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

Dissolved Pesticide Concentrations in the Sacramento-San Joaquin Delta and Grizzly Bay, California, 2011–12

Data Series 779

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

Cover. Photo was taken from the research vessel, Questuary, while traveling from San Francisco Bay to the Sacramento-San Joaquin Delta to collect samples for the project. The Richmond-San Rafael Bridge is in the background. (Photo taken by James L. Orlando, U.S. Geological Survey).

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SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2013

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
micrometer (µm)	0.00003937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
	Area	
hectare (ha)	0.003861	square mile (mi^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
microliter (µL)	0.000001057	quart (qt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
	Flow rate	
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
	Mass	
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

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

ACN	acetonitrile
ASE	accelerated solvent extractor
CDPR	California Department of Pesticide Regulation
DCM	dichloromethane
DCPMU	*N*-(3,4-Dichlorophenyl)-*N*'-methylurea
DCPU	3,4-Dichlorophenylurea
DOC	dissolved organic carbon
G	dimensionless ratio of acceleration due to centrifugal force divided by the acceleration due to gravity
GC	gas chromatography or gas chromatograph
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HCl	hydrochloric acid
HPLC	high performance liquid chromatography
L/min	liter per minute
LC/MS/MS	liquid chromatography tandem mass spectrometry
MDL	method detection limit
mL	milliliter
mL/min	milliliter per minute
mM	millimolar
MS	mass spectrometry or mass spectrometer
MSD	mass-selective detector
psi	pounds per square inch
QC	quality control
SD	standard deviation
SPE	solid-phase extraction
TIE	toxicity identification evaluation
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
V	volt
v/v	volume to volume
v/w	volume to weight
°C/min	degrees Celsius per minute
µA	microampere
µg/kg	microgram per kilogram

Acknowledgements

The authors would like to acknowledge Frank Wulff for sample collection during this project. This project was funded by the San Luis and Delta Mendota Water Authority and the U.S. Geological Survey Cooperative Water Program.

Dissolved Pesticide Concentrations in the Sacramento-San Joaquin Delta and Grizzly Bay, California, 2011–12

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

Abstract

Surface-water samples were collected from sites within the Sacramento-San Joaquin Delta and Grizzly Bay, California, during the spring in 2011 and 2012, and they were analyzed by the U.S. Geological Survey for a suite of 99 current-use pesticides and pesticide degradates. Samples were collected and analyzed as part of a collaborative project studying the occurrence and characteristics of phytoplankton in the San Francisco Estuary. Samples were analyzed by two separate laboratory methods employing gas chromatography/mass spectrometry or liquid chromatography with tandem mass spectrometry. Method detection limits ranged from 0.9 to 10.5 nanograms per liter (ng/L). Eighteen pesticides were detected in samples collected during 2011, and the most frequently detected compounds were the herbicides clomazone, diuron, hexazinone and metolachlor, and the diuron degradates 3,4-dichloroaniline and *N*-(3,4-dichlorophenyl)-*N*'-methylurea (DCPMU). Concentrations for all compounds were less than 75 ng/L, except for the rice herbicide clomazone and the fungicide tetraconazole, which had maximum concentrations of 535 and 511 ng/L, respectively. In samples collected in 2012, a total of 16 pesticides were detected. The most frequently detected compounds were the fungicides azoxystrobin and boscalid and the herbicides diuron, hexazinone, metolachlor, and simazine. Maximum concentrations for all compounds detected in 2012 were less than 75 ng/L, except for the fungicide azoxystrobin and the herbicides hexazinone and simazine, which were detected at up to 188, 134, and 140 ng/L, respectively.

Introduction

The Sacramento-San Joaquin Delta (Delta) and Grizzly Bay are areas of critical habitat for numerous species of fish, including the threatened delta smelt. Several important changes in the pelagic food web of this area have been documented over the last two decades, indicating that food for delta smelt and other threatened fishes is in short supply (Mueller-Solger and others, 2002; Sommer and others, 2007). There is evidence that primary production is inhibited in this region and that ammonium likely plays a major role in causing this inhibition (Dugdale and others, 2012; Parker and others, 2012). However, other contaminants such as current-use pesticides could also play a role in reducing phytoplankton abundance.

Previous studies have shown that herbicides can inhibit phytoplankton growth and influence species composition at environmental concentrations (Peterson and others, 1994; Ricart and others, 2009). The phenylurea herbicide, diuron in combination with other herbicides, has been shown to have additive toxic effects (Magnusson and others, 2010), and diuron in combination with its degradates 3,4-dichloroaniline, 3,4-dichlorophenylurea (DCPU), and *N*-(3,4-dichlorophenyl)-*N'*-methylurea (DCPMU) have been shown to act synergistically to inhibit phytoplankton growth (Gatidou and Thomaidis, 2007).

This study was carried out by the U.S. Geological Survey (USGS) to characterize the occurrence of current-use pesticides and pesticide degradates in the Delta and Grizzly Bay, California, during the spring of 2011 and 2012. Water samples for pesticide analysis were collected from three sites—two sites in the Delta and one site in Grizzly Bay—from mid-April to mid-June 2011. Two different Delta sites and the same Grizzly Bay site were sampled from the end of March through May 2012 (fig. 1 and table 1). The pesticides analyzed during this study included diuron and its primary degradates, which are thought to affect phytoplankton abundance.

Purpose and Scope

This report describes the methods and procedures used in measuring dissolved pesticide and organic carbon concentrations in filtered surface-water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay during 2011–12. Results are presented for a suite of 99 current-use pesticides, pesticide degradates, and dissolved organic carbon (DOC) in surface water. The purpose of the study was to determine spring current-use pesticide concentrations in the Sacramento-San Joaquin Delta and Grizzly Bay, California. These data were collected in support of a larger collaborative project attempting to better understand the occurrence and character of phytoplankton in the San Francisco Estuary. Data from this project will be used to develop toxicity identification evaluation (TIE) tests for native phytoplankton exposed to mixtures of current-use pesticides at environmental concentrations.

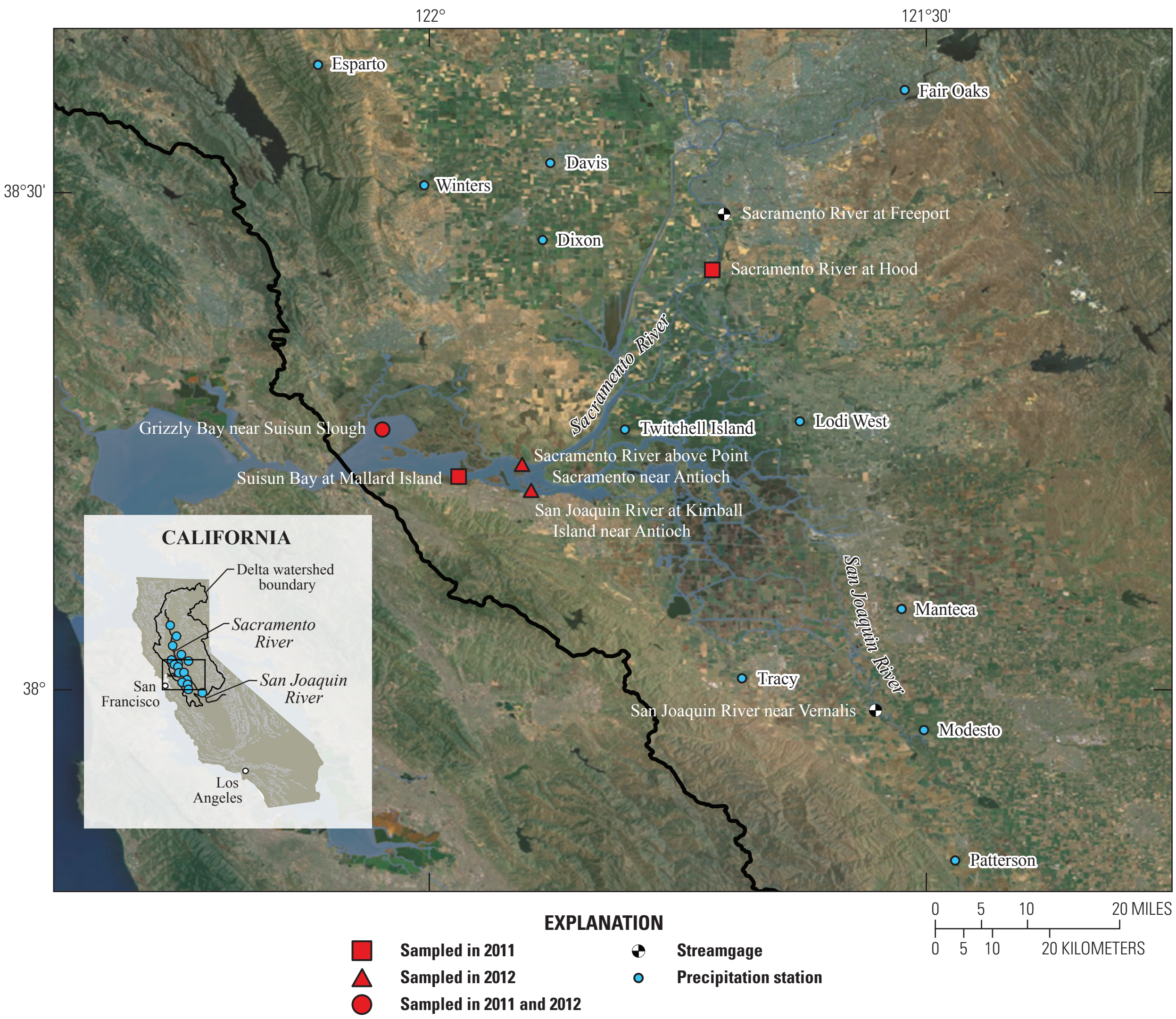

Figure 1. Locations of sampling sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California.

Table 1. Surface-water sampling sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California.

