlor	Guardian, Relay	H	34256-82-1	0.002	--	--
Alachlor	Lasso, Alanex	H	15972-60-8	0.002	2	--
Atrazine	Aatrex	H	1912-24-9	0.001	3	[1]1.8
Azinphos-methyl[2]	Guthion	I	86-50-0	0.001	--	0.01
Benfluralin	Balan, Benefin	H	1861-40-1	0.002	--	--
Butylate	Sutan+, Genate Plus	H	2008-41-5	0.002	[3]350	--
Carbaryl[2, 4]	Sevin, Carbatox	I	63-25-2	0.003	[3]700	[1]0.2
Carbofuran[2, 4]	Furadan	I	1563-66-2	0.003	40	[1]1.8
Chlorpyrifos	Lorsdan, Dursban	I	2921-88-2	0.004	[3]20	0.041
Cyanazine	Bladex	H	21725-46-2	0.004	[3]1	[5]2
DCPA	Dacthal	H	1861-32-1	0.002	--	--
p,p'-DDE	none	D	72-55-9	0.006	[6]0.1	--
Deethylatrazine[2]	none	D	6190-65-4	0.002	--	--
Diazinon	Spectracide, Basudin	I	333-41-5	0.002	[3]0.6	[7]0.08
Dieldrin	Panoram D-31, Octalox	I	60-57-1	0.001	[8]0.002	0.056
2,6-Diethylaniline	none	D	579-66-8	0.003	--	--
Disulfoton	Di-Syston	I	298-04-4	0.017	[3]0.3	--
EPTC	Eptam, Eradicane	H	759-94-4	0.002	--	--
Ethalfluralin	Sonalan	H	55283-68-6	0.004	--	--
Ethoprop	Mocap, Prophos	I	13194-48-4	0.003	--	--
Fonofos	Dyfonate	I	944-22-9	0.003	[3]10	--
alpha-HCH	none	D	319-84-6	0.002	[6]0.006	--
gamma-HCH	Lindane, Isotox	I	58-89-9	0.004	0.2	[7]0.01
Linuron[4]	Lorox, Linurex	H	330-55-2	0.002	--	[9]7
Malathion	Cythion, Malaspray	I	121-75-5	0.005	[3]200	0.1
Methyl parathion	Penncap-M	I	298-00-0	0.006	[3]2	--
Metolachlor	Dual, Bicep	H	51218-45-2	0.002	[3]70	[5]7.8
Metribuzin	Lexone, Sencor	H	21087-64-9	0.004	[3]100	[5]1
Molinate	Hydram, Ordram	H	2212-67-1	0.004	--	--
Napropamide	Devrinol	H	15299-99-7	0.003	--	--
Parathion	Alkron, Bladan	I	56-38-2	0.004	--	0.013
Pebulate	Tillam	H	1114-71-2	0.004	--	--
Pendimethalin	Prowl, Stomp	H	40487-42-1	0.004	--	--
cis-Permethrin	none	I	52341-33-00	0.005	--	--
Phorate	Thimet, Rampart	I	298-02-2	0.002	--	--
Prometon	Pramitol, Gesafram	H	1610-18-0	0.018	[10]100	--
Pronamide	Kerb	H	23950-58-5	0.003	[3]50	--

Table 5. Pesticide target analytes, method reporting limits, drinking-water standards, and aquatic-life criteria—Continued

[µg/L, micrograms per liter; H, herbicide; I, insecticide; D, pesticide degradate; F, fungicide; --, no drinking-water standard, guideline, or criteria for aquatic-life protection established; drinking-water standards are U.S. Environmental Protection Agency primary drinking-water standards; drinking-water standards and guidelines are from U.S. Environmental Protection Agency (1999a), unless otherwise noted; criteria for aquatic-life protection are chronic criteria from U.S. Environmental Protection Agency (1999b), unless otherwise noted]

Pesticide	Trade or common name	Type of pesticide	Chemical Abstract Service registry number	Method reporting limit (µg/L)	Drinking-water standard or health-advisory guideline (µg/L)	Freshwater-chronic criterion for protection of aquatic life (µg/L)
Gas Chromatography/Mass Spectrometry analysis method—Continued						
Propachlor	Ramrod, Bexton	H	1918-16-7	0.007	[3]90	--
Propanil	Stam	H	709-98-8	0.004	--	--
Propargite	Comite, Omite	I	2312-35-8	0.013	--	--
Simazine	Aquazine, Princep	H	122-34-9	0.005	4	[1]10
Tebuthiuron	Spike, Graslan	H	34014-18-1	0.01	[3]500	[5]1.6
Terbacil[2]	Sinbar, Herbicide 732	H	5902-51-2	0.007	[3]90	--
Terbufos	Counter, Contraven	I	13071-79-9	0.013	[3]0.9	--
Thiobencarb	Bolero, Saturn	H	28249-77-6	0.002	--	--
Triallate	Far-Go, Avadex BW	H	2303-17-5	0.001	--	[5]0.24
Trifluralin	Treflan, Trim	H	1582-09-8	0.002	[3]5	[1]0.2
High-Performance Liquid Chromatography analysis method						
2,4-D	Weed-Broom, Lawn-Keep	H	94-75-7	0.035 [11]0.15	70	[1]4
2,4-DB	Embutone, Venceweed	H	94-82-6	0.035 [11]0.24	--	--
2,4,5-T	Brushtox, Dacamine	H	93-76-5	0.035	[3]70	--
2,4,5-TP	Silvex, Fenoprop	H	93-72-1	0.021	50	[12]1.4
3-Hydroxy-carbofuran	none	D	16655-82-6	0.014	--	--
Acifluorfen	Blazer, Tackle	H	50594-66-6	0.035	[8]1	--
Aldicarb[13]	Temik	I	116-06-3	0.016 [11]0.55	[14]7	[15]1
Aldicarb sulfone[13]	Temik sulfone, Standak	I, D	1646-88-4	0.016 [11]0.10	[14]7	[15]1
Aldicarb sulfoxide[13]	Temik sulfoxide	D	1646-87-3	0.021	[14]7	[15]1
Bentazon	Basagran	H	25057-89-0	0.014	[3]200	--
Bromacil	Hyvar, Borea	H	314-40-9	0.035	[3]90	[5]5
Bromoxynil	Buctril, Brominal	H	1689-84-5	0.035	--	[16]5
Carbaryl[4]	Sevin, Carbatox	I	63-25-2	0.008	[3]700	[1]0.2
Carbofuran[4]	Furadan	I	1563-66-2	0.028 [11]0.12	40	[1]1.8
Chloramben[17]	Amiben, Vegiben	H	133-90-4	0.011 [11]0.42	[3]100	--
Chlorothalonil[18]	Bravo, Forturf	F	1897-45-6	0.035 [11]0.48	[8]1.5	[5]0.18
Clopyralid	Lontrel, Lontril T	H	1702-17-6	0.05 [11]0.23	--	--
Dacthal, mono-acid	DCPA, mono-acid	H	887-54-7	0.017	--	--

Table 5. Pesticide target analytes, method reporting limits, drinking-water standards, and aquatic-life criteria—Continued

[µg/L, micrograms per liter; H, herbicide; I, insecticide; D, pesticide degradate; F, fungicide; --, no drinking-water standard, guideline, or criteria for aquatic-life protection established; drinking-water standards are U.S. Environmental Protection Agency primary drinking-water standards; drinking-water standards and guidelines are from U.S. Environmental Protection Agency (1999a), unless otherwise noted; criteria for aquatic-life protection are chronic criteria from U.S. Environmental Protection Agency (1999b), unless otherwise noted]

Pesticide	Trade or common name	Type of pesti-cide	Chemical Abstract Service registry number	Method reporting limit (µg/L)	Drinking-water standard or health-advisory guideline (µg/L)	Freshwater-chronic criterion for protection of aquatic life (µg/L)
High-Performance Liquid Chromatography analysis method—Continued						
Dicamba	Banvel, Banex	H	1918-00-9	0.035	[3]200	[5]10
Dichlobenil[18]	Casoron, Prefix D	H	1194-65-6	0.02 [11]1.2	--	[12]37
Dichlorprop	2,4-DP, Kildip	H	120-36-5	0.032	--	--
Dinoseb	DNBP, Dinitro	H	88-85-7	0.035	7	[1]0.05
Diuron	Karmex, Cekiuron	H	330-54-1	0.02	[3]10	[12]1.6
DNOC[18]	Sinox, Elgetol 30	H, I	534-52-1	0.035 [11]0.42	--	--
Fenuron	Beet-Kleen	H	101-42-8	0.013	--	--
Fluometuron	Cotoran, Lanex	H	2164-17-2	0.035	[3]90	--
Linuron[4]	Lorox, Linurex	H	330-55-2	0.018	--	[9]7
MCPA	Metaxon, Kilsem	H	94-74-6	0.05 [11]0.17	[3]10	[19]2.6
MCPB	Bexane, Trifolex	H	94-81-5	0.035 [11]0.14	--	--
Methiocarb	Mesurol, Draza	I	2032-65-7	0.026	--	--
Methomyl	Lannate, Nudrin	I	16752-77-5	0.017	[3]200	--
Neburon	Neburex, Kloben	H	555-37-3	0.015	--	--
Norflurazon	Evital, Solicam	H	27314-13-2	0.024	--	--
Oryzalin	Surflan, Ryzelan	H	19044-88-3	0.019 [11]0.31	--	--
Oxamyl	Vydate	I	23135-22-0	0.018	200	--
Picloram	Tordon, Grazon PC	H	1918-02-1	0.05	500	[5]29
Propham	Chem-Hoe, IFC	H	122-42-9	0.035	[3]100	--
Propoxur	Baygon	I	114-26-1	0.035	--	--
Triclopyr	Garlon, Grazon	H	55335-06-3	0.05 [11]0.25	--	--

Table 5. Pesticide target analytes, method reporting limits, drinking-water standards, and aquatic-life criteria—Continued

[µg/L, micrograms per liter; H, herbicide; I, insecticide; D, pesticide degradate; F, fungicide; --, no drinking-water standard, guideline, or criteria for aquatic-life protection established; drinking-water standards are U.S. Environmental Protection Agency primary drinking-water standards; drinking-water standards and guidelines are from U.S. Environmental Protection Agency (1999a), unless otherwise noted; criteria for aquatic-life protection are chronic criteria from U.S. Environmental Protection Agency (1999b), unless otherwise noted]

Pesticide	Trade or common name	Type of pesticide	Chemical Abstract Service registry number	Method reporting limit (µg/L)	Drinking-water standard or health-advisory guideline (µg/L)	Freshwater-chronic criterion for protection of aquatic life (µg/L)

[1] Guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999).

[2] Concentrations for 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).

[3] U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult (about 150 pounds).

[4] Analyzed by both gas chromatography/mass spectrometry and high-performance liquid chromatography methods.

[5] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999).

[6] U.S. Environmental Protection Agency risk-specific health advisory associated with a cancer risk of 10^{-6} (U.S. Environmental Protection Agency, 1999c).

[7] Guidelines for the protection of freshwater aquatic life are from International Joint Commission Canada and United States (1978).

[8] U.S. Environmental Protection Agency risk-specific health advisory associated with a cancer risk of 10^{-6}.

[9] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999). Value applies to linuron, including linuron and its transformation products.

[10] U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult (about 150 pounds). Value is under review.

[11] New reporting level for constituent, effective 12/15/97, based on analysis of performance data for schedule 2050 from the Organic Blind Sample Program of the NWQL's Quality Assurance Unit and from routine laboratory reagent spike recovery data (National Water Quality Laboratory, 1998). No change in historical results reported for detections is needed since all reported detections and concentrations have been and still are considered reliable.

[12] Criteria for the protection of aquatic life are recommended maximum concentrations in freshwater by National Academy of Sciences and National Academy of Engineering, from Nowell and Resek (1994).

[13] Concentrations for these pesticides are qualitatively identified and reported with an E code because of (1) low and variable recoveries of aldicarb and aldicarb sulfone and (2) post-collection conversion of aldicarb to aldicarb sulfoxide, resulting in variable high bias in aldicarb sulfoxide (National Water Quality Laboratory, 1998).

[14] U.S. Environmental Protection Agency draft drinking-water standards.

[15] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999). Value is sum of aldicarb, aldicarb sulfone, and aldicarb sulfoxide.

[16] Guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999). Value applies to total bromoxynil, including the phenol, octanoate, and heptanoate forms.

[17] Compound with variable analytical performance, for which concentrations are reported as estimated values.

[18] Concentrations for these pesticides are qualitatively identified and reported with an E code because of variable recovery performance during solid-phase extraction and HPLC analysis (Werner and others, 1996; National Water Quality Laboratory, 1998).

[19] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Environment Canada (1999). Value applies to all forms of MCPA and all transformation products.

criteria during analysis, and only the concentration is estimated, not the presence (National Water Quality Laboratory, 1996). Throughout this report, estimated concentrations above the MRL were treated as normal concentrations, whereas estimated concentrations below the MRL were treated as "less than" concentrations.

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QUALITY-CONTROL METHODS AND RESULTS

Quality-control (QC) samples were used to assess the bias and variability of water-quality data that may be introduced by sample collection, processing, shipping, and analysis. Without QC samples, the quality of the data collected cannot be determined. Field-blank, replicate, and field-matrix-spike samples were collected and processed as QC samples using the same equipment and procedures as the stream-water or environmental samples in order to evaluate the bias and variability of the pesticide data. Pesticide surrogate solutions were added to each environmental and quality-assurance sample in the laboratory as an additional QC mechanism. The same QC procedures were used in the fixed-station and synoptic sampling. Quality-control data for both sampling programs were analyzed together. Further information on QC in the NAWQA Program and QC samples is described in Shelton (1994).

Field-blank samples were used to test for bias, the systematic error inherent in sampling and analytical methods (Spahr and Boulger, 1997). Blank samples were organic-free water that did not contain detectable concentrations of the pesticides of interest. The blank water, Baker Analyzed HPLC (J.T. Baker Company, Phillipsburg, New York), was processed through the sampling equipment and handled as if it were a typical stream sample. Because pesticides in a water sample can be detected at low concentrations in the laboratory, field blanks are important in determining possible contamination of a sample from collection, processing, cleaning, shipping, and analysis procedures.

Replicate samples were two or four samples collected simultaneously or in sequence in order to yield samples of nearly identical composition. Replicates provide information on the precision of concentration values and the consistency in identifying targeted pesticides. As such, replicate samples test for variability, the degree of random error in independent measurements of the same quantity (Spahr and Boulger, 1997). Replicate analysis is based on the comparison of the analytical results of the environmental sample with the analytical results of the QC sample or samples. Replicates were analyzed by the relative percent difference between replicate samples, calculated by dividing the difference in concentration between two replicate samples by the mean concentration of the two replicate samples and multiplying the result by 100. Where more than two samples were collected at a site, a range of relative percent differences was calculated.

The field-matrix-spike sample was an environmental sample that had been spiked with a solution containing targeted pesticides and then analyzed as a typical water-quality sample. Specifically, one liter of each environmental sample to be analyzed by GC/MS was spiked with the targeted pesticides at a concentration of 0.1 µg/L, while another liter, for HPLC analysis, was spiked with targeted pesticides at a concentration of 1 µg/L. The spiked samples were used to identify the recoverability of pesticides in the environmental samples. Pesticide recovery can be affected by pesticide degradation, interference from other organic substances or matter in the sample, and laboratory analysis. Spike solutions were provided by the USGS NWQL.

