Prepared in cooperation with the San Luis and Delta Mendota Water Authority

Dissolved Pesticide Concentrations Entering the Sacramento–San Joaquin Delta from the Sacramento and San Joaquin Rivers, California, 2012–13

Data Series 876

U.S. Department of the Interior
U.S. Geological Survey

Cover. View of bridge over the Sacramento River at Freeport, Sacramento, Calif. Photo taken by the author.

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By James L. Orlando, Megan McWayne, Corey Sanders, and Michelle Hladik

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SALLY JEWELL, Secretary

U.S. Geological Survey
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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
	Area	
millimeter (mm)	0.03937	inch (in.)
	Volume	
liter (L)	1.057	quart (qt)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
inch per day (in/d)	25.4	millimeter per day (mm/d)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)

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

°F=(1.8×°C)+32

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or nanograms per liter (ng/L).

Abbreviations

CDPR	California Department of Pesticide Regulation
DCM	dichloromethane
DCPMU	*N*-(3,4-Dichlorophenyl)-*N'*-methylurea
DCPU	3,4-Dichlorophenylurea
DOC	dissolved organic carbon
GC/MS	gas chromatography/mass spectrometry
HPLC	high performance liquid chromatography
LC/MS/MS	liquid chromatography with tandem mass spectrometry
MDL	method detection limit
mL	milliliter
mL/min	milliliter per minute
mM	millimolar (milimoles per liter of solution)
MSD	mass-selective detector
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
ng/L	nanograms per liter
ng/µL	nanograms per microliter
QC	quality control
SPE	solid-phase extraction
SD	standard deviation
USGS	U.S. Geological Survey
µL	microliter
µm	micrometer

Acknowledgments

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Dissolved Pesticide Concentrations Entering the Sacramento–San Joaquin Delta from the Sacramento and San Joaquin Rivers, California, 2012–13

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Abstract

Surface-water samples were collected from the Sacramento and San Joaquin Rivers where they enter the Sacramento–San Joaquin Delta, and analyzed by the U.S. Geological Survey for a suite of 99 current-use pesticides and pesticide degradates. Samples were collected twice per month from May 2012 through July 2013 and from May 2012 through April 2013 at the Sacramento River at Freeport, and the San Joaquin River near Vernalis, respectively. Samples were analyzed by two separate laboratory methods by using gas chromatography with mass spectrometry or liquid chromatography with tandem mass spectrometry. Method detection limits ranged from 0.9 to 10.5 nanograms per liter (ng/L).

A total of 37 pesticides and degradates were detected in water samples collected during the study (18 herbicides, 11 fungicides, 7 insecticides, and 1 synergist). The most frequently detected pesticides overall were the herbicide hexazinone (detected in 100 percent of the samples); 3,4-dichloroaniline (97 percent), which is a degradate of the herbicides diuron and propanil; the fungicide azoxystrobin (83 percent); and the herbicides diuron (72 percent), simazine (66 percent), and metolachlor (64 percent). Insecticides were rarely detected during the study. Pesticide concentrations varied from below the method detection limits to 984 ng/L (hexazinone).

Twenty seven pesticides and (or) degradates were detected in Sacramento River samples, and the average number of pesticides per sample was six. The most frequently detected compounds in these samples were hexazinone (detected in 100 percent of samples), 3,4-dichloroaniline (97 percent), azoxystrobin (88 percent), diuron (56 percent), and simazine (50 percent). Pesticides with the highest detected maximum concentrations in Sacramento River samples included the herbicide clomazone (670 ng/L), azoxystrobin (368 ng/L), 3,4-dichloroaniline (364 ng/L), hexazinone (130 ng/L), and propanil (110 ng/L), and all but hexazinone are primarily associated with rice agriculture.

In addition to the twice monthly sampling, surface-water samples were collected from the Sacramento River on 5 consecutive days following a rainfall event in the Sacramento urban area. Samples collected following this event contained an average of 11 pesticides. The insecticides carbaryl, fipronil, and imidacloprid; the herbicide DCPA; and the fungicide imazalil were only detected in the Sacramento River during this storm-runoff event, and two detections of fipronil during this period exceeded the U.S. Environmental Protection Agency Aquatic Life Benchmark (11 ng/L) for chronic toxicity to invertebrates in freshwater.

In San Joaquin River samples, 26 pesticides and (or) degradates were detected, and the average number detected per sample was 9. The most frequently detected compounds in these samples were hexazinone and metolachlor (detected in 100 percent of samples); diuron (96 percent); the fungicide boscalid (96 percent); the degradates 3,4-dicloroaniline (92 percent) and *N*-(3,4-Dichlorophenyl)-*N*'-methylurea (DCPMU; 83 percent); simazine (83 percent); and azoxystrobin (75 percent). The pesticides with the highest detected maximum concentrations were hexazinone (984 ng/L), diuron (695 ng/L), simazine (524 ng/L), the herbicide prometryn (155 ng/L), metolachlor (127 ng/L), boscalid (112 ng/L), DCPMU (111 ng/L), and the herbicide pendimethalin (108 ng/L).

Introduction

The Sacramento–San Joaquin Delta (hereinafter Delta) is an area of critical habitat for numerous species of concern, including chinook salmon and the threatened delta smelt (Sommer and Mejia, 2013). In recent years, multiple pelagic species within the Delta have been in sharp decline (Sommer and others, 2007). The Delta is hydrologically complex, with a great variety of man-made and natural interconnecting sloughs and channels that convey nearly one-half of California's total yearly runoff (California Department of Water Resources, 1993). In addition, the Delta provides water to approximately 25 million people living in southern California and irrigates nearly 750,000 acres of farmland in the southern Central Valley (California Department of Water Resources, 2013a). These factors point to the need for a complete and timely understanding of the quality of water entering the Delta.

Previous studies have shown that current-use pesticides associated with agricultural and urban runoff enter the Delta from the Sacramento and San Joaquin Rivers throughout the year and that the types and concentrations of these pesticides vary based on their use in the upstream watersheds (Dileanis and others, 2002; Kratzer and others, 2002; Orlando and Kuivila, 2004; Weston and Lydy, 2010; and Zhang and others, 2012). Other studies have suggested that contaminants (including current-use pesticides) may play a role in the decline of pelagic fish species in the Delta (Werner and others, 2010)

This study was conducted by the U.S. Geological Survey (USGS), in cooperation with the San Luis and Delta Mendota Water Authority, to characterize the input of current-use pesticides and pesticide degradates into the Delta from the Sacramento and San Joaquin Rivers, the Delta's two main riverine inputs, during the course of 1 calendar year. Water samples for pesticide analysis were collected twice per month from two sites (Sacramento River at Freeport, and the San Joaquin River near Vernalis) located at the furthest downstream point of each basin before entering the Delta (fig. 1 and table 1). These sites are considered representative integrator sites for the Sacramento and San Joaquin Rivers (Gilliom and others, 1995, Domagalski and others, 1998, Panshin and others, 1998) and have been sampled by the USGS for current-use pesticides since the early 1990s, with investigations performed as part of the National Stream Quality Accounting Network (NASQAN), National Water-Quality Assessment (NAWQA), and Toxics Substances Hydrology programs, as well as in collaboration with numerous State and federal agencies (Orlando, 2013).

Purpose and Scope

This report describes the methods and procedures used in measuring dissolved pesticide concentrations in filtered surface-water samples collected from the Sacramento and San Joaquin Rivers. Results are presented for a suite of 99 current-use pesticides and pesticide degradates in surface water.

Regional Setting

The Delta is an ecologically rich and hydrologically complex region of interconnecting sloughs and channels that receives runoff from a mix of agricultural, urban, and natural sources. The Delta is fed by two primary river systems, the Sacramento River and the San Joaquin River, which flow south and north, respectively, through the Central Valley, and converge in the western Delta (fig. 1). The region is characterized by a Mediterranean climate, with typically wet winters and dry summers. Precipitation falls primarily in the winter and spring as rain in the Central Valley and as snow in the higher elevations of the Sierra Nevada.

Sacramento River Watershed

The effective Sacramento River watershed upstream from Freeport encompasses over 22,300 square miles (mi^2) in northern California, and extends from the Delta northward to Oregon border, eastward to the crest of the Sierra Nevada Mountains, and westward into the Coast Range (fig. 1). The Sacramento River flows southward through the Central Valley where it is joined by a number of major tributaries, and their combined flows enter the Delta at Freeport downstream of Sacramento (fig. 1). Landuse in the watershed is primarily forest in the mountainous upper reaches of the watershed while agriculture dominates within the Central Valley portion of the watershed (roughly 1,980 mi^2; fig. 1; U.S. Geological Survey, 2014). Major crop types by area are rice, alfalfa, and orchard crops such as almonds, peaches, prunes, and walnuts (Natural Resources Conservation Service, 2013). There are also a number of major urban areas in the watershed. Together these cities cover an area of 445 mi^2 (fig. 1; U.S. Geological Survey, 2014) and support a population of nearly 2 million, based on the 2010 census (U.S. Census Bureau, 2011). Runoff from agricultural lands, along with discharge from urban waste water treatment plants and storm drains enter the Sacramento River and its tributaries at numerous locations within the watershed.

San Joaquin River Watershed

The San Joaquin River watershed encompasses over 7,300 mi^2 in central California and extends southward from the Delta (fig. 1). The San Joaquin River flows northward through the Central Valley where it is joined by a number of major tributaries, and their combined flows enter the Delta near Vernalis (fig. 1). Landuse within the Central Valley is primarily agricultural (over 1,550 mi^2) while land above the valley floor is primarily shrub, grassland and forest (fig. 1; U.S. Geological Survey, 2014). Major crops grown in the region include cotton, orchard crops and vegetable crops. There are also a number of urban areas in the watershed (fig. 1). Combined these cities cover an area of 170 mi^2 (U.S. Geological Survey, 2014) and support a population of over 700,000 based on the 2010 census (U.S. Census Bureau, 2011). Runoff from agricultural lands and urban areas enter the San Joaquin River and its tributaries at numerous locations within the watershed.

Pesticide Use

Agricultural and urban runoff enters the Delta throughout the year from sources upstream from the Delta as well as from agricultural activities and urban waste-water treatment plants within the Delta (California Department of Water Resources, 2013b). These waters can contain current-use pesticides and degradates in concentrations that vary depending in large part on spatial and temporal patterns of pesticide application and hydrologic conditions.

Since 1990, the California Department of Pesticide Regulation (CDPR) has had a full-use reporting system that requires pesticide applicators to provide detailed information on pesticide use. The CDPR system is the most comprehensive pesticide reporting system in the nation, and these data are extremely valuable in assessing trends in pesticide use, changes in application patterns, and potential for environmental contamination. The CDPR reporting system, however, does not contain information on pesticide

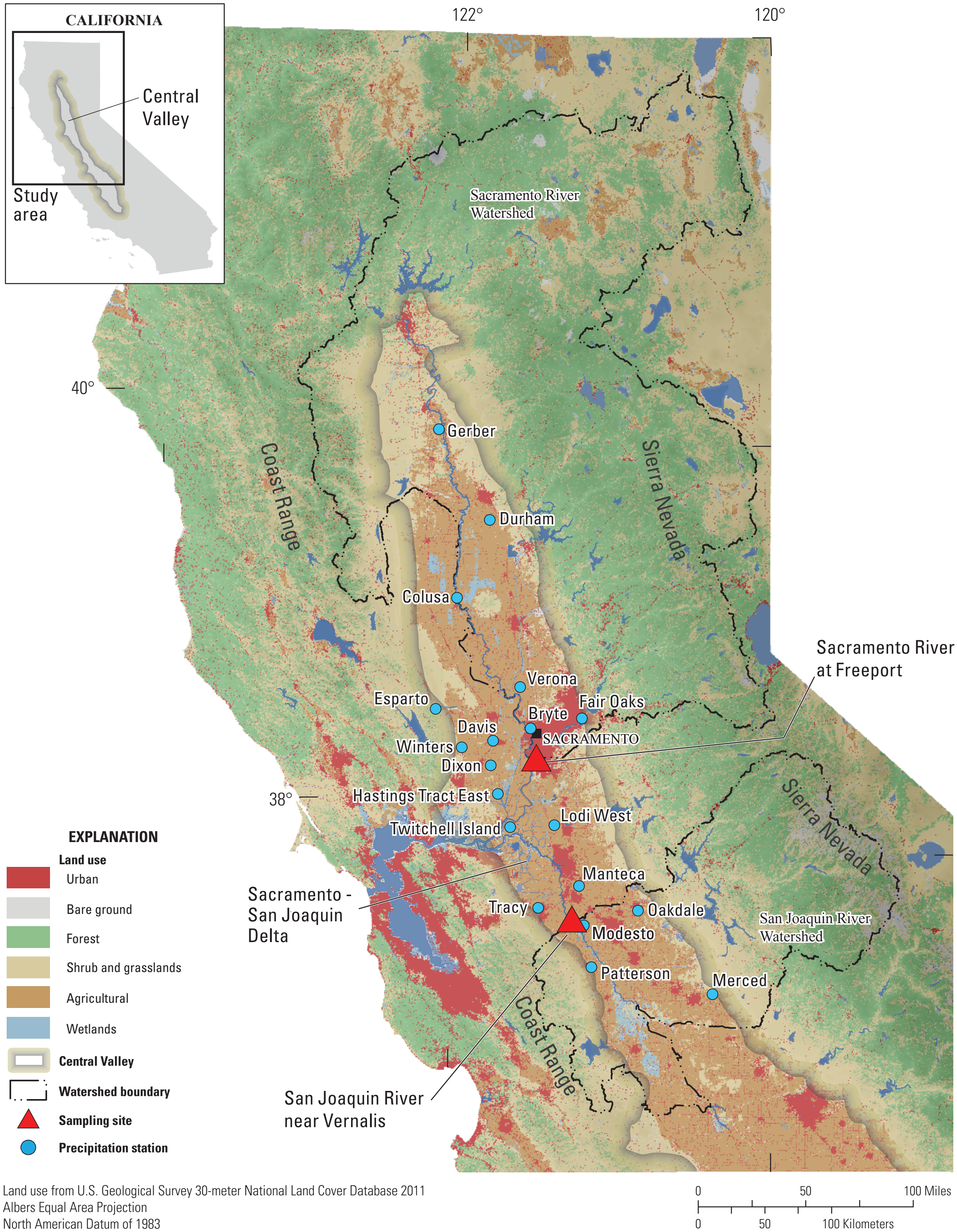

Figure 1. Locations of sampling sites in the Sacramento–San Joaquin Delta.

Table 1. Surface-water sampling sites located on the Sacramento and San Joaquin Rivers.

