Pesticides in Surface Water Measured at Select Sites in the Sacramento River Basin, California, 1996–1998

By Joseph Domagalski

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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 60 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 60 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, VERTICAL DATUM AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic meter (m^3)	35.31	cubic foot
cubic meter per second (m^3/s)	35.31	cubic foot per second
kilogram (kg)	2.205	pound (avoirdupois)
meter (m)	3.281	foot
square kilometer (km^2)	0.3861	square mile

Vertical Datum

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Acronyms

GC/MS gas chromatography/mass spectrometry
GIRAS Geographic Retrieval and Analysis System
HPLC high performance liquid chromatography
NAWQA National Water-Quality Assessment
PERA probabilistic ecological risk assessment
TMDL total maximum daily load
UVD untraviolet light detection
µg/L microgram per liter

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Abstract

Pesticides were measured in one urban stream, one agricultural stream, one site on the Sacramento River, and one large flood control channel over a period of 18 months during 1996–1998. All sites were located within the Sacramento River Basin of California. Measurements were made on 83 pesticides or pesticide transformation products by either gas chromatography/mass spectrometry or by high performance liquid chromatography with ultraviolet light spectrometry. Some pesticides were detected frequently at the agricultural stream and downstream in the Sacramento River and at the flood control channel of the Sacramento River. These were pesticides related to rice farming (molinate, carbofuran, thiobencarb, and bentazon); herbicides used both agriculturally or for roadside maintenance (diuron, simazine, and metolachlor); or insecticides used on orchards and row corps (diazinon and chlorpyrifos). No pesticide concentrations above enforceable water quality criteria were measured at either the agricultural site or the Sacramento River sites. In contrast to the agricultural site, insecticides used for household, lawn, or garden maintenance were the most frequently detected pesticides at the urban site. Diazinon, an organophosphate insecticide, exceeded recommended criteria for the protection of aquatic life, and the diazinon levels were frequently above known toxic levels for certain zooplankton species at the urban site. Because of the low discharge of the urban stream, pesticide concentrations were greatly diluted upon mixing with Sacramento River water.

INTRODUCTION

To obtain a better understanding of the current status of pesticide concentrations in the rivers of the United States, the U.S. Geological Survey has been collecting data throughout the United States as part of the National Water-Quality Assessment (NAWQA) Program. The objectives of the NAWQA Program are to describe the status of, and trends in, the quality of a large, representative part of the nation's surface- and ground-water resources and to provide a sound scientific understanding of the primary natural and human factors affecting the quality of these resources (Leahy and others, 1990). Gilliom and others (1995) detailed the general design of the NAWQA data collection program for pesticides. The program includes the collection of water samples for pesticides within relatively small watersheds, the land uses representing the major agricultural practices within a study unit or urban area, and the collection of water samples for pesticides at larger streams downstream of major agricultural and urban areas. In that way, information can be obtained on the effect of urban and agricultural runoff on receiving bodies of water of small to larger size.

Pesticide residues in streams can have adverse effects on aquatic life or limit the beneficial uses of a stream, such as the use of stream water as a source of drinking water. Insecticide residues might affect aquatic insect populations, and herbicide residues might limit the growth of certain algal species. Fish populations can suffer indirect effects such as loss of a source of food when parts of an ecological system or food web are disrupted, as well as acute or chronic toxic effects from both insecticides and herbicides (Kuivila and Foe, 1995; Bennett and others, 1998). The use of a stream as a source of drinking water also can be limited when pesticide concentrations exceed regulatory criteria or when standard water treatment is unable to lower concentrations to meet regulatory criteria.

The Sacramento River Basin of California (fig. 1) was chosen as a NAWQA study unit, and data collection activities began in 1995. Previous studies of pesticides in this river basin have demonstrated that organophosphate insecticides such as diazinon can be present in concentrations sufficiently high to result in toxicity to aquatic insects, such as zooplankton *(Ceriodaphnia dubia)*, and that residues of these organophosphate insecticides are present either seasonally after application on select crops or throughout the year, such as in urban streams (Kuivila and Foe, 1995; MacCoy and others, 1995; Domagalski, 1996; Cooke and Connor, 1998). Other pesticides detected in previous studies include organo-nitrogen herbicides, such as simazine and molinate, and insecticides, such as carbofuran and chlorpyrifos (Cornacchia and others, 1984; MacCoy and others, 1995; Domagalski, 1996; Cooke and Connor, 1998).

Diazinon and chlorpyrifos are used in orchards to control insects and in urban areas for household and garden or lawn pest control. The heaviest agricultural applications on orchards typically occur during winter, the season of highest rainfall. The organophosphate insecticides are applied to orchards during the winter to control the insect populations present in the subsequent spring. Runoff, following rainfall, may transport residues of diazinon and chlorpyrifos to receiving water bodies such as the Sacramento River (Domagalski, 1996).

Rice cultivation is the major agricultural land use of the Sacramento Valley. Rice fields are flooded during the May through September growing season, and controlled drainage of rice field water is a major source of herbicides and insecticides in agricultural streams (Domagalski and Kuivila, 1991). Herbicides are applied to rice fields during May to control aquatic grasses and other weeds, and insecticides are applied during May and June to prevent damage to the rice crop from aquatic organisms.

Purpose and Scope

The purpose of this report is to present the results of pesticide monitoring for four select streams of the Sacramento River Basin: one urban stream, one agricultural stream, one site on the Sacramento River, and a flood control channel of the Sacramento River Basin. The study spans the period from November 1996 to April 1998. The principal land use within the watershed of one stream, Arcade Creek near Del Paso Heights, was urban, whereas that of another stream, the Colusa Basin Drain at Road 99E near Knights Landing, was agricultural. The Sacramento River at Freeport, located near the mouth of the Sacramento River Basin, and another site on a flood control channel, the Yolo Bypass at Interstate 80 near West Sacramento, also were sampled for pesticides. The sites on the Sacramento River and the flood control channel represent an integration of all upstream land uses. Forest and rangeland cover about 80 percent of the basin upstream from the lower Sacramento River sampling site, agriculture is about 17 percent, and urban is about 1 percent.

Description of Study Area

The Sacramento River Basin (fig. 1) occupies nearly 70,000 km^2 in the north central part of California (Domagalski and Brown, 1994). The Sacramento River is the largest river in California, with an average annual runoff of 27,100,000,000 m^3 (California Department of Water Resources, 1993). The basin includes six physiographic provinces: the Great Basin, the Middle Cascade Mountains, the Sierra Nevada, the Klamath Mountains, the Central Valley, and the Coast Ranges (fig. 2). The northern part of the Central Valley, the Sacramento Valley, is the low-lying part of the basin; all other physiographic provinces are mountainous. Land cover or land use of the mountainous parts of the study unit is principally forest, although forest and rangeland are mixed in parts of the Coast Ranges and the Great Basin (fig. 3). Domagalski and others (1998) provide more information on the physiographic provinces of the Sacramento River Basin. The Sacramento Valley, which has the greatest population of the study unit, also is the region where the greatest effects, or potential effects, to surface water and ground water from agricultural and urban land use likely will occur. The Sacramento Valley also is the location of the greatest water use of the basin. Land uses and land cover are shown in figure 3.

The Sacramento Valley supports a diverse agricultural economy, much of which depends on the availability of irrigation water. More than 8,100 km^2 are irrigated. The major crops are rice, fruits and nuts, tomatoes, sugar beets, corn, alfalfa, and wheat. Dairy products also are important agricultural commodities. The soils of the Sacramento Valley are mostly clay with very slow to slow infiltration rates (Soil Conservation Service, 1993). Because of the widespread presence of clay soils and associated slow infiltration rates, and the availability of sufficient irrigation water from the Sacramento River, rice farming is possible. Rice production includes the seasonal creation of temporary wetlands.

The largest cities of the basin are in the Sacramento Valley, including Chico, Red Bluff,

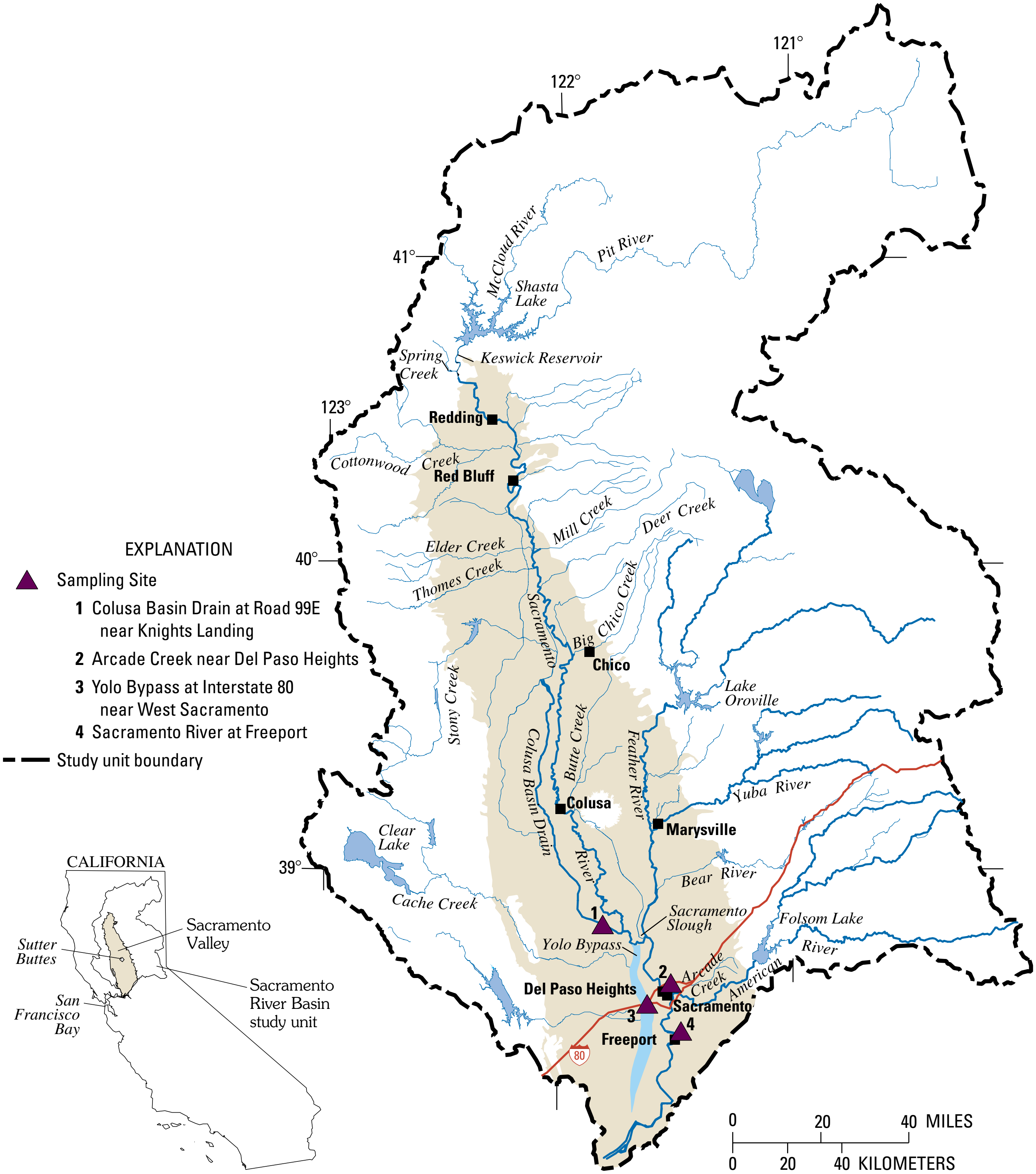

Figure 1. Map showing location of the Sacramento River Basin study unit, California.