[**Abbreviations**: NAD83; North American Datum of 1983; USGS, U.S. Geological Survey; °, degree; ’, minute; ”, second]

USGS station number	USGS station name	Latitude	Longitude	Horizontal datum	Year sampled
382205121311300	Sacramento River at Hood	38° 22’ 05”	121° 31’ 17”	NAD83	2011
11185185	Suisun Bay at Mallard Island	38° 02’ 34”	121° 55’ 13”	NAD83	2011
380701122022301	Grizzly Bay near Suisun Slough	38° 07’ 01”	121° 02’ 23”	NAD83	2011, 2012
380345121491401	Sacramento River above Point Sacramento near Antioch	38° 03’ 45”	121° 49’ 14”	NAD83	2012
380118121482301	San Joaquin River at Kimball Island near Antioch	38° 01’ 18”	121° 48’ 23”	NAD83	2012

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 within a watershed covering approximately 24.9 million acres in northern and central California (fig. 1). The Delta is fed by two major river systems, the Sacramento River and the San Joaquin River, which flow south and north, respectively, though the Central Valley and converge in the western Delta. Water transported from the Delta is used to irrigate farms in central California and is a major source of drinking water for southern California cities. Over 3.9 million acres within the Delta watershed are devoted to agriculture, and the region produces an extremely wide variety of crops (U.S. Geological Survey, 2011). The area also contains numerous large urban centers that have a combined population of approximately 4.9 million, on the basis of 2010 Census data (U.S. Census Bureau, 2011). The region is characterized by a Mediterranean climate, with wet winters and dry summers. Precipitation falls primarily in the winter and spring as rain in the Sacramento and San Joaquin Valley and as snow in the higher elevations of the Sierra Nevada.

Pesticide Use

Agricultural and urban runoff enters the Delta throughout the year from sources upstream of the Delta as well as from agricultural activities and urban waste-water treatment plants within the Delta proper. These waters can contain current-use pesticides and degradates in concentrations that vary depending in large part on pesticide-application patterns 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 applications made by homeowners using products purchased at retail stores, which could contribute substantially to total pesticide use in urban areas. In 2010 (the latest year for which data are available), it was reported that over 41 million pounds of pesticides were applied in the Delta watershed (California Department of Pesticide Regulation, 2012). Of this amount, approximately 39 million pounds were applied to agriculture, and approximately 2.4 million pounds were applied by licensed applicators in urban settings.

Rainfall and Hydrologic Conditions

Pesticide transport is strongly influenced by the timing of pesticide applications as well as by rainfall and streamflow. Dileanis and others (2003) and Orlando and others (2004) have demonstrated increased pesticide concentrations in surface water following major storm events that were preceded by pesticide applications in the Delta region.

The California Department of Water Resources classified 2011 as a "wet" runoff year in the Sacramento and San Joaquin Valley, indicating that the region received well above normal precipitation (California Department of Water Resources, 2012). During the study period (April 5, 2011, through June 6, 2011), rain fell in the Sacramento or San Joaquin Valley on 39 of the 70 days (California Irrigation Management Information System, 2012). These conditions led to above-normal streamflow on the Sacramento and San Joaquin Rivers where they enter the Delta (U.S. Geological Survey, 2012a, b). Figure 2 shows daily mean streamflow measured from March to July 2011 at two USGS gages (Sacramento River at Freeport, 11447650, and San Joaquin River near Vernalis, 11303500). The historic mean of daily mean streamflow, based on the periods October 1, 1948, to September 30, 2011, for Sacramento River at Freeport, and October 1, 1923, to September 30, 2012, for San Joaquin River near Vernalis, are shown in figures 2 and 3 for comparison.

In contrast to the previous year, 2012 was classified as a "below-normal" runoff year in the Sacramento Valley and a "dry" year for the San Joaquin Valley (California Department of Water Resources, 2012). Precipitation fell infrequently in the winter months prior to the study period, resulting in below-normal streamflow in the Sacramento and San Joaquin Rivers (fig. 3). However, four storms during March and April 2012 in the Sacramento and San Joaquin Valley caused distinct increases in streamflow in the Sacramento and San Joaquin Rivers during the study period (U.S. Geological Survey, 2012b; fig. 3).

Procedures and Methods

Water samples were collected from two sites in the Delta and one site in Grizzly Bay from mid-April to mid-June 2011 and from two different Delta sites and the same Grizzly Bay site from the end of March through May 2012 (fig. 1 and table 1). 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

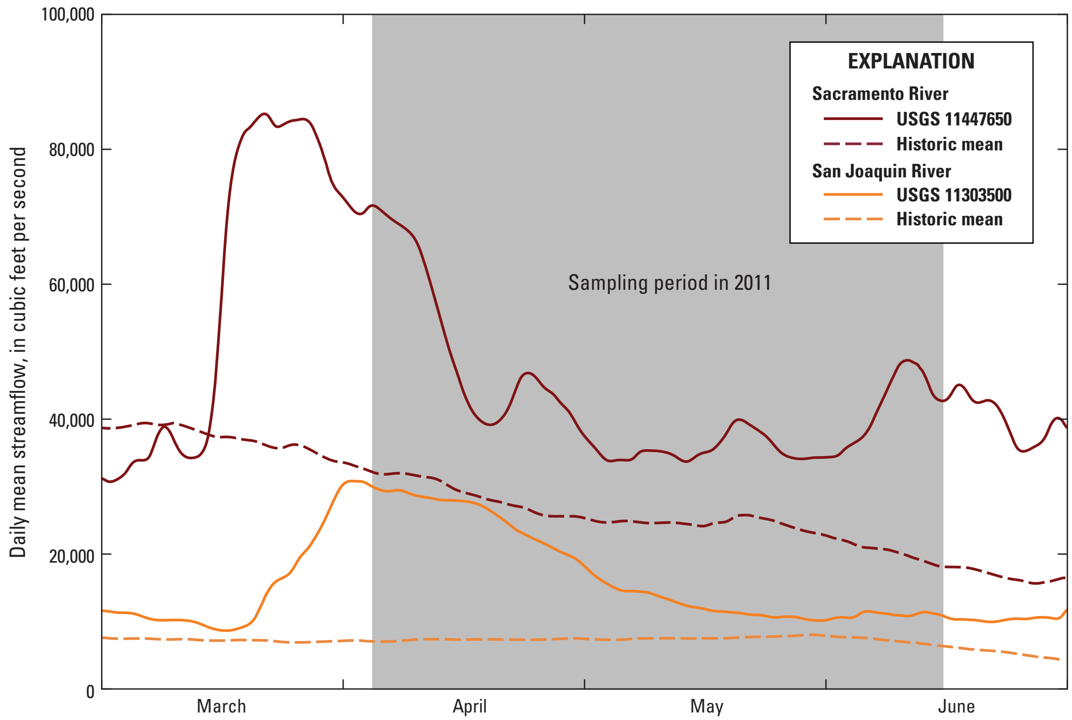

Figure 2. Daily mean streamflow from U.S. Geological Survey streamgages at Sacramento River at Freeport, California, (11447650) and San Joaquin River near Vernalis (11303500), spring 2011.

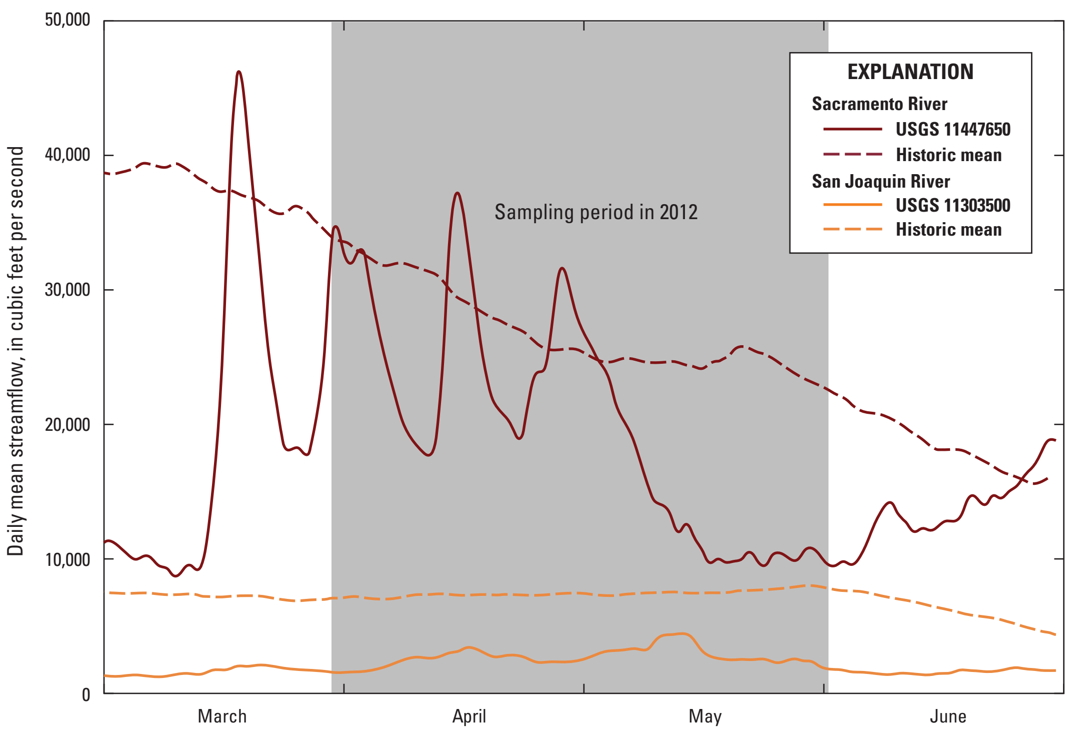

Figure 3. Daily mean streamflow from U.S. Geological Survey streamgages at Sacramento River at Freeport, California, (11447650) and San Joaquin River near Vernalis (11303500), spring 2012.

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 and field replicates and laboratory matrix-spike and matrix-spike-replicate samples. Water samples were also analyzed for DOC concentration. 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 and DOC.

Sample Collection

Surface-water samples were collected approximately weekly for 10 consecutive weeks from mid-April to mid-June 2011, and late-March to late-May 2012. Sampling events were regular intervals (rather than targeting specific flow conditions) to facilitate comparisons between 2011 and 2012. At two sites (Sacramento River at Hood and Suisun Bay at Mallard Island), samples were collected from platforms extending a few tens of meters out from the bank. At the other three sites, samples were collected from a boat stationed in the center of the channel. At all sites, water was collected as single-point grab samples 0.1 meter (m) below the surface. Sample water was collected directly into 1-liter (L), baked, amber-glass bottles by using a clean, weighted, plastic bottle holder. Field QC samples (field blanks and field replicates) were collected concurrently with the environmental samples. Field blanks were collected by pouring organic-free, deionized water directly into the sample bottles. Water-quality parameters (temperature, specific conductance, pH, and dissolved oxygen concentration) were measured at the time of sample collection, and from the same location and depth as sample collection, by using a multi-parameter meter (YSI model 6920V2) that was calibrated with appropriate standards prior to sampling. Water samples were immediately placed in coolers on ice and delivered within 24 hours to the USGS Organic Chemistry Research Laboratory in Sacramento, California.