[**Abbreviations**: Calif., California; NAD 83, North American Datum 1983; USGS, U.S. Geological Survey; °, degrees; ', minutes; ", seconds]

USGS station number	USGS station name	Latitude	Longitude	Horizontal datum	Period sampled
11447650	Sacramento River at Freeport, Calif.	38° 27' 22"	121° 30' 05"	NAD 83	May 2012–July 2013
11303500	San Joaquin River near Vernalis, Calif.	37° 40' 34"	121° 15' 59"	NAD 83	May 2012–April 2013

applications made by homeowners using products purchased at retail stores, which could contribute substantially to total pesticide use in urban areas. In 2012 (the latest year for which data are available), it was reported that over 23.3 million pounds (lb) of pesticides were applied in the Sacramento and San Joaquin River watersheds (9.0 and 14.3 million lbs, respectively; California Department of Pesticide Regulation, 2014). Of this amount, approximately 21.7 million lbs were applied to agricultural land, and approximately 1.6 million lbs were applied by licensed applicators in urban settings.

Rainfall and Hydrologic Conditions

Pesticide transport is strongly affected by the timing and location of pesticide applications as well as by rainfall and streamflow. Dileanis and others (2003), and Orlando and others (2013) have demonstrated increased pesticide concentrations in surface water following rainfall events in the Sacramento and San Joaquin Valleys that were preceded by pesticide applications.

The California Department of Water Resources classified 2012 and 2013 as “below normal” and “dry” runoff years in the Sacramento Valley, and “dry” and “critical” runoff years in the San Joaquin Valley indicating that the region received well below normal precipitation (California Department of Water Resources, 2013c). Large rainfall events (greater than 1 inch in 24 hours) were rare during the study period in both the Sacramento and San Joaquin valley floor regions. These conditions led to below-normal streamflow on the Sacramento and San Joaquin Rivers where they enter the Delta during most of the study period (U.S. Geological Survey, 2013a, 2013b). Daily mean streamflow measured from May 2012 to July 2013 at two USGS streamgages (Sacramento River at Freeport, 11447650, and San Joaquin River near Vernalis, 11303500) is shown in figure 2. The historic means of daily mean streamflow, based on the periods October 1, 1948, to September 30, 2012, for Sacramento River at Freeport; and October 1, 1923, to September 30, 2012, for San Joaquin River near Vernalis, are shown for comparison (fig. 2).

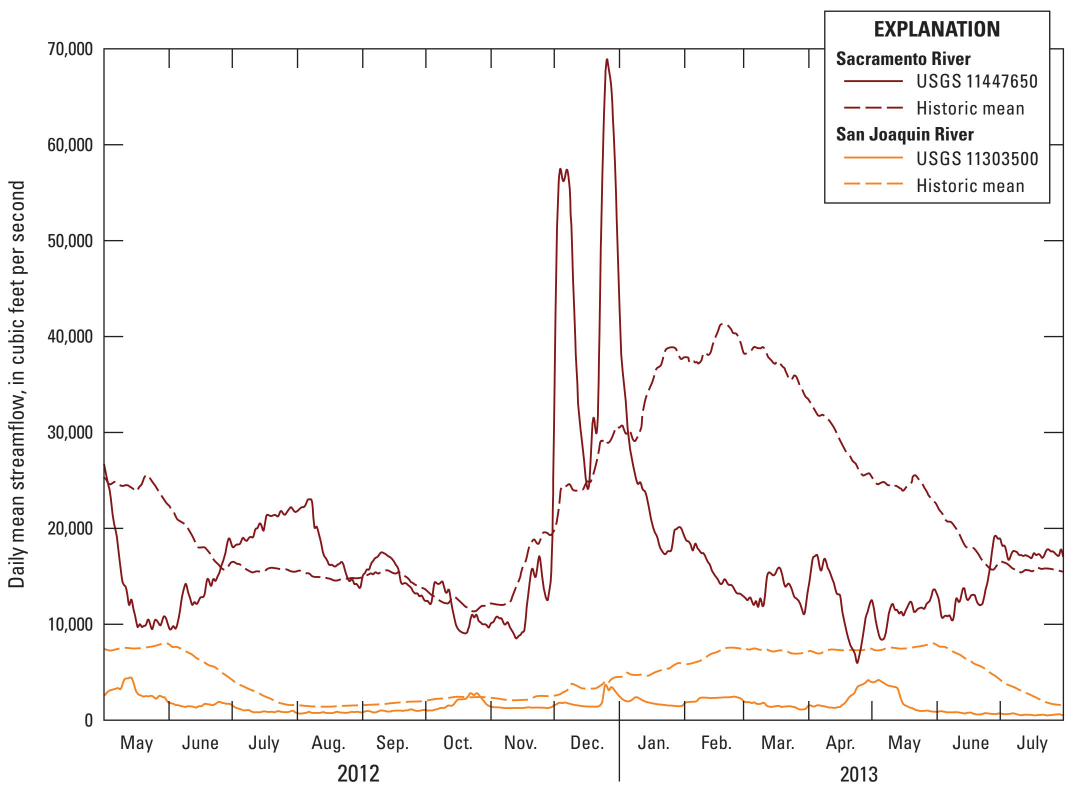

Figure 2. Daily mean streamflow from U.S. Geological Survey (USGS) streamgages at Sacramento River at Freeport (11447650), and San Joaquin River near Vernalis (11303500).

Procedures and Methods

Water samples were collected twice per month during 2012 and 2013 from the Sacramento and San Joaquin Rivers where they enter the Delta. Basic field parameters (temperature, specific conductance, pH, and dissolved oxygen concentration) were measured at the time of sample collection. Water samples were transported to the USGS Organic Chemistry Research Laboratory in Sacramento, and analyzed for pesticides using two methods, gas chromatography with mass spectrometry (GC/MS) and liquid chromatography with tandem mass spectrometry (LC/MS/MS) for a suite of 99 current-use pesticides (table 2). Extensive quality-control (QC) sampling was also performed for each method, including field blanks, field replicates, and laboratory matrix-spike and matrix-spike-replicate samples. The procedures and methods for this study included sample-collection methods in the field, sample-processing methods in the laboratory, and analytical methods for pesticides.

Sample Collection

Surface-water samples were collected from the Sacramento River at Freeport and the San Joaquin River near Vernalis twice per month from May 2012 to July 2013, and from May 2012 to April 2013, respectively (table 1). Samples were also collected from the Sacramento River at Freeport for 5 consecutive days (April 1 through April 5, 2013) following a moderate rainfall event (greater than 0.5 inches in 24 hours) in the Sacramento urban area. At the Sacramento River site all samples were collected from a boat as integrated grab samples using a US D-96 depth-integrating sampler configured with a Teflon nozzle and 3 liter (L) Teflon-lined collection bag following methods described by the Federal Interagency Sedimentation Project (2002). Sample water was obtained at five locations equally spaced across the stream channel on the ebb tide following standard USGS sampling procedures (U.S. Geological Survey, 2006). Sample water was poured into a Teflon churn splitter following collection at each location. The churn was placed on ice after all sample water was collected and delivered to the USGS Organic Chemistry Research Laboratory in Sacramento, Calif., for processing and analysis.

At the San Joaquin River site surface-water samples were collected from a bridge at 15–20 equally spaced points across the stream channel using a US DH-95 depth-integrating sampler (Federal Interagency Sedimentation Project, 2000) following standard USGS sampling procedures (U.S. Geological Survey, 2006). Sample water was collected in a 1-L Teflon collection bottle and poured into a Teflon churn splitter. After water from all sampling points had been collected, sample water was churned into 1-L amber glass bottles that were then placed on ice for transport to the USGS Organic Chemistry Research Laboratory in Sacramento, Calif., for further processing and analysis.

Prior to all sampling events, the sampler nozzle, bag or bottle, and churn were cleaned with tap water and soap, triple rinsed with organic-free deionized water, and rinsed with reagent grade methanol. All components were then allowed to air dry and stored in sealed plastic bags. On arrival at the sampling site, all equipment was triple rinsed with native water prior to sample collection. During sample collection, basic water parameters (temperature, pH, specific conductance, and dissolved oxygen concentration) were measured at a depth of approximately 2 feet (ft) at the center of the channel using a multiparameter meter (YSI model 6920V2), which was calibrated with appropriate standards and buffers prior to sampling.

Sample Processing

Sample processing was performed in the laboratory within 24 hours of sample collection. All water samples were filtered through 0.7-micrometer (μm) glass-fiber filters (Grade GF/F, Whatman, Piscataway, New Jersey) into pre-cleaned glass bottles to remove suspended material. Samples were then stored refrigerated at 2 degrees Celsius (°C) until analysis.

Analytical Methods for Pesticides

Analytical instruments were calibrated with standards in concentrations that spanned the linear range of instrument response (0.025 to 2.5 nanograms per microliter [ng/μL]). Calibration curves were determined by linear regression and considered acceptable if the coefficient of determination (R^2) for each compound was greater than 0.995. The responses of the instruments were monitored every 6–8 samples with a mid-level check standard of 0.25 ng/μL or 0.5 ng/μL. The instruments were considered to be stable if the recoveries of the check standards fell within the range of 80–120 percent of the nominal standard concentration. All environmental sample concentrations fell within the linear range of the instruments.

Gas Chromatography/Mass Spectrometry Analysis

GC/MS analysis methods were based on those previously described by Hladik and others (2008, 2009). To summarize these methods, each 1-L filtered-water sample was spiked with $^{13}C_3$-atrazine (Cambridge Isotopes, Andover, Massachusetts) as a recovery surrogate. The sample was then pumped under vacuum at a flow rate of 10 milliliters per minute (mL/min) through an Oasis HLB solid-phase extraction (SPE) cartridge (6 milliliters [mL], 500 milligrams [mg], 60 μm, Waters Corporation, Milford, Massachusetts) that had been cleaned with two column-volumes of ethyl acetate followed by two column-volumes of methanol and two column-volumes of organic-free deionized water. After extraction, approximately 1 gram (g) of sodium sulfate (Na_2SO_4) was

Table 2. Method detection limits for pesticides in water measured by the U.S. Geological Survey Organic Chemistry Research Laboratory.

[**Abbreviations**: GC/MS, gas chromatograph with mass spectrometry; LC/MS/MS, liquid chromatography with tandem mass spectrometry; ng/L, nanograms per liter; NWIS, National Water Information System]

Compound	NWIS parameter code	Chemical class	Pesticide type	Method detection limit (ng/L)	Analytical method
Acetamiprid	68302	Neonicotinoid	Insecticide	3.6	LC/MS/MS
Alachlor	65064	Chloroacetanilide	Herbicide	1.7	GC/MS
Allethrin	66586	Pyrethroid	Insecticide	6.0	GC/MS
Atrazine	65065	Triazine	Herbicide	2.3	GC/MS
Azoxystrobin	66589	Strobilurin	Fungicide	3.1	GC/MS
Bifenthrin	65067	Pyrethroid	Insecticide	4.7	GC/MS
Boscalid	67550	Pyridine	Fungicide	2.8	GC/MS
Butylate	65068	Thiocarbamate	Herbicide	1.8	GC/MS
Carbaryl	65069	Carbamate	Insecticide	6.5	GC/MS
Carbofuran	65070	Carbamate	Insecticide	3.1	GC/MS
Chlorothalonil	65071	Chloronitrile	Fungicide	4.1	GC/MS
Chlorpyrifos	65072	Organophosphate	Insecticide	2.1	GC/MS
Clomazone	67562	Isoxazlidinone	Herbicide	2.5	GC/MS
Clothianidin	68221	Neonicotinoid	Insecticide	6.2	LC/MS/MS
Cycloate	65073	Thiocarbamate	Herbicide	1.1	GC/MS
Cyfluthrin	65074	Pyrethroid	Insecticide	5.2	GC/MS
Cyhalothrin	68354	Pyrethroid	Insecticide	4.5	GC/MS
Cypermethrin	65075	Pyrethroid	Insecticide	5.6	GC/MS
Cyproconazole	66593	Triazole	Fungicide	4.7	GC/MS
Cyprodinil	67574	Pyrimidine	Fungicide	7.4	GC/MS
DCPA	65076	Benzenedicarboxylic acid	Herbicide	2.0	GC/MS
p,p'-DDD	65094	Organochlorine	Degradate	4.1	GC/MS
p,p'-DDE	65095	Organochlorine	Degradate	3.6	GC/MS
p,p'-DDT	65096	Organochlorine	Insecticide	4.0	GC/MS
Deltamethrin	65077	Pyrethroid	Insecticide	3.5	GC/MS
Desulfinylfipronil	66607	Phenylpyrazole	Degradate	1.6	GC/MS
Diazinon	65078	Organophosphate	Insecticide	0.9	GC/MS
3,4-Dichloroaniline (3,4-DCA)	66584	Urea	Degradate	5.2	LC/MS/MS
3,5-Dichloroaniline (3,5-DCA)	67536	Aniline	Degradate	7.6	GC/MS
N-(3,4-Dichlorophenyl)-*N*'-methylurea (DCPMU)	68231	Urea	Degradate	3.0	LC/MS/MS
3,4-Dichlorophenylurea (DCPU)	68226	Urea	Degradate	4.3	LC/MS/MS
Difenoconazole	67582	Triazole	Fungicide	10.5	GC/MS
(*E*)-Dimethomorph	67587	Morpholine	Fungicide	6.0	GC/MS
Dinotefuran	68379	Neonicotinoid	Insecticide	5.5	LC/MS/MS
Diuron	66598	Urea	Herbicide	3.2	LC/MS/MS
Esfenvalerate	65081	Pyrethroid	Insecticide	3.9	GC/MS
Ethalfluralin	65082	Aniline	Herbicide	3.0	GC/MS
Etofenprox	67604	Pyrethroid	Insecticide	2.2	GC/MS
S-Ethyl dipropylthiocarbamate (EPTC)	65080	Thiocarbamate	Herbicide	1.5	GC/MS
Famoxadone	67609	Oxazole	Fungicide	2.5	GC/MS
Fenarimol	67613	Pyrimidine	Fungicide	6.5	GC/MS
Fenbuconazole	67618	Triazole	Fungicide	5.2	GC/MS
Fenhexamide	67622	Anilide	Fungicide	7.6	GC/MS
Fenpropathrin	65083	Pyrethroid	Insecticide	4.1	GC/MS
Fipronil	66604	Phenylpyrazole	Insecticide	2.9	GC/MS
Fipronil sulfide	66610	Phenylpyrazole	Degradate	1.8	GC/MS
Fipronil sulfone	66613	Phenylpyrazole	Degradate	3.5	GC/MS
Fluazinam	67636	Pyridine	Fungicide	4.4	GC/MS
Fludioxinil	67640	Pyrrole	Fungicide	7.3	GC/MS
Fluoxastrobin	67645	Strobilurin	Fungicide	4.2	GC/MS

Table 2. Method detection limits for pesticides in water measured by the U.S. Geological Survey Organic Chemistry Research Laboratory.—Continued

[**Abbreviations**: GC/MS, gas chromatograph with mass spectrometry; LC/MS/MS, liquid chromatography with tandem mass spectrometry; ng/L, nanograms per liter; NWIS, National Water Information System]