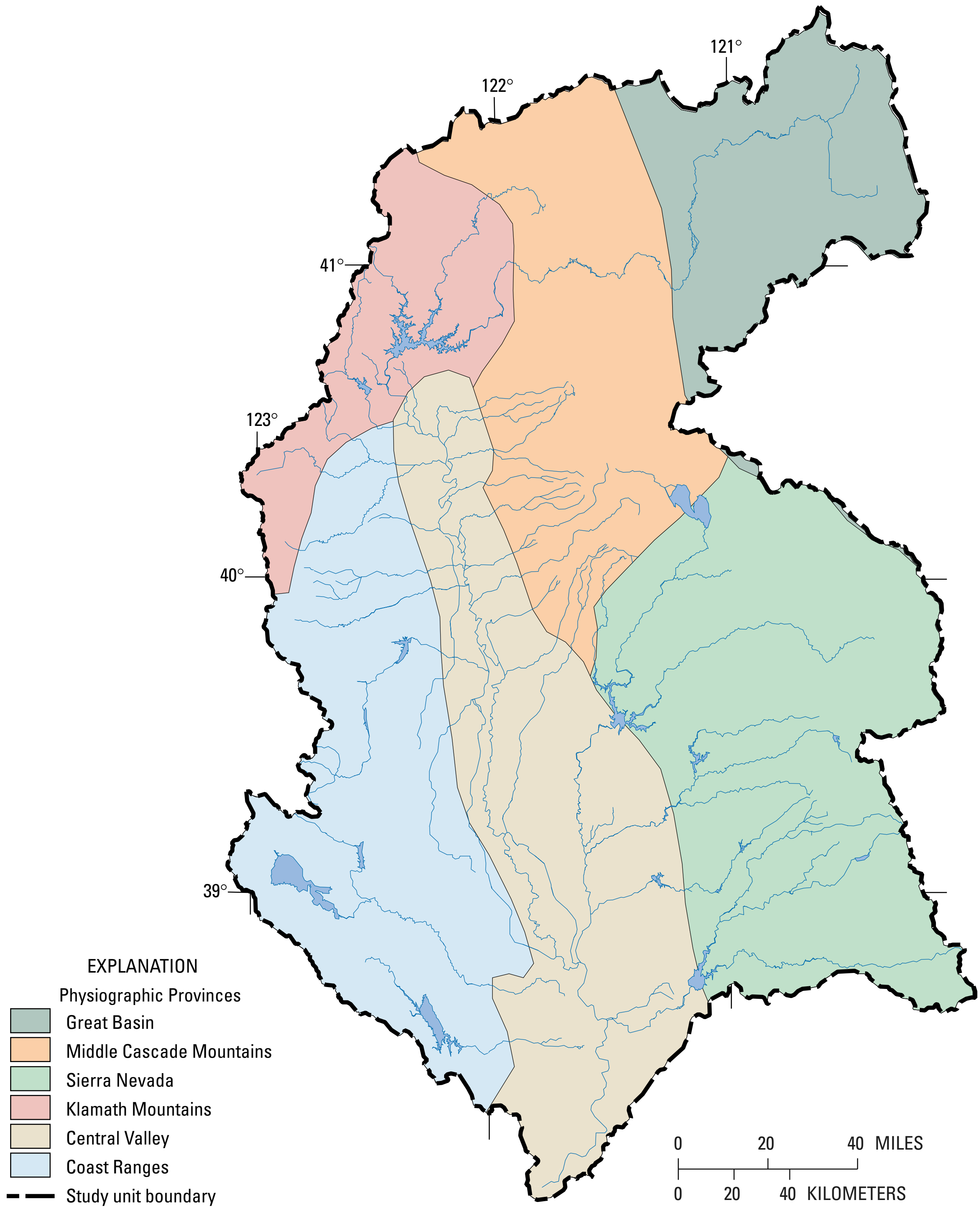

Figure 2. Map showing physiographic provinces of the Sacramento River Basin, California.

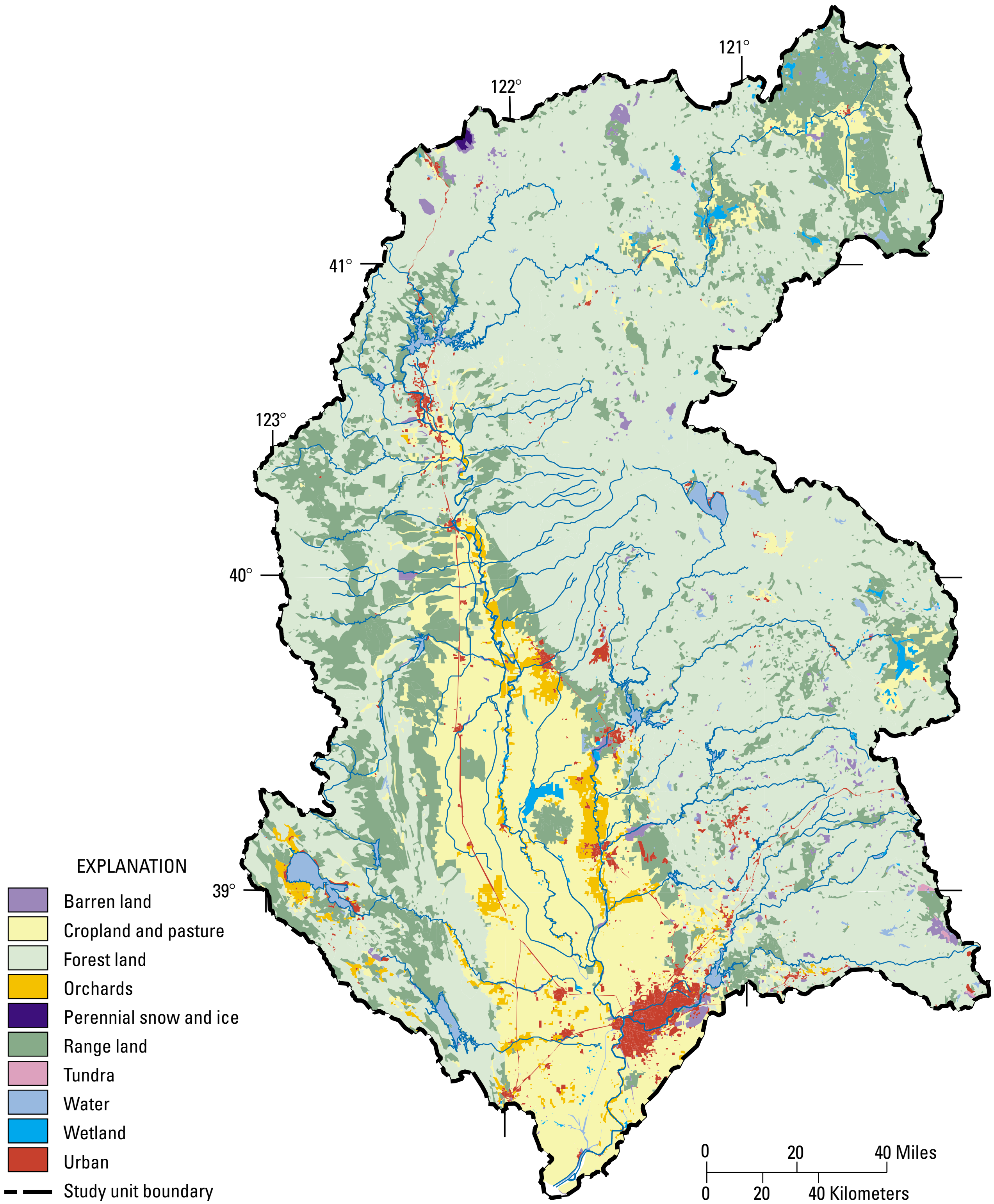

Figure 3. Map showing land uses and land cover of the Sacramento River Basin, California.

Redding, and Sacramento. The Sacramento metropolitan area is home to more than a million people, which is nearly one half of the total population of 2,208,900 people in the Sacramento Valley (U.S. Department of Commerce, 1992). Urban runoff is another potential source of pesticides to receiving bodies of waters. Because the Sacramento metropolitan area is the largest urban area in the study unit, a stream was chosen in that location to determine the effects of the urban land use on water quality.

The average annual precipitation for the Sacramento River Basin is 91.4 cm, most of which occurs as rain or snow during November through March. Irrigation water is required for agriculture during the summer growing season because there is little or no rain. Two important hydrological events or climatic conditions occurred during this period of study. The first was a major flood that started on January 1, 1997, and affected a major part of the Sacramento River below Shasta Lake and tributaries. Rainfall was especially heavy within the Feather and Yuba river basins. The second was the El Niño winter of 1997–1998. The term El Niño refers to a weather phenomenon that occurs when masses of warmer than normal water build over much of the North and South American coasts during winter. The frequent result of an El Niño winter is higher than normal precipitation in northern California because of changes in the location of the jet stream (Philander, 1990).