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) to remove suspended material. Water for DOC analysis was gravity filtered through a separate 0.45-µm glass-fiber filter into a 125-milliliter (mL) amber-glass bottle and preserved with nitric acid to a pH less than 2. Samples were then stored refrigerated at 0 degrees Celsius (°C) until analysis.

Analytical Methods

Pesticides

Instruments were calibrated by using concentration standards that spanned the linear range of instrument response (0.025 to 2.5 nanograms per microliter, ng/µL). Calibration curves, determined by linear regression, were 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 0.5 ng/µL. The instruments were considered to be stable if the recovery of the check standards fell within the range of 80–115 percent of the nominal standard concentration. All environmental sample concentrations fell within the linear range of the instruments.

GC/MS Analysis

GC/MS analysis methods were based on those previously described by Hladik and others (2008, 2009). Briefly, each 1-L filtered-water sample was spiked with $^{13}C_3$-atrazine and diazinon diethyl-d_{10} (Cambridge Isotopes, Andover, Mass.) as recovery surrogates. 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 cubic centimeters, 500 milligram, 60 µm, Waters Corporation, Milford, Massachusetts) that had been cleaned with two column-volumes of ethyl actetate 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 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 vial. The bottle rinses were reduced in volume to 1 mL under a gentle stream of nitrogen gas. Each cartridge was dried by passing carbon dioxide through the cartridge for approximately 1 hour or until the solid-phase extraction (SPE) sorbent was dry. Each cartridge was then eluted with 12 mL of ethyl acetate, and the eluate was added to its corresponding bottle rinse. The combined solution was then reduced in a fume hood under a gentle stream of dry nitrogen to a final volume of 200 microliters (µL) for analysis. An internal standard (20 µL of 2 ng/L internal standard) 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 (up to 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 and detected on a Agilent 5975C Inert XL EI/CI mass-selective detector (MSD) system with a DB-5MS analytical column (30 meter × 0.25 millimeter × 0.25 µm, Agilent, Palo Alto, California) and helium as the

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

[**Abbreviations**: GC/MS, gas chromatograph/mass spectrometery; IGR, insect growth regulator; LC/MS/MS, liquid chromatography/tandem mass spectrometry; MDL, method detection limit; ng/L, nanogram per liter; NWIS, National Water Information System]

Compound	Use type	NWIS parameter code	MDL (ng/L)	Analytical method
Acetamiprid	Insecticide	68302	3.6	LC/MS/MS
Alachlor	Herbicide	65064	1.7	GC/MS
Allethrin	Insecticide	66586	6.0	GC/MS
Atrazine	Herbicide	65065	2.3	GC/MS
Azoxystrobin	Fungicide	66589	3.1	GC/MS
Bifenthrin	Insecticide	65067	4.7	GC/MS
Boscalid	Fungicide	67550	2.8	GC/MS
Butylate	Herbicide	65068	1.8	GC/MS
Carbaryl	Insecticide	65069	6.5	GC/MS
Carbofuran	Insecticide	65070	3.1	GC/MS
Chlorothalonil	Fungicide	65071	4.1	GC/MS
Chlorpyrifos	Insecticide	65072	2.1	GC/MS
Clomazone	Herbicide	67562	2.5	GC/MS
Clothianidin	Insecticide	68221	6.2	LC/MS/MS
Cycloate	Herbicide	65073	1.1	GC/MS
Cyfluthrin	Insecticide	65074	5.2	GC/MS
Cyhalothrin	Insecticide	68354	4.5	GC/MS
Cypermethrin	Insecticide	65075	5.6	GC/MS
Cyproconazole	Fungicide	66593	4.7	GC/MS
Cyprodinil	Fungicide	67574	7.4	GC/MS
DCPA	Herbicide	65076	2.0	GC/MS
p,p′-DDD	Degradate	65094	4.1	GC/MS
p,p′-DDE	Degradate	65095	3.6	GC/MS
p,p′-DDT	Degradate	65096	4.0	GC/MS
Deltamethrin	Insecticide	65077	3.5	GC/MS
Desulfinylfipronil	Degradate	66607	1.6	GC/MS
Diazinon	Insecticide	65078	0.9	GC/MS
3,4-Dichloroaniline (3,4-DCA)	Degradate	66584	5.2	LC/MS/MS
3,5-Dichloroaniline (3,5-DCA)	Degradate	67536	7.6	GC/MS
3,4-Dichlorophenylurea (DCPU)	Degradate	68226	4.3	LC/MS/MS
Difenoconazole	Fungicide	67582	10.5	GC/MS
(*E*)-Dimethomorph	Fungicide	67587	6.0	GC/MS
Dinotefuran	Insecticide	68379	5.5	LC/MS/MS
Diuron	Herbicide	66598	3.2	LC/MS/MS
EPTC	Herbicide	65080	1.5	GC/MS
Esfenvalerate	Insecticide	65081	3.9	GC/MS
Ethalfluralin	Herbicide	65082	3.0	GC/MS
Etofenprox	Insecticide	67604	2.2	GC/MS
Famoxadone	Fungicide	67609	2.5	GC/MS
Fenarimol	Fungicide	67613	6.5	GC/MS
Fenbuconazole	Fungicide	67618	5.2	GC/MS
Fenhexamide	Fungicide	67622	7.6	GC/MS
Fenpropathrin	Insecticide	65083	4.1	GC/MS
Fipronil	Insecticide	66604	2.9	GC/MS
Fipronil sulfide	Degradate	66610	1.8	GC/MS
Fipronil sulfone	Degradate	66613	3.5	GC/MS
Fluazinam	Fungicide	67636	4.4	GC/MS
Fludioxinil	Fungicide	67640	7.3	GC/MS
Fluoxastrobin	Fungicide	67645	4.2	GC/MS
Flusilazole	Fungicide	67649	4.5	GC/MS
Flutriafol	Fungicide	67653	4.2	GC/MS
τ-Fluvalinate	Insecticide	65106	5.3	GC/MS
Hexazinone	Herbicide	65085	8.4	GC/MS
Imazalil	Fungicide	67662	10.5	GC/MS
Imidacloprid	Insecticide	68426	4.9	LC/MS/MS
Iprodione	Fungicide	66617	4.4	GC/MS
Kresoxim-methyl	Fungicide	67670	4.0	GC/MS
Malathion	Insecticide	65087	3.7	GC/MS
Metconazole	Fungicide	66620	5.2	GC/MS
Methidathion	Insecticide	65088	7.2	GC/MS
Methoprene	IGR	66623	6.4	GC/MS
Methylparathion	Insecticide	65089	3.4	GC/MS
Metolachlor	Herbicide	65090	1.5	GC/MS
Molinate	Herbicide	65091	3.2	GC/MS
Myclobutanil	Fungicide	66632	6.0	GC/MS
N-(3,4-Dichlorophenyl)-*N′*-methylurea (DCPMU)	Degradate	68231	3.0	LC/MS/MS
Napropamide	Herbicide	65092	8.2	GC/MS
Oxyfluorfen	Herbicide	65093	3.1	GC/MS
Pebulate	Herbicide	65097	2.3	GC/MS
Pendimethalin	Herbicide	65098	2.3	GC/MS
Pentachloroanisole (PCA)	Degradate	66637	4.7	GC/MS
Pentachloronitrobenzene (PCNB)	Degradate	66639	3.1	GC/MS
Permethrin	Insecticide	65099	3.4	GC/MS
Phenothrin	Insecticide	65100	5.1	GC/MS
Phosmet	Insecticide	65101	4.4	GC/MS
Piperonyl butoxide	Synergist	65102	2.3	GC/MS
Prometon	Herbicide	67702	1.8	GC/MS
Prometryn	Herbicide	65103	2.5	GC/MS
Propanil	Herbicide	66641	10.1	GC/MS
Propiconazole	Fungicide	66643	5.0	GC/MS
Propyzamide	Herbicide	67706	5.0	GC/MS
Pyraclostrobin	Fungicide	66646	2.9	GC/MS
Pyrimethanil	Fungicide	67717	4.1	GC/MS
Resmethrin	Insecticide	65104	5.7	GC/MS
Simazine	Herbicide	65105	5.0	GC/MS
Tebuconazole	Fungicide	66649	3.7	GC/MS
Tefluthrin	Insecticide	67731	4.2	GC/MS
Tetraconazole	Fungicide	66654	5.6	GC/MS
Tetramethrin	Insecticide	66657	2.9	GC/MS
Thiacloprid	Insecticide	68485	3.8	LC/MS/MS
Thiamethoxam	Insecticide	68245	3.9	LC/MS/MS
Thiobencarb	Herbicide	65107	1.9	GC/MS
Triadimefon	Fungicide	67741	8.9	GC/MS
Triadimenol	Fungicide	67746	8.0	GC/MS
Trifloxystrobin	Fungicide	66660	4.7	GC/MS
Triflumizole	Fungicide	67753	6.1	GC/MS
Trifluralin	Herbicide	65108	2.1	GC/MS
Triticonazole	Fungicide	67758	6.9	GC/MS
Zoxamide	Fungicide	67768	3.5	GC/MS

carrier gas. Injections of 1 µL were made with the injector at 275°C in pulsed splitless mode with a 50 pounds per square inch (psi) pressure pulse for 1 minute. The flow of helium through a GC column was set at 1.2 mL/min. Two separate injections were made—one for the analysis of herbicides/insecticides and one for fungicides. The herbicide/insecticide oven-temperature program was to hold at 80°C for 1.0 minute, ramp at 10°C/min until 120°C, then ramp at 3°C/min until 200°C and hold for 5 minutes, ramp at 3°C/min until 219°C, and a final ramp at 10°C/min until 300°C and hold for 10 minutes. The fungicide oven temperature program was to hold at 80°C for 0.5 min, ramp at 10°C/min until 180°C, then ramp at 5°C/min until 220°C and hold for 1 minute, ramp at 4°C/min until 280°C and hold for 1 minute, and a final ramp at 10°C/min until 300°C and hold for 10 minutes. The temperature of the transfer line from the GC to the MS was set at 280°C, while the quadrupole and the MS ion source were set at 150°C and 230°C, respectively. The MS was operated in electronionization mode. Data were collected in the selected-ion-monitoring mode.