Compound	NWIS parameter code	Chemical class	Pesticide type	Method detection limit (ng/L)	Analytical method
Flusilazole	67649	Triazole	Fungicide	4.5	GC/MS
Flutriafol	67653	Triazole	Fungicide	4.2	GC/MS
τ-Fluvalinate	65106	Pyrethroid	Insecticide	5.3	GC/MS
Hexazinone	65085	Triazone	Herbicide	8.4	GC/MS
Imazalil	67662	Triazole	Fungicide	10.5	GC/MS
Imidacloprid	68426	Neonicotinoid	Insecticide	4.9	LC/MS/MS
Iprodione	66617	Dicarboxamide	Fungicide	4.4	GC/MS
Kresoxim-methyl	67670	Strobilurin	Fungicide	4.0	GC/MS
Malathion	65087	Organophosphate	Insecticide	3.7	GC/MS
Metconazole	66620	Azole	Fungicide	5.2	GC/MS
Methidathion	65088	Organophosphate	Insecticide	7.2	GC/MS
Methoprene	66623	Terpene	Insecticide	6.4	GC/MS
Methylparathion	65089	Organophosphate	Insecticide	3.4	GC/MS
Metolachlor	65090	Chloroacetanilide	Herbicide	1.5	GC/MS
Molinate	65091	Thiocarbamate	Herbicide	3.2	GC/MS
Myclobutanil	66632	Triazole	Fungicide	6.0	GC/MS
Napropamide	65092	Amide	Herbicide	8.2	GC/MS
Oxyfluorfen	65093	Nitrophenyl ether	Herbicide	3.1	GC/MS
Pebulate	65097	Thiocarbamate	Herbicide	2.3	GC/MS
Pendimethalin	65098	Aniline	Herbicide	2.3	GC/MS
Pentachloroanisole (PCA)	66637	Organochlorine	Insecticide	4.7	GC/MS
Pentachloronitrobenzene (PCNB)	66639	Organochlorine	Fungicide	3.1	GC/MS
Permethrin	65099	Pyrethroid	Insecticide	3.4	GC/MS
Phenothrin	65100	Pyrethroid	Insecticide	5.1	GC/MS
Phosmet	65101	Organophosphate	Insecticide	4.4	GC/MS
Piperonyl butoxide	65102	Unclassified	Synergist	2.3	GC/MS
Prometon	67702	Triazine	Herbicide	1.8	GC/MS
Prometryn	65103	Triazine	Herbicide	2.5	GC/MS
Propanil	66641	Anilide	Herbicide	10.1	GC/MS
Propiconazole	66643	Azole	Fungicide	5.0	GC/MS
Propyzamide	67706	Benzamide	Herbicide	5.0	GC/MS
Pyraclostrobin	66646	Strobilurin	Fungicide	2.9	GC/MS
Pyrimethanil	67717	Pyrmidine	Fungicide	4.1	GC/MS
Resmethrin	65104	Pyrethroid	Insecticide	5.7	GC/MS
Simazine	65105	Triazine	Herbicide	5.0	GC/MS
Tebuconazole	66649	Azole	Fungicide	3.7	GC/MS
Tefluthrin	67731	Pyrethroid	Insecticide	4.2	GC/MS
Tetraconazole	66654	Azole	Fungicide	5.6	GC/MS
Tetramethrin	66657	Pyrethroid	Insecticide	2.9	GC/MS
Thiacloprid	68485	Neonicotinoid	Insecticide	3.8	LC/MS/MS
Thiamethoxam	68245	Neonicotinoid	Insecticide	3.9	LC/MS/MS
Thiobencarb	65107	Thiocarbamate	Herbicide	1.9	GC/MS
Triadimefon	67741	Triazole	Fungicide	8.9	GC/MS
Triadimenol	67746	Triazole	Fungicide	8.0	GC/MS
Trifloxystrobin	66660	Strobilurin	Fungicide	4.7	GC/MS
Triflumizole	67753	Azole	Fungicide	6.1	GC/MS
Trifluralin	65108	Aniline	Herbicide	2.1	GC/MS
Triticonazole	67758	Azole	Fungicide	6.9	GC/MS
Zoxamide	67768	Benzamide	Fungicide	3.5	GC/MS

added to the sample bottle to remove any residual water, and the bottles were rinsed three times with approximately 2 mL of dichloromethane (DCM) into a collection tube. The bottle rinses were concentrated to 1 mL under a gentle stream of nitrogen gas. Each cartridge was dried on a manifold by passing carbon dioxide through the cartridge for approximately 1 hour or until the SPE sorbent was dry. Each cartridge was then eluted with 12 mL of ethyl acetate, and the eluate was combined with its corresponding bottle rinse. The combined solution was then reduced under a gentle stream of dry nitrogen to a final volume of 200 microliters (µL) for analysis. An internal standard (20 µL of 2 nanograms per liter [ng/L]) containing the deuterated polycyclic aromatic hydrocarbon compounds acenaphthene-d_{10} and pyrene-d_{10} was then added to each sample. The sample extracts were stored (not to exceed 30 days) in a freezer at –20 °C until instrumental analysis.

Water extracts were analyzed for 89 current-use pesticides on an Agilent 7890A GC chromatograph with an Agilent 5975C Inert XL EI mass-selective detector (MSD) system using a DB-5MS analytical column (30 meter [m] by 0.25 millimeter [mm] by 0.25 µm, Agilent, Palo Alto, Calif.) for separation and helium as the carrier gas. Data were collected in the selected-ion-monitoring mode. Additional details of the GC/MS method can be found in Hladik and others (2008, 2009).

One sample (Sacramento River at Freeport, June 26, 2013) to be analyzed by GC/MS was lost during laboratory processing, and no results are available for pesticides measured by GC/MS, although the same environmental sample was analyzed by LC/MS/MS, and those results are reported.

Liquid Chromatography With Tandem Mass Spectrometry Analysis

Each 1-L filtered-water sample was spiked with the recovery surrogate standards monuron (Chem Service, West Chester, Pennsylvania) and imidacloprid-d_4 (Cambridge Isotope Laboratories, Andover, Massachusetts). The sample was then pumped under vacuum at a flow rate of 10 mL/min through an Oasis HLB SPE (6 mL, 500 mg, 60 µm, Waters Corporation, Milford, Massachusetts) cartridge that had been cleaned with one column-volume of DCM, followed by one column-volume of acetone and two column-volumes of deionized water. The SPE cartridge was then dried using a stream of carbon dioxide for approximately 1 hour or until the SPE sorbent was dry. The cartridges were eluted into a clean, glass concentrator tube by using 10 mL of a solution of 1 DCM:1 acetone. The eluent was evaporated to less than 0.5 mL in a fume hood under a gentle stream of nitrogen, then solvent-exchanged into acetonitrile and further evaporated to 200 µL. The internal standard ($^{13}C_3$-caffeine, Cambridge Isotope Laboratories) was then added (10 µL of a 1-ng/µL solution). The sample extracts were stored (not to exceed 30 days) in a freezer at –20 °C until analysis.

Water extracts were analyzed for the herbicide diuron, three diuron degredates (DCPMU, 3,4-Dichlorophenylurea (DCPU), and 3,4-dichloroaniline), and six neonicotinoid insecticides (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid, and thiamethoxam) by LC/MS/MS. Aliquots of the sample extracts (10 µL) were injected, and the compounds were separated on an Agilent (Palo Alto, Calif.) 1100 Series high performance liquid chromatograph (HPLC) coupled to a 6430 tandem mass spectrometry (MS)system with a Zorbax Eclipse XDB-C18 column (2.1 mm by 150 mm by 3.5 mm, Agilent). The mobile phases were acetonitrile (A channel) and 5 millimolar (mM) formic acid in water (B channel). Data were collected in the multiple-reaction-monitoring mode. Additional details of the LC/MS/MS analytical method can be found in Hladik and Calhoun (2012).

Method Detection Limits

Method detection limits (MDL) for surface-water samples were validated in previous studies (Hladik and others, 2008; Hladik and Calhoun, 2012) by using the procedure described in 40 CFR Part 136 appendix B (U.S. Environmental Protection Agency, 1992). MDLs for pesticides in surface water ranged from 0.9 to 10.5 ng/L (table 2). Analytes can sometimes be identified at concentrations less than the MDLs with lower confidence in the numerical value; therefore, concentrations of compounds detected below the MDLs are reported as estimates.

Quality-Assurance and Quality-Control Methods and Results

Pesticide concentrations were validated against a comprehensive set of performance based QC criteria, including field blanks, field replicates, laboratory matrix-spike and matrix spike-replicate samples, and surrogate recoveries. QC samples were analyzed using the GC/MS and LC/MS/MS methods described earlier.

During the study, six field blanks consisting of pesticide-grade organic-free blank water were processed to test the cleanliness of the field procedures. Field blanks were processed in the same manner as the environmental samples. Blank samples were analyzed using both the GC/MS and LC/MS/MS methods. No pesticides were detected in any of the field blanks, so no results are shown.

Twelve field replicate sample pairs were analyzed (7 by GC/MS and 5 by LC/MS/MS; tables 3 and 4) to test the reproducibility of results, and there were 49 paired detections of pesticides. The relative standard deviations between replicate samples were less than the control limit of 25 percent in all cases (tables 3 and 4). There were no instances where a pesticide was detected in either the environmental or replicate sample and not in the corresponding sample (tables 3 and 4).

Table 3. Pesticide concentrations measured by gas chromatograph with mass spectrometry (GC/MS) in environmental and field replicate water samples from the Sacramento and San Joaquin Rivers, and the relative standard deviations between results.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: alachlor, allethrin, atrazine, bifenthrin, butylate, carbofuran, chlorothalonil, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, cyprodinil, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, EPTC, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, tau-fluvalinate, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, prometon, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; RSD, relative standard deviation; %, percent; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	Azoxystrobin [66589]	Boscalid [67550]	Carbaryl [65069]	Chlorpyrifos [65072]	Clomazone [67562]	DCPA [65076]	Fipronil [66604]	Hexazinone [65085]	Imazalil [67662]
Sacramento River at Freeport	10/18/2012	12:23	Environmental	13.4	—	—	—	—	—	—	32.8	—
Sacramento River at Freeport	10/18/2012	12:23	Field replicate	11.8	—	—	—	—	—	—	31.3	—
			RSD	9%							3%	
Sacramento River at Freeport	01/22/2013	13:33	Environmental	32.0	—	—	—	—	—	—	44.1	—
Sacramento River at Freeport	01/22/2013	13:33	Field replicate	36.9	—	—	—	—	—	—	46.8	—
			RSD	10%							4%	
Sacramento River at Freeport	04/01/2013	13:03	Environmental	29.1	—	20.6	—	—	5.4	20.4	82.3	30.7
Sacramento River at Freeport	04/01/2013	13:03	Field replicate	30.9	—	23.3	—	—	5.3	23.1	85.6	34.1
			RSD	4%		9%			2%	9%	3%	7%
Sacramento River at Freeport	07/11/2013	12:08	Environmental	102	—	—	—	20.1	—	—	62.7	—
Sacramento River at Freeport	07/11/2013	12:08	Field replicate	106	—	—	—	20.8	—	—	65.3	—
			RSD	3%				2%			3%	
San Joaquin River near Vernalis	05/16/2012	11:00	Environmental	—	11.4	—	14.7	—	—	—	99.1	—
San Joaquin River near Vernalis	05/16/2012	11:00	Field replicate	—	12.9	—	15.9	—	—	—	110	—
			RSD		9%		6%				7%	
San Joaquin River near Vernalis	12/18/2012	11:33	Environmental	7.5	7.7	—	—	—	—	—	69.6	—
San Joaquin River near Vernalis	12/18/2012	11:33	Field replicate	7.9	8.1	—	—	—	—	—	72.0	—
			RSD	3%	4%						2%	
San Joaquin River near Vernalis	04/11/2013	10:23	Environmental	3.7	53.7	—	—	—	—	—	255	—
San Joaquin River near Vernalis	04/11/2013	10:23	Field replicate	(2.8)	50.4	—	—	—	—	—	238	—
			RSD	20%	5%						5%	

Table 3. Pesticide concentrations measured by gas chromatograph with mass spectrometry (GC/MS) in environmental and field replicate water samples from the Sacramento and San Joaquin Rivers, and the relative standard deviations between results.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: alachlor, allethrin, atrazine, bifenthrin, butylate, carbofuran, chlorothalonil, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, cyprodinil, *p,p*'-DDD, *p,p*'-DDE, *p,p*'-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, EPTC, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, tau-fluvalinate, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, prometon, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: mm/dd/yyyy, month/day/year; hh:mm, hours:minutes; RSD, relative standard deviation; %, percent; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	Metolachlor [65090]	Oxyflurofen [65093]	Pendimethalin [65098]	Piperonyl butoxide [65102]	Prometryn [65103]	Propanil [66641]	Propiconazole [66643]	Simazine [65105]
Sacramento River at Freeport	10/18/2012	12:23	Environmental	—	—	—	—	—	—	—	—
Sacramento River at Freeport	10/18/2012	12:23	Field replicate	—	—	—	—	—	—	—	—
			RSD								
Sacramento River at Freeport	01/22/2013	13:33	Environmental	—	—	—	—	—	—	—	28.9
Sacramento River at Freeport	01/22/2013	13:33	Field replicate	—	—	—	—	—	—	—	24.4
			RSD								12%
Sacramento River at Freeport	04/01/2013	13:03	Environmental	—	—	—	—	—	—	26.7	38.1
Sacramento River at Freeport	04/01/2013	13:03	Field replicate	—	—	—	—	—	—	28.6	41.0
			RSD							5%	5%
Sacramento River at Freeport	07/11/2013	12:08	Environmental	11.4	—	—	14.6	—	77.6	12.8	(4.4)
Sacramento River at Freeport	07/11/2013	12:08	Field replicate	11.9	—	—	16.0	—	79.6	12.9	(4.5)
			RSD	3%			7%		2%	1%	2%
San Joaquin River near Vernalis	05/16/2012	11:00	Environmental	38.0	—	—	—	—	—	—	39.8
San Joaquin River near Vernalis	05/16/2012	11:00	Field replicate	39.7	—	—	—	—	—	—	37.5
			RSD	3%							4%
San Joaquin River near Vernalis	12/18/2012	11:33	Environmental	7.9	—	9.4	—	—	—	—	29.2
San Joaquin River near Vernalis	12/18/2012	11:33	Field replicate	7.8	—	10.5	—	—	—	—	32.8
			RSD	1%		8%					8%
San Joaquin River near Vernalis	04/11/2013	10:23	Environmental	26.4	10.8	—	—	6.5	—	(3.8)	101
San Joaquin River near Vernalis	04/11/2013	10:23	Field replicate	25.6	9.1	—	—	6.3	—	(3.3)	93.6
			RSD	2%	12%			2%		10%	5%

Table 4. Pesticide concentrations measured by liquid chromatography with tandem mass spectrometry (LC/MS/MS) in environmental and field replicate water samples from the Sacramento and San Joaquin Rivers, and the relative standard deviations between results.