All of the major rivers of the basin—the Sacramento, the Feather, the American, and the Yuba—are impounded just above the margin of the Sacramento Valley (fig. 1). The reservoirs are managed to collect snowmelt and to provide flood protection during the winter and irrigation water during the summer. The upper Sacramento, the McCloud, and the Pit rivers supply water to Shasta Lake, which has a capacity of 5,614,809,153 m^3. Lake Oroville, on the Feather River, has a capacity of 4,363,565,216 m^3. The reservoirs are managed for flood protection during the winter and provide water for irrigation to farms during the spring and summer and for cities throughout the year. The water entering most of the reservoirs tends to be of high quality because it originates as melting snow.

The rocks of the Sacramento River Basin are of a diverse assemblage. The Coast Ranges consist of ocean sediments and volcanics. The Klamath Mountains include accreted terrains, oceanic crust, and subduction zone complexes. The Cascade Mountains and the Great Basin consist predominantly of volcanics. The Sierra Nevada assemblage includes granitic plutons, volcanic, sedimentary, and metamorphic rocks. The Sacramento Valley is mainly composed of a thick assemblage of sediments derived from these adjacent highlands. The uppermost layer of Sacramento Valley sediments tends to produce clay soils over much of the valley. The coarser-grained soils found near the river channels are where most of the orchards are located (Domagalski and others, 1998).

SAMPLING COLLECTION AND ANALYSIS

Selection of Sampling Sites

Four sampling sites were chosen for this study: Arcade Creek near Del Paso Heights, located in an urban basin; Colusa Basin Drain at Road 99E near Knights Landing, located downstream of primarily agricultural land uses; Sacramento River at Freeport, located on the Sacramento River, integrated urban, agricultural, and other land uses; and Yolo Bypass at Interstate 80 near West Sacramento, a flood control channel used to control flooding on the lower Sacramento River system. Water is diverted to the Yolo Bypass when flow on the Sacramento River is projected to exceed channel capacity. Site locations and drainage basin boundaries associated with these sites are shown in figures 4 through 7. The drainage basin sizes of Arcade Creek, Colusa Basin Drain, Sacramento River at Freeport, and Yolo Bypass are 88; 4,274; 59,570; and 59,388 km^2, respectively.

Different land-use settings were investigated as part of this study. Agricultural land use within the Colusa Basin Drain is mainly rice production with lesser amounts of land planted in row crops or orchards. Variable amounts of land are placed in rice, depending on water availability for irrigation and crop rotation management. Orchard crops include walnuts, almonds, prunes, and other fruits. Water samples were collected at the Colusa Basin Drain at Road 99E near Knights Landing monthly from November 1996–March 1997 and August 1997–April 1998, and twice per month from April 1997–July 1997. Water samples were collected at the Sacramento River at Freeport, a large river site where water quality is affected by different land uses, monthly from November 1996–March 1997 and from August 1997–February 1998, and twice per month from April 1997–July 1997. For both the Colusa Basin Drain at Road 99E near Knights Landing and the Sacramento River at Freeport sites, the twice per month sampling was designed to coincide with the most intense use of pesticides in rice production. The Arcade Creek drainage basin is mainly urban land use. Water samples were collected monthly at the Arcade Creek near Del Paso Heights from November–December 1996 and December 1997–April 1998, and twice per month from January–November 1997. Water was collected at the Yolo Bypass at Interstate 80 near West

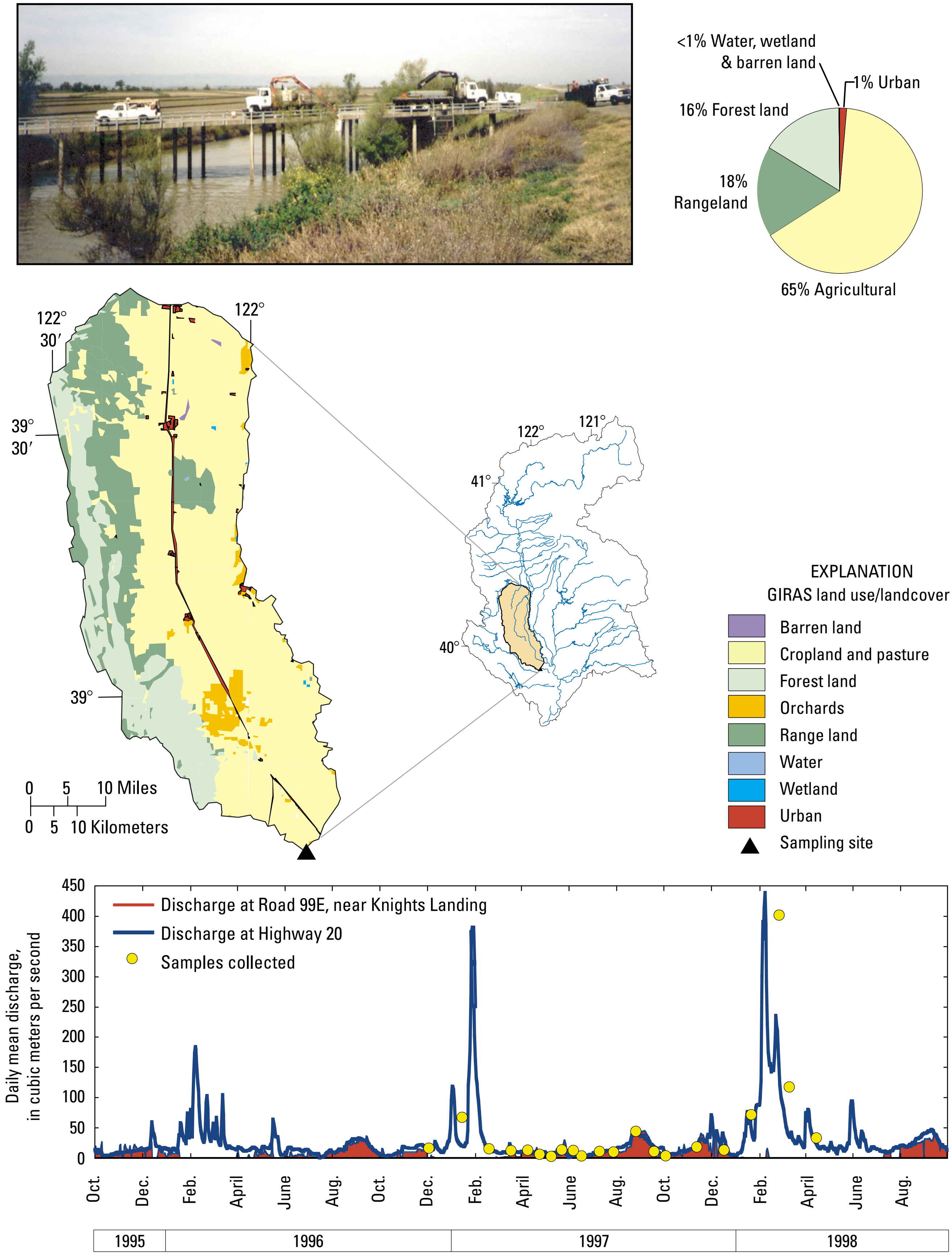

Figure 4. Drainage basin boundary, land uses, and land cover of the Colusa Basin Drain drainage basin and location of the Colusa Basin Drain at Road 99E near Knights Landing site, Sacramento River Basin, California. GIRAS, Geographic Retrieval and Analysis System.

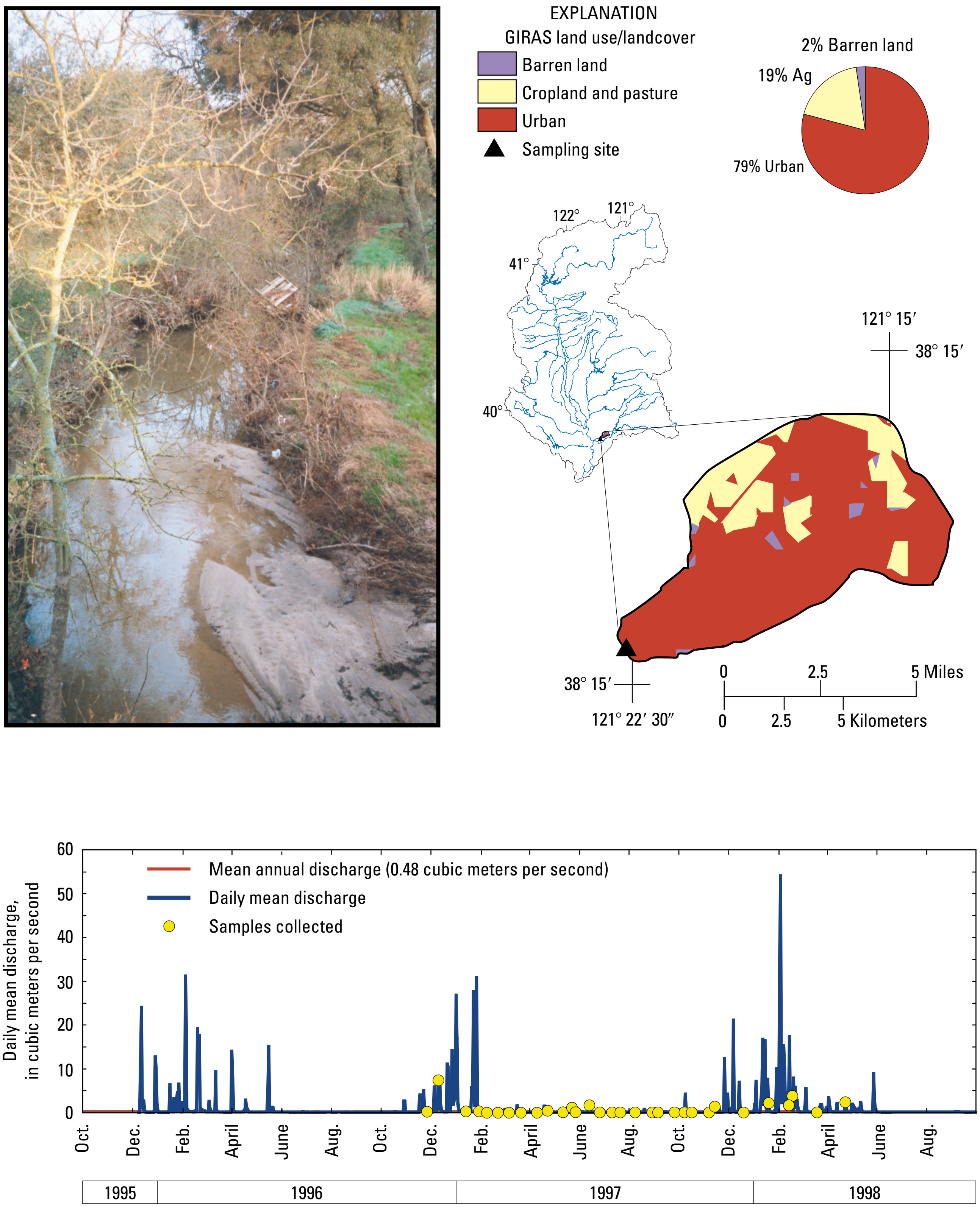

Figure 5. Drainage basin boundary, land uses, and land cover of the Arcade Creek drainage basin and location of the Arcade Creek near Del Paso Heights site, Sacramento River Basin, California. GIRAS, Geographic Retrieval and Analysis System.