LC/MS/MS Analysis

Each 1-L filtered-water sample was spiked with recovery surrogate standards, monuron (Chem Service, West Chester, Pennsylvania) and imidacloprid-d_4 (Cambridge Isotope Laboratories, Andover, Massachusetts). These surrogates were chosen because they are similar in structure to the target analytes; deuterated imidacloprid is not found in the environment, and monuron was canceled for use in the United States in 1977 (U.S. Environmental Protection Agency, 1998). The sample was then pumped under vacuum at a flow rate of 10 mL/min through an Oasis HLB SPE (6 mL, 500 mg; Waters, 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 50 percent DCM and 50 percent acetone. The eluent was evaporated to less than 0.5 mL in a fume hood by using a gentle stream of nitrogen, then solvent-exchanged into acetonitrile (ACN), and further evaporated to less than 0.2 mL. 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 (up to 30 days) in a freezer at –20°C until analysis.

Water extracts were analyzed for the herbicide diuron, three diuron degredates (DCPMU, DCPU, and 3,4-Dichloroaniline), and three neonicotinoid insecticides (clothianidin, imidacloprid, and thiamethoxam) by LC/MS/MS in 2011. The diuron degredates dinotefuran, acetamiprid, and thiacloprid were added to the method and analyzed in samples during 2012. Aliquots of the sample extracts (10 µL) were injected, and the compounds were separated on an Agilent (Palo Alto, California) 1100 high performance liquid chromatography (HPLC) coupled to a 6430 tandem MS system with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm, Agilent). The column flow rate was 0.6 mL/min, and the column temperature was 30°C. The mobile phases were ACN (A channel) and 5 millimolar (mM) formic acid in water (B channel). The column gradient program was to hold at 2:98 percent (A:B) for 2 minutes, ramp over 2 minutes to 50:50 percent (A:B) and hold for 3 minutes, then decrease over 0.5 minute to 2:98 percent (A:B) and hold for 4.5 minutes (12 minutes total). MS/MS conditions were electrospray ionization, positive mode, drying gas temperature 350°C, drying gas flow 10 liter per minute (L/min), capillary voltage 4,000 volts, and nebulizer pressure 40 psi. 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 (MDLs) 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). Water samples used to determine MDLs for insecticides and herbicides analyzed by GC/MS were collected in 2005 from the Sacramento River at Miller Park, and water samples used to determine fungicide MDLs were collected in 2008 from the American River near the California State University, Sacramento, campus. In 2012, MDLs for compounds analyzed by LC/MS/MS were determined by using water collected from the Lower American River (California) that had zero pesticide detections for the target compounds. The MDLs were calculated for each compound by using the following equation:

$$MDL = S \times t_{(n-1,\ 1-\alpha=0.99)} \quad (1)$$

where

S is the standard deviation of replicate analyses, and

$t_{(n-1,\ 1-\alpha=0.99)}$ is the Student's *t* value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom.

MDLs for pesticides in surface water ranged from 0.9 to 10.5 ng/L. Analytes can sometimes be identified at concentrations less than the MDL with lower confidence in the numerical value; therefore, concentrations of compounds detected below the MDLs are reported as estimates.

Dissolved Organic Carbon

Filtered water samples were analyzed for DOC at the USGS Organic Chemistry Research Laboratory in Sacramento, California, by high-temperature catalytic combustion on a Shimadzu TOC-VCNS total organic carbon analyzer (Shimadzu Scientific Instruments, Columbia, Maryland) using a modified version of U.S. Environmental Protection Agency (USEPA) Method 415.3 (Potter and Wimsatt, 2005). The instrument was calibrated by using potassium hydrogen phthalate standards prepared in organic-free water with concentrations ranging from 0.0 to 4.0 milligrams per liter (mg/L). Samples were acidified with concentrated sulfuric acid in order to lower the pH to approximately 1.9 prior to analysis. The accuracy and precision of the measurements were within 3 percent of expected values as indicated by internal standards (potassium hydrogen phthalate and caffeine).

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 by using the GC/MS and LC/MS/MS methods describe earlier. Quality control for the analysis of DOC consisted of laboratory blanks and replicates.

Pesticides

Six field blanks consisting of pesticide-grade organic-free blank water were processed during the study to test the cleanliness of the field procedures. Field blanks were collected once from each site in both 2011 and 2012. Field blanks were processed in the same manner as the environmental samples and were analyzed by using the GC/MS and LC/MS/MS methods. No pesticides were detected in any of the field blanks.

Six field replicate sample pairs were analyzed (by using both analytical methods) to test the reproducibility of results, and there were 14 paired detections of pesticides in 2011 and 26 paired detections in 2012. 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.

Six laboratory matrix-spike samples paired with six matrix-spike-replicate samples were analyzed (by using both analytical methods) to assess pesticide recovery, degradation, sorption, and interferences caused by the sampling matrix. Percent recoveries for all pesticides in all 12 samples met the data-quality objective of 70 to 130 percent. These six 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. 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-d4, 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.

Dissolved Organic Carbon

A total of 198 laboratory blank samples were analyzed in instrument batches in which DOC samples for this project were analyzed. There were no detections of DOC above the laboratory control limit of 0.3 mg/L in any blank sample, and this met the project data-quality objectives. Five laboratory replicate samples were analyzed to test the reproducibility of results. The relative standard deviation between the environmental and replicate samples ranged from 0 to 9 percent, which met the data-quality objectives.

Results

Spring 2011

At least one pesticide or pesticide degradate was detected in every water sample collected in 2011, and 19 of the 30 samples (63 percent) contained a mixture of 5 or more pesticides (table 6). A total of 18 compounds were detected: 5 fungicides, 8 herbicides, 3 herbicide degradates, and 2 insecticides (fig. 4). The most frequently detected compounds were the herbicides clomazone, diuron, hexazinone, and metolachlor, and the diuron degradates 3,4-Dichloroaniline and DCPMU (fig. 4). Fungicides were detected in over half the samples, whereas insecticides were only detected in two samples (both collected at Grizzly Bay near Suisun Slough; table 6). The numbers of pesticides detected varied during the sampling period and tended to increase following rainfall events, as shown in figure 5, which depicts the numbers of pesticides detected at Suisun Bay at Mallard Island and average daily rainfall on the basis of data from 17 measurement sites in the Sacramento and San Joaquin Valley (California Irrigation Management Information System, 2012). During the sampling period, the number of pesticides detected by site was least at Sacramento River at Hood (12 compounds), whereas greater numbers of pesticides were detected in Suisun Bay at Mallard Island (15 compounds) and Grizzly Bay near Suisun Slough samples (18 compounds).

Table 3. Pesticide concentrations measured by gas chromatography/mass spectrometry (GC/MS) in environmental and field replicate water samples from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, collected during the spring of 2011 and 2012 and the relative standard deviations between results.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. The following compounds were analyzed but were not detected in any samples: alachlor, allethrin, atrazine, bifenthrin, butylate, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, 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, fipronil sulfide, fipronil sulfone, τ-fluvalinate, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propiconazole, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanograms per liter; RSD, relative standard deviation; %, percent; –, not detected]

Site	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	Azoxystrobin (ng/L) [66589]	Boscalid (ng/L) [67550]	Clomazone (ng/L) [67562]	Hexazinone (ng/L) [65085]	Imazalil (ng/L) [67662]
Sacramento River at Hood	06/06/2011	10:30	Environmental	–	–	419	–	–
Sacramento River at Hood	06/06/2011	10:30	Field replicate	–	–	445	–	–
			RSD			4%		
Suisun Bay at Mallard Island	05/09/2011	12:50	Environmental	–	–	–	20.3	63.0
Suisun Bay at Mallard Island	05/09/2011	12:50	Field replicate	–	–	–	23.5	71.1
			RSD				10%	9%
Grizzly Bay near Suisun Slough	05/24/2011	10:15	Environmental	–	–	44.5	26.5	–
Grizzly Bay near Suisun Slough	05/24/2011	10:15	Field replicate	–	–	50.9	28.0	–
			RSD			9%	4%	
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	Environmental	18.4	31.5	–	134	–
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	Field replicate	17.1	29.1	–	127	–
			RSD	5%	6%		4%	
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	Environmental	7.4	11.8	–	118	–
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	Field replicate	8.1	12.5	–	127	–
			RSD	6%	4%		5%	
Grizzly Bay near Suisun Slough	04/10/2012	11:00	Environmental	11.3	19.9	–	56.7	–
Grizzly Bay near Suisun Slough	04/10/2012	11:00	Field replicate	10.1	20.2	–	53.6	–
			RSD	8%	1%		4%	

Table 3. Pesticide concentrations measured by gas chromatography/mass spectrometry (GC/MS) in environmental and field replicate water samples from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, collected during the spring of 2011 and 2012 and the relative standard deviations between results.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. The following compounds were analyzed but were not detected in any samples: alachlor, allethrin, atrazine, bifenthrin, butylate, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, 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, fipronil sulfide, fipronil sulfone, τ-fluvalinate, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, iprodione, kresoxim-methyl, malathion, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propiconazole, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanograms per liter; RSD, relative standard deviation; %, percent; –, not detected]

Site	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	Metolachlor (ng/L) [65090]	Napropamide (ng/L) [65092]	Pendimethalin (ng/L) [65098]	Simazine (ng/L) [65105]	Tetraconazole (ng/L) [66654]
Sacramento River at Hood	06/06/2011	10:30	Environmental	8.3	–	–	–	30.9
Sacramento River at Hood	06/06/2011	10:30	Field replicate	8.8	–	–	–	33.5
			RSD	4%				6%
Suisun Bay at Mallard Island	05/09/2011	12:50	Environmental	–	–	–	–	–
Suisun Bay at Mallard Island	05/09/2011	12:50	Field replicate	–	–	–	–	–
			RSD					
Grizzly Bay near Suisun Slough	05/24/2011	10:15	Environmental	7.4	–	–	–	–
Grizzly Bay near Suisun Slough	05/24/2011	10:15	Field replicate	10.4	–	–	–	–
			RSD	24%				
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	Environmental	29.3	–	–	126	–
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	Field replicate	26.4	–	–	119	–
			RSD	7%			4%	
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	Environmental	17.7	51.5	–	88.7	–
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	Field replicate	19.9	57.0	–	91.7	–
			RSD	8%	7%		2%	
Grizzly Bay near Suisun Slough	04/10/2012	11:00	Environmental	9.1	–	8.0	35.3	–
Grizzly Bay near Suisun Slough	04/10/2012	11:00	Field replicate	8.1	–	8.7	31.2	–
			RSD	8%		6%	9%	