[Numbers in brackets are U.S Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, clothianidin, DCPU, dinotefuran, imidacloprid, thiacloprid, and thiamethoxam. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; RSD, relative standard deviation; %, percent; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	3,4-Dichloroaniline [66584]	DCPMU [68231]	Diuron [66598]
Sacramento River at Freeport	08/07/2012	11:05	Environmental	50.5	—	—
Sacramento River at Freeport	08/07/2012	11:05	Field replicate	43.2	—	—
			RSD	11%		
Sacramento River at Freeport	11/27/2012	11:03	Environmental	60.8	—	7.9
Sacramento River at Freeport	11/27/2012	11:03	Field replicate	58.1	—	7.5
			RSD	3%		4%
Sacramento River at Freeport	02/19/2013	09:53	Environmental	9.4	—	—
Sacramento River at Freeport	02/19/2013	09:53	Field replicate	10.0	—	—
			RSD	4%		
San Joaquin River near Vernalis	07/02/2012	12:00	Environmental	5.2	17.2	19.2
San Joaquin River near Vernalis	07/02/2012	12:00	Field replicate	5.9	19.8	20.7
			RSD	9%	10%	5%
San Joaquin River near Vernalis	10/30/2012	10:48	Environmental	(2.3)	—	(3.1)
San Joaquin River near Vernalis	10/30/2012	10:48	Field replicate	(2.2)	—	(2.8)
			RSD	3%		7%

Eleven laboratory matrix-spike samples paired with 11 matrix-spike-replicate samples were analyzed (5 by GC/MS and 6 by LC/MS/MS; table 5) to assess pesticide recovery, degradation, sorption, and potential interferences caused by the sampling matrix. Percent recoveries for all pesticides in all 22 samples met the data-quality objective of 70 to 130 percent (table 5). These 11 pairs of laboratory matrix-spike and matrix-spike-replicate samples were also tested for reproducibility, and the relative standard deviations were less than the control limit of 25 percent in all cases (table 5). Minimum, maximum, and median recoveries and standard deviations of these recoveries for all pesticides are shown in table 5.

To assess the efficiency of sample extraction for the GC/MS and LC/MS/MS analytical methods, ring-$^{13}C_3$-atrazine and diethyl-d_{10} diazinon, and monuron and imidacloprid-d_4, respectively, were used as recovery surrogates. Percentage recoveries of surrogates for all samples analyzed (including QC samples) met the data-quality objective of 70 to 130 percent.

Results

A total of 37 pesticides or pesticide degradates (table 6) were detected in water samples collected from the Sacramento and San Joaquin Rivers during this study, and each sample contained a mixture of at least 3 compounds. The most frequently detected pesticides overall were the herbicide hexazinone (100 percent); 3,4-dichloroaniline (97 percent); which is a degradate of the herbicides diuron and propanil; the fungicide azoxystrobin (83 percent); and the herbicides diuron (72 percent), simazine (66 percent), and metolachlor (64 percent; table 6). Concentrations ranged from below method detection limits to 984 ng/L (hexazinone; tables 6, 7, and 8).

To provide context for the pesticide concentration data collected during this study, results from the field measurements of the water-quality parameters (water temperature, specific conductance, dissolved oxygen, and pH) are provided in table 9.

Table 5. Minimum, maximum, and median recovery, and standard deviation of the recoveries, represented as a percentage for all compounds added to laboratory spiked water samples.

[Five spiked samples and five spiked replicate samples were analyzed by gas chromatography with mass spectrometry (GC/MS). Compounds noted with ** were analyzed in six spiked samples and six spiked replicate samples by liquid chromatography with tandem mass spectrometry (LC/MS/MS). **Abbreviations**: %, percent; ±, plus or minus]

Compound	Minimum recovery (in percent)	Maximum recovery (in percent)	Median recovery (in percent)	Standard deviation (in percent)
Acetamiprid**	74	113	88	± 11
Alachlor	93	110	99	± 5
Allethrin	83	110	93	± 8
Atrazine	82	113	100	± 10
Azoxystrobin	79	109	98	± 9
Bifenthrin	85	100	92	± 5
Boscalid	75	111	102	± 11
Butylate	79	101	89	± 7
Carbaryl	78	108	95	± 11
Carbofuran	79	110	100	± 11
Chlorothalonil	73	103	84	± 10
Chlorpyrifos	74	101	91	± 8
Clomazome	90	109	99	± 6
Clothianidin**	74	95	82	± 7
Cycloate	86	117	99	± 9
Cyfluthrin	81	119	99	± 12
Cyhalothrin	85	105	97	± 7
Cypermethrin	81	103	95	± 7
Cyproconazole	77	103	86	± 7
Cyprodinil	78	114	89	± 11
DCPA	91	112	97	± 7
p,p'-DDD	73	101	89	± 9
p,p'-DDE	72	114	85	± 12
p,p'-DDT	77	103	94	± 10
Deltamethrin	75	113	97	± 11
Desulfinylfipronil	82	104	96	± 7
Diazinon	91	110	99	± 6
3,4-Dichloroaniline (3,4-DCA)**	77	110	98	± 9
3,5-Dichloroaniline (3,5-DCA)	72	102	89	± 11
N-(3,4-Dichlorophenyl)-*N*'-methylurea (DCPMU)**	76	106	93	± 10
3,4-Dichlorophenylurea (DCPU)**	72	101	89	± 10
Difenoconazole	78	103	93	± 7
(*E*)-Dimethomorph	78	106	95	± 8
Dinotefuran**	72	108	86	± 12
Diuron**	76	117	93	± 12
Esfenvalerate	74	118	99	± 14
Ethalfluralin	78	113	98	± 13
Etofenprox	85	103	91	± 5
S-Ethyl dipropylthiocarbamate (EPTC)	83	108	97	± 10
Famoxadone	78	110	93	± 11
Fenarimol	81	104	90	± 7
Fenbuconazole	78	107	97	± 9
Fenhexamide	83	103	92	± 7
Fenpropathrin	77	102	92	± 8
Fipronil	90	120	105	± 12
Fipronil sulfide	87	113	100	± 8
Fipronil sulfone	89	114	105	± 9
Fluazinam	70	80	75	± 4
Fludioxinil	82	103	90	± 7
Fluoxastrobin	72	113	93	± 14

Table 5. Minimum, maximum, and median recovery, and standard deviation of the recoveries, represented as a percentage for all compounds added to laboratory spiked water samples.—Continued

[Five spiked samples and five spiked replicate samples were analyzed by gas chromatography with mass spectrometry (GC/MS). Compounds noted with ** were analyzed in six spiked samples and six spiked replicate samples by liquid chromatography with tandem mass spectrometry (LC/MS/MS). **Abbreviations**: %, percent; ±, plus or minus]

Compound	Minimum recovery (in percent)	Maximum recovery (in percent)	Median recovery (in percent)	Standard deviation (in percent)
Flusilazole	70	105	84	± 11
Flutriafol	88	118	101	± 8
τ-Fluvalinate	76	98	87	± 7
Hexazinone	79	112	94	± 11
Imazalil	80	117	99	± 13
Imidacloprid**	76	110	88	± 11
Iprodione	79	111	98	± 12
Kresoxim-methyl	79	103	86	± 8
Malathion	87	110	102	± 8
Metconazole	85	116	99	± 9
Methidathion	88	114	104	± 9
Methoprene	81	106	94	± 9
Methylparathion	93	113	104	± 7
Metolachlor	94	112	101	± 5
Molinate	85	107	95	± 7
Myclobutanil	78	109	89	± 11
Napropamide	90	107	102	± 5
Oxyfluorfen	92	119	105	± 9
Pebulate	81	100	92	± 7
Pendimethalin	83	130	106	± 13
Pentachloroanisole (PCA)	70	97	81	± 9
Pentachloronitrobenzene (PCNB)	76	93	83	± 5
Permethrin	85	107	97	± 6
Phenothrin	72	105	86	± 10
Phosmet	92	120	104	± 10
Piperonyl butoxide	96	112	105	± 5
Prometon	88	120	104	± 8
Prometryn	82	106	94	± 7
Propanil	89	109	102	± 7
Propiconazole	83	97	90	± 5
Propyzamide	92	113	103	± 6
Pyraclostrobin	93	119	102	± 8
Pyrimethanil	79	112	87	± 11
Remethrin	70	104	87	± 12
Simazine	97	119	107	± 7
Tebuconazole	80	121	101	± 14
Tefluthrin	77	104	87	± 9
Tetraconazole	74	110	86	± 9
Tetramethrin	76	103	90	± 9
Thiacloprid**	72	105	82	± 10
Thiamethoxam**	70	113	86	± 13
Thiobencarb	93	105	99	± 4
Triadimefon	78	101	90	± 8
Triadimenol	86	114	101	± 8
Trifloxystrobin	74	106	89	± 10
Triflumizole	71	116	91	± 14
Trifluralin	76	96	86	± 7
Triticonazole	78	107	96	± 9
Zoxamide	76	110	95	± 13

Table 6. Pesticide detection frequencies and maximum concentrations measured in environmental water samples collected from the Sacramento and San Joaquin Rivers.

[**Abbreviations**: ng/L, nanograms per liter; %, percent; —, not detected]

Compound	Pesticide type	Sacramento River at Freeport		San Joaquin River near Vernalis	
		Detection frequency (in percent)	Maximum concentration (ng/L)	Detection frequency (in percent)	Maximum concentration (ng/L)
Atrazine	Herbicide	—	—	4%	39.1
Azoxystrobin	Fungicide	88%	368	75%	39.8
Boscalid	Fungicide	15%	82.9	96%	112
Carbaryl	Insecticide	9%	26.5	8%	55.9
Chlorothalonil	Fungicide	6%	3.0	—	—
Chlorpyrifos	Insecticide	—	—	8%	14.7
Clomazone	Herbicide	35%	670	—	—
Clothianidin	Insecticide	—	—	13%	1.9
Cyprodinil	Fungicide	3%	6.6	4%	9.2
DCPA	Herbicide	15%	5.4	8%	5.3
Desulfinylfipronil	Degradate	—	—	4%	6.3
3,4-Dichloroaniline (3,4-DCA)	Degradate	97%	364	92%	9.0
N-(3,4-Dichlorophenyl)-*N*'-methylurea (DCPMU)	Degradate	14%	8.5	83%	111
3,4-Dichlorophenylurea (DCPU)	Degradate	—	—	13%	10.8
Difenoconazole	Fungicide	—	—	4%	18.2
Diuron	Herbicide	56%	42.6	96%	695
S-Ethyl dipropylthiocarbamate (EPTC)	Herbicide	—	—	4%	49.2
Famoxadone	Fungicide	12%	21.6	—	—
Fipronil	Insecticide	15%	20.4	—	—
Hexazinone	Herbicide	100%	130	100%	984
Imazalil	Fungicide	15%	30.7	4%	53.4
Imidacloprid	Insecticide	6%	1.7	8%	2.3
Iprodione	Fungicide	—	—	4%	21.5
Metolachlor	Herbicide	38%	41.9	100%	127
Myclobutanil	Fungicide	3%	1.6	—	—
Napropamide	Herbicide	3%	31.4	—	—
Oxyfluorfen	Herbicide	3%	21.5	8%	14.2
Pendimethalin	Herbicide	9%	21.4	33%	108
Permethirn	Insecticide	3%	5.3	—	—
Piperonyl butoxide	Synergist	6%	79.9	—	—
Prometryn	Herbicide	—	—	17%	155
Propanil	Herbicide	12%	110	—	—
Propiconazole	Fungicide	29%	28.4	17%	15.3
Pyraclostrobin	Fungicide	—	—	8%	20.2
Simazine	Herbicide	53%	87.7	83%	524
Thiobencarb	Herbicide	12%	81.9	—	—
Trifluralin	Herbicide	3%	2.3	—	—

Table 7. Pesticide concentrations measured in environmental water samples collected from the Sacramento River, May 2012 through July 2013.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, atrazine, bifenthrin, butylate, carbofuran, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p*'-DDD, *p,p*'-DDE, *p,p*'-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,4-dichlorophenylurea (DCPU), 3,5-dichloroaniline, difenoconazole, (*E*)-Dimethomorph, dinotefuran, *S*-Ethyl dipropylthiocarbamate (EPTC), esfenvalerate, ethalfluralin, etofenprox, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, pebulate, pentachloroanisole, pentachloronitrobenzene, phenothrin, phosmet, prometon, prometryn, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, triadimefon, triadimenol, trifloxstrobin, triflumizole, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost and was not analyzed; ng/L, nanograms per liter; —, not detected; *, storm sample]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Azoxystrobin (ng/L) [66589]	Boscalid (ng/L) [67550]	Carbaryl (ng/L) [65069]	Chlorothalonil (ng/L) [65071]	Clomazone (ng/L) [67562]	Cyprodinil (ng/L) [67574]	DCPA (ng/L) [65076]	DCPMU (ng/L) [68231]	3,4-Dichloroaniline (ng/L) [66584]
Sacramento River at Freeport	05/17/2012	11:35	—	—	—	—	65.9	—	—	—	—
Sacramento River at Freeport	05/30/2012	10:45	7.2	—	—	—	374	—	—	—	6.4
Sacramento River at Freeport	06/12/2012	11:05	9.9	7.4	—	—	537	(6.6)	—	—	18.1
Sacramento River at Freeport	06/20/2012	10:15	—	—	—	—	143	—	—	—	25.9
Sacramento River at Freeport	07/09/2012	13:15	—	—	—	—	32.0	—	—	—	333
Sacramento River at Freeport	07/24/2012	10:45	48.6	—	—	—	23.3	—	—	—	191
Sacramento River at Freeport	08/07/2012	11:05	128	—	—	—	10.0	—	—	—	50.5
Sacramento River at Freeport	08/22/2012	11:00	368	—	—	—	—	—	—	—	33.0
Sacramento River at Freeport	09/05/2012	10:45	201	3.8	—	—	—	—	—	—	30.8
Sacramento River at Freeport	09/18/2012	10:30	140	—	—	—	—	—	—	—	37.7
Sacramento River at Freeport	10/18/2012	12:23	13.4	—	—	—	—	—	—	—	5.8
Sacramento River at Freeport	10/29/2012	12:48	46.9	—	—	—	—	—	—	—	13.4
Sacramento River at Freeport	11/14/2012	10:18	88.0	—	—	—	—	—	—	—	27.7
Sacramento River at Freeport	11/27/2012	11:03	164	—	—	—	—	—	—	—	60.8
Sacramento River at Freeport	12/04/2012	11:23	33.0	—	—	—	—	—	—	8.5	45.5
Sacramento River at Freeport	12/19/2012	14:33	158	—	—	—	—	—	—	—	22.3
Sacramento River at Freeport	01/08/2013	13:33	99.3	—	—	—	—	—	—	—	26.4
Sacramento River at Freeport	01/22/2013	13:33	32.0	—	—	—	—	—	—	—	14.2
Sacramento River at Freeport	02/05/2013	12:43	53.6	—	—	—	—	—	—	—	15.9
Sacramento River at Freeport	02/19/2013	09:53	45.1	—	—	—	—	—	—	—	9.4
Sacramento River at Freeport	03/12/2013	11:33	22.2	—	—	(3.0)	—	—	—	—	6.5
Sacramento River at Freeport	03/28/2013	11:28	16.2	—	—	—	—	—	—	—	(3.3)
Sacramento River at Freeport	04/01/2013*	13:03	29.1	—	20.6	—	—	—	5.4	(1.9)	(4.0)
Sacramento River at Freeport	04/02/2013*	13:13	25.8	—	9.8	—	—	—	4.8	(1.9)	(3.3)
Sacramento River at Freeport	04/03/2013*	13:18	24.8	—	—	—	—	—	4.6	(1.9)	(3.5)
Sacramento River at Freeport	04/04/2013*	13:43	16.5	—	—	—	—	—	4.4	—	(1.7)
Sacramento River at Freeport	04/05/2013*	09:48	20.0	—	26.5	—	—	—	4.3	—	(2.3)
Sacramento River at Freeport	04/11/2013	11:03	(1.3)	6.4	—	—	—	—	—	—	(2.7)
Sacramento River at Freeport	04/26/2013	10:58	(2.6)	82.9	—	—	—	—	—	(2.3)	(4.5)
Sacramento River at Freeport	05/07/2013	11:38	—	—	—	—	96.6	—	—	—	(4.6)
Sacramento River at Freeport	05/30/2013	11:03	16.2	—	—	(2.3)	670	—	—	—	25.1
Sacramento River at Freeport	06/13/2013	11:28	43.5	7.0	—	—	216	—	—	—	363
Sacramento River at Freeport	06/26/2013	12:03	NA	NA	NA	NA	NA	NA	NA	—	364
Sacramento River at Freeport	07/11/2013	12:08	102	—	—	—	20.1	—	—	—	175
Sacramento River at Freeport	07/29/2013	12:33	299	—	—	—	8.6	—	—	—	42.9