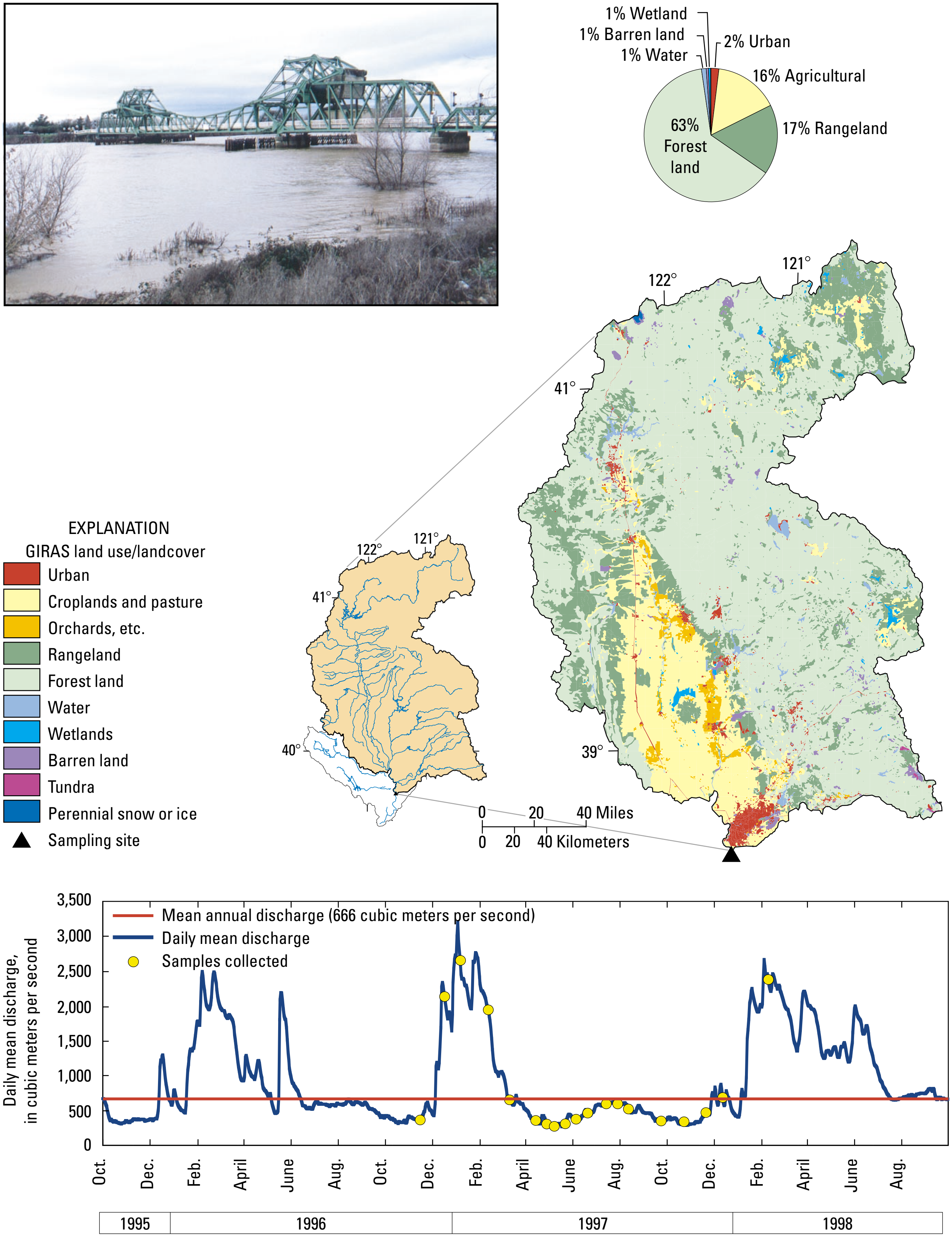

Figure 6. Drainage basin boundary, land uses, and land cover of the Sacramento River at Freeport drainage basin and location of the Sacramento River at Freeport site, Sacramento River Basin, California. GIRAS, Geographic Retrieval and Analysis System.

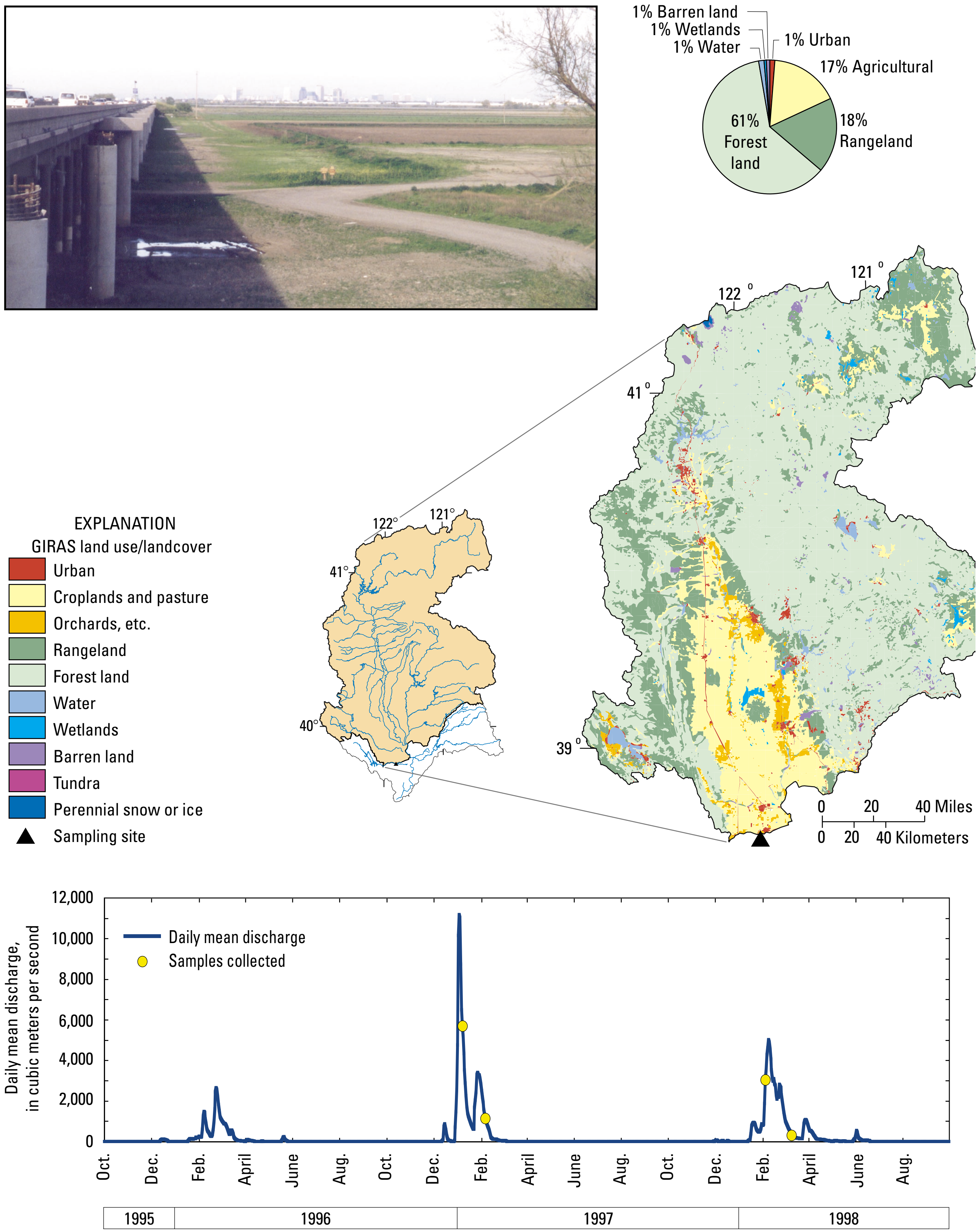

Figure 7. Drainage basin boundary, land uses, and land cover of the Yolo Bypass at Interstate 80 near West Sacramento drainage basin, and location of the Yolo Bypass at Interstate 80 near West Sacramento site, Sacramento River Basin, California. GIRAS, Geographic Retrieval and Analysis System.

Sacramento on a monthly basis whenever water was flowing.

Sampling site selection was based on known water quality impairments of these streams with respect to pesticides. Several streams within the Sacramento River Basin are on the recent 303(d) (U.S. Environmental Protection Agency, accessed October 1, 1999) listing of impaired water bodies with the impairment attributed to pesticides. The Clean Water Act of the United States requires states to list rivers with known water quality impairments and to rank the impairment according to severity. The most recent listing available for the Sacramento River Basin is 1998. Both Colusa Basin Drain and Arcade Creek are listed as impaired by pesticides. The Colusa Basin Drain impairment is attributed to carbofuran, organochlorine pesticides, malathion, and methyl parathion. The impairment of Arcade Creek is attributed to chlorpyrifos and diazinon. Other streams listed as impaired by pesticides are the lower American River (organochlorine pesticides), the lower Feather River (diazinon), and the lower Sacramento River (diazinon). The impairment priority for both the lower Feather and Sacramento rivers is listed as high (U.S. Environmental Protection Agency, accessed October 1, 1999), which indicates that action should be taken to establish a control plan for pesticides, including the establishment of a total maximum daily load (TMDL). Sites listed as a medium to low priority will be given a TMDL plan only after all those for high priority sites are completed. The severity of impairments for the Colusa Basin Drain and Arcade Creek are listed as medium. The stream segments listed have been known to have concentrations of pesticides, periodically, in excess of amounts known to be toxic, or have been positively linked to toxicity (Cooke and Connor, 1998).