Table 4. Pesticide concentrations measured by liquid chromatography tandem mass spectrometry (LC/MS/MS) in environmental and field replicate water samples from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, collected during the spring of 2011 and 2012 and the relative standard deviations between results.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. 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, thiacloprid, and thiamethoxam. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanograms per liter; RSD, relative standard deviation; %, percent; –, not detected]

Site	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Sample type	DCPMU (ng/L) [68231]	3,4-Dichloroaniline (ng/L) [66584]	Diuron (ng/L) [66598]	Imidacloprid (ng/L) [68426]
Sacramento River at Hood	05/16/2011	12:10	Environmental	–	3.1	–	–
Sacramento River at Hood	05/16/2011	12:10	Field replicate	–	3.0	–	–
			RSD		2%		
Suisun Bay at Mallard Island	04/25/2011	13:40	Environmental	4.4	–	14.7	–
Suisun Bay at Mallard Island	04/25/2011	13:40	Field replicate	4.2	–	13.9	–
			RSD	3%		4%	
Grizzly Bay near Suisun Slough	04/12/2011	12:25	Environmental	8.4	6.7	21.6	–
Grizzly Bay near Suisun Slough	04/12/2011	12:25	Field replicate	9.0	6.8	21.1	–
			RSD	5%	1%	2%	
Sacramento River above Point Sacramento near Antioch	04/17/2012	11:30	Environmental	3.1	(3.6)	23.4	(2.0)
Sacramento River above Point Sacramento near Antioch	04/17/2012	11:30	Field replicate	3.0	(3.0)	21.3	(2.2)
			RSD	2%	13%	7%	7%
San Joaquin River at Kimball Island near Antioch	05/08/2012	09:15	Environmental	–	–	5.9	–
San Joaquin River at Kimball Island near Antioch	05/08/2012	09:15	Field replicate	–	–	6.6	–
			RSD			8%	
Grizzly Bay near Suisun Slough	03/27/2012	10:35	Environmental	(2.8)	(4.6)	36.8	(3.8)
Grizzly Bay near Suisun Slough	03/27/2012	10:35	Field replicate	(2.2)	(4.2)	31.7	(3.1)
			RSD	17%	6%	11%	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.

[Number of samples analyzed for each compound is 12. **Abbreviation**: Max, maximum; Min, minimum; %, percent]

Compound	Min recovery (%)	Max recovery (%)	Median recovery (%)	Standard deviation (%)
Acetamiprid	71	86	79	5
Alachlor	81	114	96	13
Allethrin	77	112	93	11
Atrazine	85	130	103	17
Azoxystrobin	78	111	95	11
Bifenthrin	73	116	83	14
Boscalid	90	116	96	7
Butylate	77	115	93	14
Carbaryl	82	118	97	12
Carbofuran	85	128	102	16
Chlorothalonil	70	94	84	7
Chlorpyrifos	73	121	91	16
Clomazone	92	130	99	12
Clothianidin	71	96	86	9
Cycloate	82	122	106	14
Cyfluthrin	77	117	92	12
Cyhalothrin	73	111	80	13
Cypermethrin	72	119	86	14
Cyproconazole	73	115	99	13
Cyprodinil	81	100	93	6
DCPA	85	120	102	12
p,p′-DDD	71	113	74	15
p,p′-DDE	73	98	80	7
p,p′-DDT	70	114	79	13
Deltamethrin	72	124	84	16
Desulfinylfipronil	87	128	102	12
Diazinon	91	125	106	11
3,4-Dichloroaniline (3,4-DCA)	83	119	94	12
3,5-Dichloroaniline (3,5-DCA)	78	119	87	12
N-(3,4-Dichlorophenyl)-*N′*-methylurea (DCPMU)	76	106	83	10
3,4-Dichlorophenylurea (DCPU)	71	89	79	5
Difenoconazole	78	118	100	13
(*E*)-Dimethomorph	72	108	89	11
Dinotefuran	72	82	77	4
Diuron	83	112	96	9
EPTC	74	125	97	16
Esfenvalerate	73	112	82	13
Ethalfluralin	70	120	87	15
Etofenprox	71	116	77	15
Famoxadone	79	121	101	14
Fenarimol	70	101	85	12
Fenbuconazole	89	106	96	6
Fenhexamide	85	115	99	11
Fenpropathrin	74	111	87	12
Fipronil	80	116	98	10
Fipronil sulfide	86	124	106	12
Fipronil sulfone	86	127	108	14
Fluazinam	71	105	83	11
Fludioxinil	81	118	94	11
Fluoxastrobin	71	118	103	14
Flusilazole	79	96	88	6
Flutriafol	75	113	97	14
τ-Fluvalinate	71	118	86	15
Hexazinone	94	128	114	9
Imazalil	76	114	94	11
Imidacloprid	71	97	86	9
Iprodione	81	125	103	14
Kresoxim-methyl	73	90	85	5
Malathion	81	119	107	12
Metconazole	78	121	104	16
Methidathion	79	128	111	14
Methoprene	73	124	90	18
Methylparathion	81	124	108	12
Metolachlor	89	125	110	12
Molinate	81	127	98	15
Myclobutanil	78	102	85	9
Napropamide	92	121	108	10
Oxyfluorfen	75	119	81	16
Pebulate	78	122	99	16
Pendimethalin	74	107	81	12
Pentachloroanisole (PCA)	71	90	81	6
Pentachloronitrobenzene (PCNB)	79	99	85	8
Permethrin	70	117	79	15
Phenothrin	73	115	87	12
Phosmet	73	125	100	17
Piperonyl butoxide	79	126	95	13
Prometon	74	128	109	16
Prometryn	89	125	108	11
Propanil	82	119	99	14
Propiconazole	76	126	100	17
Propyzamide	85	121	98	12
Pyraclostrobin	88	120	104	12
Pyrimethanil	82	96	91	5
Resmethrin	71	111	77	14
Simazine	89	119	107	9
Tebuconazole	73	117	92	15
Tefluthrin	74	92	79	7
Tetraconazole	82	103	94	6
Tetramethrin	77	105	89	9
Thiacloprid	74	85	77	4
Thiamethoxam	72	90	79	5
Thiobencarb	88	125	102	14
Triadimefon	78	112	106	14
Triadimenol	74	104	85	11
Trifloxystrobin	72	97	86	6
Triflumizole	77	108	95	12
Trifluralin	73	105	79	10
Triticonazole	77	122	100	17
Zoxamide	84	127	98	12

Table 6. Pesticide concentrations measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. 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, butylate, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, DCPA, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, imidacloprid, iprodione, kresoxim-methyl, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propiconazole, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiamethoxam, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanograms per liter; –, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Azoxystrobin (ng/L) [66589]	Bifenthrin (ng/L) [65067]	Boscalid (ng/L) [67550]	Clomazone (ng/L) [67562]	Cyprodinil (ng/L) [67574]	DCPU (ng/L) [68226]	DCPMU (ng/L) [68231]	3,4-Dichloroaniline (ng/L) [66584]	Diuron (ng/L) [66598]
Sacramento River at Hood	04/11/2011	09:00	–	–	–	–	–	–	–	6.8	–
Sacramento River at Hood	04/18/2011	12:10	(2.0)	–	(1.4)	–	–	–	–	–	3.5
Sacramento River at Hood	04/25/2011	11:20	–	–	–	–	–	–	–	–	15.2
Sacramento River at Hood	05/02/2011	11:40	–	–	–	–	–	–	–	–	5.2
Sacramento River at Hood	05/09/2011	11:00	–	–	–	13.0	–	–	–	(3.2)	–
Sacramento River at Hood	05/16/2011	12:10	–	–	–	33.1	–	–	–	(3.1)	–
Sacramento River at Hood	05/23/2011	11:00	–	–	–	156	–	–	–	6.0	–
Sacramento River at Hood	06/01/2011	10:20	–	–	–	535	–	–	–	7.4	–
Sacramento River at Hood	06/06/2011	10:30	–	–	–	419	–	–	–	15.6	–
Sacramento River at Hood	06/13/2011	11:50	–	–	–	203	–	–	–	15.3	–
Suisun Bay at Mallard Island	04/11/2011	14:30	(2.0)	–	7.5	–	–	–	15.0	–	36.2
Suisun Bay at Mallard Island	04/18/2011	10:30	–	–	3.2	–	–	–	15.0	7.5	32.4
Suisun Bay at Mallard Island	04/25/2011	13:40	–	–	(2.5)	–	(0.2)	–	4.4	–	14.7
Suisun Bay at Mallard Island	05/02/2011	10:10	–	–	–	–	–	–	5.7	–	17.9
Suisun Bay at Mallard Island	05/09/2011	12:50	–	–	–	–	–	–	–	(4.0)	15.5
Suisun Bay at Mallard Island	05/16/2011	10:40	–	–	–	7.4	–	–	6.7	(4.7)	11.6
Suisun Bay at Mallard Island	05/23/2011	12:50	–	–	–	45.3	–	–	5.7	(4.2)	9.0
Suisun Bay at Mallard Island	06/01/2011	09:40	–	–	–	130	–	–	–	(3.6)	7.5
Suisun Bay at Mallard Island	06/06/2011	11:50	3.1	–	–	288	–	–	4.5	8.6	7.7
Suisun Bay at Mallard Island	06/13/2011	10:15	(2.4)	–	–	225	–	–	3.8	9.2	6.8
Grizzly Bay near Suisun Slough	04/05/2011	11:32	5.1	–	9.1	–	(0.4)	5.1	–	–	16.0
Grizzly Bay near Suisun Slough	04/12/2011	12:25	(1.9)	4.1	5.4	–	–	–	8.4	6.7	21.6
Grizzly Bay near Suisun Slough	04/21/2011	10:42	3.3	–	4.5	–	–	–	4.4	(4.9)	11.3
Grizzly Bay near Suisun Slough	04/26/2011	13:11	–	–	(2.5)	–	–	–	4.2	(4.9)	13.7
Grizzly Bay near Suisun Slough	05/03/2011	10:20	–	–	–	–	–	–	–	–	18.5
Grizzly Bay near Suisun Slough	05/10/2011	10:05	–	–	–	–	–	–	4.7	(4.3)	11.6
Grizzly Bay near Suisun Slough	05/17/2011	10:00	–	–	–	–	–	–	5.6	6.9	14.4
Grizzly Bay near Suisun Slough	05/24/2011	10:15	–	–	–	44.5	–	–	5.9	5.5	10.4
Grizzly Bay near Suisun Slough	05/31/2011	09:40	–	–	–	85.2	–	–	–	6.4	–
Grizzly Bay near Suisun Slough	06/07/2011	10:05	–	–	–	292	–	–	5.1	11.8	9.2