Table 7. Pesticide concentrations measured in environmental water samples collected from the Sacramento River, May 2012 through July 2013.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, atrazine, bifenthrin, butylate, carbofuran, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,4-dichlorophenylurea (DCPU), 3,5-dichloroaniline, difenoconazole, (*E*)-Dimethomorph, dinotefuran, *S*-Ethyl dipropylthiocarbamate (EPTC), esfenvalerate, ethalfluralin, etofenprox, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, pebulate, pentachloroanisole, pentachloronitrobenzene, phenothrin, phosmet, prometon, prometryn, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, triadimefon, triadimenol, trifloxstrobin, triflumizole, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost and was not analyzed; ng/L, nanograms per liter; —, not detected; *, storm sample]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Diuron (ng/L) [66598]	Famoxadone (ng/L) [67609]	Fipronil (ng/L) [66604]	Hexazinone (ng/L) [65085]	Imazalil (ng/L) [67662]	Imidacloprid (ng/L) [68426]	Metolachlor (ng/L) [65090]	Myclobutanil (ng/L) [66632]	Napropamide (ng/L) [65092]
Sacramento River at Freeport	05/17/2012	11:35	4.8	—	—	130	—	—	24.6	—	—
Sacramento River at Freeport	05/30/2012	10:45	7.3	—	—	128	—	—	27.4	—	31.4
Sacramento River at Freeport	06/12/2012	11:05	6.7	—	—	82.6	—	—	24.4	—	—
Sacramento River at Freeport	06/20/2012	10:15	(2.1)	—	—	44.7	—	—	15.9	—	—
Sacramento River at Freeport	07/09/2012	13:15	—	—	—	51.4	—	—	—	—	—
Sacramento River at Freeport	07/24/2012	10:45	—	—	—	54.2	—	—	—	—	—
Sacramento River at Freeport	08/07/2012	11:05	—	—	—	74.2	—	—	—	—	—
Sacramento River at Freeport	08/22/2012	11:00	—	—	—	57.4	—	—	—	—	—
Sacramento River at Freeport	09/05/2012	10:45	—	21.6	—	47.0	—	—	—	—	—
Sacramento River at Freeport	09/18/2012	10:30	—	15.4	—	46.5	—	—	—	—	—
Sacramento River at Freeport	10/18/2012	12:23	26.0	—	—	32.8	—	—	—	—	—
Sacramento River at Freeport	10/29/2012	12:48	25.1	—	—	38.9	—	—	—	—	—
Sacramento River at Freeport	11/14/2012	10:18	(2.6)	9.1	—	58.6	—	—	—	—	—
Sacramento River at Freeport	11/27/2012	11:03	7.9	16.6	—	57.4	—	—	—	—	—
Sacramento River at Freeport	12/04/2012	11:23	25.6	—	—	28.4	—	—	9.4	—	—
Sacramento River at Freeport	12/19/2012	14:33	—	—	—	79.4	—	—	7.5	—	—
Sacramento River at Freeport	01/08/2013	13:33	(2.5)	—	—	67.8	—	—	4.6	—	—
Sacramento River at Freeport	01/22/2013	13:33	—	—	—	44.1	—	—	—	—	—
Sacramento River at Freeport	02/05/2013	12:43	—	—	—	46.2	—	—	—	—	—
Sacramento River at Freeport	02/19/2013	09:53	—	—	—	36.4	—	—	—	—	—
Sacramento River at Freeport	03/12/2013	11:33	—	—	—	77.8	—	—	—	—	—
Sacramento River at Freeport	03/28/2013	11:28	—	—	—	80.3	—	—	—	—	—
Sacramento River at Freeport	04/01/2013*	13:03	42.6	—	20.4	82.3	30.7	(1.1)	—	—	—
Sacramento River at Freeport	04/02/2013*	13:13	17.3	—	13.0	83.9	27.6	(1.7)	—	—	—
Sacramento River at Freeport	04/03/2013*	13:18	42.2	—	8.2	96.8	29.0	—	—	—	—
Sacramento River at Freeport	04/04/2013*	13:43	11.8	—	10.0	85.4	29.4	—	—	—	—
Sacramento River at Freeport	04/05/2013*	09:48	7.8	—	8.3	87.0	24.6	—	—	—	—
Sacramento River at Freeport	04/11/2013	11:03	3.2	—	—	73.4	—	—	—	—	—
Sacramento River at Freeport	04/26/2013	10:58	18.2	—	—	55.0	—	—	22.7	(1.6)	—
Sacramento River at Freeport	05/07/2013	11:38	(2.5)	—	—	109	—	—	20.6	—	—
Sacramento River at Freeport	05/30/2013	11:03	3.9	—	—	42.2	—	—	41.9	—	—
Sacramento River at Freeport	06/13/2013	11:28	—	—	—	54.2	—	—	9.4	—	—
Sacramento River at Freeport	06/26/2013	12:03	—	NA	NA	NA	NA	—	NA	NA	NA
Sacramento River at Freeport	07/11/2013	12:08	—	—	—	62.7	—	—	11.4	—	—
Sacramento River at Freeport	07/29/2013	12:33	—	—	—	49.1	—	—	5.7	—	—

Table 7. Pesticide concentrations measured in environmental water samples collected from the Sacramento River, May 2012 through July 2013.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, atrazine, bifenthrin, butylate, carbofuran, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,4-dichlorophenylurea (DCPU), 3,5-dichloroaniline, difenoconazole, (*E*)-Dimethomorph, dinotefuran, EPTC, esfenvalerate, ethalfluralin, etofenprox, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, pebulate, pentachloroanisole, pentachloronitrobenzene, phenothrin, phosmet, prometon, prometryn, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, triadimefon, triadimenol, trifloxstrobin, triflumizole, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost and was not analyzed; ng/L, nanograms per liter; —, not detected; *, storm sample]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Oxyflurofen (ng/L) [65093]	Pendimethalin (ng/L) [65098]	Permethrin (ng/L) [65099]	Piperonyl butoxide (ng/L) [65102]	Propanil (ng/L) [66641]	Propiconazole (ng/L) [66643]	Simazine (ng/L) [65105]	Thiobencarb (ng/L) [65107]	Trifluralin (ng/L) [65108]
Sacramento River at Freeport	05/17/2012	11:35	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	05/30/2012	10:45	—	—	—	—	—	—	—	59.7	—
Sacramento River at Freeport	06/12/2012	11:05	—	—	—	—	—	8.2	—	81.9	—
Sacramento River at Freeport	06/20/2012	10:15	—	—	—	—	—	—	—	17.9	—
Sacramento River at Freeport	07/09/2012	13:15	—	—	—	—	97.6	—	—	—	—
Sacramento River at Freeport	07/24/2012	10:45	—	—	—	—	41.9	—	—	—	—
Sacramento River at Freeport	08/07/2012	11:05	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	08/22/2012	11:00	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	09/05/2012	10:45	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	09/18/2012	10:30	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	10/18/2012	12:23	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	10/29/2012	12:48	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	11/14/2012	10:18	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	11/27/2012	11:03	—	—	—	—	—	(4.9)	41.6	—	—
Sacramento River at Freeport	12/04/2012	11:23	—	—	—	—	—	—	78.6	—	—
Sacramento River at Freeport	12/19/2012	14:33	—	21.4	—	—	—	—	63.0	—	—
Sacramento River at Freeport	01/08/2013	13:33	—	5.0	—	—	—	—	87.7	—	—
Sacramento River at Freeport	01/22/2013	13:33	—	—	—	—	—	—	28.9	—	—
Sacramento River at Freeport	02/05/2013	12:43	—	—	—	—	—	—	9.4	—	—
Sacramento River at Freeport	02/19/2013	09:53	—	15.1	—	—	—	—	17.8	—	—
Sacramento River at Freeport	03/12/2013	11:33	—	—	—	—	—	—	29.0	—	—
Sacramento River at Freeport	03/28/2013	11:28	21.5	—	—	—	—	—	45.3	—	—
Sacramento River at Freeport	04/01/2013*	13:03	—	—	—	—	—	26.7	38.1	—	—
Sacramento River at Freeport	04/02/2013*	13:13	—	—	—	—	—	9.8	73.0	—	—
Sacramento River at Freeport	04/03/2013*	13:18	—	—	—	—	—	5.8	43.1	—	—
Sacramento River at Freeport	04/04/2013*	13:43	—	—	—	—	—	9.6	62.5	—	—
Sacramento River at Freeport	04/05/2013*	09:48	—	—	—	—	—	9.5	66.5	—	—
Sacramento River at Freeport	04/11/2013	11:03	—	—	—	—	—	—	23.7	—	—
Sacramento River at Freeport	04/26/2013	10:58	—	—	—	—	—	—	—	—	—
Sacramento River at Freeport	05/07/2013	11:38	—	—	5.3	—	—	—	11.6	—	2.3
Sacramento River at Freeport	05/30/2013	11:03	—	—	—	—	—	—	—	71.9	—
Sacramento River at Freeport	06/13/2013	11:28	—	—	—	—	110	11.8	5.2	—	—
Sacramento River at Freeport	06/26/2013	12:03	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sacramento River at Freeport	07/11/2013	12:08	—	—	—	14.6	77.6	12.8	(4.4)	—	—
Sacramento River at Freeport	07/29/2013	12:33	—	—	—	79.9	—	28.4	—	—	—

Table 8. Pesticide concentrations measured in environmental water samples collected from the San Joaquin River, May 2012 through April 2013.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, bifenthrin, butylate, carbofuran, chlorothalonil, clomazone, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, diazinon, 3,5-dichloroaniline, (*E*)-Dimethomorph, dinotefuran, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, t-fluvalinate, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, propanil, propyzamide, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost; ng/L, nanograms per liter; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Atrazine ng/L [65065]	Azoxystrobin ng/L [66589]	Boscalid ng/L [67550]	Carbaryl ng/L [65069]	Chlorpyrifos ng/L [65072]	Clothianidin ng/L [68221]	Cyprodinil ng/L [67574]	DCPA ng/L [65076]	DCPMU ng/L [68231]
San Joaquin River near Vernalis	05/16/2012	11:00	—	—	11.4	—	14.7	—	—	—	21.9
San Joaquin River near Vernalis	05/30/2012	12:00	—	—	10.7	—	13.5	—	—	—	11.4
San Joaquin River near Vernalis	06/06/2012	12:00	39.1	14.3	25.8	—	—	—	9.2	—	32.3
San Joaquin River near Vernalis	06/21/2012	12:30	—	—	5.7	—	—	—	—	—	19.3
San Joaquin River near Vernalis	07/02/2012	12:00	—	—	10.5	—	—	—	—	—	17.2
San Joaquin River near Vernalis	07/25/2012	11:00	—	12.2	11.8	—	—	(1.9)	—	—	13.6
San Joaquin River near Vernalis	08/08/2012	11:50	—	7.0	7.5	—	—	(0.9)	—	—	6.6
San Joaquin River near Vernalis	08/23/2012	12:30	—	24.5	18.4	—	—	—	—	—	5.7
San Joaquin River near Vernalis	09/06/2012	14:00	—	39.8	9.7	—	—	—	—	—	4.6
San Joaquin River near Vernalis	09/20/2012	10:10	—	19.9	—	—	—	(1.9)	—	—	5.1
San Joaquin River near Vernalis	10/17/2012	11:43	—	14.9	6.8	—	—	—	—	—	—
San Joaquin River near Vernalis	10/30/2012	10:48	—	17.6	9.0	(1.1)	—	—	—	—	—
San Joaquin River near Vernalis	11/14/2012	11:13	—	8.3	4.9	—	—	—	—	—	—
San Joaquin River near Vernalis	11/26/2012	12:23	—	6.8	7.8	—	—	—	—	—	—
San Joaquin River near Vernalis	12/05/2012	15:43	—	9.1	12.1	—	—	—	—	—	10.7
San Joaquin River near Vernalis	12/18/2012	11:33	—	7.5	7.7	—	—	—	—	—	4.8
San Joaquin River near Vernalis	01/10/2013	11:03	—	25.6	112	—	—	—	—	—	11.5
San Joaquin River near Vernalis	01/24/2013	11:03	—	9.0	10.0	—	—	—	—	—	4.6
San Joaquin River near Vernalis	02/07/2013	10:13	—	9.1	10.4	55.9	—	—	—	—	10.5
San Joaquin River near Vernalis	02/27/2013	11:23	—	9.2	9.7	—	—	—	—	—	85.1
San Joaquin River near Vernalis	03/14/2013	12:03	—	—	91.4	—	—	—	—	4.7	111
San Joaquin River near Vernalis	03/25/2013	11:48	—	16.3	100	—	—	—	—	5.3	97.9
San Joaquin River near Vernalis	04/11/2013	10:23	—	3.7	53.7	—	—	—	—	—	50.2
San Joaquin River near Vernalis	04/23/2013	12:43	—	—	21.6	—	—	—	—	—	42.4