Collection Procedures

Water samples were collected by either the equal width increment method or the equal discharge increment method (Edwards and Glysson, 1999). A modification of the method was necessary for the Sacramento River at the Freeport site. The method of Edwards and Glysson (1999) is only applicable to depths of approximately 5 m. Although the depth of water at the Sacramento River at the Freeport site was more than 5 m, only the upper 5 m were sampled. All sampling material was constructed of Teflon to minimize contamination or sampling artifacts. The sampling methods conformed to guidelines specified for the NAWQA Program (Shelton, 1994). After collection, the water sample was split for analyses of pesticides and other water quality constituents using a Teflon cone splitter (Capel and others, 1995).

Water samples for pesticide analyses were filtered shortly after collection using 0.7-micrometer glass fiber filters in an aluminum filter support and pumped through Teflon tubing. Following filtration, water samples were spiked with surrogate pesticide compounds. The surrogate compounds were either isotopically labeled pesticides that could be distinguished from pesticides used agriculturally or were of a similar chemical structure to agriculturally used pesticides. The purpose of the surrogate was to assess the overall efficiency of the analytical procedure. Pesticides were then extracted from water onto C-18 and Carbopak-B cartridges. The cartridges were then shipped to the U.S. Geological Survey Laboratory in Denver, Colo., where the pesticides were eluted from the cartridges using appropriate solvents and analyzed according to the methods of Zaugg and others (1995) and Werner and others (1996). The method of Zaugg and others (1995) utilizes gas chromatography/mass spectrometry (GC/MS) and that of Werner and others (1996) utilizes high performance liquid chromatography (HPLC) with ultraviolet light spectrometry. Pesticides analyzed and their reporting limit by GC/MS or HPLC with ultraviolet light spectrometry are listed in table 1.

Quality control procedures included the collection of blank, replicate, and spiked samples. The procedure for blank samples was to place pesticide-free water through all of the sampling, filtration, and extraction steps to determine whether any artifacts interfered with the analysis. The results of the blanks indicated that no problems were present. Only one detection, EPTC, was noted at an estimated concentration of 0.0011 µg/L (microgram per liter). EPTC was measured in environmental samples, but usually at higher levels than 0.0011 µg/L. Because only one detection of EPTC occurred out of six blank analyses, the environmental data for that compound were not censured. Replicates are designed to show the reproducibility of the method. The interpretation of replicate samples depends on the presence of pesticides in the environmental samples. For those compounds present, the replicate analyses were within the precision specified by Zaugg and others (1995) and Werner and others (1996). Spiked samples provide a better representation of analytical performance as known amounts of selected analytes are added to a water sample. Samples are equally split and pesticides are measured in both unspiked and spiked samples. The overall recovery of pesticides can then be calculated and compared to the published precision of the analytical method for each pesticide. The recoveries of pesticides spiked into water and analyzed by GC/MS and high performance liquid chromatography/ultraviolet light spectrometry are shown in tables 2 and 3, respectively. Not all pesticides

Table 1. Pesticides analyzed and reporting limits in water samples, in the Sacramento River Basin, California

[*, transformation product; number in parentheses indicates method reporting limit, in micrograms per liter]

Compound	Compound	Compound
Amides		
Alachlor (0.002)[1]	Napropamide (0.003)[1]	Propanil (0.004)[1]
Metolachlor (0.002)[1]	Propachlor (0.007)[1]	Propyzamide (0.003)[1]
Carbamates		
Aldicarb (0.016)[2]	Carbofuran, 3-Hydroxy* (0.014)[2]	Pebulate (0.004)[1]
Aldicarb sulfone* (0.016)[2]	EPTC (0.002)[1]	Propham (0.035)[2]
Aldicarb sulfoxide* (0.021)[2]	Methiocarb (0.026)[2]	Propoxur (0.035)[2]
Butylate (0.002)[1]	Methomyl (0.017)[2]	Thiobencarb (0.002)[1]
Carbaryl (0.003)[1], (0.008)[2]	Molinate (0.004)[1]	Triallate (0.001)[1]
Carbofuran (0.003)[1], (0.028)[2]	Oxamyl (0.018)[2]	
Chlorophenoxy herbicides		
2,4,5-T (0.035)[2]	Dacthal, mono-acid* (0.017)[2]	MCPB (0.035)[2]
2,4-D (acid) (0.035)[2]	Dichlorprop (2,4-DP) (0.032)[2]	Silvex (2,4,5-TP) (0.021)[2]
2,4-DB (0.035)[2]	MCPA (0.05)[2]	Triclopyr (0.05)[2]
Dinitroanilines		
Benfluralin (0.002)[1]	Trifluralin (0.002)[1]	Pendimethalin (0.004)[1]
Ethafluralin (0.004)[1]	Oryzalin (0.019)[2]	
Organochlorines		
Chlorothalonil (0.035)[2]	Dichlobenil (0.02)[2]	alpha-HCH* (0.002)[1]
Dacthal (DCPA) (0.002)[1]	Dieldrin (0.001)[1]	GAMMA -HCH (0.004)[1]
p,p′–DDE* (0.006)[1]		
Organophosphates		
Azinphos-methyl (0.001)[1]	Ethoprop (0.003)[1]	Parathion (0.004)[1]
Chlorpyrifos (0.004)[1]	Fonofos (0.003)[1]	Phorate (0.002)[1]
Diazinon (0.002)[1]	Malathion (0.005)[1]	Terbufos (0.013)[1]
Disulfoton (0.017)[1]	Methyl parathion (0.006)[1]	
Triazine herbicides:		
Atrazine (0.001)[1]	Cyanazine (0.004)[1]	Prometon (0.018)[1]
Atrazine, desethyl* (0.002)[1]	Metribuzin (0.004)[1]	Simazine (0.005)1
Uracils		
Bromacil (0.035)[2]	Terbacil (0.007)[1]	
Ureas		
Fenuron (0.013)[2]	Fluometuron (0.035)[2]	Neburon (0.015)[2]
Diuron (0.020)[2]	Linuron (0.002)[1], (0.018)[2]	Tebuthiuron (0.010)[1]
Miscellaneous:		
2,6-Diethylanaline* (0.003)[1]	Chloramben (0.011)[2]	DNOC (0.035)[2]
Acetochlor (0.002)[1]	*cis*-Permethrin (0.05)[1]	Norflurazon (0.024)[2]
Acifluorfen (0.035)[2]	Clopyralid (0.05)[2]	Picloram (0.05)[2]
Bentazon (0.014)[2]	Dicamba (0.035)[2]	Propargite (0.013)[1]
Bromoxynil (0.035)[2]	Dinoseb (0.035)[2]	

[1] Solid-phase extraction and gas chromatography/mass spectrometry (GC/MS) correspond to the method reporting limit.

[2] Solid-phase extraction and high performance liquid chromatography (HPLC) with ultraviolet light spectrometry correspond to the method reporting limit.

Table 2. Recoveries and standard deviations of pesticides measured by gas chromatography/mass spectrometry

[All recoveries and standard deviation are expressed as percentages. The medians and standard deviations are calculated from six trials. na, not available because of poor analytical results; GC/MS, gas chromatography/mass spectrometry]

Pesticides measured by GC/MS	Median recovery	Lowest recovery	Highest recovery	Standard deviation
Acetochlor	97	92	106	5
Alachlor	100	88	118	10
Alpha-BHC	96	84	102	7.8
Atrazine	94	79	111	11.5
Atrazine, desethyl	na	na	na	na
Azinphos-methyl	na	na	na	na
Benfluralin	89	79	95	7.9
Butylate	98	90	118	9.7
Carbaryl	na	na	na	na
Carbofuran	na	na	na	na
Chlorpyrifos	85	63	104	15.3
Cyanazine	110	88	131	18.6
Dacthal	99	76	122	15.1
p,p'-DDE	48.5	37	82	16.3
Diazinon	90.5	67	101	24.3
Dieldrin	94	86	107	7.9
2,6-Diethylaniline	85.5	77	91	5.4
Disulfoton	59	42	84	16.5
EPTC	96.5	85	106	7.9
Ethalfluralin	103	96	129	13.2
Ethoprop	98	81	106	8.3
Fonofos	86.5	80	99	7.4
Lindane	92	81	105	9.7
Linuron	78.5	67	104	21.9
Malathion	98.5	71	108	18.4
Metolachlor	106	90	124	11.7
Metribuzin	100	82	127	16
Molinate	101.5	90	109	7.6
Napropamide	96	79	112	13.1
Parathion	116.5	96	139	14.7
Parathion, methyl	104	91	179	37.9
Pebulate	99	89	107	6.6
Pendimethalin	94.5	66	103	13.9
Permethrin	28.5	16	59	15.5
Phorate	64.5	40	81	16.9
Prometon	94	22	119	35.7
Propachlor	109	93	129	13.6
Propanil	106.5	90	113	9.3
Propargite	82	60	91	11.7
Pronamide	101.5	93	113	7.1
Simazine	91	62	114	19.2
Tebuthiuron	118.5	36	158	40.3
Terbacil	na	na	na	na
Terbufos	83	45	110	21.6
Thiobencarb	95.5	84	101	7.3
Triallate	91.5	80	102	7.3
Trifluralin	97	82	123	13.5

Table 3. Recoveries and standard deviations of pesticides measured by high performance liquid chromatography/ultraviolet light spectrometry

[All recoveries and standard deviation are expressed as percentages. The medians and standard deviations are calculated from five trials. na, not available because of poor analytical results; HPLC/UVS, high performance liquid chromatography/ultraviolet light spectrometry]