Pesticide-spike-recovery data were calculated in three steps. First, the expected or theoretical concentration of the spiked sample was determined by multiplying the concentration of the spike solution with the amount of spike added to the environmental sample and then dividing the result by the sample volume.

Next, the concentration of the pesticide in the environmental sample (zero if reported less than or estimated below the MRL) was subtracted from the concentration in the spiked sample. Finally, this result was multiplied by 100 and then divided by the expected or theoretical concentration of the spiked sample to determine the pesticide recovery percentage.

Pesticide surrogates were used to assess analytical recovery and precision for each analysis. Surrogate solutions containing known concentrations of organic compounds were added in the laboratory to each of the 155 environmental and quality-assurance samples prior to analysis. The surrogates were not expected to be found in the environmental samples but were expected to have similar chemical properties as the pesticides of interest. The surrogates diazinon-d_{10}, terbuthylazine, and *alpha*-HCH-d_6 were added to the samples analyzed by GC/MS, and the surrogate BDMC was added to the samples analyzed by HPLC. Surrogates were reported as percent surrogate recovered and analyzed by mean surrogate recovery.

No pesticides were detected in the seven field-blank samples. For four of the blank samples, the sites sampled just prior to the blank processing had various pesticides detected above the MRLs. Field-cleaning procedures were, therefore, effective in preventing contamination from one sample to another during equipment use. The potential for contamination of samples during sample collection, processing, cleaning, shipping, and analysis procedures was minimal.

As a result of the replicate sampling, 88 replicate groups for 20 pesticides were studied (table 6), a replicate group here having at least one detected concentration equal to or greater than the MRL for the respective pesticide. Relative percent differences were determined for these replicate groups, and the differences generally were small (table 6). Differences ranged from 0.0 to 100 percent, and most were less than 20 percent. The only pesticide with a relative percent difference above 41 percent was 2,4-D. As such, variability in concentrations for the pesticide sampling generally was low. Forty-seven of the 88 replicate groups consisted of a single pair of replicates, and 18 of these had a relative percent difference of 0.0 percent. Of the 41 replicate groups with multiple pairs of replicates, 22 contained at least one pair with no relative percent difference. Of the 88 replicate groups studied, only 7 contained concentrations that were reported both above and below the MRL for the respective pesticides and, thus, did not have a relative percent difference computed. Except for bromoxynil, these concentrations were less than 0.008 µg/L. Overall, there was good consistency in identifying the targeted pesticides, and only at very low concentrations were pesticides apt to have concentrations detected above and below the detection limit for the same replicate group.

Mean pesticide recoveries in the 30 samples spiked in the field for analysis by GC/MS ranged from 34 to 227 percent with a median of 98 percent (table 7). Deethylatrazine, *p,p'*-DDE, disulfoton, *cis*-permethrin, and phorate all had mean recoveries below 70 percent, with deethylatrazine and *cis*-permethrin having the lowest recoveries, below 40 percent. Azinphos-methyl, carbaryl, and carbofuran had high and variable recovery percentages. During testing of the GC/MS analytical method, Zaugg and others (1995) found azinphos-methyl, carbaryl, carbofuran, deethylatrazine, and terbacil to have low or highly variable spike recoveries. Because of this, analytical results for these five pesticides are reported by the NWQL as estimated (E) concentrations. There is increased uncertainty in analytical precision for estimated concentrations, but there is no increase in uncertainty of analytical detection (Rinella and Janet, 1998).

Mean recoveries for the spiked samples analyzed by the HPLC method were lower than those for the GC/MS method; the recoveries ranged from 13 to 90 percent, and the median was 77 percent (table 8). Low and/or variable recoveries were reported for aldicarb, aldicarb sulfone, carbofuran, chlorothalonil, clopyralid, dicamba, dichlobenil, methomyl, oryzalin, and picloram. Based on low or variable recovery performance, the NWQL reports concentrations of aldicarb, aldicarb sulfone, aldicarb sulfoxide, chloramben, chlorothalonil, dichlobenil, and DNOC as estimated values (Werner and others, 1996; National Water Quality Laboratory, 1998). As with the estimated concentrations for the GC/MS analysis method, the analytical results for the pesticides with estimated concentrations as determined by the HPLC method are reliable detections with greater than average uncertainty for numerical precision.

As mentioned previously, carbaryl and carbofuran were analyzed by both the GC/MS and the HPLC methods. The mean recoveries for carbaryl for the two methods were 196 and 75 percent, respectively, whereas the mean recoveries for carbofuran

Table 6. Concentrations and relative percent differences for pesticides detected in replicate samples

[µg/L, microgram per liter; <, less than; nc, not computed; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference
Acetochlor	0.008 0.007	13	Alachlor (continued)	0.031 0.034	9.2	Atrazine (continued)	0.235 0.219 0.216 0.216	0.0 - 8.4
	0.017 0.015 0.014 0.018	5.7 - 25		0.102 0.009 0.011 0.011 0.012 0.011	3.0 0.0 - 8.7		0.019 0.020 0.127 0.127 0.123 0.125	5.1 0.0 - 3.2
Alachlor	0.003 0.002	40						
	0.022 0.020	9.5	Atrazine	0.003 0.004	29		0.083 0.082 0.079 0.087	1.2 - 9.6
	0.031 0.030 0.031 0.029	0.0 - 6.7		0.076 0.068 0.105 0.106 0.105 0.104	11 0.0 - 1.9		0.011 0.011	0.0
	0.110 0.086 0.083 0.092	3.6 - 28		0.004 0.004	0.0	Benfluralin	0.003 0.004 0.003 0.004	0.0 - 29

Table 6. Concentrations and relative percent differences for pesticides detected in replicate samples—Continued

[µg/L, microgram per liter; <, less than; nc, not computed; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference
Benfluralin (continued)	0.004 0.004	0.0	Carbofuran (GC/MS) (continued)	0.007 0.007 0.007 0.007	0.0	Carbofuran (HPLC) (continued)	0.570 0.480 0.560 0.470	1.8 - 19
	0.004 0.004	0.0		0.982 0.978 0.986 0.953	0.41 - 3.4	Chlorpyrifos	0.004 0.004 0.004 0.005	0.0 - 22
Bromoxynil	<0.035 0.070 0.040 <0.035	nc		0.784 0.809 0.770 0.806	0.37 - 4.9		0.013 0.014	7.4
Carbaryl (GC/MS)	0.006 0.007	15		0.009 0.008	12		0.006 0.006	0.0
	0.003 0.003	0.0	Carbofuran (HPLC)	0.470 0.310	41		0.005 0.005 0.006 0.005	0.0 - 18
Carbofuran (GC/MS)	0.009 0.009	0.0		0.620 0.600 0.580 0.630	1.6 - 8.3	Cyanazine	0.004 0.005 0.005 0.004	0.0 - 22
	0.480 0.485	1.0						

Table 6. Concentrations and relative percent differences for pesticides detected in replicate samples—Continued

[µg/L, microgram per liter; <, less than; nc, not computed; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference
Cyanazine (continued)	0.007 0.007	0.0	2,4-D (continued)	0.490 0.370	28	DCPA (continued)	0.002 <0.002	nc
	<0.004 0.007 0.006 <0.004	nc		0.870 0.860 0.800 0.880	1.1 - 9.5		0.005 0.005 0.002 0.002	0.0 0.0
	0.016 0.014 0.013 0.015	6.5 - 21		0.210 0.070 0.150 0.140	6.9 - 100		0.004 0.004	0.0
	0.023 0.024	4.3	2,4-DB	0.830 1.00	19		0.005 0.005	0.0
	0.008 0.009	12					0.003 0.003	0.0
2,4-D	0.390 0.360	8.0	DCPA	0.015 0.014 0.014 0.015	0.0 - 6.9	Deethylatrazine	0.003 0.004	29
	0.620 0.560 0.660 0.550	1.8 - 18		0.010 0.012 0.011 0.011	0.0 - 18		0.016 0.018 0.015 0.015	0.0 - 18

Table 6. Concentrations and relative percent differences for pesticides detected in replicate samples—Continued

[µg/L, microgram per liter; <, less than; nc, not computed; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference
Deethylatrazine (continued)	0.009 0.007	25	Diazinon (continued)	<0.002 0.002 <0.002 <0.002	nc	EPTC (continued)	0.053 0.054 0.054 0.051	0.0 - 5.7
	0.007 0.009 0.010 0.008	11 - 35	Dicamba	0.150 0.150	0.0	Ethalfluralin	0.009 0.008 0.008 0.010	0.0 - 22
	0.006 0.005 0.005 0.006	0.0 - 18	EPTC	0.003 0.003	0.0			
	0.004 0.004	0.0		0.002 0.003	40	Metolachlor	0.003 0.002	40
	0.003 <0.002 <0.002 <0.002	nc		0.199 0.202	1.5		0.005 0.006	18
	0.003 0.003	0.0		0.061 0.046 0.046 0.059	0.0 - 28		<0.002 <0.002 0.004 <0.002	nc
Diazinon	0.004 0.005	22		0.003 0.003	0.0		0.043 0.044 0.043 0.042	0.0 - 4.7

Table 6. Concentrations and relative percent differences for pesticides detected in replicate samples—Continued

[µg/L, microgram per liter; <, less than; nc, not computed; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference	Pesticide	Concentration in replicates (µg/L)	Relative percent difference
Metolachlor (continued)	0.016 0.017	6.1	Terbufos	0.017 0.017 0.017 0.015	0.0 - 12	Trifluralin (continued)	0.006 0.005 0.005 0.006	0.0 - 18
	0.130 0.137	5.2					0.012 0.012 0.012 0.009	0.0 - 29
	0.065 0.068 0.062 0.066	3.0 - 6.2	Trifluralin	0.005 0.005 0.005 0.006	0.0 - 18		0.003 0.004 <0.002 0.003	nc
				0.019 0.024	23			

Table 7. Mean and standard deviation of pesticide recovery in 30 field-spiked samples determined by gas chromatography/mass spectrometry (GC/MS)

Pesticide	Mean recovery (percent)	Standard deviation (percent)	Pesticide	Mean recovery (percent)	Standard deviation (percent)
Acetochlor	107	7.8	Malathion	89	17
Alachlor	108	9.0	Methyl parathion	96	16
Atrazine	102	7.2	Metolachlor	112	13
Azinphos-methyl	154	62	Metribuzin	74	9.7
Benfluralin	77	12	Molinate	97	4.8
Butylate	105	8.0	Napropamide	102	10
Carbaryl	196	130	Parathion	96	16
Carbofuran	227	310	Pebulate	100	6.9
Chlorpyrifos	89	8.2	Pendimethalin	85	18
Cyanazine	100	15	*cis*-Permethrin	39	11
DCPA	110	16	Phorate	67	14
p,p'-DDE	60	4.8	Prometon	97	8.0
Deethylatrazine	34	7.6	Pronamide	96	10
Diazinon	97	13	Propachlor	114	12
Dieldrin	99	12	Propanil	110	15
2,6-Diethylaniline	92	6.9	Propargite	100	27
Disulfoton	69	14	Simazine	98	6.9
EPTC	107	31	Tebuthiuron	114	27
Ethalfluralin	89	19	Terbacil	75	16
Ethoprop	106	14	Terbufos	77	5.5

Table 8. Mean and standard deviation of pesticide recovery in 30 field-spiked samples determined by high-performance liquid chromatography (HPLC)

Pesticide	Mean recovery (percent)	Standard deviation (percent)	Pesticide	Mean recovery (percent)	Standard deviation (percent)
Acifluorfen	85	13	DNOC	78	8.8
Aldicarb	41	11	Fenuron	81	7.4
Aldicarb sulfone	20	16	Fluometuron	85	5.0
Aldicarb sulfoxide	66	13	3-Hydroxy-carbofuran	75	11
Bentazon	78	8.2	Linuron	78	7.0
Bromacil	71	5.9	MCPA	77	7.6
Bromoxynil	85	4.6	MCPB	70	6.4
Carbaryl	75	6.1	Methiocarb	67	4.8
Carbofuran	90	39	Methomyl	77	23
Chloramben[1]	75	8.3	Neburon	77	8.8
Chlorothalonil	54	17	Norflurazon	82	6.5
Clopyralid	13	13	Oryzalin	78	30
2,4-D	76	15	Oxamyl	63	8.6
2,4-DB	75	8.9	Picloram	51	26
Dacthal, mono-acid	73	10	Propham	71	9.2
Dicamba	58	27	Propoxur	79	16
Dichlobenil	46	16	Silvex	87	10
Dichlorprop	79	7.9	2,4,5-T	85	2.8
Dinoseb	85	11	Triclopyr	79	6.6
Diuron	81	6.2			

[1] Mean recovery and standard deviation are based on seven May 1998 samples.

were 227 and 90 percent, respectively (tables 7 and 8). Because the recovery rates for the HPLC method were closer to 100 percent than the recovery rates for the GC/MS method, only the carbaryl and carbofuran occurrences and concentrations resulting from the HPLC method will be discussed in later sections of the report. With recovery rates below 100 percent, the carbaryl and carbofuran results from the HPLC method may be biased slightly low; however, the results from the GC/MS method would have a very high bias because of the recovery rates being around 200 percent.

For the pesticides with low recovery percentages, the detection frequencies and concentration ranges may be biased low. False negatives occur when a pesticide is present in a sample at a concentration greater than the MRL but is not detected because of analytical problems. In the UCOL study, for example, the mean recovery for dicamba was 58 percent (table 8). Because of this low recovery, dicamba may not have been detected in a sample even though it was actually present above the MRL. The probability of a false positive (the detection of a pesticide at a concentration greater than the MRL when the actual concentration is below the reporting limit) is much lower than a false negative when the data are censored at the MRL (National Water Quality Laboratory, 1994).

Mean recoveries for the pesticide surrogates terbuthylazine, diazinon-d_{10}, *alpha*-HCH-d_6, and BDMC were 112, 100, 99.9, and 84.0 percent, respectively (table 9). As with the spiked samples, the mean surrogate recovery for the BDMC samples analyzed by HPLC was lower than the mean recoveries for the terbuthylazine, diazinon-d_{10}, *alpha*-HCH-d_6 samples analyzed by GC/MS. Recoveries for all samples but one ranged between 64 and 141 percent, and most recoveries fell between 80 and 120 percent. A recovery of 0 percent was reported for one BDMC sample; this surrogate may have accidentally been omitted from the sample. These results of the surrogate recoveries show that no significant bias occurred in the pesticide data, and variabilities in recovery, as shown by the standard deviations in table 9, were similar for the four surrogates.