Table 6. Pesticide concentrations measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. 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, butylate, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, DCPA, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, imidacloprid, iprodione, kresoxim-methyl, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, napropamide, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propiconazole, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetramethrin, thiamethoxam, triadimefon, triadimenol, trifloxstrobin, triflumizole, trifluralin, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanograms per liter; –, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	EPTC (ng/L) [65080]	Hexazinone (ng/L) [65085]	Imazalil (ng/L) [67662]	Malathion (ng/L) [65087]	Metolachlor (ng/L) [65090]	Pendimethalin (ng/L) [65098]	Simazine (ng/L) [65105]	Tetraconazole (ng/L) [66654]	Thiobencarb (ng/L) [65107]
Sacramento River at Hood	04/11/2011	09:00	(0.4)	–	–	–	–	–	–	–	–
Sacramento River at Hood	04/18/2011	12:10	–	15.4	–	–	–	19.7	–	–	–
Sacramento River at Hood	04/25/2011	11:20	–	–	–	–	–	–	–	–	–
Sacramento River at Hood	05/02/2011	11:40	–	47.1	–	–	–	–	–	–	–
Sacramento River at Hood	05/09/2011	11:00	–	26.3	–	–	–	–	–	–	–
Sacramento River at Hood	05/16/2011	12:10	–	17.2	–	–	–	–	–	–	–
Sacramento River at Hood	05/23/2011	11:00	–	27.1	–	–	–	–	–	–	–
Sacramento River at Hood	06/01/2011	10:20	–	28.3	17.3	–	–	–	–	227	43.6
Sacramento River at Hood	06/06/2011	10:30	–	–	–	–	8.3	–	–	30.9	–
Sacramento River at Hood	06/13/2011	11:50	–	19.4	–	–	28.4	–	–	37.0	11.0
Suisun Bay at Mallard Island	04/11/2011	14:30	–	12.6	–	–	8.3	20.8	15.1	–	–
Suisun Bay at Mallard Island	04/18/2011	10:30	15.5	10.6	–	–	–	–	–	–	–
Suisun Bay at Mallard Island	04/25/2011	13:40	16.2	20.8	11.6	–	9.8	–	–	–	–
Suisun Bay at Mallard Island	05/02/2011	10:10	–	28.6	–	–	12.7	–	–	–	–
Suisun Bay at Mallard Island	05/09/2011	12:50	–	20.3	63.0	–	–	–	–	–	–
Suisun Bay at Mallard Island	05/16/2011	10:40	–	11.8	–	–	–	–	–	–	–
Suisun Bay at Mallard Island	05/23/2011	12:50	–	24.7	–	–	13.3	–	–	–	–
Suisun Bay at Mallard Island	06/01/2011	09:40	–	19.1	–	–	19.2	–	–	463	–
Suisun Bay at Mallard Island	06/06/2011	11:50	–	20.2	–	–	11.1	–	–	54.5	20.0
Suisun Bay at Mallard Island	06/13/2011	10:15	–	16.8	–	–	11.3	–	–	22.6	16.9
Grizzly Bay near Suisun Slough	04/05/2011	11:32	(1.1)	16.3	–	16.1	7.4	19.4	17.7	–	–
Grizzly Bay near Suisun Slough	04/12/2011	12:25	–	19.0	–	–	–	20.5	–	–	–
Grizzly Bay near Suisun Slough	04/21/2011	10:42	–	16.6	–	–	8.8	–	–	–	–
Grizzly Bay near Suisun Slough	04/26/2011	13:11	–	21.4	(10.3)	–	9.4	–	–	–	–
Grizzly Bay near Suisun Slough	05/03/2011	10:20	–	–	–	–	10.1	–	–	–	–
Grizzly Bay near Suisun Slough	05/10/2011	10:05	–	25.0	–	–	–	–	–	–	–
Grizzly Bay near Suisun Slough	05/17/2011	10:00	–	21.7	53.4	–	–	–	–	–	–
Grizzly Bay near Suisun Slough	05/24/2011	10:15	–	26.5	–	–	7.4	–	–	–	–
Grizzly Bay near Suisun Slough	05/31/2011	09:40	–	22.7	–	–	13.0	–	–	511	–
Grizzly Bay near Suisun Slough	06/07/2011	10:05	–	20.6	(10.3)	–	14.9	–	–	16.5	20.8

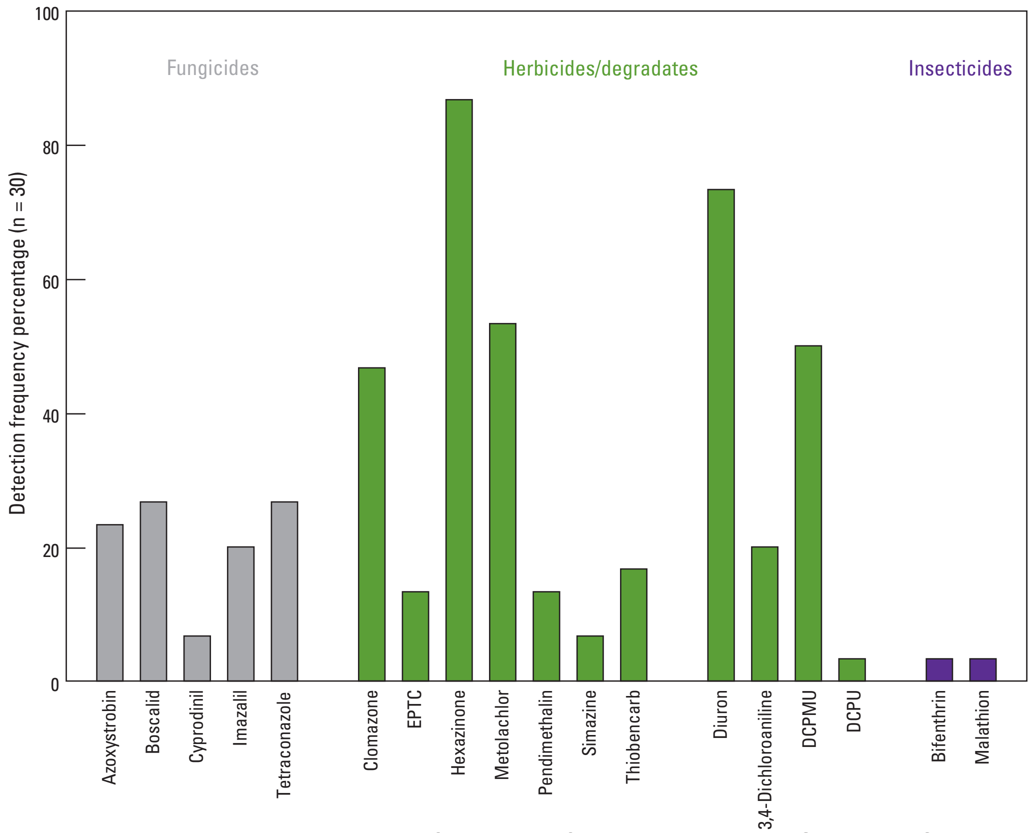

Figure 4. Pesticide detection frequencies from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011.

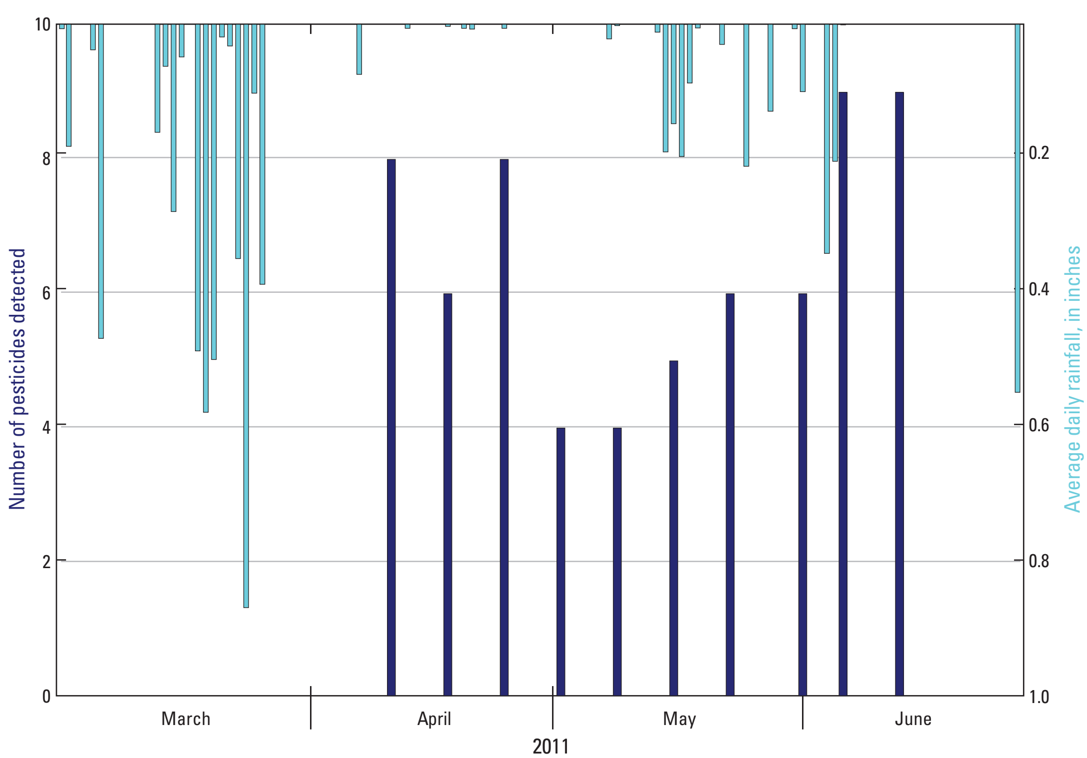

Figure 5. Pesticide detections at Suisun Bay at Mallard Island, California, by sampling event and average daily rainfall in the Sacramento and San Joaquin Valley during spring 2011.

Maximum concentrations for all detected compounds were less than 75 ng/L, with two exceptions: the rice herbicide clomazone and the fungicide tetraconazole, which were detected at up to 535 and 511 ng/L, respectively (table 6). Median concentrations for the most frequently detected pesticides were less than 20 ng/L (fig. 6). Maximum concentrations of clomazone, 3,4-Dichloroaniline, hexazinone, and metolachlor were highest in samples collected from Sacramento River at Hood, whereas diuron and DCPMU maximum concentrations were highest in samples from Suisun Bay at Mallard Island. Pesticide concentrations generally did not increase immediately following rainfall events during the sampling period. The insecticide bifenthrin was detected in one sample (Grizzly Bay near Suisun Slough, on April 12, 2011) at a concentration above the aquatic-life benchmark for chronic toxicity to invertebrates of 1.3 ng/L (U.S. Environmental Protection Agency, 2012). All other pesticides with established aquatic-life benchmarks were detected at concentrations below those benchmarks.