Pesticides measured by HPLC/UVS	Median recovery	Lowest recovery	Highest recovery	Standard deviation
2,4,5-T	73	43	92	21.3
2,4-D	na	na	na	na
2,4-DB	61.5	41	83	20.8
Silvex	89	51	100	21.1
3-Hydroxycarbofuran	71	28	100	28.5
DNOC	na	na	na	na
Acifluorfen	49	0	94	43.9
Aldicarb	na	na	na	na
Aldicarb sulfone	na	na	na	na
Aldicarb sulfoxide	na	na	na	na
Bentazon	na	na	na	na
Bromacil	74	58	79	11.2
Bromoxynil	84	39	86	22
Carbaryl	73	66	88	10.5
Carbofuran	69	47	92	17.2
Chloramben	na	na	na	na
Chlorothalonil	na	na	na	na
Clopyralid	0	0	25	11.2
Dacthal monoacid	48.5	0	79	33
Dicamba	na	na	na	na
Dichlobenil	na	na	na	na
Dichlorprop	73	25	87	28
Dinoseb	84	51	103	20.9
Diuron	84.5	51	103	20.9
Fenuron	83	47	97	20.2
Fluometuron	80	66	93	12.4
Linuron	81	65	86	10.1
MCPA	75	0	78	35.9
MCPB	na	na	na	na
Methiocarb	82	70	89	10.6
Methomyl	88	51	133	33.3
Neburon	78	67	79	6.8
Norfluorazon	87	63	91	14.1
Oryzalin	64	0	68	28.9
Oxamyl	48	0	80	34
Picloram	0	0	60	30
Propham	na	na	na	na
Propoxur	41	38	86	26.9
Triclopyr	80	35	87	21.5

were recovered in acceptable amounts. Poor performance was noted for azinphos-methyl, carbaryl, carbofuran, atrazine desethyl, and terbacil. Those five pesticides were analyzed by GC/MS. Poor analytical performance was noted for several compounds analyzed by high performance liquid chromatography/ultraviolet light spectrometry, especially 2,4-D, DNOC, aciflurofen, aldicarb and its metabolites, bentazon, chloramben, chlorothalonil, dicamba, dichlobenil, MCPB, picloram, and propham. Other compounds analyzed by high performance liquid chromatography/ultraviolet light spectrometry also had less than ideal performance as indicated by the calculated recovery. Few pesticides analyzed by high performance liquid chromatography/ultraviolet light spectrometry were detected in the water samples, although the lack of detections of some compounds may be related to the poor analytical performance.

DETECTION FREQUENCY

Detection frequency of pesticides analyzed by GC/MS is listed in tables 4 through 7. Detection frequency of pesticides analyzed by high performance liquid chromatography/ultraviolet light spectrometry is listed in tables 8 through 11. The pesticides are listed in order of detection frequency.

The Colusa Basin Drain at Road 99E near Knights Landing site had the greatest number of

Table 4. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by gas chromatography/mass spectrometry, in Colusa Basin Drain at Road 99E near Knights Landing, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency percent
Propanil	H	0.045	0.045	<0.004	4.8
Propargite	I	0.052	0.052	<0.013	4.8
Alachlor	H	0.012	0.011	<0.002	9.5
Atrazine, desethyl	D	e0.004	e0.003	<0.002	9.5
Pebulate	H	0.011	0.011	<0.004	9.5
Tebuthiuron	H	0.013	e0.009	<0.010	9.5
Prometon	H	e0.01	e0.005	<0.018	14.3
Atrazine	H	e0.003	0.005	<0.001	19
Metribuzin	H	0.031	0.013	<0.004	19
Chlorpyrifos	I	0.016	0.007	<0.004	28.6
Malathion	I	0.054	0.0055	<0.005	33.3
Napropamide	H	0.43	e0.004	<0.003	33.3
Pronamide	H	0.035	0.0094	<0.003	38.1
Carbaryl	I	e0.1	e0.009	<0.003	42.9
Cyanazine	H	0.44	0.005	<0.004	42.9
Dacthal	H	0.0086	e0.001	e0.001	52.4
Trifluralin	H	0.016	e0.002	e0.002	52.4
EPTC	H	0.72	e0.003	e0.003	57.1
Diazinon	I	0.098	e0.002	0.014	71.4
Metolachlor	H	0.39	e0.004	0.024	90.5
Thiobencarb	H	4.4	0.014	0.026	90.5
Simazine	H	0.15	e0.003	0.014	95.2
Carbofuran	I	e0.4	e0.01	e0.03	100
Molinate	H	19	0.009	0.1	100

pesticides detected by GC/MS (table 4). A total of 24 out of 47 pesticides analyzed were detected at that site. In contrast, only 20 of these 47 pesticides were detected at the Arcade Creek near Del Paso Heights site (table 5), 16 of 47 at the Sacramento River at Freeport site (table 6), and 13 of 47 at the Yolo Bypass at Interstate 80 near West Sacramento site (table 7).

Nine pesticides were detected at a frequency of 50 percent or higher at the agricultural site (Colusa Basin Drain at Road 99E near Knights Landing), and eight pesticides were detected at a frequency of 50 percent or higher at the urban site (Arcade Creek near Del Paso Heights). There were some differences in which pesticides were detected at this frequency, and those differences are related to either pesticide use or land use. For example, thiobencarb, carbofuran, and molinate were detected in 90.5 to 100 percent of the samples at the Colusa Basin Drain at Road 99E near Knights Landing site (table 4), but were detected at much lower frequency at Arcade Creek near Del Paso Heights site (table 5), which is the urban site. In the Sacramento Valley, thiobencarb and molinate are only used on rice. Carborfuran also is used on rice, but has uses on other crops, such as alfalfa.

Molinate is the most heavily used pesticide on rice. It is applied during early May to control aquatic grasses prior to the planting of rice. During 1996, a total of 639,000 kg of molinate were applied to fields prior to rice planting. Most of that molinate was applied during May (California Department of Pesticide Regulation, 1996). A time series plot of molinate concentrations at the Colusa Basin Drain at Road 99E near Knights Landing site is shown in figure 8. Consistent with the pesticide use, the highest concentrations of molinate are detected in May and June, but residues of molinate can be detected throughout the year. Molinate also is one of the most frequently detected pesticides downstream at the Sacramento River at Freeport site. Although the Colusa Basin Drain is one of the largest sources of agricultural pesticide residues to the Sacramento River (Foe and Connor, 1991; Bennett and others, 1998) the much greater discharge of the Sacramento River dilutes

Table 5. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by gas chromatography/mass spectrometry, in Arcade Creek near Del Paso Heights, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
2,6-Diethylaniline	D	e0.002	e0.002	<0.003	3.3
Molinate	H	0.054	0.054	<0.004	3.3
Propanil	H	0.091	0.091	<0.004	3.3
Thiobencarb	H	e0.004	e0.004	<0.002	3.3
Carbofuran	I	e0.05	e0.05	<0.003	6.7
Metribuzin	H	0.18	0.052	<0.004	6.7
Benfluralin	H	0.013	e0.0014	<0.002	10
EPTC	H	0.014	e0.001	<0.002	13.3
Atrazine	H	0.027	0.027	<0.001	16.7
Pendimethalin	H	0.16	0.011	<0.004	16.7
Tebuthiuron	H	0.078	0.013	<0.010	23.3
Trifluralin	H	0.02	e0.002	<0.002	33.3
Malathion	I	0.63	0.012	0.013	53.3
Chlorpyrifos	I	0.045	0.0048	0.0076	73.3
Simazine	H	0.19	0.008	0.019	73.3
Metolachlor	H	0.67	e0.003	0.008	80
Dacthal	H	0.019	e0.0004	0.0041	83.3
Prometon	H	0.52	0.03	0.1	96.7
Carbaryl	I	e2	e0.02	e0.2	100
Diazinon	I	1.4	0.081	0.28	100

agricultural pesticide concentrations. The highest concentrations of molinate in the Sacramento River also are measured during the May–June period.

Thiobencarb, the other major rice herbicide, also was detected in water samples collected from the Sacramento River at Freeport site with the highest concentrations during the same period as that for molinate. The concentrations of molinate, carbofuran, and thiobencarb, measured in the Colusa Basin Drain or the Sacramento River, are below any existing water quality goals. However, the Colusa Basin Drain is listed on the 303(d) list as having a water quality impairment attributable to carbofuran (U.S. Environmental Protection Agency, accessed October 1, 1999). The impairment is listed as a medium priority.

Other herbicides, including simazine, metolachlor, dacthal, and EPTC, also were detected in the water samples from either the Sacramento River or the Colusa Basin Drain, or other sites.

The concentrations of molinate and other pesticides used in rice farming, as measured in this study, either in the Colusa Basin Drain or the Sacramento River, were greatly reduced over concentrations measured in past years and this represents a significant improvement. During the late 1970s, the levels of rice pesticides in the Colusa Basin Drain were periodically acutely toxic to fish (Bennet and others, 1998); acute toxicity to carp *(Cyprinus carpio)* was attributable to molinate. During the early 1980s, consumers of drinking water in the city of Sacramento reported an objectionable taste during May and June, which was attributable to thiobencarb. Concentrations of molinate, measured in the Colusa Basin Drain by various state agencies, were as high as 340 µg/L during the early 1980s (Cornacchia and others, 1984). Concentrations of thiobencarb were as high as 110 µg/L in the Colusa Basin Drain in the early 1980s (Cornacchia and others, 1984). The concentrations of molinate and thiobencarb were as high as 27 µg/L and 6 µg/L, respectively, in the lower Sacramento River during the same period (Cornacchia and others, 1984). A management program began in 1990 to reduce the levels of these pesticides in receiving bodies of water. The program consisted of requiring rice field water to be retained on the field for a specified period to allow pesticide concentrations in water to be reduced through some mechanism, such as volatilization, biological processes, or sunlight-induced degradation. Currently, water is required to be held on the field for about 1 month. Because of this requirement, the drainage water is no longer toxic to aquatic

Table 6. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by gas chromatography/mass spectrometry, in Sacramento River at Freeport, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
Chlorpyrifos	I	e0.003	e0.003	<0.004	5.3
Dacthal	H	e0.002	e0.002	<0.002	5.3
Atrazine, desethyl	D	e0.001	e0.001	<0.002	5.3
Malathion	I	e0.004	e0.004	<0.005	5.3
Pebulate	H	0.0056	0.0056	<0.004	5.3
Propanil	H	0.029	0.029	<0.004	5.3
Cyanazine	H	0.02	0.01	<0.004	10.5
Atrazine	H	e0.002	e0.001	<0.001	15.8
EPTC	H	0.022	e0.001	<0.002	15.8
Carbofuran	I	e0.04	e0.01	<0.003	26.3
Carbaryl	I	e0.06	e0.03	<0.003	31.6
Diazinon	I	0.046	e0.002	<0.002	42.1
Thiobencarb	H	0.17	e0.004	<0.002	42.1
Simazine	H	0.02	e0.003	0.006	68.4
Molinate	H	1.6	e0.002	0.0077	73.7
Metolachlor	H	0.026	e0.002	0.0041	78.9

organisms, and concentrations in the Sacramento River are extremely low due to dilution (Bennet and others, 1998).