Table 9. Mean and standard deviation of pesticide surrogate recovery

Pesticide surrogate	Mean recovery (percent)	Standard deviation (percent)
Gas Chromatography/Mass Spectrometry (GC/MS) analysis		
alpha-HCH-d_6	99.9	13
diazinon-d_{10}	100	11
terbuthylazine	112	10
High-Performance Liquid Chromatography (HPLC) analysis		
BDMC	84.0	11

HYDROLOGIC CONDITIONS DURING SAMPLING

Streamflow and runoff were higher than normal in the study unit during water year (WY) 1997 (October 1996 through September 1997). The annual mean streamflow and total runoff for the Colorado River near the Colorado-Utah State Line (encompassing streamflow from the entire study unit) for WY 1997 were 9,826 ft^3/s and 7,114,000 acre-ft, respectively (U.S. Geological Survey, 1998b). In comparison, the long-term (WY 1970–97) mean annual streamflow and runoff amounts were 6,847 ft^3/s and 4,960,000 acre-ft, respectively. The annual mean streamflow and runoff amounts for the Gunnison River near Grand Junction for WY 1997 also were above the long-term (WY 1970–97) averages for this site. For calender year 1997, precipitation was 35 percent above normal at Grand Junction, mainly in April, May, August, and September. At Montrose, precipitation in 1997 was 21 percent above normal, mainly in April, May, June, and September (National Oceanic and Atmospheric Administration, 1998a).

Streamflow for the Colorado River near State Line and Gore Creek at mouth was dependent on snowmelt runoff; streamflow was generally highest in June during snowmelt (fig. 3). In contrast, streamflow in Reed Wash was caused primarily by irrigation and irrigation-return flow, with high streamflow from April into November. Streamflow for Dry Creek near Begonia Road was primarily dependent on irrigation and irrigation-return flow but also included snowmelt runoff from the Uncompahgre Plateau. For all four fixed-station sites, water-quality samples were collected over a wide range of streamflow conditions (fig. 3). In figure 3, samples were positioned based on instantaneous streamflow at the time of collection and, thus, may not plot on the line representing daily mean streamflow.

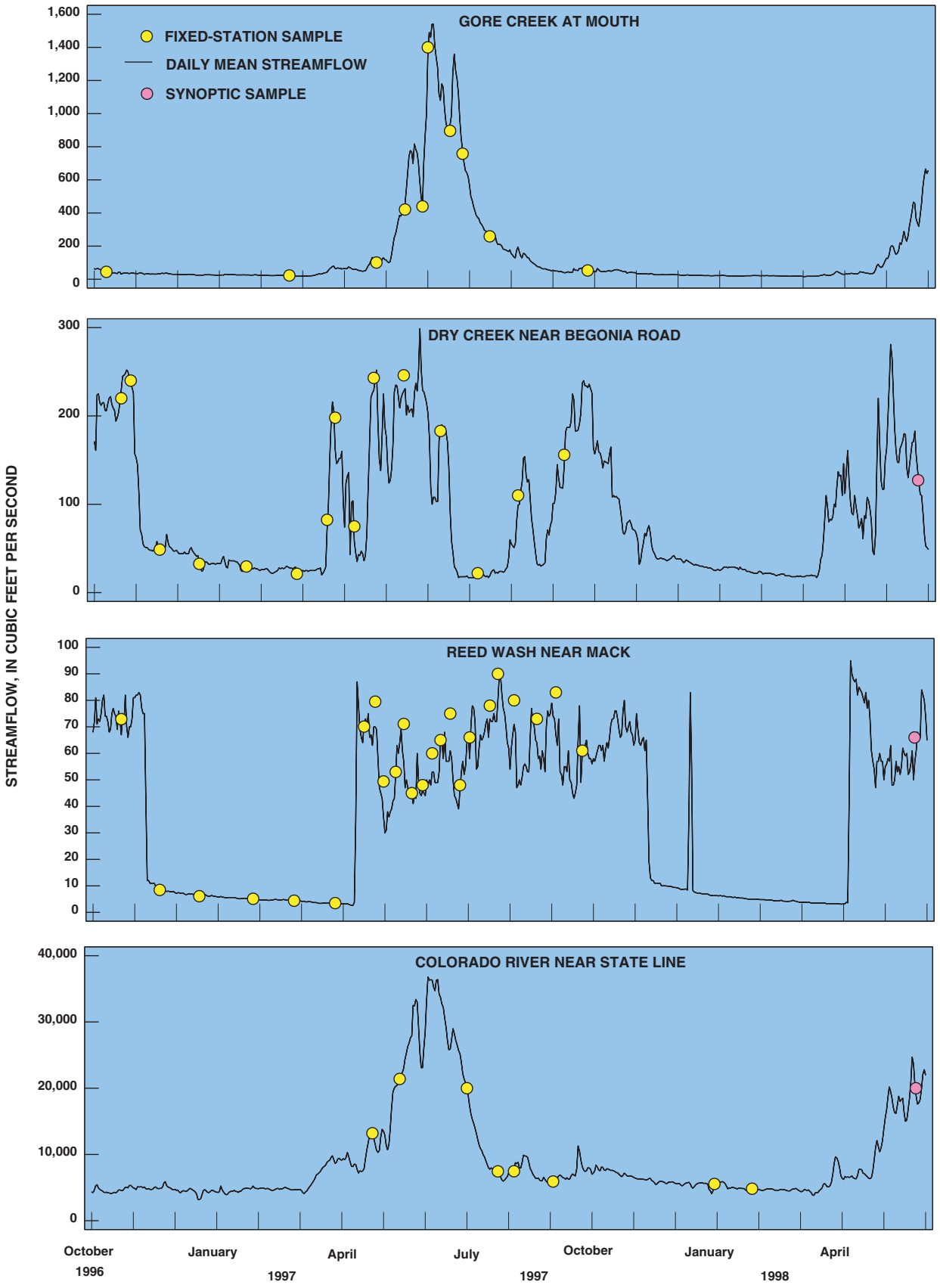

Figure 3. Streamflow and pesticide sample-collection dates for fixed-station sites, Upper Colorado River Basin, October 1996–May 1998. (Streamflow at sampling time is instantaneous measurement; graphs have different vertical scales.)

During the synoptic study in May 1998, the monthly mean streamflows for the Colorado River near State Line and Gunnison River near Grand Junction were 23 and 16 percent, respectively, above the long-term (WY 1970–98) May mean monthly streamflows for the two sites. Above average streamflow at each site may have been due to a greater snowpack or more snowmelt in each basin. As irrigation return flow, streamflow in the drains of the agricultural areas was affected by irrigation practices, which in turn were influenced by precipitation and temperature. Precipitation in the Grand Valley and Uncompahgre River Valley was slightly (less than 1 inch) below normal during the synoptic study, as measured at Grand Junction and Montrose, while the temperature was slightly (less than 1°F) above normal at the two sites (National Oceanic and Atmospheric Administration, 1998b). Precipitation and temperature values greatly different from normal would affect irrigation practices and growing conditions, pesticide applications, and, therefore, pesticides in streams and drains.

OCCURRENCE AND DISTRIBUTION OF PESTICIDES

The occurrence and distribution of pesticides in surface water and whether pesticides are detected in a water sample or not depend on many factors, such as the time, rate, and location of pesticide application, crop type, precipitation or irrigation events, physical and chemical characteristics of pesticides, and atmospheric transport and deposition. The time of pesticide application affects when pesticides are detected in streams. In surface water, pesticide detections typically occur after the first precipitation/irrigation event following pesticide application. Also, small amounts of pesticides applied per acre are less likely to be detected than pesticides applied in large amounts. The spatial distribution of pesticides detected in a stream depends on the spatial distribution of pesticide application and crop type or agricultural practice. For example, atrazine is a very common herbicide used for corn and is commonly detected in streams near corn fields, whereas it is not used and not commonly detected in fruit-growing areas (U.S. Geological Survey, 1998a; Gianessi and Puffer, 1990). Pesticides applied just before or during a rainstorm may be transported more quickly in surface runoff to streams and drains than pesticides applied during dry conditions. The potential of pesticides to be transported from an agricultural field into runoff water differs among pesticides and depends on the physical and chemical characteristics of each pesticide. Factors such as water solubility, persistence, and acid/base, ionic, and sorption properties determine the runoff potential of a pesticide (Larson and others, 1997). Pesticides with large runoff potentials, such as atrazine, carbofuran, and pendimethalin, are more likely to be transported out of an agricultural field into surface water through runoff than a pesticide that has a small runoff potential, such as malathion. Malathion has low soil persistence due to rapid degradation and, thus, is not readily present or available to be included in runoff. Atrazine, carbofuran, and pendimethalin, in contrast, are moderately to highly persistent in soil and are readily available for inclusion in runoff. Depending on the characteristics of individual pesticides, storm runoff can be an important mechanism in the transport of pesticides to receiving waters. Finally, some pesticide detections may not be due to local use of the pesticide at all. It is possible that very low levels of detected pesticides may be related to atmospheric transport and deposition. As Majewski and Capel (1995) reported, pesticides have been detected in the atmosphere throughout the Nation, and pesticides applied in one area may be transported and deposited in another area.

In the UCOL study unit, 35 pesticides were detected at least once in 82 of the 100 samples collected during the fixed-station and synoptic sampling periods of October 1996 through January 1998 and May 1998 (table 10), respectively, a detection for this report being defined as a concentration of a pesticide equal to or greater than the MRL of the pesticide. Almost 93 percent (76 of 82) of these samples contained two or more pesticide detections. For the 100 samples, 8,248 individual pesticide analyses were performed, and there were 476 detections (5.8 percent of the possible total). Fifty-two additional analyses were unreported because of difficulties in the laboratory determination of concentration. Almost 82 percent (390 of 476) of the detections were for the 11 most frequently occurring pesticides. Of these 11 pesticides, 9 were herbicides, 1 (carbofuran) was an insecticide, and 1 (deethylatrazine) was a degradation product of atrazine. Atrazine and alachlor, used on corn and dry beans, were the most commonly detected herbicides, whereas carbofuran, used on pests in alfalfa, corn, and grains, was the most commonly detected insecticide. Pesticide concentrations in the

Table 10. Summary of pesticide occurrence and concentrations for all 44 surface-water sites sampled in the UCOL study unit, October 1996 through January 1998 and May 1998

[≥, greater than or equal to; µg/L, micrograms per liter; MRL, method reporting limit, <, less than; E, estimated; --, method reporting limit greater than detection threshold; HPLC, high-performance liquid chromatography]

Pesticide	Number of samples	Number of detections	Percentage detected	Percentage detected ≥0.01 (µg/L)	Percentage detected ≥0.05 (µg/L)	MRL (µg/L)	Concentration at indicated percentile (µg/L)					Maximum concentration (µg/L)
							10th	25th	50th	75th	90th	
Atrazine	100	69	69	35	12	0.001	<0.001	<0.001	0.005	0.019	0.061	1.04
Alachlor	100	57	57	33	13	0.002	<0.002	<0.002	0.003	0.014	0.086	0.751
Metolachlor	100	46	46	23	10	0.002	<0.002	<0.002	<0.002	0.009	0.053	0.442
Deethylatrazine	100	37	37	5.0	0.0	0.002	<0.002	<0.002	<0.002	0.004	0.008	E 0.028
2,4-D	100	32	32	--	--	0.035 [1]0.15	<0.035	<0.035	<0.15	0.170	0.385	E 3.50
Cyanazine	100	30	30	14	4.0	0.004	<0.004	<0.004	<0.004	0.006	0.013	0.618
DCPA	100	30	30	8.0	1.0	0.002	<0.002	<0.002	<0.002	0.002	0.007	0.109
Trifluralin	100	30	30	9.0	1.0	0.002	<0.002	<0.002	<0.002	0.003	0.007	0.051
EPTC	100	21	21	10	5.0	0.002	<0.002	<0.002	<0.002	<0.002	0.014	0.853
Acetochlor	100	19	19	15	7.0	0.002	<0.002	<0.002	<0.002	<0.002	0.022	2.61
Carbofuran (HPLC)	98	19	19	--	--	0.028 [1]0.12	<0.028	<0.028	<0.12	<0.12	0.447	E 1.80
Chlorpyrifos	100	13	13	2.0	0.0	0.004	<0.004	<0.004	<0.004	<0.004	0.005	0.029
Benfluralin	100	10	10	0.0	0.0	0.002	<0.002	<0.002	<0.002	<0.002	0.002	0.009
Diazinon	100	8	8.0	3.0	1.0	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.104
Pendimethalin	100	8	8.0	6.0	1.0	0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.099
Propargite	100	6	6.0	--	3.0	0.013	<0.013	<0.013	<0.013	<0.013	<0.013	0.230
Simazine	100	5	5.0	5.0	1.0	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.065
Carbaryl (HPLC)	98	3	3.1	3.1	3.1	0.008	<0.008	<0.008	<0.008	<0.008	<0.008	0.780
Diuron	98	3	3.1	--	1.0	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	E 18.0
Azinphos-methyl	100	3	3.0	1.0	1.0	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	E 0.062
Dicamba	99	3	3.0	--	3.0	0.035	<0.035	<0.035	<0.035	<0.035	<0.035	E 1.50
Ethalfluralin	100	3	3.0	0.0	0.0	0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.009
Terbufos	100	3	2.0	--	0.0	0.013	<0.013	<0.013	<0.013	<0.013	<0.013	0.018
2,4-DB	100	2	2.0	--	--	0.035	<0.035	<0.035	<0.035	<0.24	<0.24	0.830
Dieldrin	100	2	2.0	0.0	0.0	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	E 0.004
gamma-HCH	100	2	2.0	1.0	0.0	0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.012
Malathion	100	2	2.0	2.0	0.0	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.026
Metribuzin	100	2	2.0	1.0	0.0	0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.011

Table 10. Summary of pesticide occurrence and concentrations for all 44 surface-water sites sampled in the UCOL study unit, October 1996 through January 1998 and May 1998—Continued

[≥, greater than or equal to; µg/L, micrograms per liter; MRL, method reporting limit, <, less than; E, estimated; --, method reporting limit greater than detection threshold; HPLC, high-performance liquid chromatography]

Pesticide	Number of samples	Number of detections	Percentage detected	Percentage detected ≥0.01 (µg/L)	Percentage detected ≥0.05 (µg/L)	MRL (µg/L)	Concentration at indicated percentile (µg/L)					Maximum concentration (µg/L)
							10th	25th	50th	75th	90th	
Prometon	100	2	2.0	--	1.0	0.018	<0.018	<0.018	<0.018	<0.018	<0.018	0.399
Bentazon	98	1	1.0	1.0	1.0	0.014	<0.014	<0.014	<0.014	<0.014	<0.014	E 2.60
Bromoxynil	99	1	1.0	1.0	1.0	0.035	<0.035	<0.035	<0.035	<0.035	<0.035	0.090
MCPB	99	1	1.0	1.0	1.0	0.035 [1]0.14	<0.035	<0.035	<0.035	<0.14	<0.14	0.22
Oryzalin	98	1	1.0	1.0	0.0	0.019 [1]0.31	<0.019	<0.019	<0.019	<0.31	<0.31	E 0.030
Phorate	100	1	1.0	0.0	0.0	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	E 0.003
Pronamide	100	1	1.0	1.0	0.0	0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.012

[1] New reporting level for constituent, effective 12/15/97 (National Water Quality Laboratory, 1998).