Table 8. Pesticide concentrations measured in environmental water samples collected from the San Joaquin River, May 2012 through April 2013.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, bifenthrin, butylate, carbofuran, chlorothalonil, clomazone, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, diazinon, 3,5-dichloroaniline, (*E*)-Dimethomorph, dinotefuran, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, t-fluvalinate, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, propanil, propyzamide, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost; ng/L, nanograms per liter; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	DCPU ng/L [68226]	Desulfinylfipronil ng/L [66607]	3,4-Dichloroaniline ng/L [66584]	Difenoconazole ng/L [67582]	Diuron ng/L [66598]	EPTC ng/L [65080]	Hexazinone ng/L [65085]	Imazalil ng/L [67662]
San Joaquin River near Vernalis	05/16/2012	11:00	—	—	—	—	44.6	—	99.1	—
San Joaquin River near Vernalis	05/30/2012	12:00	—	—	—	—	17.3	—	116	—
San Joaquin River near Vernalis	06/06/2012	12:00	—	—	(2.6)	18.2	37.1	—	108	53.4
San Joaquin River near Vernalis	06/21/2012	12:30	—	—	7.3	—	23.8	—	21.7	—
San Joaquin River near Vernalis	07/02/2012	12:00	—	—	5.2	—	19.2	—	71.5	—
San Joaquin River near Vernalis	07/25/2012	11:00	—	—	8.3	—	13.5	—	29.5	—
San Joaquin River near Vernalis	08/08/2012	11:50	—	—	(4.9)	—	8.1	49.2	19.6	—
San Joaquin River near Vernalis	08/23/2012	12:30	—	6.3	(3.0)	—	4.9	—	32.7	—
San Joaquin River near Vernalis	09/06/2012	14:00	—	—	(2.4)	—	5.0	—	(5.5)	—
San Joaquin River near Vernalis	09/20/2012	10:10	—	—	6.1	—	6.3	—	15.5	—
San Joaquin River near Vernalis	10/17/2012	11:43	—	—	(2.3)	—	—	—	14.7	—
San Joaquin River near Vernalis	10/30/2012	10:48	—	—	(2.3)	—	(3.1)	—	18.2	—
San Joaquin River near Vernalis	11/14/2012	11:13	—	—	(5.1)	—	(1.9)	—	37.9	—
San Joaquin River near Vernalis	11/26/2012	12:23	—	—	(4.6)	—	(1.9)	—	35.0	—
San Joaquin River near Vernalis	12/05/2012	15:43	—	—	7.0	—	64.0	—	49.9	—
San Joaquin River near Vernalis	12/18/2012	11:33	—	—	(3.1)	—	21.9	—	69.6	—
San Joaquin River near Vernalis	01/10/2013	11:03	—	—	(3.4)	—	429	—	116	—
San Joaquin River near Vernalis	01/24/2013	11:03	—	—	(3.9)	—	24.2	—	48.1	—
San Joaquin River near Vernalis	02/07/2013	10:13	—	—	6.3	—	114	—	58.5	—
San Joaquin River near Vernalis	02/27/2013	11:23	8.4	—	5.4	—	695	—	589	—
San Joaquin River near Vernalis	03/14/2013	12:03	10.8	—	9.0	—	539	—	984	—
San Joaquin River near Vernalis	03/25/2013	11:48	—	—	5.3	—	409	—	926	—
San Joaquin River near Vernalis	04/11/2013	10:23	—	—	6.4	—	123	—	255	—
San Joaquin River near Vernalis	04/23/2013	12:43	5.8	—	(4.4)	—	69.4	—	171	—

Table 8. Pesticide concentrations measured in environmental water samples collected from the San Joaquin River, May 2012 through April 2013.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. Concentrations are in nanograms per liter. Results in parenthesis ( ) are below method detection limits and are estimates. The following compounds were analyzed but were not detected in any samples: acetamiprid, alachlor, allethrin, bifenthrin, butylate, carbofuran, chlorothalonil, clomazone, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, deltamethrin, diazinon, 3,5-dichloroaniline, (*E*)-Dimethomorph, dinotefuran, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, t-fluvalinate, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, propanil, propyzamide, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hours:minutes; mm/dd/yyyy, month/day/year; NA, sample lost; ng/L, nanograms per liter; —, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Imidacloprid ng/L [68426]	Iprodione ng/L [66617]	Metolachlor ng/L [65090]	Oxyflurofen ng/L [65093]	Pendimethalin ng/L [65098]	Prometryn ng/L [65103]	Propiconazole ng/L [66643]	Pyraclostrobin ng/L [66646]	Simazine ng/L [65105]
San Joaquin River near Vernalis	05/16/2012	11:00	—	—	38.0	—	—	—	—	—	39.8
San Joaquin River near Vernalis	05/30/2012	12:00	—	—	127	—	—	—	—	—	83.3
San Joaquin River near Vernalis	06/06/2012	12:00	—	—	122	—	—	—	15.3	20.2	58.9
San Joaquin River near Vernalis	06/21/2012	12:30	—	—	43.7	—	—	—	—	—	—
San Joaquin River near Vernalis	07/02/2012	12:00	—	—	85.3	—	16.3	—	—	—	9.8
San Joaquin River near Vernalis	07/25/2012	11:00	—	—	122	—	—	—	—	—	24.9
San Joaquin River near Vernalis	08/08/2012	11:50	—	—	59.0	—	—	—	—	—	12.7
San Joaquin River near Vernalis	08/23/2012	12:30	—	—	36.8	—	—	—	—	—	—
San Joaquin River near Vernalis	09/06/2012	14:00	—	—	4.8	—	—	—	—	—	—
San Joaquin River near Vernalis	09/20/2012	10:10	—	—	7.7	—	—	—	—	—	—
San Joaquin River near Vernalis	10/17/2012	11:43	—	—	6.0	—	—	—	—	—	(3.9)
San Joaquin River near Vernalis	10/30/2012	10:48	—	—	6.7	—	7.5	—	—	—	(3.1)
San Joaquin River near Vernalis	11/14/2012	11:13	—	—	4.3	—	—	155	—	—	10.7
San Joaquin River near Vernalis	11/26/2012	12:23	—	—	9.0	—	—	—	—	—	8.7
San Joaquin River near Vernalis	12/05/2012	15:43	—	—	21.9	—	—	—	—	—	270
San Joaquin River near Vernalis	12/18/2012	11:33	—	—	7.9	—	9.4	—	—	—	29.2
San Joaquin River near Vernalis	01/10/2013	11:03	—	—	18.2	—	44.0	—	—	—	524
San Joaquin River near Vernalis	01/24/2013	11:03	—	—	4.2	—	17.7	—	—	—	48.9
San Joaquin River near Vernalis	02/07/2013	10:13	—	—	(1.4)	—	—	—	—	—	21.1
San Joaquin River near Vernalis	02/27/2013	11:23	(2.3)	21.5	53.0	—	58.8	—	—	—	26.4
San Joaquin River near Vernalis	03/14/2013	12:03	(2.2)	—	98.0	—	108	28.0	12.2	—	51.4
San Joaquin River near Vernalis	03/25/2013	11:48	—	—	47.2	14.2	89.2	19.8	8.7	14.3	76.5
San Joaquin River near Vernalis	04/11/2013	10:23	—	—	26.4	10.8	—	6.5	(3.8)	—	101
San Joaquin River near Vernalis	04/23/2013	12:43	—	—	30.3	—	—	—	—	—	27.8

Table 9. Water-quality parameter data measured in water samples collected from the Sacramento and San Joaquin Rivers, May 2012 through July 2013.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. **Abbreviations**: hh:mm, hours:minutes; mg/L, miligrams/liter; mm/dd/yyyy, month/day/year; —, data not collected; °C, degrees Celsius; µS/cm, microsiemens per centimeter]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Water temperature (°C) [00010]	Specific conductance (µS/cm) [00095]	Dissolved oxygen (mg/L) [00300]	pH [00400]
Sacramento River at Freeport	05/17/2012	11:35	19.2	114	9.0	7.8
Sacramento River at Freeport	05/30/2012	10:45	19.6	139	9.1	7.7
Sacramento River at Freeport	06/12/2012	11:05	19.9	133	9.3	7.6
Sacramento River at Freeport	06/20/2012	10:15	21.4	—	8.7	7.6
Sacramento River at Freeport	07/09/2012	13:15	22.0	—	8.8	7.6
Sacramento River at Freeport	07/24/2012	10:45	20.9	119	8.8	7.5
Sacramento River at Freeport	08/07/2012	11:05	20.2	118	—	7.7
Sacramento River at Freeport	08/22/2012	11:00	21.2	—	8.7	7.8
Sacramento River at Freeport	09/05/2012	10:45	20.0	—	8.9	7.8
Sacramento River at Freeport	09/18/2012	10:30	19.2	—	8.9	7.8
Sacramento River at Freeport	10/18/2012	12:23	18.6	128	9.2	7.7
Sacramento River at Freeport	10/29/2012	12:48	15.3	236	10.0	7.6
Sacramento River at Freeport	11/14/2012	10:18	12.3	155	—	—
Sacramento River at Freeport	11/27/2012	11:03	12.4	160	9.0	7.5
Sacramento River at Freeport	12/04/2012	11:23	12.9	102	8.3	7.0
Sacramento River at Freeport	12/19/2012	14:33	9.2	168	10.3	7.7
Sacramento River at Freeport	01/08/2013	13:33	7.9	178	12.6	7.6
Sacramento River at Freeport	01/22/2013	13:33	7.7	172	—	7.9
Sacramento River at Freeport	02/05/2013	12:43	9.9	177	10.8	7.8
Sacramento River at Freeport	02/19/2013	09:53	10.6	151	10.8	7.5
Sacramento River at Freeport	03/12/2013	11:33	12.9	152	8.6	8.0
Sacramento River at Freeport	03/28/2013	11:28	14.8	135	10.1	7.7
Sacramento River at Freeport	04/01/2013	13:03	16.8	129	10.9	8.1
Sacramento River at Freeport	04/02/2013	13:13	16.7	143	11.2	8.2
Sacramento River at Freeport	04/03/2013	13:18	16.7	134	11.1	8.2
Sacramento River at Freeport	04/04/2013	13:43	16.6	125	10.4	8.0
Sacramento River at Freeport	04/05/2013	09:48	16.0	125	9.7	7.8
Sacramento River at Freeport	04/11/2013	11:03	15.8	146	7.3	7.8
Sacramento River at Freeport	04/26/2013	10:58	19.0	142	8.6	7.8
Sacramento River at Freeport	05/07/2013	11:38	19.4	122	8.0	7.6
Sacramento River at Freeport	05/30/2013	11:03	20.3	174	8.8	7.6
Sacramento River at Freeport	06/13/2013	11:28	21.4	141	8.0	7.6
Sacramento River at Freeport	06/26/2013	12:03	19.8	134	14.3	7.7
Sacramento River at Freeport	07/11/2013	12:08	21.5	126	8.0	7.9
Sacramento River at Freeport	07/29/2013	12:33	21.3	139	7.7	7.5
San Joaquin River near Vernalis	05/16/2012	11:00	17.9	264	9.2	7.7
San Joaquin River near Vernalis	05/30/2012	12:00	19.5	317	9.9	8.1
San Joaquin River near Vernalis	06/06/2012	12:00	19.1	525	10.4	8.3
San Joaquin River near Vernalis	06/21/2012	12:30	22.1	397	11.0	8.8
San Joaquin River near Vernalis	07/02/2012	12:00	23.5	—	—	—
San Joaquin River near Vernalis	07/25/2012	11:00	24.6	514	11.2	8.7
San Joaquin River near Vernalis	08/08/2012	11:50	24.6	581	9.9	8.6
San Joaquin River near Vernalis	08/23/2012	12:30	25.0	629	9.2	8.5
San Joaquin River near Vernalis	09/06/2012	14:00	23.0	640	8.9	8.1
San Joaquin River near Vernalis	09/20/2012	10:10	20.0	—	—	7.9
San Joaquin River near Vernalis	10/17/2012	11:43	17.3	402	9.5	7.8
San Joaquin River near Vernalis	10/30/2012	10:48	16.0	—	—	—
San Joaquin River near Vernalis	11/14/2012	11:13	12.0	712	10.3	7.9
San Joaquin River near Vernalis	11/26/2012	12:23	12.5	699	—	7.8
San Joaquin River near Vernalis	12/05/2012	15:43	—	—	—	—

Table 9. Water-quality parameter data measured in water samples collected from the Sacramento and San Joaquin Rivers, May 2012 through July 2013.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. **Abbreviations**: hh:mm, hours:minutes; mg/L, miligrams/liter; mm/dd/yyyy, month/day/year; —, data not collected; °C, degrees Celsius; µS/cm, microsiemens per centimeter]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Water temperature (°C) [00010]	Specific conductance (µS/cm) [00095]	Dissolved oxygen (mg/L) [00300]	pH [00400]
San Joaquin River near Vernalis	12/18/2012	11:33	10.7	840	9.9	7.8
San Joaquin River near Vernalis	01/10/2013	11:03	8.2	652	12.9	7.7
San Joaquin River near Vernalis	01/24/2013	11:03	9.9	969	9.9	7.8
San Joaquin River near Vernalis	02/07/2013	10:13	11.3	767	10.2	7.9
San Joaquin River near Vernalis	02/27/2013	11:23	17.3	402	9.5	7.8
San Joaquin River near Vernalis	03/14/2013	12:03	17.1	822	9.8	8.2
San Joaquin River near Vernalis	03/25/2013	11:48	16.0	10	10.0	7.9
San Joaquin River near Vernalis	04/11/2013	10:23	19.3	—	—	—
San Joaquin River near Vernalis	04/23/2013	12:43	17.5	276	8.6	7.9

Sacramento River

At least three pesticides or pesticide degradates were detected in every Sacramento River water sample analyzed by GC/MS and LC/MS/MS. A total of 27 compounds were detected: 8 fungicides, 14 herbicides/degradates, 4 insecticides, and 1 synergist (fig. 3). The most frequently detected compounds were the herbicide hexazinone (100 percent of samples), followed by the degradate 3,4-dichloroaniline (97 percent), the fungicide azoxystrobin (88 percent), and the herbicides diuron (56 percent) and simazine (50 percent; table 6 and fig. 3). Insecticides were infrequently detected except during storm samples as described later in this section. The numbers of pesticides detected varied during the sampling period and tended to increase following rainfall events, as shown in figure 4, which depicts the numbers of pesticides detected in samples collected during the study and average daily rainfall calculated from data recorded at 19 measurement sites in the Central Valley (fig. 1) (California Irrigation Management Information System, 2013). The timing of pesticide detections corresponded to patterns of pesticide use in the upstream watershed as shown in figure 5, which depicts concentrations of four pesticides applied primarily to rice (azoxystrobin, clomazone, propanil, and thiobencarb), along with 3,4-dichloroaniline, which is a degradate of propanil in samples collected in 2012; and application amounts of these pesticides to rice in 2012 (California Department of Pesticide Regualtion, 2014).