In contrast to the agricultural basin, insecticides tend to be detected at a higher frequency and at higher concentrations at the urban site, Arcade Creek near Del Paso Heights. Herbicides also were detected at a frequency of greater than 50 percent at the urban site. Chlorpyrifos was detected at a frequency of 73.3 percent at the urban site (table 5), but at a frequency of only 28.6 percent at the agricultural site, Colusa Basin Drain at Road 99E (table 4). Both carbaryl and diazinon

Table 7. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by gas chromatography/mass spectrometry, in Yolo Bypass at Interstate 80 near West Sacramento, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
Dacthal	H	e0.0010	e0.0010	<0.002	25
EPTC	H	e0.0025	e0.0025	<0.002	25
Malathion	I	0.015	0.015	<0.005	25
Metribuzin	H	0.009	0.009	<0.004	25
Napropamide	H	0.017	0.017	<0.003	25
Pronamide	H	e0.0031	e0.0031	<0.003	25
Trifluralin	H	e0.0031	e0.0031	<0.002	25
Carbaryl	I	e0.0089	e0.0035	<0.003	50
Thiobencarb	H	0.0077	0.0065	<0.002	50
Diazinon	I	0.053	0.017	0.017	75
Molinate	H	0.0181	e0.0038	0.01	75
Metolachlor	H	0.01	0.004	0.007	100
Simazine	H	0.0491	0.021	0.0325	100

Table 8. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by high performance liquid chromatography/ultraviolet light spectrometry, in Colusa Basin Drain at Road 99E near Knights Landing, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
Bromoxynil	H	0.06	0.06	<0.035	4.8
Linuron	H	e0.03	e0.03	<0.018	4.8
Oryzalin	H	e0.03	e0.03	<0.019	4.8
Norfluorazon	H	0.06	e0.02	<0.024	9.5
Carbaryl	I	0.04	e0.0010	<0.008	14.3
Carbofuran	I	0.2	0.15	<0.028	14.3
2,4-D	H	0.78	0.11	<0.035	19
Triclopyr	H	1.1	0.22	<0.05	19
MCPA	H	0.94	0.08	<0.05	33.3
Bentazon	H	0.13	e0.05	<0.014	47.6
Diuron	H	0.69	0.04	0.08	66.7

were detected at 100 percent frequency at the urban site (table 5) compared to 42.9 and 71.4 percent, respectively, at the agricultural site (table 4). Of greater significance are the higher concentrations of diazinon measured throughout the year at the urban site. A time series plot of diazinon for the urban and agricultural sites is shown in figure 9. The higher concentrations of diazinon at the agricultural site tend to be measured during the winter, the time of greatest agricultural use, but higher concentrations of diazinon can be measured throughout the year at the urban site. The measured concentrations of diazinon at the urban site are frequently above the levels toxic to *Ceriodaphnia dubia*, an aquatic invertebrate frequently used for

Table 9. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by high performance liquid chromatography/ultraviolet light spectrometry, in Arcade Creek near Del Paso Heights, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. H, herbicide; I, insecticide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
Linuron	H	e0.03	e0.03	<0.018	3.6
MCPA	H	0.06	0.06	<0.05	3.6
Oryzalin	H	1.5	0.08	<0.019	21.4
2,4-D	H	1.4	e0.02	<0.035	28.6
Triclopyr	H	e3	0.09	<0.05	32.1
Carbaryl	I	e0.6	0.05	<0.008	42.9
Diuron	H	1.4	0.12	0.5	85.7

Table 10. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by high performance liquid chromatography/ultraviolet light spectrometry, in Sacramento River at Freeport, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. H, herbicide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
Bentazon	H	e0.002	e0.002	<0.014	5.6
Dichlobenil	H	e0.08	e0.08	<0.02	5.6
Triclopyr	H	e0.03	e0.03	<0.05	5.6
Diuron	H	0.12	e0.004	e0.006	61.1

Table 11. Maximum, minimum, and median concentrations, and detection frequency of pesticides in water samples analyzed by high performance liquid chromatography/ultraviolet light spectrometry, in Yolo Bypass at Interstate 80 near West Sacramento, Sacramento River Basin, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. H, herbicide; e, estimated concentration; <, less than]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency, percent
MCPA	H	0.06	<0.05	0.05	50
Oryzalin	H	e0.0200	<0.02	0.02	50
Diuron	H	0.13	e0.002	0.07	100

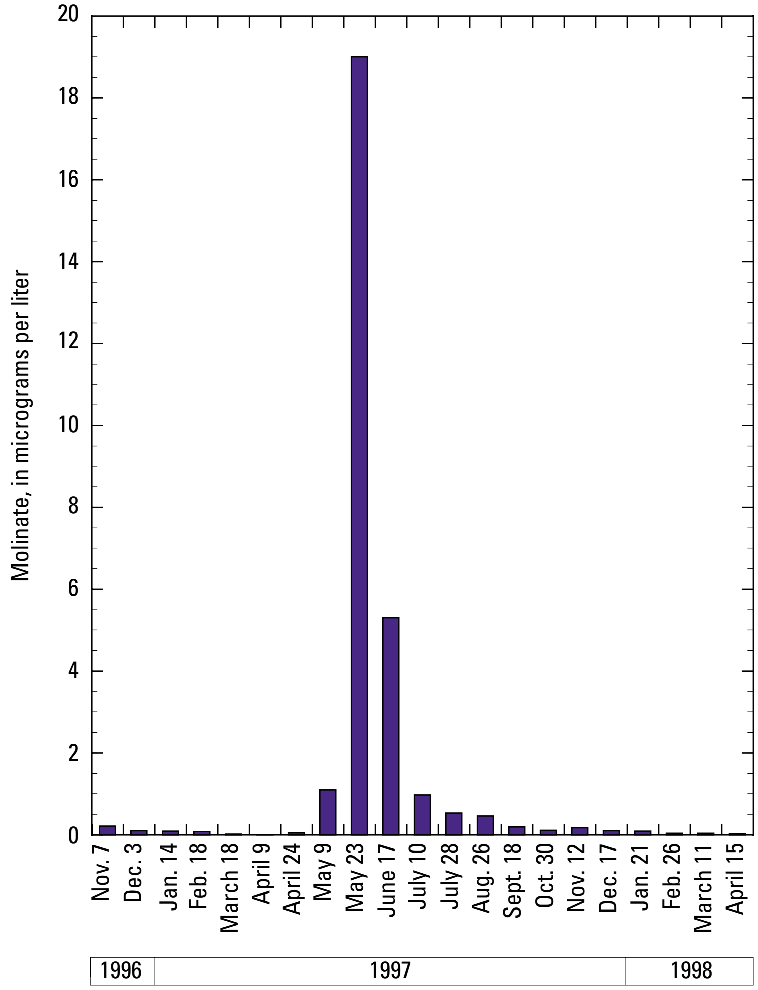

Figure 8. Time series plot of molinate concentrations at the Colusa Basin Drain at Road 99E near Knights Landing site, Sacramento River Basin, California.

toxicity testing (Cooke and Connor, 1998). The International Joint Commission for the Great Lakes suggested a more recent guideline of 0.080 µg/L (fig. 9). The greater frequency and higher concentration of insecticides in the Arcade Creek is consistent with the use of these compounds for household or garden pest control. Diazinon is a major pesticide used for that purpose.

If Arcade Creek can be characterized as a typical urban stream for the Sacramento metropolitan area, then it is likely that toxic levels of diazinon also are present in other urban drainages. The Arcade Creek watershed is entirely contained within the Sacramento metropolitan area. The flow in the stream throughout most of the year is entirely urban runoff either from rain or lawn irrigation, with minor amounts of flow attributable to ground water. Flow in Arcade Creek is extremely low in November, the month in which lawn irrigation generally does not occur and before the rainy season. Other similar urban streams or drainage canals within the Sacramento metropolitan area probably have similar toxicity levels. In fact, insecticides such as diazinon, chlorpyrifos, and carbaryl have high detection frequency at many urban streams across the United States (Larson and others, 1999).

Relatively few pesticides analyzed by high performance liquid chromatography/ultraviolet light spectrometry were detected at the sampling sites. Three exceptions were bentazon, carbaryl, and diuron. The use of bentazon, an herbicide used on rice, was suspended in California in 1989 pending a review and formally banned in 1992 by the California Department of Pesticide Regulation (Miller-Maes and others, 1993) because of frequent detections in ground water samples. Bentazon was detected at a frequency of 47.6 percent at the agricultural site (table 8) and a frequency of 5.6 percent at the Sacramento River at Freeport site (table 10). Despite not being in use for at least 6 years, bentazon can still be detected in water samples from both the agricultural stream and