UCOL study unit generally were low. Including all samples and analyses, only atrazine and alachlor had median concentrations (50th percentile in table 10) greater than their MRLs, and the median concentrations were only slightly greater than the respective MRLs (table 10). Carbofuran and 2,4-D were the only pesticides having detections at consistently higher concentrations than the other pesticides studied (table 10). Carbofuran concentrations exceeded 0.447 µg/L in 10 percent of the samples. Concentrations of 2,4-D exceeded 0.17 µg/L in 25 percent of the samples and 0.385 µg/L in 10 percent of the samples. Pesticides were detected at 41 of the 44 pesticide-sampling sites in the UCOL, all 4 sites of the fixed-station network, and 40 of the 43 synoptic sites.

Pesticides at Fixed-Station Network

Fifty-seven water samples collected from October 1996 through January 1998 from the four fixed-station network sites in the UCOL study unit were analyzed for 83 pesticides. Twenty-three pesticides were detected at least once (table 11) in 42 samples. Forty samples contained two or more pesticides. For the fixed-station samples, 4,687 individual pesticide analyses were performed. Detections occurred in 253 analyses, or 5.4 percent of the total. The 10 most frequently occurring pesticides accounted for almost 85 percent of the 253 detections. The frequency of detection for all 23 pesticides and their measured detected concentrations are shown in figure 4, in descending order of frequency. Sixteen herbicides and seven insecticides were detected, with only the herbicides atrazine (70 percent) and alachlor (54 percent) being detected in more than 50 percent of the samples. Carbofuran and chlorpyrifos, detected in 18 percent of the samples, were the most frequently detected insecticides. Concentrations of the detected pesticides in the fixed-station network generally were low, ranging from 0.001 µg/L to 2.60 µg/L. More than 36 percent of the detections were greater than or equal to 0.01 µg/L, and almost 22 percent were greater than or equal to 0.05 µg/L. Carbofuran and 2,4-D accounted for 47 percent of the detections that were greater than or equal to 0.05 µg/L. Statistical summaries of the detected pesticide concentrations for each of the four fixed-station sites individually and combined are in table 11.

For the samples collected at the fixed-station sites, no pesticide concentrations exceeded U.S. Environmental Protection Agency (USEPA) drinking-water standards or health-advisory guidelines; maximum pesticide concentrations were much lower than these water-quality criteria. The criterion for the protection of freshwater aquatic life, however, was exceeded for one pesticide at Reed Wash on May 21, 1997. The estimated azinphos-methyl concentration of 0.062 µg/L was greater than the USEPA freshwater-chronic criterion for aquatic-life protection of 0.01 µg/L (table 5).

Interpretation of water-quality data based on standards and guidelines has to be done with qualifications. The description of water quality in an area has to be tempered by the knowledge that water-quality criteria have not been set for many pesticides, pesticide mixtures and degradation products have not been evaluated, and not all pesticide effects have been studied.

Temporal Distribution

For the fixed-station sampling, pesticides were detected throughout most of the October 1996 through January 1998 sampling period (fig. 5). The mean number of pesticide detections per sample by month was greatest for April through August 1997 (fig. 6). Detections of herbicides were more common than insecticides. Herbicides were detected in every month that a detection occurred, while insecticides were detected only from April through August 1997 (fig. 6). Atrazine was the only herbicide detected every month in which a detection occurred, and it was present in 40 of the 42 samples with detections. Atrazine is used as a season-long weed control in corn, so its detection during much of the year is common. Carbofuran and chlorpyrifos, the most commonly detected insecticides, were found in 10 of the 42 samples with detections. All 10 detections occurred in the spring and summer months, April through August 1997. Because of their use as insecticides, carbofuran and chlorpyrifos would not be expected to be detected year round but would be more common during the times of insect activity.

The concentrations of detected pesticides in the fixed-station study were elevated from April through August or September 1997, which corresponded to the time of higher streamflows because of irrigation and irrigation return flows and also snowmelt in May and

Table 11. Statistical summary of concentrations of detected pesticides at fixed-station sites in the Upper Colorado River Basin, October 1996–January 1998

[µg/L, micrograms per liter; --, not computed; E, estimated; HPLC, high-performance liquid chromatography]

Pesticide	Number of samples	Number of detections	Percentage detected	Method reporting limit (µg/L)	Statistics for detections		
					Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Gore Creek at mouth near Minturn (urban/forest site)							
Atrazine	10	1	10	0.001	--	--	0.014
Benfluralin	10	1	10	0.002	--	--	E 0.002
Cyanazine	10	1	10	0.004	--	--	0.006
Metolachlor	10	1	10	0.002	--	--	0.007
Dry Creek near Begonia Road, near Delta (agriculture site)							
Atrazine	15	15	100	0.001	E 0.003	0.021	0.105
Deethylatrazine	15	14	93	0.002	E 0.003	E 0.009	E 0.028
Alachlor	15	9	60	0.002	E0.003	0.011	0.031
DCPA	15	6	40	0.002	E 0.002	E 0.004	0.016
Cyanazine	15	5	33	0.004	0.004	0.008	0.013
Benfluralin	15	4	27	0.002	E 0.003	E 0.004	0.004
EPTC	15	3	20	0.002	E 0.002	E 0.002	E 0.003
Metolachlor	15	3	20	0.002	E 0.002	E 0.003	E 0.003
Diazinon	15	2	13	0.002	0.004	0.006	0.008
Ethalfluralin	15	2	13	0.004	0.004	0.006	0.009
Trifluralin	15	2	13	0.002	E 0.003	E 0.004	0.006
Oryzalin	[1]14	1	7.1	0.019	--	--	E 0.030
Acetochlor	15	1	6.7	0.002	--	--	0.008
Azinphos-methyl	15	1	6.7	0.001	--	--	E 0.003
2,4-D	15	1	6.7	0.035	--	--	E 0.620
Propargite	15	1	6.7	0.013	--	--	0.046
Reed Wash near Mack (agriculture site)							
Atrazine	24	18	75	0.001	E 0.001	0.009	0.127
Metolachlor	24	17	71	0.002	E 0.003	0.043	0.281
Alachlor	24	16	67	0.002	E 0.002	0.008	0.513
Trifluralin	24	14	58	0.002	E 0.002	0.006	0.021
2,4-D	24	13	54	0.035	0.120	0.270	E 0.980
Carbofuran (HPLC)	24	10	42	0.028	0.040	0.200	E 1.60
Chlorpyrifos	24	10	42	0.004	0.005	0.006	0.013
DCPA	24	9	38	0.002	E 0.002	E 0.003	0.026
EPTC	24	9	38	0.002	E 0.003	0.025	0.853
Cyanazine	24	8	33	0.004	0.006	0.020	0.159
Deethylatrazine	24	7	29	0.002	E 0.002	E 0.004	E 0.006
Propargite	24	4	17	0.013	0.043	0.168	0.230
2,4-DB	24	2	8.3	0.035	0.050	0.440	0.830
Dicamba	24	2	8.3	0.035	E 0.090	E 0.120	E 0.150
Terbufos	24	2	8.3	0.013	0.017	0.017	0.017
Azinphos-methyl	24	1	4.2	0.001	--	--	E 0.062
Benfluralin	24	1	4.2	0.002	--	--	E 0.003
Bentazon	24	1	4.2	0.014	--	--	E 2.60
Malathion	24	1	4.2	0.005	--	--	0.026

Table 11. Statistical summary of concentrations of detected pesticides at fixed-station sites in the Upper Colorado River Basin, October 1996–January 1998

[µg/L, micrograms per liter; --, not computed; E, estimated; HPLC, high-performance liquid chromatography]

Pesticide	Number of samples	Number of detections	Percentage detected	Method reporting limit (µg/L)	Statistics for detections		
					Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Colorado River near Colorado-Utah State Line (integrator site)							
Alachlor	8	6	75	0.002	E 0.003	0.006	0.015
Atrazine	8	6	75	0.001	E 0.004	0.005	0.011
Metolachlor	8	6	75	0.002	E 0.003	0.005	0.007
DCPA	8	5	62	0.002	E 0.002	E 0.003	0.005
2,4-D	8	3	38	0.035	0.080	0.100	0.160
Cyanazine	8	2	25	0.004	0.006	0.007	0.008
Deethylatrazine	8	2	25	0.002	E 0.003	E 0.003	E 0.004
EPTC	8	2	25	0.002	E 0.002	E 0.002	E 0.003
Propargite	8	1	12	0.013	--	--	0.014
Trifluralin	8	1	12	0.002	--	--	0.004
All fixed-station sites combined							
Atrazine	57	40	70	0.001	E 0.001	0.010	0.127
Alachlor	57	31	54	0.002	E 0.002	0.008	0.513
Metolachlor	57	27	47	0.002	E 0.002	0.016	0.281
Deethylatrazine	57	23	40	0.002	E 0.002	E 0.006	E 0.028
DCPA	57	20	35	0.002	E 0.002	E 0.003	0.026
2,4-D	57	17	30	0.035	0.080	0.270	E 0.980
Trifluralin	57	17	30	0.002	E 0.002	0.006	0.021
Cyanazine	57	16	28	0.004	0.004	0.008	0.159
EPTC	57	14	25	0.002	E 0.002	0.014	0.853
Carbofuran (HPLC)	[1]55	10	18	0.028	0.040	0.200	E 1.60
Chlorpyrifos	57	10	18	0.004	0.005	0.006	0.013
Benfluralin	57	6	11	0.002	E 0.002	0.004	0.004
Propargite	57	6	11	0.013	0.014	0.077	0.230
Azinphos-methyl	57	2	3.5	0.001	E 0.003	E 0.032	E 0.062
Diazinon	57	2	3.5	0.002	0.004	0.006	0.008
2,4-DB	57	2	3.5	0.035	0.050	0.440	0.830
Dicamba	57	2	3.5	0.035	E 0.090	E 0.120	E 0.150
Ethalfluralin	57	2	3.5	0.004	0.004	0.006	0.009
Terbufos	57	2	3.5	0.013	0.017	0.017	0.017
Acetochlor	57	1	1.8	0.002	--	--	0.008
Bentazon	57	1	1.8	0.014	--	--	E 2.60
Malathion	57	1	1.8	0.005	--	--	0.026
Oryzalin	[1]55	1	1.8	0.019	--	--	E 0.030

[1] Number of samples is different because the results for one or more samples are unreported due to difficulties in the laboratory determination of concentration.

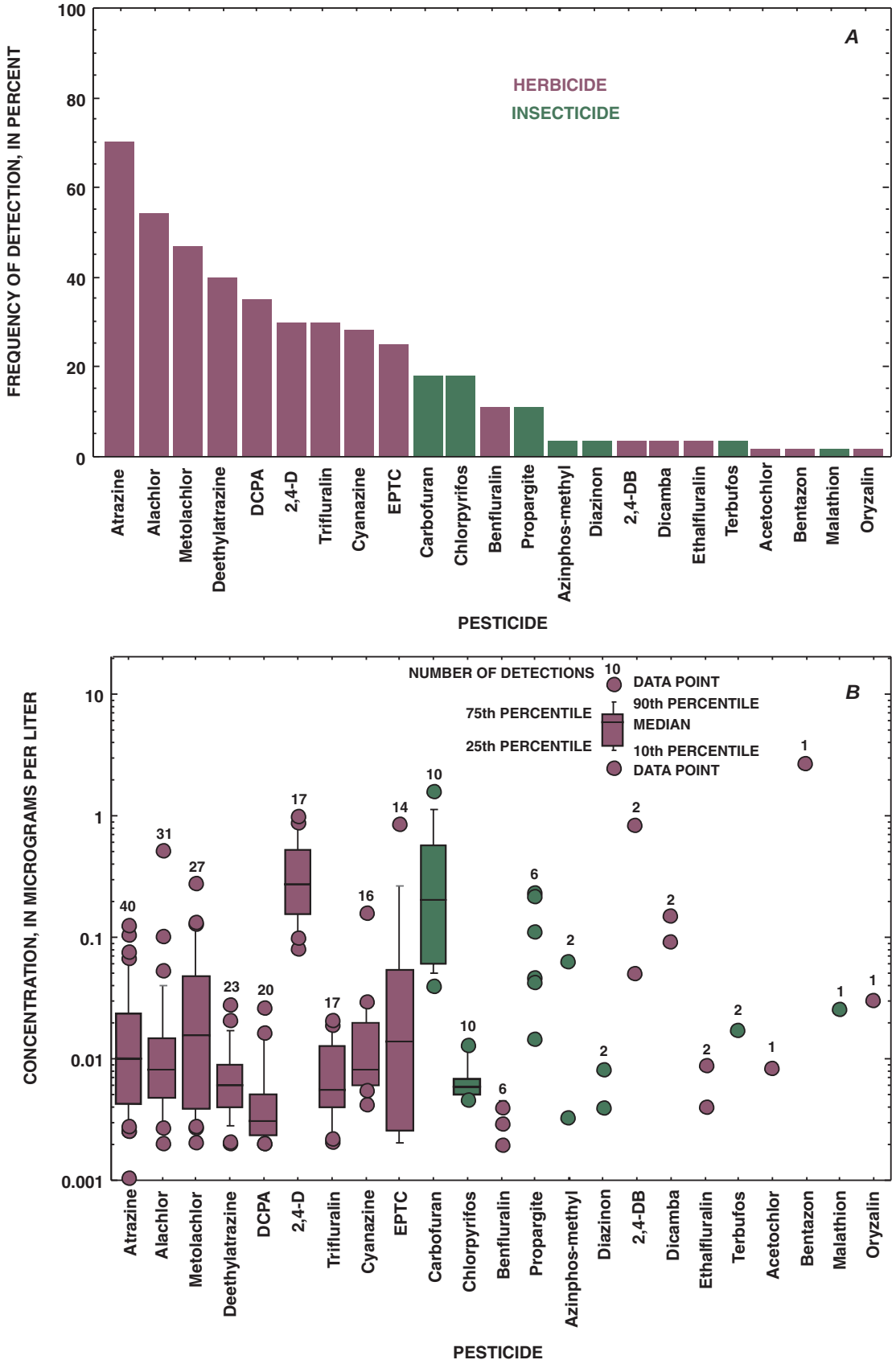

Figure 4. (*A*) Frequency of pesticide detections and (*B*) concentrations of detected pesticides for the fixed-station sites sampled in the Upper Colorado River Basin study unit, October 1996–January 1998. (Individual data points were plotted when fewer than 10 data points were available.)