Dissolved organic carbon concentrations ranged from 1.2 to 3.2 mg/L and are shown in table 7. The median DOC concentration of samples collected in 2011 from the Sacramento River at Hood was lower (1.4 mg/L) than for samples collected from either Suisun Bay at Mallard Island or Grizzly Bay near Suisun Slough (2.2 and 2.1 mg/L, respectively). The DOC concentrations tended to increase over the course of the sampling period at the Sacramento River at Hood, whereas they decreased over time at the other two sites. Water-quality parameters (water temperature, specific conductance, dissolved oxygen, and pH) measured in surface-water samples collected in 2011 are shown in table 7.

Spring 2012

A minimum of 6 pesticides were detected in every sample collected in 2012, and a total of 16 compounds were detected during the course of sampling (table 8). Pesticides detected included three fungicides, eight herbicides, two herbicide degradates, and three insecticides (fig. 7). The most frequently detected pesticides were the fungicides azoxystrobin and boscalid and the herbicides diuron, hexazinone, metolachlor, and simazine. Insecticides were detected in only four samples, and all concentrations were below the MDLs. The numbers of pesticides detected tended to increase following rainfall events, as shown in figure 8, which depicts the numbers of pesticides detected at Sacramento River above Point Sacramento and average daily rainfall in the Sacramento and San Joaquin Valley (California Irrigation Management Information System, 2012). The pesticides detected were similar for each of the sampling sites during each weekly sampling event.

Maximum concentrations for all detected compounds were less than 75 ng/L, with the exceptions of the fungicide azoxystrobin and the herbicides hexazinone and simazine, which were detected at up to 188, 134, and 140 ng/L, respectively (table 8). Median concentrations for the most frequently detected pesticides ranged from 8.8 (azoxystrobin) to 92.9 ng/L (hexazinone), as shown in figure 9. For the majority of the pesticides detected, median and maximum concentrations were similar between sites. For the most frequently detected compounds, concentrations generally tended to increase following storm events, as shown in figure 10 for simazine detected at the Sacramento River above Point Sacramento site. All pesticides with established aquatic-life benchmarks were detected at concentrations below those benchmarks.

Dissolved organic carbon concentrations measured in 2012 ranged from 2.4 to 4.1 mg/L and are shown in table 7. The median DOC concentrations were similar for all three sites: 3.3 mg/L for Sacramento River above Point Sacramento, 3.5 mg/L for San Joaquin River at Kimball Island, and 3.1 mg/L for Grizzly Bay near Suisun Slough. The DOC concentrations varied slightly during the sampling period. Water-quality parameters (air temperature, water temperature, specific conductance, dissolved oxygen, and pH) measured in surface-water samples collected in 2012 are shown in table 7.

Summary

Concentrations of dissolved pesticides and pesticide degradates were measured at sites in the Sacramento-San Joaquin Delta and Grizzly Bay during the spring months of 2011 and 2012. Hydrologic conditions during the two sampling periods differed substantially: the spring of 2011 was characterized by high flows on the major rivers entering the Delta, whereas flows were below normal during spring 2012. Weather conditions during the sampling periods were similar, however, with rainfall just prior to the initiation of sampling as well as during the sampling period. Overall, the numbers of pesticides detected during both years were similar, as were the types of pesticides detected. Detection frequencies, however, were higher for many compounds during 2012 compared to 2011. In both years, the numbers of pesticides detected increased following rainfall events. In both years, maximum concentrations of most pesticides were generally less than 75 ng/L. Exceptions were tetraconazole and clomazone in 2011 and azoxystrobin, hexazinone, and simazine in 2012. Results from this study demonstrate that mixtures of current-use pesticides and pesticide degradates can enter the Sacramento/San Joaquin Delta and Grizzly Bay under widely varying streamflow conditions.

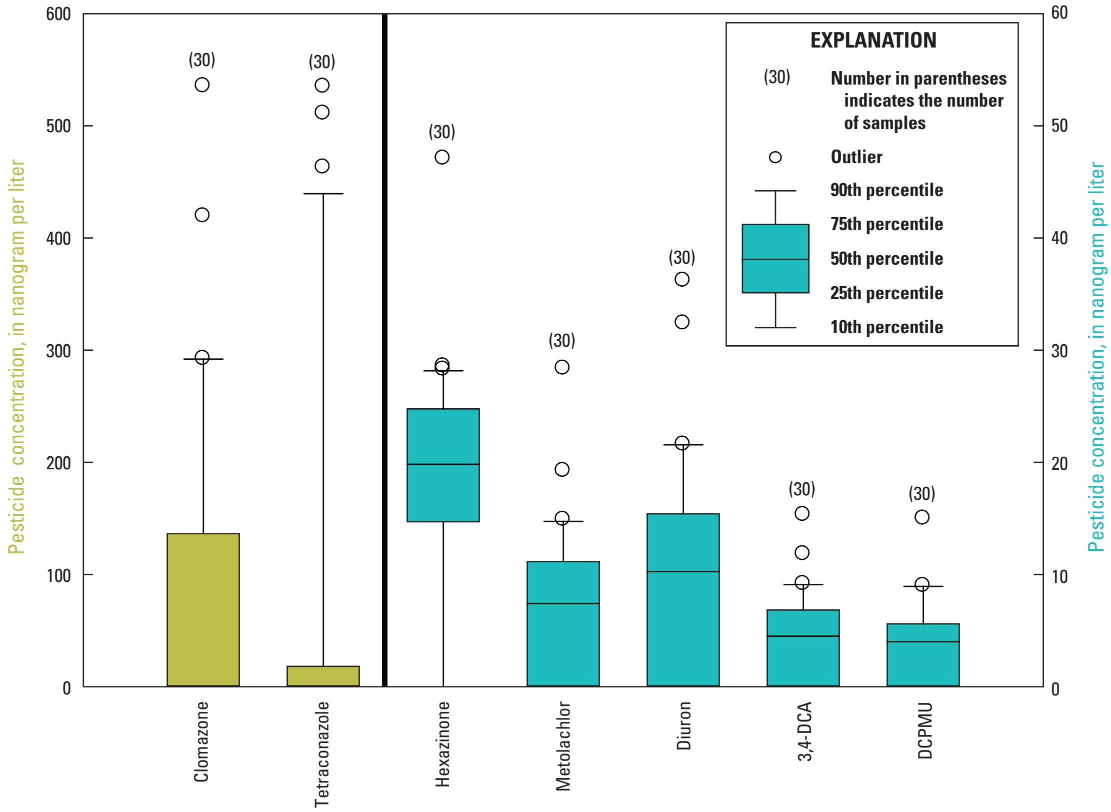

Figure 6. Concentrations of the most frequently detected pesticides from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011.

Table 7. Dissolved organic carbon concentration and water-quality parameter data measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011 and 2012.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. **Abbreviations**: hh:mm, hour:minute; mg/L, milligram per liter; mm/dd/yyyy, month/day/year; –, data not collected; °C, degree Celsius; µS/cm, microsiemen per centimeter]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Water temperature (°C) [00010]	Specific conduc-tance (µS/cm) [00095]	Dissolved oxygen (mg/L) [00300]	pH [00400]	Dissolved organic carbon (mg/L) [00681]
Sacramento River at Hood	04/11/2011	09:00	13.7	189	9.7	7.8	1.2
Sacramento River at Hood	04/18/2011	12:10	15.4	193	9.6	7.7	1.2
Sacramento River at Hood	04/25/2011	11:20	15.6	167	9.5	7.8	1.3
Sacramento River at Hood	05/02/2011	11:40	15.3	156	9.6	7.7	1.4
Sacramento River at Hood	05/09/2011	11:00	16.6	143	9.3	7.8	1.4
Sacramento River at Hood	05/16/2011	12:10	16.4	138	9.2	7.7	1.5
Sacramento River at Hood	05/23/2011	11:00	16.3	138	9.4	7.7	1.5
Sacramento River at Hood	06/01/2011	10:20	16.6	151	9.0	7.7	1.6
Sacramento River at Hood	06/06/2011	10:30	16.1	165	8.9	7.7	1.7
Sacramento River at Hood	06/13/2011	11:50	18.1	146	8.9	7.7	1.4
Suisun Bay at Mallard Island	04/11/2011	14:30	14.7	184	9.2	7.6	3.2
Suisun Bay at Mallard Island	04/18/2011	10:30	15.3	197	9.4	7.7	2.6
Suisun Bay at Mallard Island	04/25/2011	13:40	16.0	165	9.4	7.7	2.0
Suisun Bay at Mallard Island	05/02/2011	10:10	15.4	156	9.6	7.7	2.3
Suisun Bay at Mallard Island	05/09/2011	12:50	16.9	145	9.3	7.8	2.3
Suisun Bay at Mallard Island	05/16/2011	10:40	16.6	140	9.2	7.7	2.2
Suisun Bay at Mallard Island	05/23/2011	12:50	16.8	145	9.4	7.7	1.8