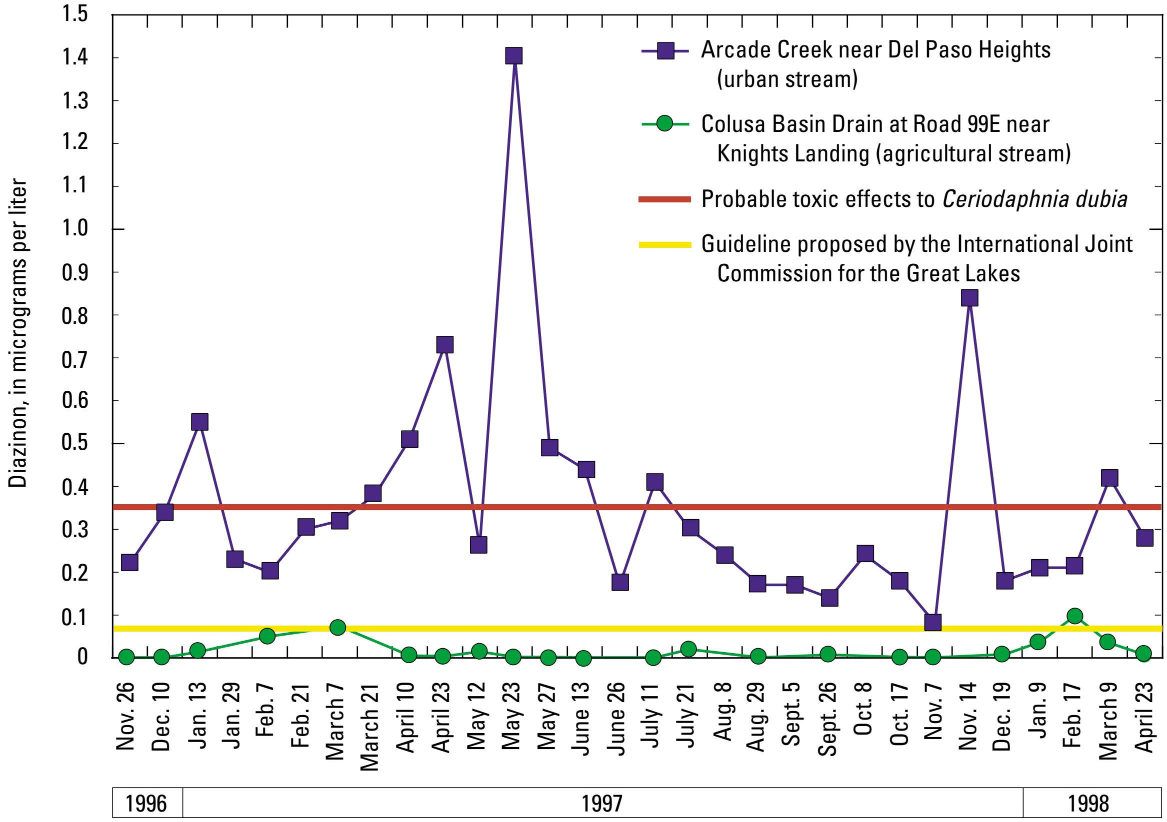

Figure 9. Time series plot of diazinon concentrations at the Arcade Creek near Del Paso Heights site and the Colusa Basin Drain at Road 99E near Knights Landing site, Sacramento River Basin, California.

downstream in the Sacramento River. Carbaryl is an insecticide with widespread use, especially in the urban environment. Diuron is an herbicide used on various agricultural commodities, with the most use occurring during the winter and the lowest use during the summer. Other pesticides analyzed by high performance liquid chromatography/ultraviolet light spectrometry were the herbicides linuron, MCPA, oryzalin, and triclopyr.

STORM-WATER RUNOFF

Pesticides in storm-water runoff have been previously reported by Domagalski (1996) for agricultural streams, sites on large tributaries to the Sacramento River, and the Sacramento River. In that study, it was shown that diazinon concentrations on the lower Sacramento River increase with discharge, reaching a peak concentration just prior to peak river flow, with decreasing concentrations measured thereafter due to dilution. In the present study, storm water was not collected across a storm hydrograph, but rather samples were collected from the Yolo Bypass, a channel that only has water in response to flood management of the Sacramento River. When the channel capacity of the Sacramento River is expected to be exceeded, water can be diverted to the Yolo Bypass to prevent flooding in downstream areas, such as the city of Sacramento. Therefore, storm-water runoff is present in the Yolo Bypass as water is diverted out of the Sacramento River.

The same suite of pesticides detected at either the agricultural site or the urban site is detected at the Yolo Bypass site (table 7). Most pesticides detected at the Yolo Bypass, with the exception of simazine, generally had lower concentrations than those measured at either the agricultural or urban site. Run-off from Arcade Creek, however, does not flow into the Yolo Bypass. Therefore, it would be expected that urban-use pesticides would have low concentrations in the Yolo Bypass. The two most frequently detected compounds at the Yolo Bypass at Interstate 80 near West Sacramento site were the herbicides metolachlor and simazine, which are used on either orchards or for roadside and highway weed control. Molinate, the rice herbicide, was detected at a frequency of 75 percent. Diazinon also was detected at a frequency of

75 percent. Although diazinon was detected at a high frequency, and the concentrations measured were above the National Academy Sciences guidelines of 0.009 µg/L (Nowell and Resek, 1994) for the protection of aquatic health, the water was not acutely toxic to *C. dubia* with respect to diazinon. Acute toxicity for *C. dubia* occurs at a concentration of approximately 0.35 µg/L (Amato and others, 1992).

The high flows occurring during the flood of January 1999 could possibly have resulted in an initial pulse of pesticides to the Sacramento River or its tributaries, followed by a considerable amount of dilution. Rainfall amounts during the El Niño year were different in that no single high-flow event, comparable in magnitude to the January 1997 flood, occurred. Rainfall amounts were higher than normal throughout the Sacramento Valley, which would likely result in early pesticide runoff events, followed by relatively lower concentrations or detection frequency later in the rainy season.

COMPARISON OF SAMPLING FREQUENCIES

The sampling frequency of the NAWQA Program was limited mainly to monthly or twice per month sampling and, as a result, the actual exposures of aquatic organisms to pesticides are difficult to assess. However, other agencies or programs within the U.S. Geological Survey have completed a considerable amount of pesticide sampling within the Sacramento River Basin. The U.S. Geological Survey Toxic Substances Hydrology Program sampled the Sacramento River at Freeport three times a week for almost 3 years and also completed several storm samplings for pesticides (Kuivila and Foe, 1995; MacCoy and others, 1995).

A high frequency of sampling allows for the completion of a probabilistic ecological risk assessment (PERA). A PERA is a statistically valid model of pesticide or other toxic contaminant exposure to aquatic organisms and allows water quality managers to determine what percentage of aquatic organisms will be adversely affected by pesticides within a stream system at given concentrations. A control program can then be designed that will allow managers to decide what level of protection is desired for a given stream. Therefore, the design of a protection program for a specific percentage of organisms on the basis of statistically relevant information is possible by development of a PERA. Completion of a PERA requires that toxicological information is available on the organisms of concern and the toxicants of concern, as well as adequate data on actual toxicant concentrations.

A PERA has been completed for the lower Sacramento River with respect to the exposure of aquatic organisms (fish and invertebrates) to levels of diazinon (Norvatis Crop Protection, 1997). The PERA considered the long-term viability of fish populations in the lower Sacramento River and the productivity of invertebrate communities. The study assessed the exposure to diazinon because it is the most frequently detected organophosphate insecticide in the Sacramento River Basin and it has been linked to toxicity to aquatic organisms, especially invertebrates (Foe, 1995; Kuivila and Foe, 1995; Domagalski, 1996).

The usage or guidelines for establishing a PERA have been given by the U.S. Environmental Protection Agency (1992, 1996) and Environment Canada (1996a,b). An example of a pesticide PERA has been published by Solomon and others, 1996.

A PERA requires knowledge of the exposure effects on an organism from a chemical and detailed knowledge about the duration of exposure and the variation in chemical concentration during exposure. The PERA, with respect to pesticides, requires toxicological information and concentration data across a range of flow conditions so that a valid statistical evaluation of exposure can be completed. In practice, the toxicological information may be available, but sufficient data on exposure are lacking, especially for aquatic systems. Invertebrates were considered because they are important in the diet of fish and any chemical exposure, which limits their productivity, could have consequences for the predatory organisms. Nine fish species, including salmon *(Oncorhynchus tshawytscha)* and striped bass *(Morone saxatilis)*, were part of the assessment. The prey organisms for these fish include copepoda *(Eurytemora, Cyclops,* and *Sinocalanus)*, mysids *(Neomysis)*, amphipods *(Corophium)*, and cladocera *(Daphnia, Bosmina,* and *Diaphonosoma)*. The PERA showed that fish are not at risk from direct toxic levels of diazinon because the concentrations are well below toxic levels (Norvatis Crop Protection, 1997). The assessment did show, however, that invertebrate populations are at greater risk, but mainly in agriculturally dominated streams or drainage channels throughout the Central Valley, and mainly during January and February (Norvatis Crop Protection, 1997). This PERA did not address urban risk due to insufficient data. However, it was pointed out that any ecological damage would be brief and limited to cladocerans (Norvatis Crop Protection, 1997). Norvatis Crop Protection (1997) cited four lines of evidence to support this conclusion for fish and for invertebrates. The first is that the diazinon concentrations lethal to cladocerans (toxic levels are approximately 0.5 to 1.5 µg/L) are nontoxic to most other invertebrates and are orders of magnitude lower than those toxic to fish. The second line of evidence is that cladocerans, such as *C. dubia*, reproduce rapidly, and any short term toxic effects are rapidly offset by rapid reproduction. The third line of evidence is that none of the fish species of concern depend on cladocerans as the critical component of their diets and, therefore, would not be affected by sharp decreases in cladoceran biomass. A final line of evidence was that microcosm and mesocosm studies with diazinon have shown that severe reductions in cladoceran populations can occur with little or no measurable effect on the rest of the ecosystem, and that cladoceran populations do in fact recover rapidly following lethal exposures to diazinon. Most of the data used by Norvatis Crop Protection for the risk assessment was collected prior to the sampling of the current NAWQA investigation. Although data from the NAWQA Program was not used in the PERA developed by Norvatis, the exposure data collected by the NAWQA Program is consistent with the findings of that risk assessment. There were no detections of diazinon within the lower Sacramento River at levels in excess of 0.35 µg/L, which are toxic to *C. dubia* (Amato and others, 1992). However, concentrations in excess of 1 µg/L were measured at the urban stream, indicating that probable adverse effects may occur.

SUMMARY AND CONCLUSIONS

Detection of pesticides in surface waters of the Sacramento River Basin can be attributed to pesticide use. Consistent with the mainly agricultural land use in rice cultivation in the Colusa Basin Drain, pesticides used on rice were the most frequently detected at the Colusa Basin Drain at Road 99E near Knights Landing sampling site and at the downstream site on the Sacramento River, the Sacramento River at Freeport. There were no measured concentrations at either the agricultural site or the large river site, which exceeded water quality criteria for specific rice pesticides, nor were any concentrations sufficiently high to affect aquatic life. Other pesticides detected at the agricultural site and downstream at the Sacramento River site were herbicides and insecticides used either on orchards or for the control of weeds along roadways.

In contrast to the agricultural stream, pesticides most frequently detected at the urban stream were insecticides used for the control of insects on lawns, gardens, or buildings. The concentrations of diazinon, an organophosphate insecticide that was detected in every water sample collected at the urban stream, were always above the recommended guidelines established by the International Joint Commission for the Great Lakes for the protection of aquatic health or were frequently at levels of acute toxicity to aquatic invertebrates such as *C. dubia*. Mixing with the Sacramento River dilutes the concentrations of diazinon and other insecticides to generally low to nondetectable levels.

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