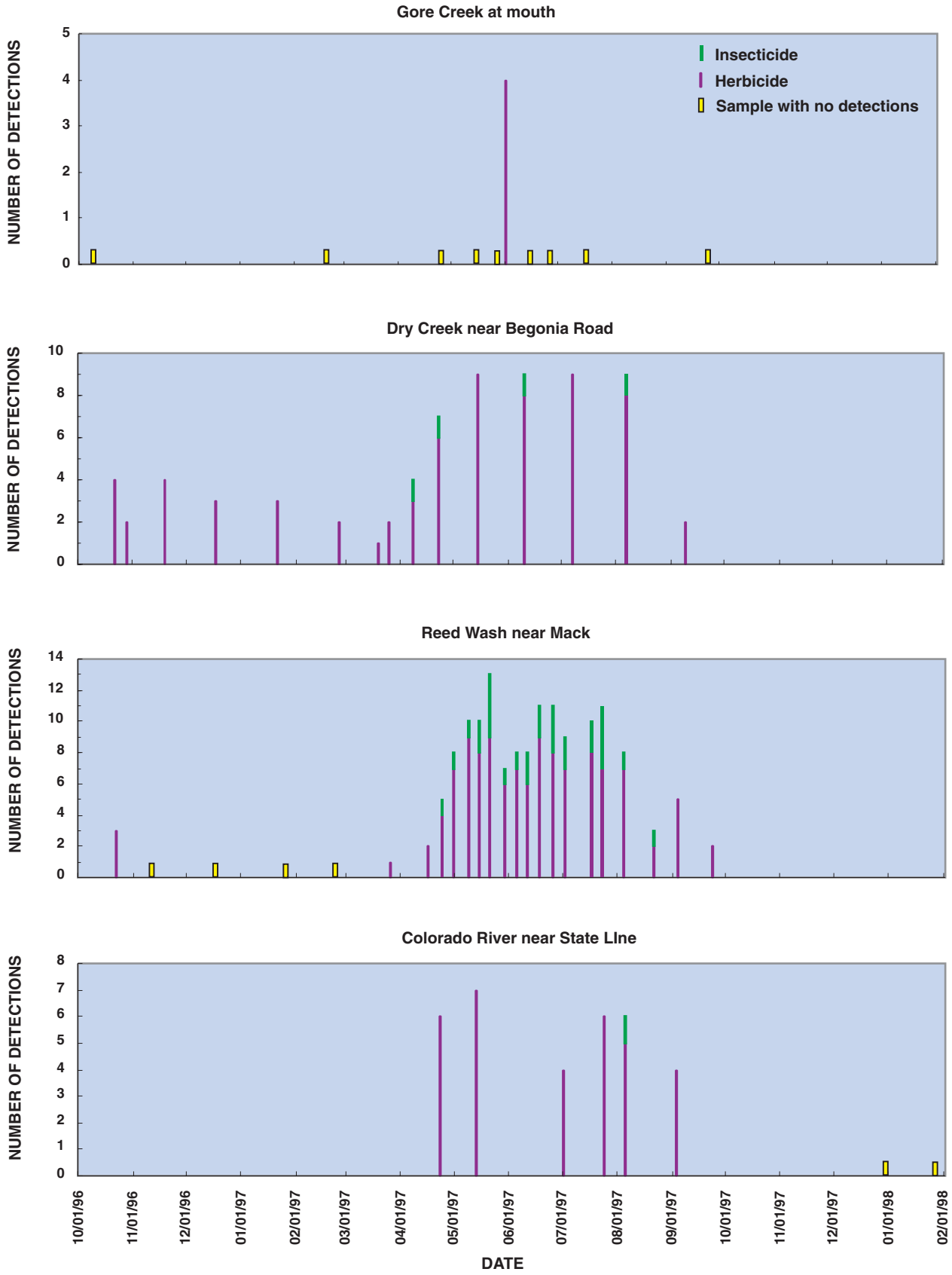

Figure 5. Number of pesticide detections per sampling date, fixed-station sites, Upper Colorado River Basin, October 1996–January 1998. (Graphs have different vertical scales.)

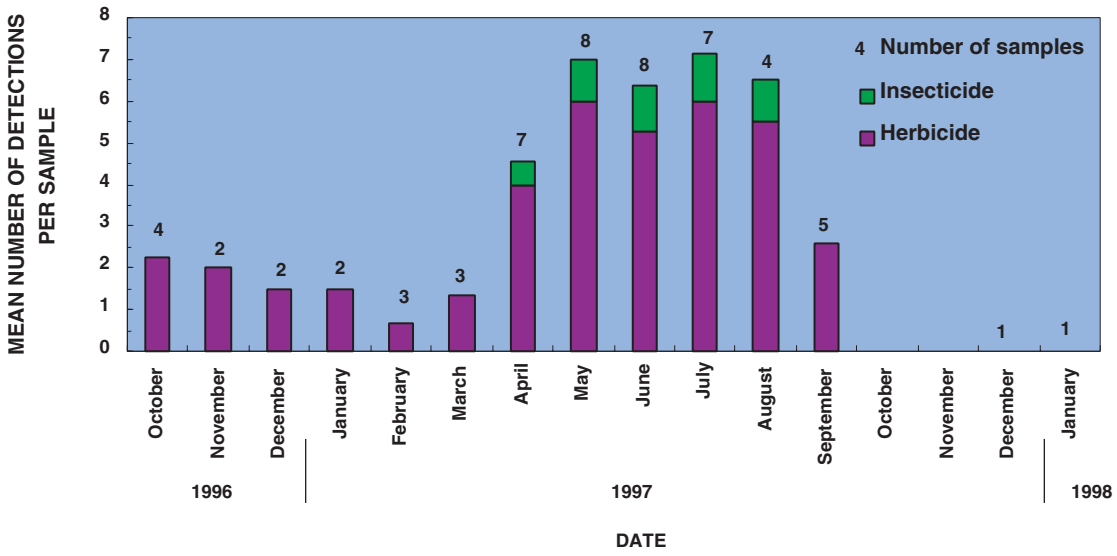

Figure 6. Mean number of pesticide detections per sample by month, all fixed-station sites combined, Upper Colorado River Basin, October 1996–January 1998.

June (fig. 3). The highest pesticide concentrations occurred primarily in May, June, and July. This can be seen, for example, with atrazine concentrations at Dry Creek, Reed Wash, and Colorado River near State Line and carbofuran and 2,4-D concentrations at Reed Wash (figs. 7 and 8). At Dry Creek, detectable concentrations of atrazine were present in most samples, with the highest concentrations occurring in May through August. At Reed Wash, atrazine concentrations were highest in May through July and were below the detection limit prior to May. For Dry Creek and Reed Wash, atrazine concentrations were greater in the irrigation return flows and snowmelt of the spring and summer months and were undetected or detected at lower levels in the winter and early spring months when streamflow was at a minimum (fig. 7). The atrazine concentration at Colorado River near State Line was highest during snowmelt (fig. 7). At Reed Wash, carbofuran and 2,4-D were detected in the April through August irrigation return flows and undetected in the low-flow winter and early spring months (fig. 8). For both Dry Creek and Reed Wash, irrigation return flows and snowmelt were important mechanisms in the transport of pesticides from agricultural fields to drainage streams.

Although it can be assumed that the atrazine, carbofuran, and 2,4-D detections at Dry Creek and Reed Wash in the irrigation return flows of the summer months were related to pesticide use during the same time period, it is not possible to correlate some of the pesticide detections directly to pesticide use without recent (1996–98) pesticide-application data. A few of the detections in the summer months were at much higher concentrations than the rest of the summer detections (figs. 7 and 8); however, without application data, these spikes in the concentration data cannot be correlated to recent pesticide applications. In addition, it cannot be determined if some of the pesticides that were detected infrequently were not used in the study unit or if any of the pesticides that were used went undetected.

Spatial Distribution

Pesticide detections varied among the different land uses and site types in the UCOL study unit (table 12). Detections were most common at the agriculture sites. One or more pesticides were detected in 100 percent and 83 percent of the samples at Dry Creek and Reed Wash, respectively. Seventy-five percent of the samples at the integrator site, Colorado River near State Line, contained at least one pesticide detection, while only 10 percent of the samples at the urban/forest site of Gore Creek had one or more detections. At each site, herbicides were detected more often than insecticides (table 12). A list of the pesticides detected at each site, along with concentration statistics, is in table 11. Only the herbicides atrazine, cyanazine, and metolachlor were detected at all four fixed-station sites. Twelve pesticides (six herbicides and six insecticides) were detected only at the agriculture sites.

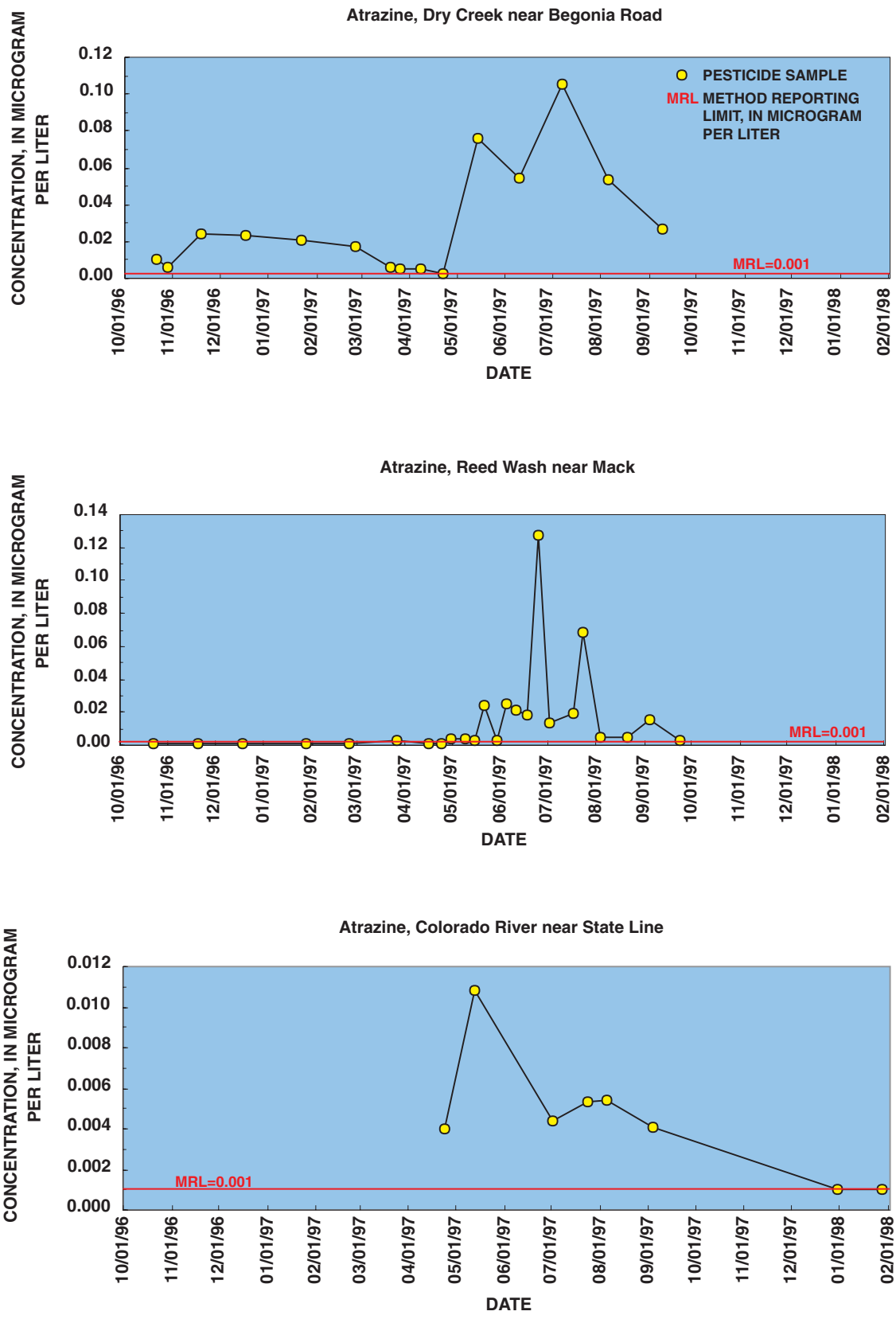

Figure 7. Atrazine concentrations at Dry Creek near Begonia Road, Reed Wash near Mack, and Colorado River near State Line, October 1996–January 1998. (Graphs have different vertical scales.)

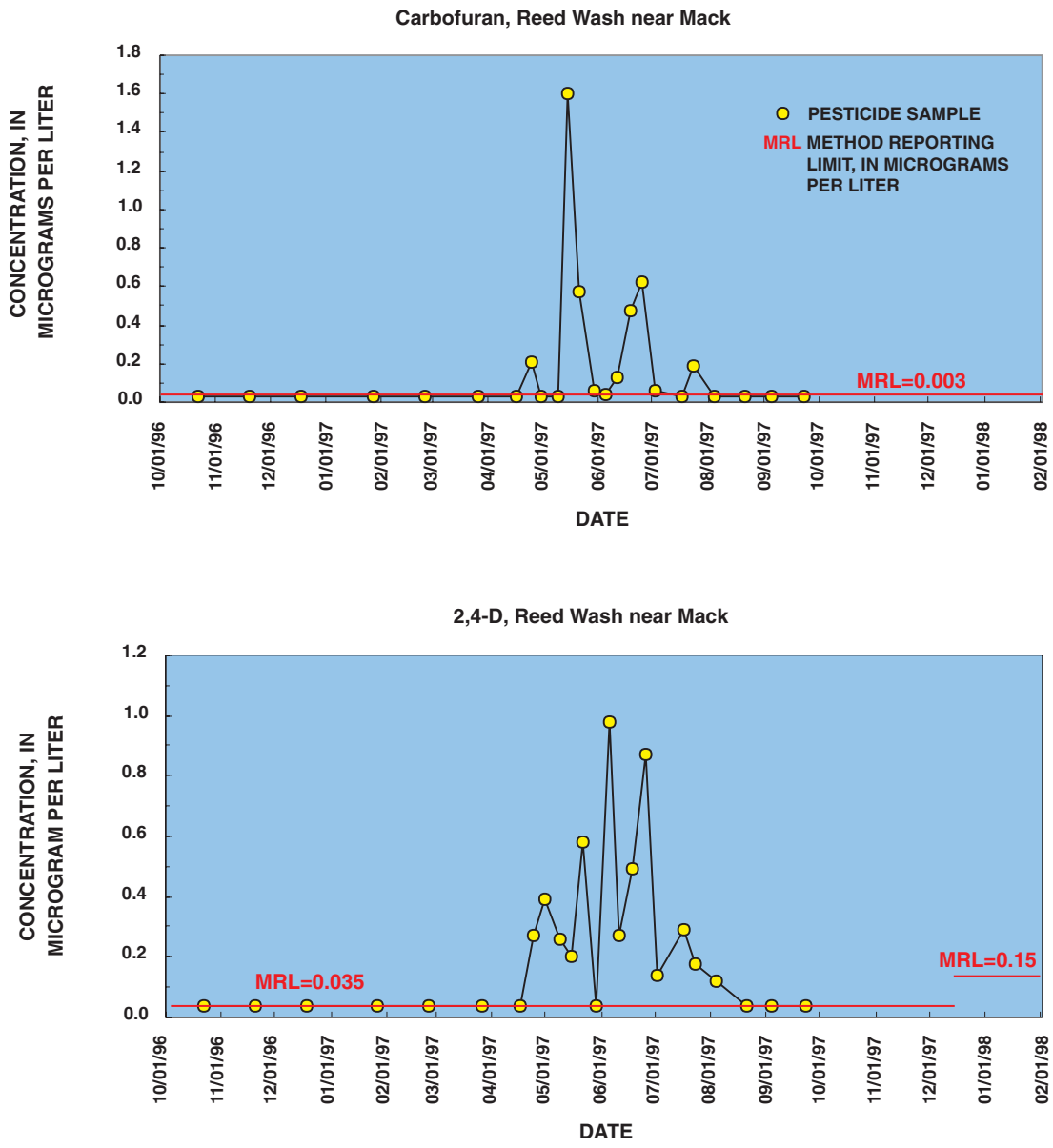

Figure 8. Carbofuran and 2,4-D concentrations at Reed Wash near Mack, October 1996–January 1998. (Graphs have different vertical scales.)