Samples were collected from the Sacramento River at Freeport for 5 consecutive days following a moderate rainfall event (greater than 0.5 inch per day) that occurred in the Sacramento urban area on March 31, 2013. A second similar storm took place on April 4, 2013, during the 5-day sampling period. Twelve pesticides and (or) degradates were detected during the storm sampling period, including five (carbaryl, DCPA, fipronil, imazalil, and imidacloprid) that were not detected in any other Sacramento River samples (table 7). The average number of compounds detected in storm samples was 11, whereas the average number of compounds detected in non-storm samples during the study was 6.

Pesticide concentrations in Sacramento River samples ranged from below the respective MDLs to 670 ng/L (clomazone). Maximum concentrations of the compounds detected were less than 100 ng/L with the exceptions of azoxystrobin, clomazone, 3,4-dichloroaniline, hexazinone, and propanil (table 6). Box plots of concentrations of the most frequently detected pesticides in Sacramento River samples are shown in figure 6.

A number of pesticides had increased concentrations (compared to non-storm samples) or were only detected during the storm event sampled in April 2013. Concentrations of the fungicides imazalil and propiconazole; and the insecticides carbaryl, fipronil, and imidacloprid, which showed increased concentrations in response to the two episodes of rainfall that occurred during the storm-sampling period, are shown in figure 7. The insecticide fipronil was detected in two consecutive storm samples (April 1–2, 2013) at concentrations above the aquatic-life benchmark for chronic toxicity to invertebrates of 11 ng/L.

In addition, the pyrethroid insecticide permethrin was detected in one non-storm sample (May 7, 2013) at a concentration above the aquatic-life benchmark for chronic toxicity to invertebrates of 1.4 ng/L (U.S. Environmental Protection Agency, 2012). All other pesticides with established aquatic-life benchmarks were detected at concentrations below those benchmarks.

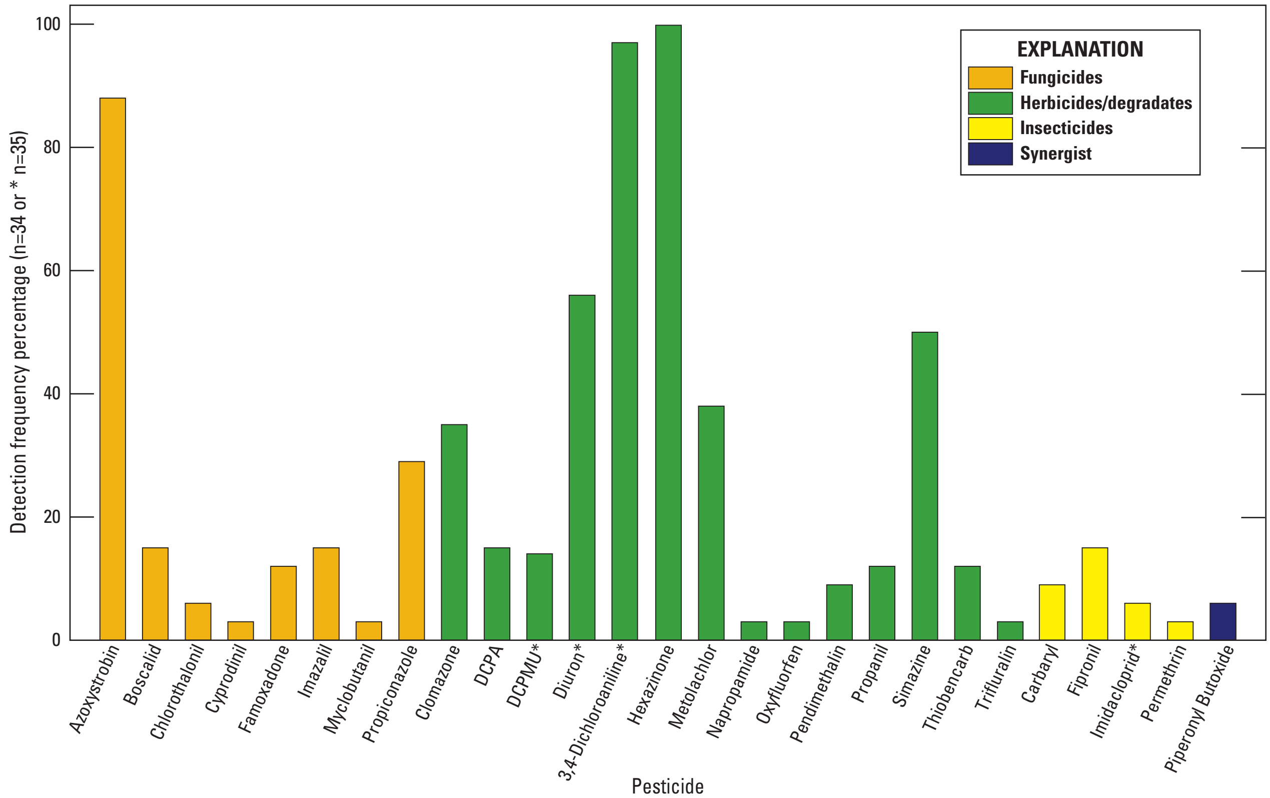

Figure 3. Pesticide detection frequencies at the Sacramento River at Freeport, May 2012 through July 2013.

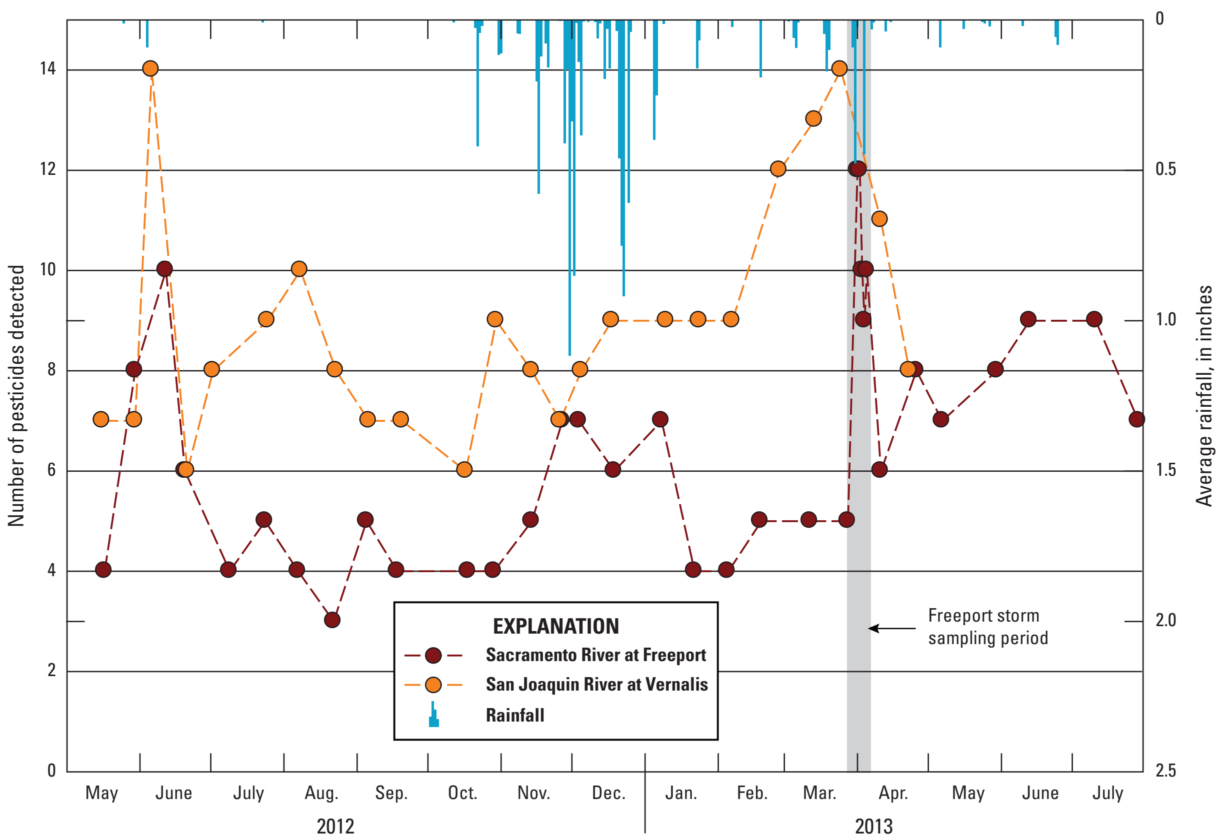

Figure 4. Numbers of pesticides detected in Sacramento River samples and San Joaquin River samples, and average daily rainfall in the Central Valley.

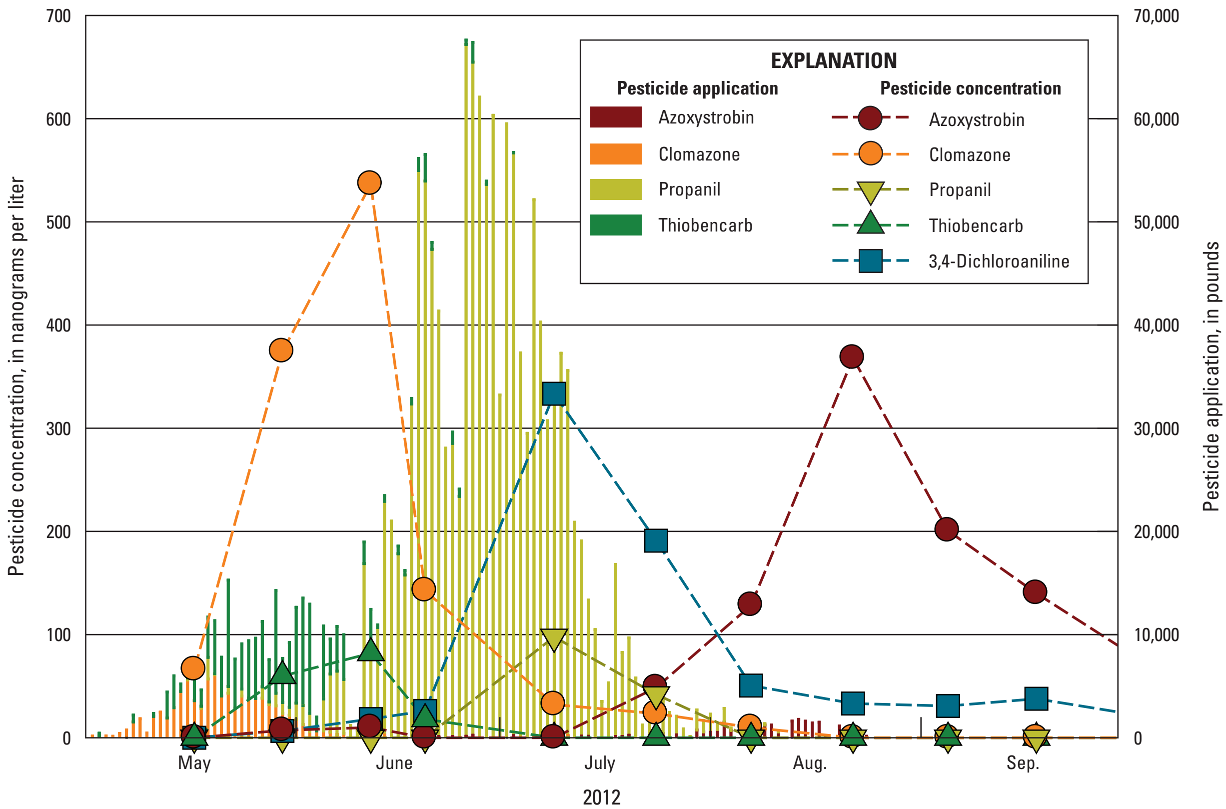

Figure 5. Concentrations of rice pesticides detected in Sacramento River samples, May 2012 through July 2013.

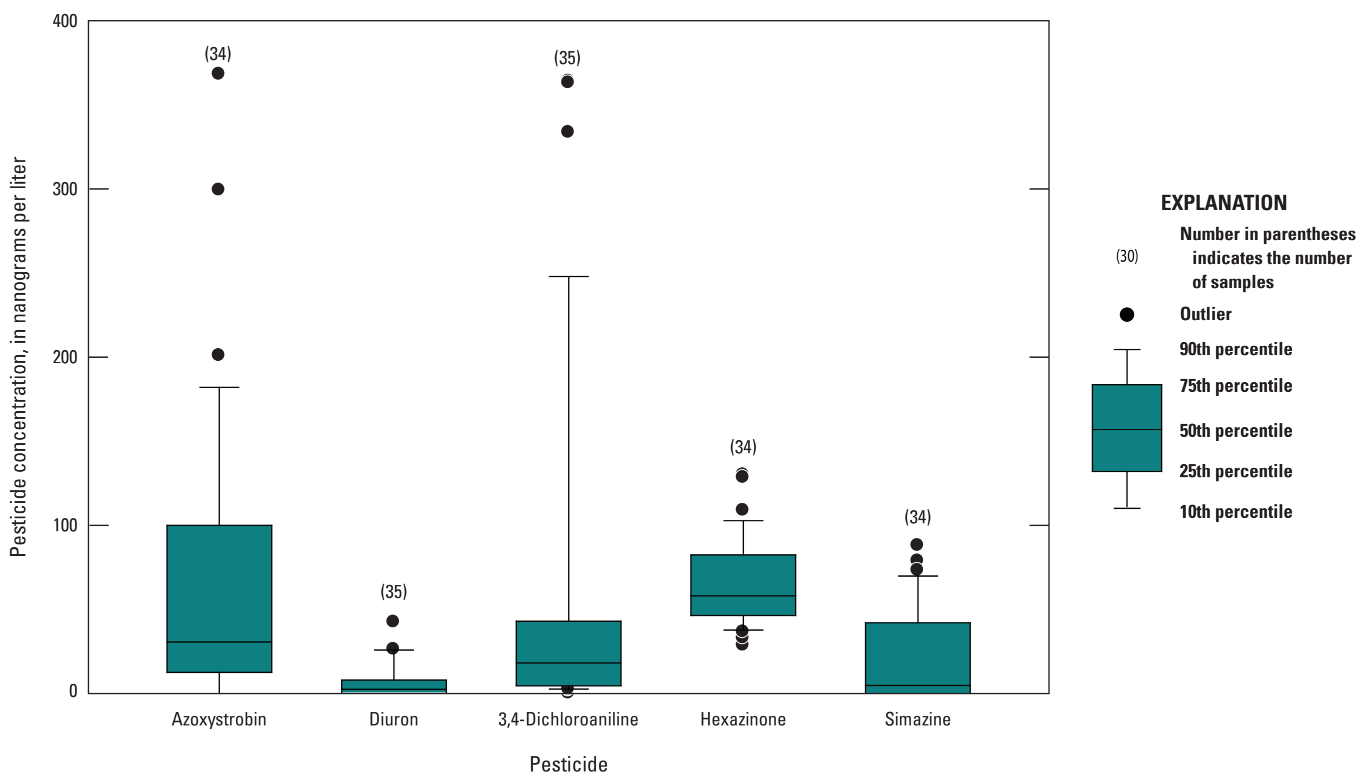

Figure 6. Concentrations of the most frequently detected pesticides in Sacramento River samples, May 2012 through July 2013.