Among the land-use/site-type classifications, the median concentrations (maximum concentrations for single detections at Gore Creek) of atrazine, cyanazine, and metolachlor were greatest at the two agriculture sites (table 11). The median concentration for the atrazine detections was highest at Dry Creek, and the median concentrations of cyanazine and metolachlor were highest at Reed Wash. The median concentrations for these three pesticides were 0.021, 0.020, and 0.043 µg/L, respectively (table 11). All three median concentrations were much lower than water-quality criteria—the drinking-water standard for atrazine of 3 µg/L and the lifetime-health advisories for cyanazine and metolachlor of 1 µg/L and 70 µg/L, respectively (table 5). Detecting the highest median concentrations at the agriculture sites would be expected, as pesticide use would be more concentrated in the agriculture areas as compared to the urban/forest area or in the study unit as a whole (integrator site). The remaining median concentrations of atrazine, cyanazine, and metolachlor for the different land-use/site-type classifications were low, 0.014 µg/L or less. In comparing the urban/forest Gore Creek site to the integrator site Colorado River near State Line, median atrazine and

Table 12. Pesticide detections per land use and site type at fixed-station sites in the Upper Colorado River Basin, October 1996–January 1998

Site name	Land use	Site type	Number of samples (excluding quality assurance)	Number of samples with pesticide detections	Number of pesticides detected	Number of herbicides detected	Number of insecticides detected
Dry Creek near Begonia Road, near Delta	Agriculture	Indicator	15	15	16	13	3
Reed Wash near Mack	Agriculture	Indicator	24	20	19	13	6
Colorado River near Colorado-Utah State Line	All[1]	Integrator	8	6	10	9	1
Gore Creek at mouth near Minturn	Urban/forest	Indicator	10	1	4	4	0

[1]Includes agriculture, forest, mining, rangeland, and urban.

metolachlor concentrations were greater at the urban/forest site, and the median cyanazine concentration was greater at the integrator site. These differences between the two sites, however, were low, 0.009 µg/L or less.

Eight other pesticides were detected in common at sites representing two of the land-use/site-type classifications. Benfluralin was jointly detected at the urban/forest site and the agriculture sites (table 11). Alachlor, DCPA, 2,4-D, deethylatrazine, EPTC, propargite, and trifluralin were all detected at the agriculture sites and the integrator site (table 11). For all eight pesticides, the highest median concentration was again at either of the two agriculture sites. Some of these median concentrations at the agriculture sites were low, only a few nanograms per liter or so above the reporting limit for the respective pesticides. Only EPTC, propargite, and 2,4-D had median concentrations substantially larger than their reporting limits, up to a difference of 0.585 µg/L for the 2,4-D reporting limit and detected concentration. The median concentrations for pesticides detected at the integrator and urban/forest sites overall tended to be low, within a few nanograms per liter of the reporting limit for most pesticides (table 11).

In comparing the pesticide data for Dry Creek and Reed Wash, there are some differences in detections even though both are agricultural areas. Metolachlor, trifluralin, 2,4-D, carbofuran, chlorpyrifos, and deethylatrazine all had at least a 40-percent difference in percentage of samples with detected pesticides at the two sites (table 11). The first three pesticides had a detection rate of greater than 50 percent at Reed Wash but 20 percent or less at Dry Creek. Carbofuran and chlorpyrifos were each detected at Reed Wash in 42 percent of the samples but were not detected at Dry Creek. These differences may be related to pesticide use, especially with carbofuran and chlorpyrifos, but also may be related to the sampling schedule. Reed Wash was sampled weekly or biweekly for pesticides from April through September 1997, while Dry Creek was only sampled monthly from late April through September 1997 (fig. 5). The detection percentages for Dry Creek may have been higher with more samples. Trifluralin, for example, was detected at Dry Creek in 13 percent (2 of 15) of the samples, with the detections occurring monthly in July and August. Presuming that trifluralin was present the entire 2-month period, the trifluralin detection frequency would have been higher if Dry Creek had also been sampled weekly or biweekly during this time. Deethylatrazine was more commonly detected in Dry Creek (93 percent) than Reed Wash (29 percent), possibly because atrazine, the parent compound, was more common in Dry Creek and had a higher median concentration. Reed Wash and Dry Creek also had differences in the number and concentration of pesticides detected in more than 30 percent of the samples at each site. At Reed Wash, 10 pesticides were detected in more than 30 percent of the samples, and five had median concentrations greater than or equal to 0.020 µg/L: 2,4-D (0.270 µg/L), carbofuran (0.200 µg/L), metolachlor (0.043 µg/L), EPTC (0.025 µg/L), and cyanazine (0.020 µg/L). At Dry Creek, five pesticides were detected in more than 30 percent of the samples, and only atrazine (0.021 µg/L) had a median concentration above 0.020 µg/L. These differences between Reed Wash and Dry Creek may, again, be related to pesticide use and sampling schedule.

Pesticides at Synoptic Network

Forty-three sites in the Grand Valley and Uncompahgre River Valley were sampled once for pesticides in May 1998 as part of a synoptic study of the water quality of rivers, streams, and drains in agricultural areas of the UCOL study unit. Thirty-one pesticides were detected at least once (table 13) in samples for 40 of the 43 sites. Of these 40 samples with detections, 36 contained two or more detected pesticides. For the synoptic samples, 3,561 individual pesticide analyses were performed. Detections occurred in 223 analyses, or 6.3 percent. Almost 75 percent (167 of 223) of the detections were for the 10 most frequently occurring pesticides. The frequency of detection for all 31 pesticides and their measured concentrations are shown in figure 9, in descending order of frequency. Twenty-one herbicides

Table 13. Statistical summary of concentrations of detected pesticides at 43 agricultural synoptic sites in the Upper Colorado River Basin, May 1998

[µg/L, micrograms per liter; E, estimated; HPLC, high-performance liquid chromatography; --, not computed]

Pesticide	Number of samples	Number of detections	Percentage detected	Method reporting limit (µg/L)	Statistics for detections		
					Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Atrazine	43	29	67	0.001	E 0.002	0.009	1.04
Alachlor	43	26	60	0.002	E 0.002	0.021	0.751
Metolachlor	43	19	44	0.002	E 0.002	0.009	0.442
Acetochlor	43	18	42	0.002	0.007	0.028	2.61
2,4-D	43	15	35	0.15	0.15	0.25	E 3.50
Cyanazine	43	14	33	0.004	0.004	0.009	0.618
Deethylatrazine	43	14	33	0.002	E 0.003	E 0.006	E 0.013
Trifluralin	43	13	30	0.002	E 0.003	0.006	0.051
DCPA	43	10	23	0.002	E 0.002	0.010	0.109
Carbofuran (HPLC)	43	9	21	0.12	0.22	0.53	E 1.80
Pendimethalin	43	8	19	0.004	0.006	0.021	0.099
EPTC	43	7	16	0.002	E 0.003	0.006	0.061
Diazinon	43	6	14	0.002	E 0.003	0.008	0.104
Simazine	43	5	12	0.005	0.012	0.014	0.065
Benfluralin	43	4	9.3	0.002	E 0.004	E 0.006	0.009
Carbaryl (HPLC)	43	3	7.0	0.008	0.050	0.230	0.780
Chlorpyrifos	43	3	7.0	0.004	0.006	0.007	0.029
Diuron	43	3	7.0	0.02	E 0.02	0.04	E 18.0
Dieldrin	43	2	4.7	0.001	E 0.003	E 0.003	E 0.004
gamma-HCH	43	2	4.7	0.004	0.007	0.009	0.012
Metribuzin	43	2	4.7	0.004	0.006	0.009	0.011
Prometon	43	2	4.7	0.018	0.031	0.215	0.399
Azinphos-methyl	43	1	2.3	0.001	--	--	E 0.006
Bromoxynil	[1]42	1	2.3	0.035	--	--	0.090
Dicamba	[1]42	1	2.3	0.035	--	--	E 1.50
Ethalfluralin	43	1	2.3	0.004	--	--	0.005
Malathion	43	1	2.3	0.005	--	--	0.014
MCPB	43	1	2.3	0.14	--	--	0.22
Phorate	43	1	2.3	0.002	--	--	E 0.003
Pronamide	43	1	2.3	0.003	--	--	0.012
Terbufos	43	1	2.3	0.013	--	--	0.018

[1] Number of samples is different because the result for one sample is unreported due to difficulties in the laboratory determination of concentration.

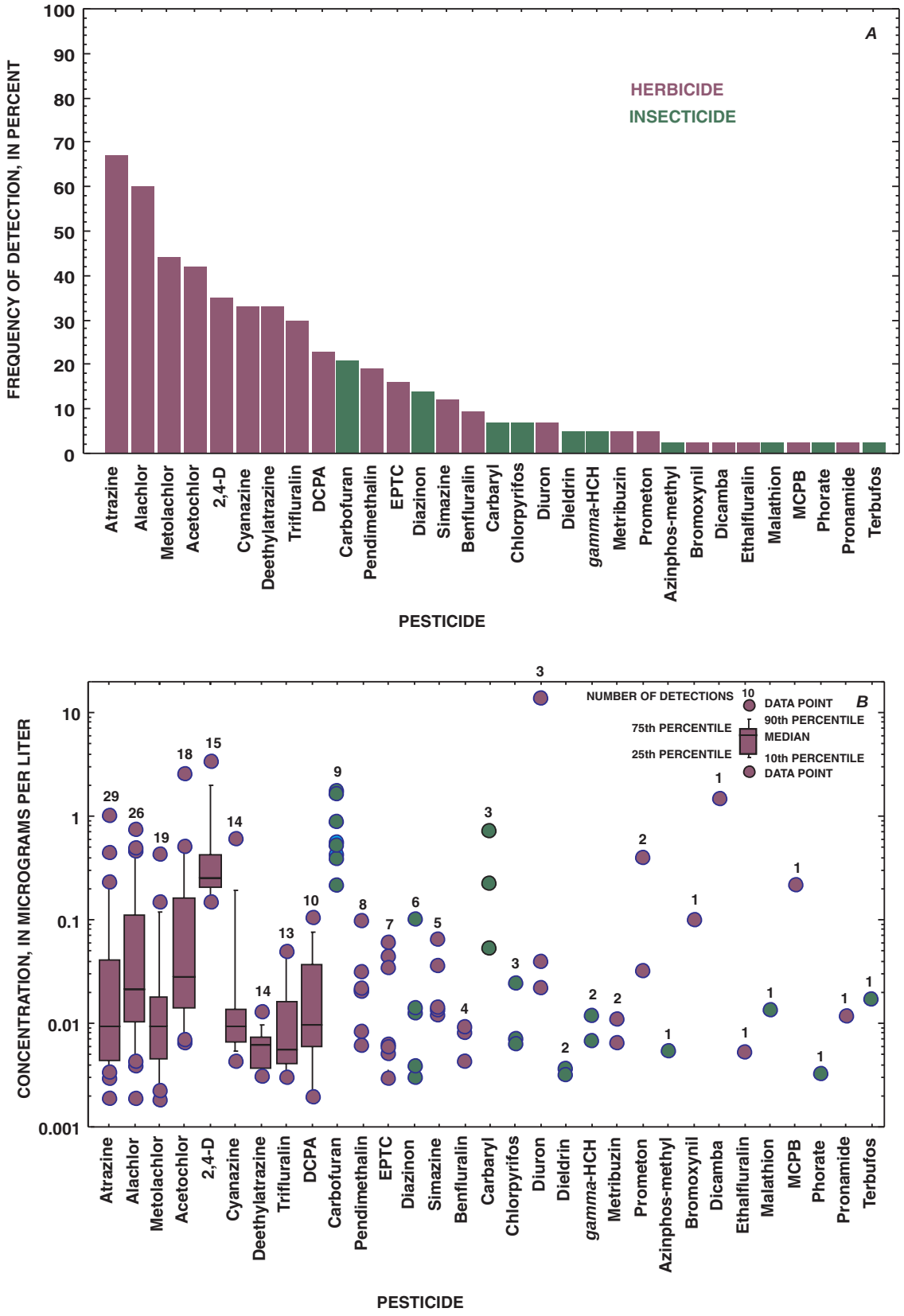

Figure 9. (*A*) Frequency of pesticide detections and (*B*) concentrations of detected pesticides for the agricultural synoptic sites sampled in the Upper Colorado River Basin, May 1998. (Individual data points were plotted when fewer than 10 data points were available.)

and 10 insecticides were detected in the synoptic study. Herbicides accounted for almost 87 percent (194 of 223) of the detections. Only two herbicides were detected in more than 50 percent of the samples—atrazine (67 percent) and alachlor (60 percent). Carbofuran, with a detection rate of 21 percent, was the most common insecticide.

Pesticide concentrations in the synoptic study ranged from 0.002 to 18.0 µg/L (table 13). Many concentrations were low. The highest concentration of 18.0 µg/L (an estimated value) was very uncommon, as the next highest concentration, also estimated, was 3.50 µg/L. More than 59 percent of the detections were greater than or equal to 0.01 µg/L. More than 30 percent of the detections were greater than or equal to 0.05 µg/L, with more than 35 percent of these detections due to high carbofuran and 2,4-D concentrations.

Twenty-two pesticides were detected more than once in the synoptic study. The maximum concentration of each of the 22 pesticides was detected among 10 sites having stream discharges between 1.45 and 185 ft^3/s. Almost 82 percent (18 of 22) of the maximum concentrations were found in two distinct discharge ranges. The maximum concentrations of nine pesticides were detected in samples from streams or drains having a discharge between 12.7 and 20 ft^3/s, and nine other pesticides had maximum concentrations in streams or drains with discharges between 75 and 185 ft^3/s. Three pesticides had maximum concentrations at discharges of less than 4.5 ft^3/s, and one pesticide had a maximum concentration at a discharge of 40 ft^3/s. It is possible that in areas with lower discharges, there was not enough surface runoff or subsurface percolation to transport pesticides from the fields to streams and drains. In larger streams and drains, in contrast, pesticide concentrations were diluted because of the higher streamflows. In the synoptic study, stream discharge ranged between 0.33 and 18,190 ft^3/s, with a median of 37.0 ft^3/s. Discharge values below 23 ft^3/s were common for drains, such as the 33 Road Drain near Clifton (17 ft^3/s), while discharge values above 429 ft^3/s were mainly found at the Colorado, Gunnison, and Uncompahgre River sites. Ninety percent of the discharge values were less than 561 ft^3/s, with other discharge percentiles and discharge values being 70 percent, 145 ft^3/s; 25 percent, 9.12 ft^3/s; and 10 percent, 2.06 ft^3/s.

In both the Grand Valley and the Uncompahgre River Valley, sampling sites were named as rivers, creeks, washes and arroyos, drains, runs, gulches, and canals (tables 3 and 4). During the synoptic sampling, the nonriver sites all functioned as drains for irrigation return flows in the agricultural areas, whether they were natural water features or manmade ditches. Some, such as the Dry Creek sites and Roubideau Creek at mouth, also carried snowmelt runoff. But because all sites functioned as drains, it was not possible to determine if there were major differences in pesticide detections and concentrations between the natural and manmade watercourses. There were differences in pesticide detections and concentrations among the river sites, though. The number of pesticide detections per site for four river sites—Uncompahgre River at Delta, Gunnison River above Escalante Creek, Gunnison River near Grand Junction, and Colorado River near State Line—was in the mid-range of detections for all synoptic sites. Only one pesticide was detected at the site Uncompahgre River at Montrose, upstream from the main agricultural areas in the Uncompahgre River Valley. The Uncompahgre River at Delta site had the most detections among the river sites, and the concentrations tended to be higher than at the other river sites. This site is just downstream from most of the irrigated land in the Uncompahgre River Valley and, thus, had water that was more concentrated with pesticides than the river sites farther downstream. In general, the concentration of a pesticide detected at the river sites was either below the median concentration for the particular pesticide at all synoptic sites or just above the median.

No pesticide concentrations from the synoptic study were detected above USEPA drinking-water standards; however, one pesticide had a detected concentration above USEPA health-advisory guidelines. The diuron concentration of 18 µg/L for the sample from Indian Wash was almost double the lifetime health advisory of 10 µg/L for a 70-kilogram adult. This sample was collected during a rainstorm, an event that may have contributed to the high concentration value in the stream. Runoff from the storm may have been large enough to wash diuron from the soils in the area and transport the pesticide to the receiving stream. The diuron concentration of 18 µg/L was estimated because the concentration was above the HPLC upper calibration standard of 1.4 µg/L for diuron (R. Brenton, U.S. Geological Survey, oral commun., 1999). Criteria for the protection of freshwater aquatic

life for four pesticides (carbaryl, diazinon, diuron, and *gamma*-HCH) were exceeded in five analyses (table 14), of which concentrations of three (for carbaryl, diazinon, and *gamma*-HCH) only slightly exceeded criteria concentrations.

Pesticide detections in the synoptic study differed somewhat between the Grand Valley and the Uncompahgre River Valley. The number of herbicide and insecticide detections for each synoptic site per valley is shown in figure 10. The Colorado River near State Line site, while located near the Grand Valley, is shown separately because it is the integrator site and drains both the Grand Valley and Uncompahgre River Valley. The Colorado River near State Line is, thus, not included in the calculations for the Grand Valley. Only Drain at D and 29 3/4 Roads in the Grand Valley and Tongue Creek and Currant Creek in the Uncompahgre River Valley had no pesticide concentrations detected above the MRLs.

Pesticide detections were slightly more frequent in the Uncompahgre River Valley than the Grand Valley. Just over 7.1 percent of the analyses performed on the samples for the Uncompahgre River Valley had detected pesticides, whereas 5.4 percent of the analyses for the Grand Valley had detected pesticides. The particular pesticides detected in each valley differed, as did the frequency of detections (fig. 11). Of the 31 pesticides detected in the synoptic study, 21 pesticides (15 herbicides and 6 insecticides) were detected in the Grand Valley and 21 pesticides (16 herbicides and 5 insecticides) were detected in the Uncompahgre River Valley. Nine pesticides detected in the Grand Valley were not found in the Uncompahgre River Valley: carbofuran, simazine, carbaryl, diuron, metribuzin, prometon, azinphos-methyl, malathion, and MCPB. Nine pesticides detected in the Uncompahgre River Valley were not found in the Grand Valley: EPTC, benfluralin, chlorpyrifos, *gamma*-HCH, bromoxynil, dicamba, ethalfluralin, pronamide, and terbufos. Twelve pesticides were detected in both basins; three (2,4-D, metolachlor, and diazinon) were more frequently detected in the Grand Valley and seven (atrazine, alachlor, cyanazine, deethylatrazine, acetochlor, pendimethalin, and trifluralin) were more frequently detected in the Uncompahgre River Valley. DCPA and dieldrin were detected at almost the same frequencies in both basins.

As stated previously, a pesticide detection depends on many factors. The time, rate, and location of pesticide application, crop type, precipitation or irrigation events, physical and chemical characteristics

Table 14. Pesticide concentrations exceeding freshwater criteria guidelines for the protection of aquatic life, Grand Valley and Uncompahgre River Valley, Upper Colorado River Basin agricultural synoptic study, May 1998

[µg/L, micrograms per liter; HPLC, high-performance liquid chromatography; GV, Grand Valley; URV, Uncompahgre River Valley; NAS/NAE, National Academy of Sciences/National Academy of Engineering; E, estimated]

Pesticide	Detected concentration (µg/L)	Criterion concentration (µg/L)	Site name and number (see fig. 2, tables 3 and 4)	Sampling date	Basin
Environment Canada (1999) guidelines for protection of freshwater aquatic life					
Carbaryl (HPLC)	0.780	0.2	Indian Wash (GV7)	05/06/98	GV
	0.230	0.2	Orchard Mesa Drain (GV8)	05/07/98	GV
International Joint Commission Canada and United States (1978) objectives for the protection of aquatic life					
Diazinon	0.104	0.08	Indian Wash (GV7)	05/06/98	GV
gamma-HCH	0.012	0.01	Drain at Blossom Road (URV5)	05/19/98	URV
NAS/NAE freshwater criteria for protection of aquatic life (Nowell and Resek, 1994)					
Diuron	E 18.0[1]	1.6	Indian Wash (GV7)	05/06/98	GV

[1] Concentration was designated as estimated because the concentration value exceeded the HPLC upper calibration standard of 1.4 µg/L for diuron (R. Brenton, U.S. Geological Survey, oral commun., 1999).

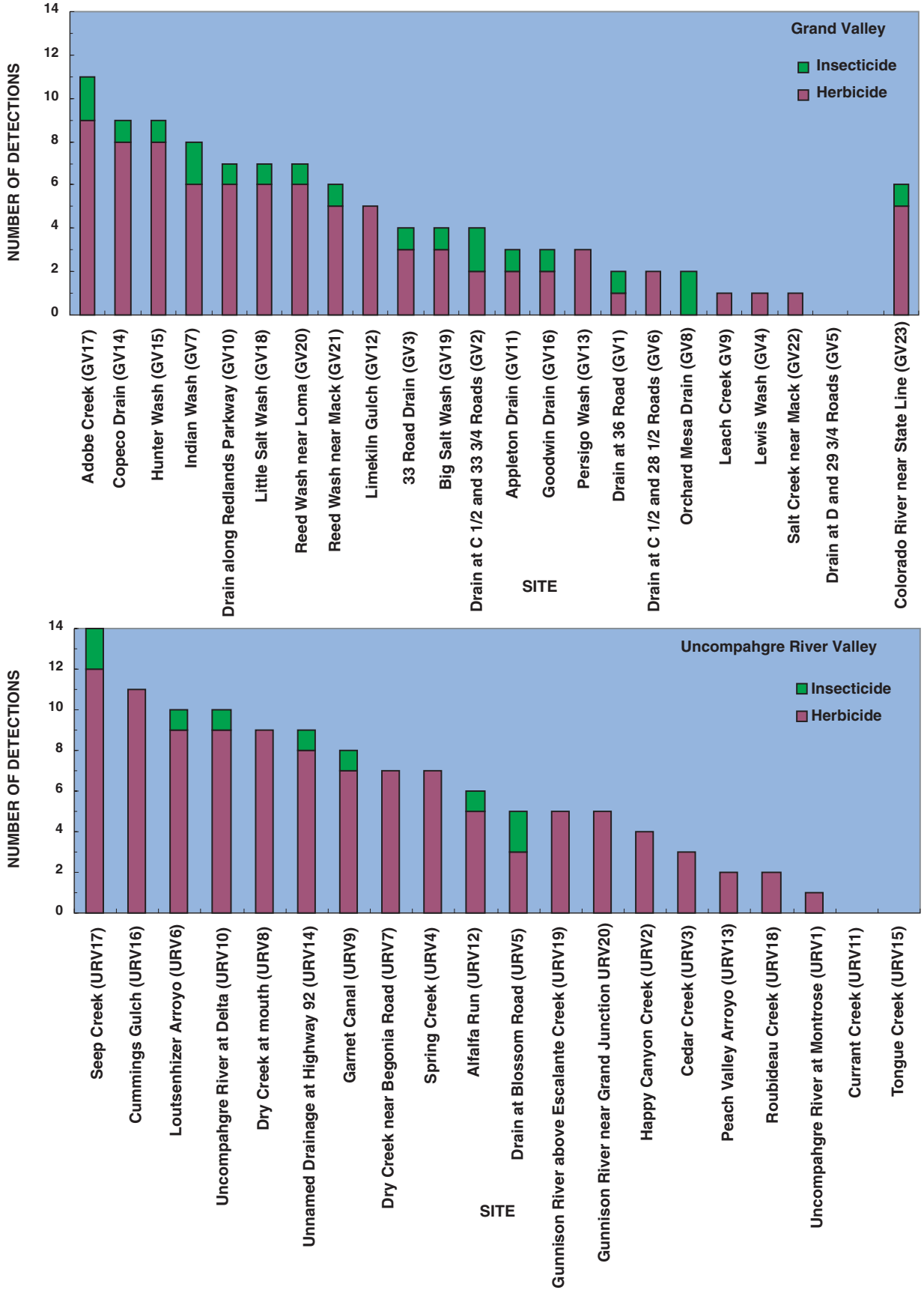

Figure 10. Number of pesticide detections per site in the Grand Valley and Uncompahgre River Valley, May 1998. (Letters and numbers in parentheses refer to site locations described in figure 2 and tables 3 and 4.)

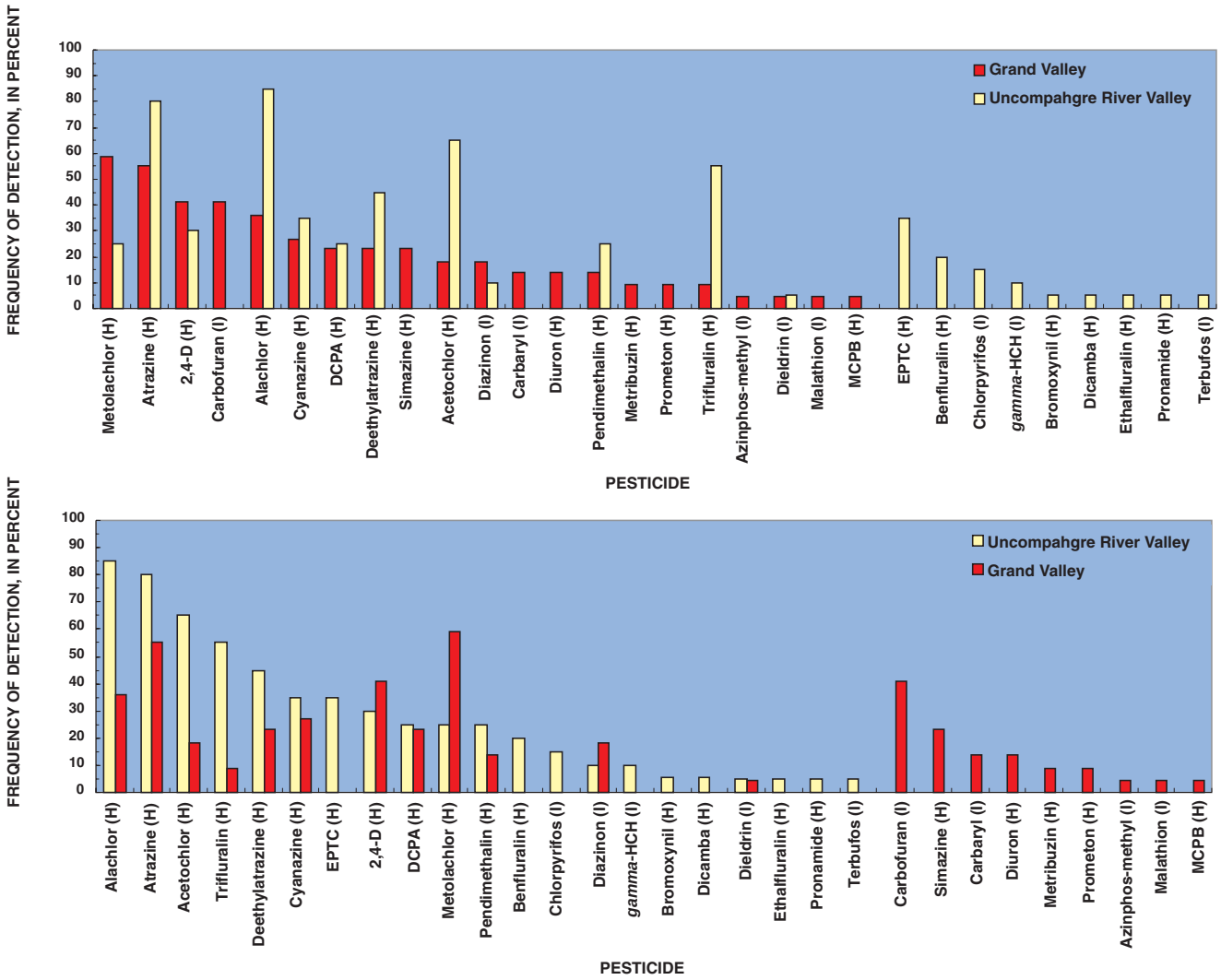

Figure 11. Frequency of pesticide detections in the Grand Valley and Uncompahgre River Valley, May 1998. Pesticides are shown from highest to lowest frequency of detection for each valley (H, herbicide; I, insecticide).

of pesticides, and atmospheric transport and deposition may affect whether or not a pesticide is detected.

The number of sites with the maximum concentrations for the 12 pesticides detected in both basins were almost evenly split between the two basins. Concentrations of five pesticides (atrazine, DCPA, diazinon, metolachlor, and pendimethalin) were highest at four sites (Adobe Creek, Copeco Drain, Indian Wash, and Reed Wash near Loma) in the Grand Valley. The maximum concentrations of seven pesticides (acetochlor, alachlor, cyanazine, 2,4-D, deethylatrazine, dieldrin, and trifluralin) were detected at three sites (Loutsenhizer Arroyo, Seep Creek, and Unnamed Drainage at Highway 92) in the Uncompahgre River Valley.

Comparison of Pesticides at Fixed-Station Network and Synoptic Network

Of the 35 pesticides detected in the UCOL, 23 pesticides (16 herbicides, 7 insecticides) were detected in samples from the fixed-station network and 31 pesticides (21 herbicides, 10 insecticides) were detected in samples from the synoptic network. Nineteen pesticides were detected in common at least once in both networks, and 13 pesticides were detected in common at least twice in both networks. Of the 19 pesticides detected in common in the two networks, 10 pesticides had higher median concentrations (maximum concentrations for single detections) detected in the synoptic study, and 7 pesticides had

higher median concentrations detected in the fixed-station network. Some of the differences in the detected median concentrations were large (0.33 µg/L for carbofuran), while seven of the differences were very small (0.002 µg/L or less). Two pesticides, deethylatrazine and trifluralin, had the same median concentration detected in both networks. Of the 13 pesticides detected two or more times in each network, the maximum detected concentrations of 11 were from in the synoptic network, and only 2 were greatest in the fixed-station network. As stated previously, more than 59 percent of the pesticide detections in the synoptic network had concentrations greater than or equal to 0.01 µg/L, and more than 30 percent had concentrations greater than or equal to 0.05 µg/L. This compares to more than 36 percent and almost 22 percent, respectively, in the fixed-station network. Standards and guidelines for the protection of human and aquatic health were exceeded more frequently in the synoptic sampling. The concentration of one diuron analysis in the synoptic study was above the lifetime human health advisory, and the concentrations of four pesticides were detected above criteria for the protection of freshwater aquatic life in five synoptic analyses. In the fixed-station network, no human health advisories were exceeded, and only one pesticide had a concentration detected above the freshwater aquatic-life criterion.