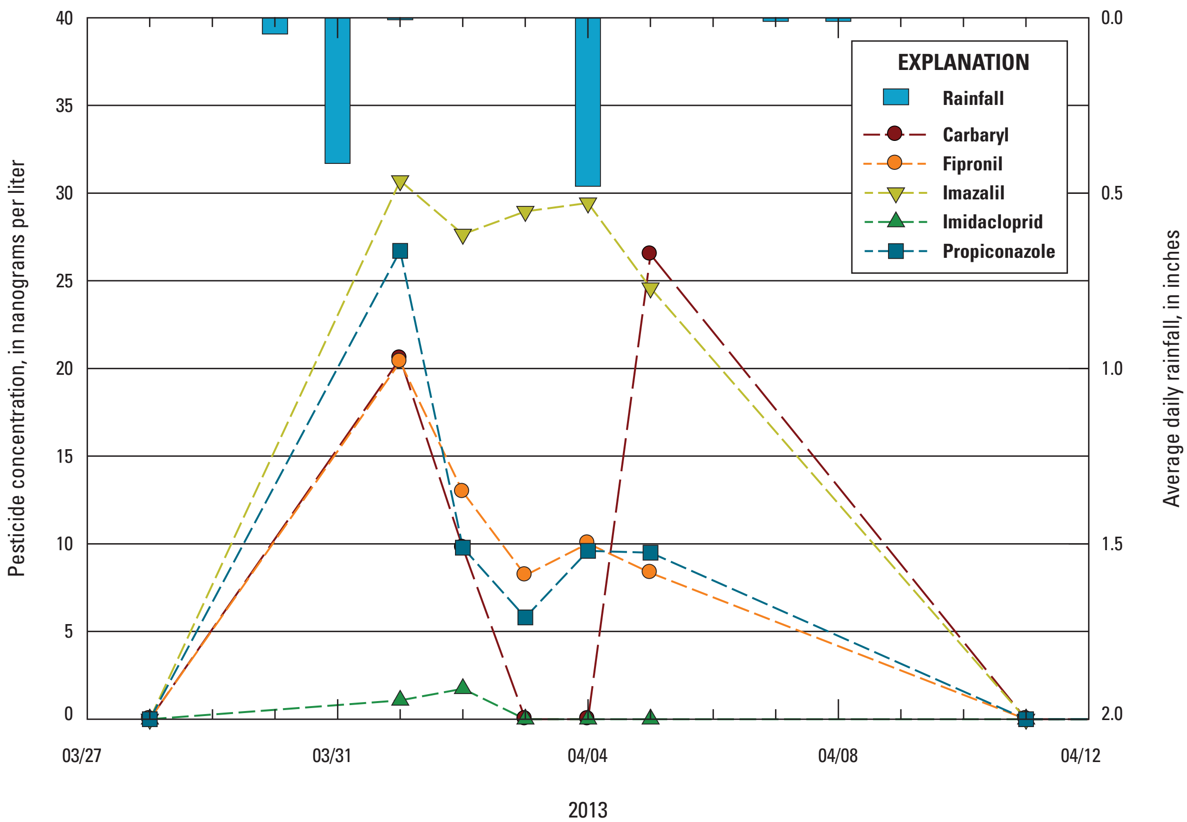

Figure 7. Concentrations of selected pesticides in Sacramento River storm samples collected April 1, 2013, through April 5, 2013, and average daily rainfall in the Sacramento Valley.

San Joaquin River

Surface-water samples collected from the San Joaquin River contained mixtures of 6–14 pesticides and (or) degradates (fig. 4). A total of 27 compounds were detected: 9 fungicides, 13 herbicides/degradates, and 5 insecticides/degradates (fig. 8). The most frequently detected compounds were the herbicides hexazinone and metolachlor (detected in 100 percent of samples), and diuron (96 percent); the fungicide boscalid (96 percent); the degradates 3,4-dicloroaniline (92 percent) and DCPMU (83 percent); the herbicide simazine (83 percent); and the fungicide azoxystrobin (75 percent; table 6, fig. 8). Insecticides were detected infrequently during the study. The numbers of pesticides detected varied during the sampling period (fig. 8) and did not consistently increase following rainfall events (fig. 4).

Maximum concentrations in San Joaquin River samples ranged from below the MDLs to as much as 984 ng/L (hexazinone; table 8). Maximum concentrations were less than 100 ng/L, with the exception of eight pesticides (boscalid, DCPMU, diuron, hexazinone, metolachlor, pendimethalin, prometryn, and simazine; table 6). Box plots showing the range in concentrations of the most frequently detected pesticides are shown in figure 9. Pesticide concentrations varied during the study, likely in response to applications in the watershed, and with the exception of the herbicide simazine, concentrations did not consistently increase following rainfall events. Measured concentrations of pesticides with established aquatic-life benchmarks were all below those benchmarks (U.S. Environmental Protection Agency, 2012).

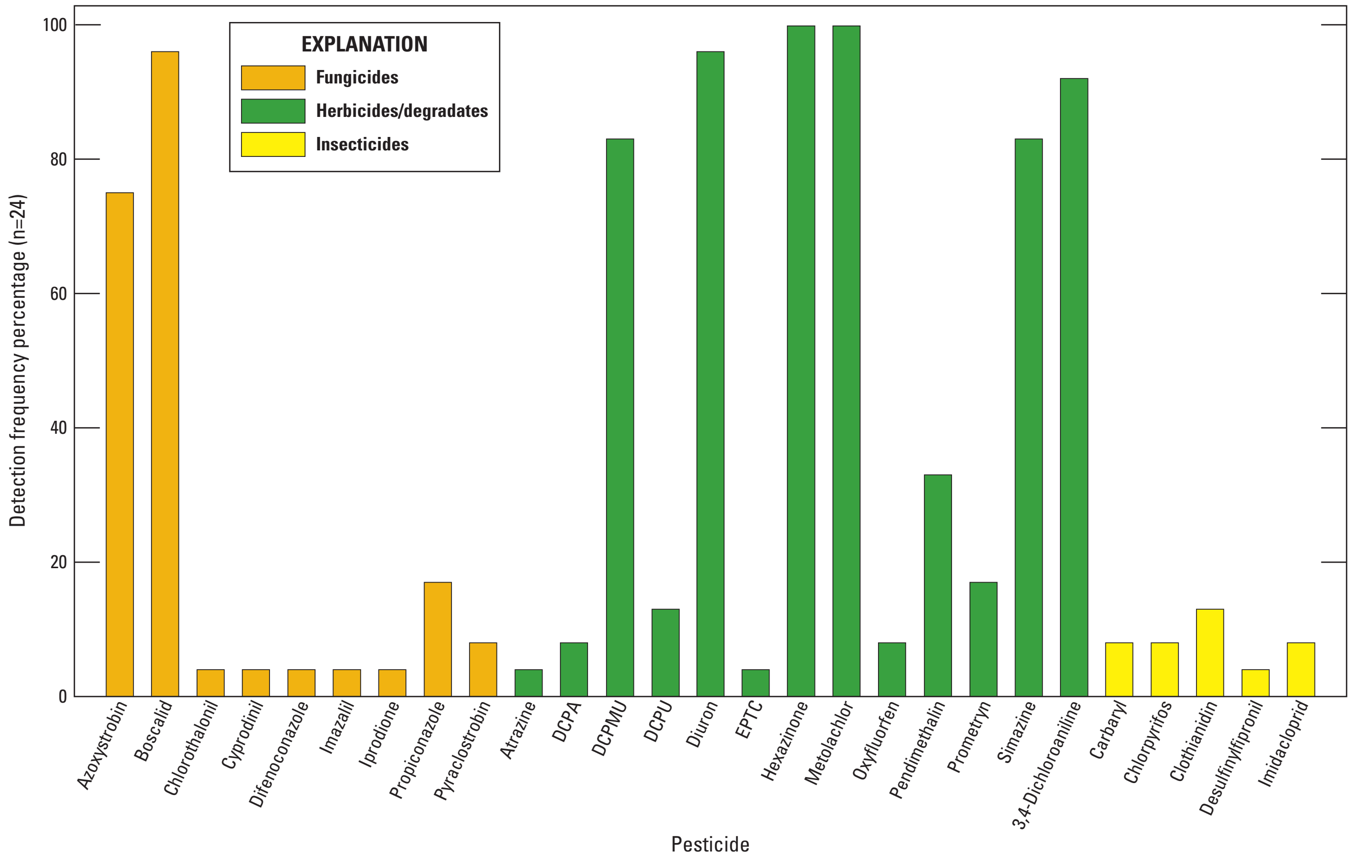

Figure 8. Pesticide detection frequencies at the San Joaquin River near Vernalis, May 2012 through April 2013.

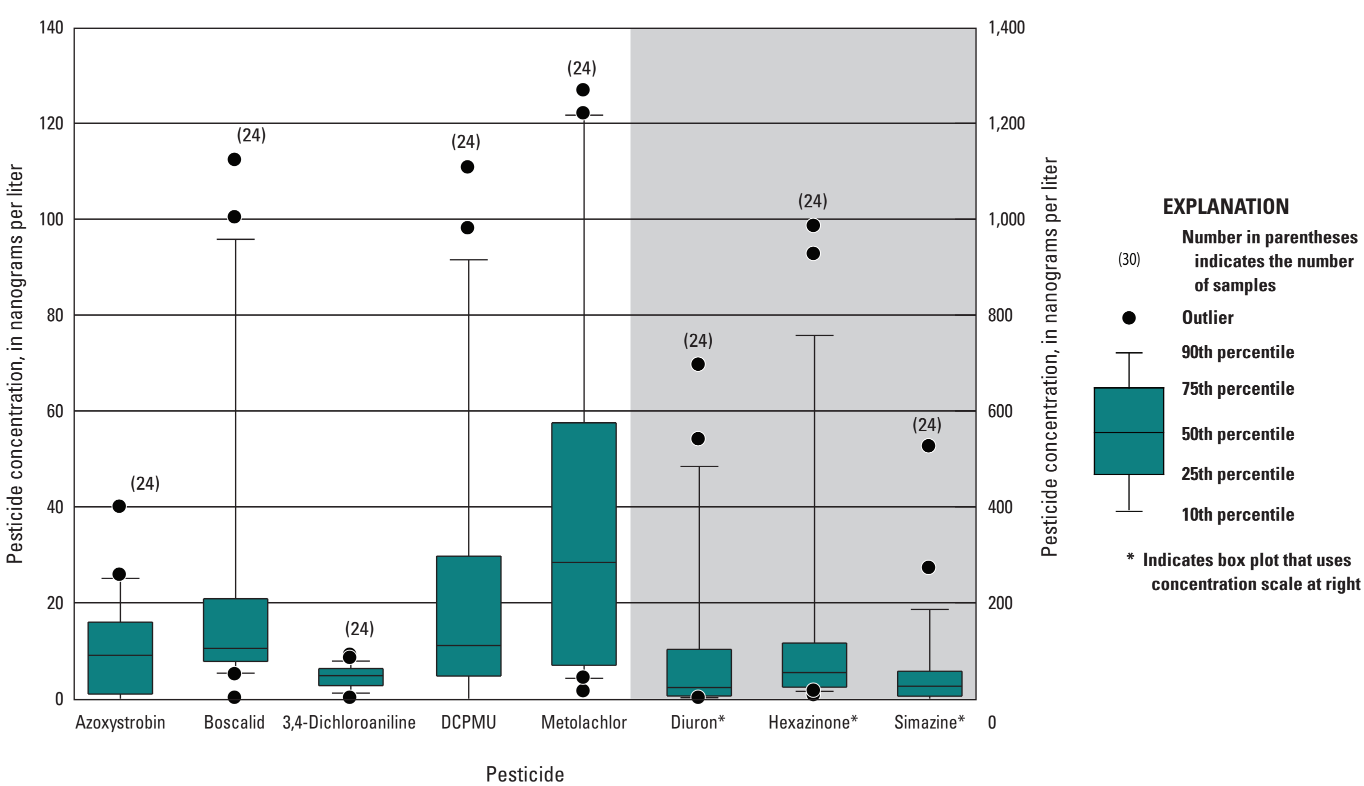

Figure 9. Concentrations of the most frequently detected pesticides in San Joaquin River samples, May 2012 through April 2013.

Summary

Concentrations of dissolved pesticides and pesticide degradates were measured twice per month from May 2012 through July 2013, and May 2012 through April 2013 at the Sacramento River at Freeport and the San Joaquin River near Vernalis, respectively. Hydrologic conditions during the sampling period were characterized by below-normal flows for the Sacramento River during most of the sampling period, while San Joaquin River flows were below normal throughout the period. Rainfall events of greater than 1 inch in 24 hours were rare in the Sacramento and San Joaquin Valley floor regions throughout the study period.

A total of 37 pesticides and degradates were detected during the study including 11 fungicides, 18 herbicides/degradates, 7 insecticides/degradates, and 1 synergist. The fungicide azoxystrobin; herbicides diuron, hexazinone metolachlor, and simazine; and the herbicide degradate 3,4-dichloroaniline were frequently detected in Sacramento and San Joaquin River samples. The fungicide boscalid, herbicide metolachlor, and herbicide degradate DCPMU were also frequently detected in San Joaquin River samples. All samples contained mixtures of multiple pesticides. Non-storm Sacramento River samples contained an average of 6 pesticides, and San Joaquin River samples contained an average of 9 pesticides, while storm samples collected from the Sacramento River contained an average of 11 pesticides. The number of pesticides in Sacramento River samples tended to increase following rainfall events, but this was generally not the case for pesticides detected in San Joaquin River samples. Insecticides were infrequently detected during the study except in storm-samples from the Sacramento River.

Maximum pesticide concentrations measured during the study ranged from below the respective method detection limits to 984 ng/L (hexazinone). In general the most frequently detected pesticides were measured at higher concentrations than less frequently detected pesticides. Pesticides detected at the highest concentrations in Sacramento River samples were, with the exception of hexazinone, primarily associated with rice agriculture. For those compounds frequently detected in both Sacramento and San Joaquin River samples (azoxystrobin, 3,4-dichloroaniline, diuron, hexazinone, metolachlor, and simazine), maximum concentrations were higher in San Joaquin River samples with the exceptions of azoxystrobin and 3,4-dichloroaniline. The insecticide fipronil was detected in two consecutive Sacramento River storm-samples at concentrations above the aquatic-life benchmark for chronic toxicity to invertebrates of 11 ng/L, and the pyrethroid insecticide permethrin was detected above its aquatic-life benchmark for chronic toxicity to invertebrates of 1.4 ng/L in one Sacramento River non-storm sample (U.S. Environmental Protection Agency, 2012). In San Joaquin River samples, concentrations of pesticides with established aquatic-life benchmarks were all below those benchmarks.

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For more information concerning this report, contact:

Director
U.S. Geological Survey
California Water Science Center
6000 J Street, Placer Hall
Sacramento, CA 95819
dc_ca@usgs.gov

or visit our Web site at:
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