Acetochlor and pendimethalin were the two pesticides with the greatest differences in percentage of detection between the two networks. Acetochlor was detected much more frequently in the synoptic sampling than in the fixed-station sampling, 42 percent as compared to 1.8 percent, respectively. Pendimethalin was detected in 19 percent of the synoptic samples and was undetected in the fixed-station samples. Acetochlor is a preplant and preemergence herbicide and thus would be more common early in the growing season, such as the May synoptic time period, rather than being detected year round, as in the fixed-station sampling. A similar situation would exist for pendimethalin, a preemergence and early postemergence herbicide.

COMPARISON WITH RESULTS OF PREVIOUS STUDIES

The results from the UCOL fixed-station and synoptic sampling can be compared to the occurrence and concentrations of pesticides from 20 NAWQA study units that collected water-quality data from 1992 through 1996. Table 15 lists the study results for selected pesticides from this NAWQA group—the 10 most commonly detected pesticides and four others that are common in the UCOL study unit. Fifty-seven percent (8 of 14) of the selected pesticides were detected less frequently in the UCOL study unit than in the larger NAWQA group, and 64 percent (9 of 14) had lower concentrations at the 90th percentile in the UCOL (tables 10 and 15). For example, atrazine, the most commonly detected pesticide in both groups, was detected in 69 percent of the samples in the UCOL study unit and in 79 percent of the NAWQA group samples. Twelve percent of all atrazine samples in the UCOL study unit had detected concentrations greater than or equal to 0.05 µg/L, whereas 41 percent of all atrazine samples for the NAWQA group had detected concentrations greater than or equal to 0.05 µg/L. Considering only the samples with pesticide detections, almost 50 percent of the samples with detections in the UCOL had concentrations greater than or equal to 0.01 µg/L, and 20 percent were greater than or equal to 0.05 µg/L. Nationally, again among only the pesticide samples with detections, most of the NAWQA group samples with detected concentrations had concentration values greater than 0.01 µg/L, and more than one-half were greater than or equal to 0.05 µg/L (U.S. Geological Survey, 1998a).

Some pesticides that were commonly detected in the NAWQA group were rare or undetected in the UCOL study unit (tables 10 and 15). Simazine, prometon, diazinon, and tebuthiuron were detected in 25 percent or more of the samples in the NAWQA group but only in 8 percent or less (undetected for tebuthiuron) of the UCOL samples. All four pesticides have substantial urban and suburban use nationally but are probably used less frequently in the UCOL study unit because of its predominantly rural and undeveloped character. Sites classified as urban in the NAWQA group consisted of sites in or near major metropolitan areas of the Nation, including Atlanta, Georgia; Denver, Colorado; and Washington, D.C. In contrast, the urban site in the UCOL, Gore Creek at the mouth, is located downstream from the small resort town of Vail, Colorado, and most of the Gore Creek watershed is forest land in the White River National Forest rather than urban land. For these reasons, Gore Creek at the mouth is a very different

Table 15. Summary of selected pesticide occurrences and concentrations for all 1,058 surface-water sites sampled as part of 20 NAWQA study units, 1992–96 (U.S. Geological Survey, 1998a)

[Percentages are rounded; ≥, greater than or equal to; µg/L, micrograms per liter; MRL, method reporting limit; <, less than; E, estimated; --, method reporting limit greater than detection threshold]

Pesticide	Number of samples	Percentage detected	Percentage detected ≥ 0.01 (µg/L)	Percentage detected ≥ 0.05 (µg/L)	MRL (µg/L)	Concentration at indicated percentile (µg/L)			Maximum concentration (µg/L)
						10th	50th	90th	
Atrazine	5,196	79	66	41	0.001	< MRL	0.026	0.70	E 120
Metolachlor	5,191	69	52	28	0.002	< MRL	0.011	0.33	E 70
Simazine	5,198	66	54	25	0.005	< MRL	0.012	0.17	E 20
Deethylatrazine	5,197	57	38	18	0.002	< MRL	0.096	0.096	E 1.1
Prometon	5,198	49	40	14	0.018	< MRL	< MRL	0.066	E 4.2
Diazinon	5,158	36	25	10	0.002	< MRL	< MRL	0.051	3.8
Cyanazine	5,198	32	29	15	0.004	< MRL	< MRL	0.11	E 160
Alachlor	5,198	31	23	9.9	0.002	< MRL	< MRL	0.049	E 25
Tebuthiuron	5,198	25	17	2.8	0.01	< MRL	< MRL	0.018	E 6.4
DCPA	5,196	24	7.1	2.4	0.002	< MRL	< MRL	0.006	E 100
EPTC	5,195	18	11	4.0	0.002	< MRL	< MRL	0.012	E 40
Trifluralin	5,196	15	5.8	0.8	0.002	< MRL	< MRL	0.01	0.51
Acetochlor	1,987	12	9.4	4.4	0.002	< MRL	< MRL	0.008	3.8
2,4-D	3,400	12	--	10	0.035	< MRL	< MRL	0.050	E 15

urban site than the sites classified as urban in the NAWQA group. In comparing agricultural areas between the two groups, alachlor and 2,4-D were detected more frequently in the UCOL. This may be a reflection of the amount of alfalfa, corn, dry beans, and various grains grown in the UCOL as compared to the NAWQA group. In studying agricultural land use, the focus of the 1992–96 NAWQA study units was limited to the most important agricultural settings within the study units; thus, the results are not an unbiased representation of all streams in agricultural settings nationally (U.S. Geological Survey, 1998a). Some crops grown and pesticides used in certain parts of the country may not be represented by this NAWQA group. In this comparison of the UCOL study unit and the NAWQA group, carbofuran has been excluded from the discussion because the carbofuran results for the two groups have been reported for different analysis methods: HPLC for the UCOL study unit and GC/MS for the NAWQA group.

In 1995–96, streambed sediment and whole-body fish were collected at selected sites in the UCOL basin and analyzed for particular organochlorine pesticides and PCB's (Stephens and Deacon, 1998). Nine sites were common to that study and the pesticide sampling described in this report: Gore Creek at mouth, Dry Creek near Begonia Road, Tongue Creek at Cory, Gunnison River near Grand Junction, 33 Road Drain at mouth, Appleton Drain near mouth, Copeco Drain near mouth, Reed Wash near Mack, and Colorado River near State Line. Six pesticides were analyzed for in both studies: *alpha*-HCH, *gamma*-HCH, DCPA, dieldrin, *p,p'*-DDE, and *cis*-permethrin. Concentrations of DCPA, dieldrin, and/or *p,p'*-DDE were detected in the streambed sediments and/or whole-body fish at many of the nine sites. For the surface-water sampling, DCPA was the only pesticide detected at any of the nine sites in common. Dieldrin was not detected at any common sites, and *p,p'*-DDE was undetected in the surface-water sampling. Since 1974, the use of dieldrin has been restricted to termite control and nonfood plant treatment, whereas DDT, the parent compound of *p,p'*-DDE, has been banned from use in the United States since 1972. The presence of DCPA, dieldrin, and *p,p'*-DDE in streambed sediment and whole-body fish is not uncommon, though, because organochlorine compounds are extremely persistent in the environment and bind to sediment and to fatty tissue in aquatic biota. As can be seen with the nondetections of dieldrin and *p,p'*-DDE in the water column and the detections in sediment and fish, the absence of a pesticide in a water sample from a partic-

ular site does not necessarily mean that the pesticide is not present at the site. The pesticide may have accumulated in the sediment and aquatic biota.

Butler and others (1991, 1994) collected water samples for pesticide analysis in the Uncompahgre River Valley in July 1988 and the Grand Valley in June and August 1991 as part of a reconnaissance investigation of irrigation-project areas. Two sites and 14 pesticides in the Uncompahgre River Valley reconnaissance study were also studied as part of the 1998 synoptic pesticide investigation in the UCOL study unit. Three pesticides—malathion, methyl parathion, and parathion—were detected at the Uncompahgre River Valley reconnaissance sites in July 1988. For the Grand Valley reconnaissance investigation in June and August 1991, 9 sites from the June sampling and 20 insecticides were in common with the UCOL synoptic pesticide sampling. Parathion and 3-hydroxycarbofuran were detected once above their respective MRLs at two different sites in the Grand Valley reconnaissance, whereas diazinon was detected above the reporting limit once at four sites. Of the five pesticides—3-hydroxycarbofuran, diazinon, malathion, methyl parathion, and parathion—detected in the reconnaissance investigation that were also analyzed for as part of the UCOL study, only diazinon and malathion were detected. This difference in pesticide detections may depend on sampling time and sites sampled, crops grown and insects or weeds common to the particular crops, pesticide usage, and the reporting limits for the various pesticides being studied. The reconnaissance investigation of Butler and others (1991, 1994) occurred later in the growing season, from June through August, than the UCOL pesticide synoptic sampling in May. Also, the UCOL fixed-station sites sampled in June through August were not the same sites sampled in the June through August reconnaissance investigation. Pesticide application varies depending on the time of year; for example, preemergence herbicides are applied before or at the beginning of the growing season, while insecticides are commonly applied later in the growing season. Different crops may have been grown in 1988 and 1991 as compared to 1997, resulting in different pesticides being applied and, therefore, detected. Finally, the MRLs for the pesticides studied in the reconnaissance investigation were generally much higher than those in the UCOL study; the MRL for carbaryl was 0.5 µg/L in 1988 and 1991 and 0.008 µg/L (for HPLC) in 1997, for example.

SUMMARY AND CONCLUSIONS

Forty-four sites in the Upper Colorado River Basin study unit were sampled for pesticides during 1996–98. Four fixed-station sites in the UCOL surface-water network were sampled from October 1996 through January 1998. These sites were sampled approximately monthly for up to 1 year, and samples were collected more frequently during the spring and summer growing season. Forty-three sites in the Grand Valley and Uncompahgre River Valley, intensive agricultural areas in the UCOL, were each sampled once in May 1998 as part of a water-quality study of rivers, streams and drains in these agricultural areas. Pesticides were detected at 41 of the 44 UCOL sites. Concentrations generally were low. For all samples and analyses, only atrazine and alachlor had median concentrations greater than their respective MRLs; in both cases, only slightly above the MRLs. Carbofuran and 2,4-D were the only pesticides to be detected consistently at concentrations higher than the other pesticides studied, with 90th percentile concentrations of 0.447 and 0.385 µg/L, respectively. Increased pesticide detections and concentrations occurred after the probable time of pesticide application and runoff from storm events and in agricultural areas during the growing season.

For the fixed-station sites, herbicides were more commonly detected than insecticides. The herbicides atrazine and alachlor were the only pesticides detected in more than 50 percent of the samples, with atrazine being the most commonly detected pesticide (70-percent detection rate). Carbofuran and chlorpyrifos were the most commonly detected insecticides, each with a detection rate of 18 percent. Detected concentrations of all pesticides in the fixed-station network generally were low, ranging from 0.001 to 2.60 µg/L. Pesticide detections and concentrations in the fixed-station study differed seasonally and across land uses and site types. The mean number of pesticides detected and pesticide concentrations were higher in the summer months and at the two agriculture sites. Only one detection, for azinphos-methyl at the agriculture site of Reed Wash, exceeded the criterion for the protection of freshwater aquatic life.

In the synoptic study, as in the fixed-station study, herbicides were more common than insecticides, and atrazine and alachlor were the only pesticides detected in more than 50 percent of the samples, 67 and 60 percent, respectively. Carbofuran

(21 percent) was the most commonly detected insecticide. Concentrations for the pesticides detected in the synoptic study ranged from 0.002 to 18.0 µg/L, and many were low. The maximum concentration of 18.0 µg/L was an estimated concentration for diuron, which exceeded the lifetime human-health advisory for a 70-kilogram adult. This sample was collected during a rainstorm, which may have contributed to the high concentration. Four pesticides—carbaryl, diazinon, diuron, and *gamma*-HCH—had five detections above criteria for the protection of freshwater aquatic life. Pesticides were detected only slightly more frequently in the Uncompahgre River Valley than in the Grand Valley. Of the 12 pesticides detected in both areas, the maximum concentrations of 5 pesticides were detected at four sites in the Grand Valley, and the maximum concentrations of 7 pesticides were detected at three sites in the Uncompahgre River Valley.

Pesticides in the synoptic study were more frequently detected above 0.01 and 0.05 µg/L than in the fixed-station study—more than 59 and 30 percent, respectively, for the synoptic study and more than 36 and almost 22 percent, respectively, for the fixed-station study. The synoptic study focused only on agriculture sites during the growing season when greater pesticide use would be expected. The fixed-station study included samples from urban/forest and integrator sites along with two agriculture sites for up to one year. Human-health advisories and criteria for the protection of freshwater aquatic life were exceeded more frequently in the synoptic sampling.

Most pesticides detected in the UCOL study unit during the fixed-station and synoptic sampling periods were not detected at concentrations of concern, and beneficial uses of water were not being impaired by the presence of pesticides in surface waters. No pesticides were detected above drinking-water standards. Slightly more than one-half of the pesticides in the UCOL were detected less frequently than in the larger 1992–96 NAWQA group, and concentrations generally were lower in the UCOL. In the agricultural areas of the study unit, concentrations of various pesticides were occasionally detected above human-health guidelines and criteria for the protection of freshwater aquatic life. The few pesticides that had detected concentrations above water-quality guidelines may be of concern, but without more intensive sampling of the agricultural synoptic sites, it cannot be stated that the exceedances reflect a chronic problem or are a rare occurrence. With regard to water-quality guidelines and standards, though, it must be stated again that not all pesticides have had standards and criteria established, and for those with standards and criteria, the values have been based on the effects of the pesticides individually. Most samples for the UCOL study unit had more than one pesticide detected per sample, and the effects of combinations of pesticides on human and aquatic health are not known. Also, it is not possible to know if pesticide detections and concentrations in the UCOL study unit have decreased or increased over time because of the short (1996–98) sampling period. Only through long-term sampling would it be possible to determine trends in pesticide detections and concentrations in the study unit. As was shown by the detection of pesticides in streambed sediment and whole-body fish in the UCOL during 1995–96 that were undetected in water samples collected during 1996–98, pesticides may be present at a particular site and not be detected in a stream-water sample for that site. Many organochlorine pesticides bind to sediment and fatty tissues of aquatic biota and are extremely persistent in the environment. These pesticides may be undetected in the stream-water sample but still be present at the site in streambed sediment and fish.

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