Table 7. Dissolved organic carbon concentration and water-quality parameter data measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2011 and 2012.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. **Abbreviations**: hh:mm, hour:minute; mg/L, milligram per liter; mm/dd/yyyy, month/day/year; –, data not collected; °C, degree Celsius; µS/cm, microsiemen 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]	Dissolved organic carbon (mg/L) [00681]
Suisun Bay at Mallard Island	06/01/2011	09:40	16.5	149	9.0	7.7	2.0
Suisun Bay at Mallard Island	06/06/2011	11:50	16.1	161	8.9	7.7	2.1
Suisun Bay at Mallard Island	06/13/2011	10:15	18.2	147	8.8	7.7	2.0
Grizzly Bay near Suisun Slough	04/05/2011	11:32	14.3	–	10.0	7.6	2.5
Grizzly Bay near Suisun Slough	04/12/2011	12:25	14.6	–	10.2	7.7	2.2
Grizzly Bay near Suisun Slough	04/21/2011	10:42	15.6	195	10.0	7.9	2.0
Grizzly Bay near Suisun Slough	04/26/2011	13:11	16.3	177	9.9	7.9	2.1
Grizzly Bay near Suisun Slough	05/03/2011	10:20	16.0	182	10.1	8.0	2.1
Grizzly Bay near Suisun Slough	05/10/2011	10:05	16.6	188	9.7	8.0	2.0
Grizzly Bay near Suisun Slough	05/17/2011	10:00	15.0	202	9.6	7.8	2.2
Grizzly Bay near Suisun Slough	05/24/2011	10:15	15.9	148	9.9	7.9	1.8
Grizzly Bay near Suisun Slough	05/31/2011	09:40	15.8	151	9.5	7.7	1.9
Grizzly Bay near Suisun Slough	06/07/2011	10:05	15.8	161	9.8	7.8	1.8
Sacramento River above Point Sacramento near Antioch	03/27/2012	09:10	12.3	208	9.6	7.6	4.0
Sacramento River above Point Sacramento near Antioch	04/03/2012	11:35	13.3	208	9.8	7.7	3.2
Sacramento River above Point Sacramento near Antioch	04/10/2012	09:20	13.9	235	9.5	7.7	2.5
Sacramento River above Point Sacramento near Antioch	04/17/2012	11:30	14.9	198	9.4	7.7	2.4
Sacramento River above Point Sacramento near Antioch	04/24/2012	08:45	17.4	220	8.9	7.7	3.4
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	18.4	191	9.2	7.8	3.6
Sacramento River above Point Sacramento near Antioch	05/08/2012	09:40	17.8	183	8.9	7.7	2.8
Sacramento River above Point Sacramento near Antioch	05/15/2012	11:55	18.6	211	8.8	7.8	3.4
Sacramento River above Point Sacramento near Antioch	05/22/2012	09:10	18.8	458	9.0	7.9	3.7
Sacramento River above Point Sacramento near Antioch	05/29/2012	11:05	18.5	758	8.9	7.9	2.7
San Joaquin River at Kimball Island near Antioch	03/27/2012	08:45	12.3	300	9.8	7.6	3.7
San Joaquin River at Kimball Island near Antioch	04/03/2012	11:05	13.9	235	9.8	7.8	3.8
San Joaquin River at Kimball Island near Antioch	04/10/2012	08:55	13.8	223	9.4	7.7	2.5
San Joaquin River at Kimball Island near Antioch	04/17/2012	11:00	15.2	223	9.6	7.8	4.1
San Joaquin River at Kimball Island near Antioch	04/24/2012	08:20	17.6	221	8.8	7.8	3.8
San Joaquin River at Kimball Island near Antioch	05/01/2012	11:00	18.9	226	9.0	7.9	2.7
San Joaquin River at Kimball Island near Antioch	05/08/2012	09:15	18.0	197	8.9	7.7	2.4
San Joaquin River at Kimball Island near Antioch	05/15/2012	11:15	19.1	217	8.7	7.8	3.6
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	19.1	481	8.7	7.8	3.3
San Joaquin River at Kimball Island near Antioch	05/29/2012	10:40	18.8	456	8.8	7.8	3.1
Grizzly Bay near Suisun Slough	03/27/2012	10:35	12.0	1,490	10.2	7.9	3.4
Grizzly Bay near Suisun Slough	04/03/2012	13:45	14.0	1,900	10.0	7.4	2.8
Grizzly Bay near Suisun Slough	04/10/2012	11:00	14.0	1,292	9.7	7.9	2.5
Grizzly Bay near Suisun Slough	04/17/2012	13:15	15.2	684	9.7	7.9	3.9
Grizzly Bay near Suisun Slough	04/24/2012	10:10	17.7	2,370	9.2	7.9	3.6
Grizzly Bay near Suisun Slough	05/01/2012	13:20	18.6	352	9.3	8.0	2.8
Grizzly Bay near Suisun Slough	05/08/2012	11:05	19.2	1,780	10.0	8.2	3.3
Grizzly Bay near Suisun Slough	05/15/2012	13:30	19.0	4,910	9.0	7.9	3.5
Grizzly Bay near Suisun Slough	05/22/2012	11:10	19.0	659	9.0	7.9	2.9
Grizzly Bay near Suisun Slough	05/29/2012	12:40	19.2	7,600	9.2	7.9	2.6

Table 8. Pesticide concentrations measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2012.

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. 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, carbaryl, chlorothalonil, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, cyprodinil, DCPA, DCPU, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, dinotefuran, EPTC, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, imazalil, iprodione, kresoxim-methyl, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanogram per liter; –, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Azoxystrobin (ng/L) [66589]	Boscalid (ng/L) [67550]	Carbofuran (ng/L) [65070]	Clomazone (ng/L) [67562]	DCPMU (ng/L) [68231]	3,4-Dichloroaniline (ng/L) [66584]	Diuron (ng/L) [66598]	Hexazinone (ng/L) [65085]
Sacramento River above Point Sacramento near Antioch	03/27/2012	09:10	188	16.0	(1.3)	–	3.3	5.6	30.1	41.6
Sacramento River above Point Sacramento near Antioch	04/03/2012	11:35	15.0	23.6	–	–	3.9	5.3	27.8	62.5
Sacramento River above Point Sacramento near Antioch	04/10/2012	09:20	6.0	17.8	–	–	3.0	(4.4)	23.3	28.0
Sacramento River above Point Sacramento near Antioch	04/17/2012	11:30	8.9	18.7	–	–	3.1	(3.6)	23.4	43.3
Sacramento River above Point Sacramento near Antioch	04/24/2012	08:45	5.4	15.3	–	–	(1.1)	–	12.8	19.4
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	18.4	31.5	–	–	–	–	8.3	134
Sacramento River above Point Sacramento near Antioch	05/08/2012	09:40	5.8	10.9	–	–	–	–	(1.8)	119
Sacramento River above Point Sacramento near Antioch	05/15/2012	11:55	9.4	13.2	–	–	(2.0)	–	7.3	127
Sacramento River above Point Sacramento near Antioch	05/22/2012	09:10	5.6	9.1	–	–	–	–	3.3	114
Sacramento River above Point Sacramento near Antioch	05/29/2012	11:05	5.5	10.1	–	26.3	–	–	4.2	127
San Joaquin River at Kimball Island near Antioch	03/27/2012	08:45	29.2	16.2	–	–	3.1	(3.9)	35.0	56.1
San Joaquin River at Kimball Island near Antioch	04/03/2012	11:05	21.6	–	–	–	3.3	(4.8)	26.7	63.9
San Joaquin River at Kimball Island near Antioch	04/10/2012	08:55	5.4	–	–	–	(2.1)	(2.5)	16.3	21.0
San Joaquin River at Kimball Island near Antioch	04/17/2012	11:00	12.0	18.7	–	–	4.5	(2.2)	22.5	17.7
San Joaquin River at Kimball Island near Antioch	04/24/2012	08:20	4.7	14.5	–	–	(1.9)	(2.5)	16.8	16.7
San Joaquin River at Kimball Island near Antioch	05/01/2012	11:00	8.8	14.4	–	–	(2.5)	–	15.4	122
San Joaquin River at Kimball Island near Antioch	05/08/2012	09:15	6.7	11.6	–	–	–	–	5.9	119
San Joaquin River at Kimball Island near Antioch	05/15/2012	11:15	8.7	15.2	–	–	4.2	–	12.7	125
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	7.4	11.8	–	–	–	–	3.7	118
San Joaquin River at Kimball Island near Antioch	05/29/2012	10:40	6.8	13.1	–	–	–	–	3.8	131
Grizzly Bay near Suisun Slough	03/27/2012	10:35	36.8	–	–	–	(2.8)	(4.6)	36.8	71.9
Grizzly Bay near Suisun Slough	04/03/2012	13:45	17.9	–	–	–	(2.6)	(4.6)	22.8	50.8
Grizzly Bay near Suisun Slough	04/10/2012	11:00	11.3	19.9	–	–	3.4	(4.7)	26.5	56.7
Grizzly Bay near Suisun Slough	04/17/2012	13:15	12.7	25.1	–	–	(2.6)	7.0	16.6	61.2
Grizzly Bay near Suisun Slough	04/24/2012	10:10	8.7	–	–	–	–	–	3.4	44.1
Grizzly Bay near Suisun Slough	05/01/2012	13:20	10.5	18.2	–	–	(1.4)	–	11.9	123
Grizzly Bay near Suisun Slough	05/08/2012	11:05	8.8	12.7	–	–	–	–	6.2	121
Grizzly Bay near Suisun Slough	05/15/2012	13:30	9.0	12.2	–	–	(1.7)	(2.3)	9.6	120
Grizzly Bay near Suisun Slough	05/22/2012	11:10	9.0	12.3	–	–	–	–	4.3	122
Grizzly Bay near Suisun Slough	05/29/2012	12:40	7.9	9.6	–	–	–	–	5.1	117

Table 8. Pesticide concentrations measured in water samples collected from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2012.—Continued

[Numbers in brackets are U.S. Geological Survey (USGS) National Water Information System (NWIS) parameter codes. 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, carbaryl, chlorothalonil, chlorpyrifos, clothianidin, cycloate, cyfluthrin, cyhalothrin, cypermethrin, cyproconazole, cyprodinil, DCPA, DCPU, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, deltamethrin, desulfinylfipronil, diazinon, 3,5-dichloroaniline, difenoconazole, (*E*)-dimethomorph, dinotefuran, EPTC, esfenvalerate, ethalfluralin, etofenprox, famoxadone, fenarimol, fenbuconazole, fenhexamide, fenpropathrin, fipronil, fipronil sulfide, fipronil sulfone, fluazinam, fludioxinil, fluoxastrobin, flusilazole, flutriafol, τ-fluvalinate, imazalil, iprodione, kresoxim-methyl, metconazole, methidathion, methoprene, methylparathion, molinate, myclobutanil, oxyflurofen, pebulate, pentachloroanisole, pentachloronitrobenzene, permethrin, phenothrin, phosmet, piperonyl butoxide, prometon, prometryn, propanil, propyzamide, pyraclostrobin, pyrimethanil, resmethrin, tebuconazole, tefluthrin, tetraconazole, tetramethrin, thiacloprid, thiamethoxam, thiobencarb, triadimefon, triadimenol, trifloxstrobin, triflumizole, triticonazole, and zoxamide. **Abbreviations**: hh:mm, hour:minute; mm/dd/yyyy, month/day/year; ng/L, nanogram per liter; –, not detected]

USGS station name	Sample date (mm/dd/yyyy)	Sample time (hh:mm)	Imidacloprid (ng/L) [68426]	Malathion (ng/L) [65087]	Metolachlor (ng/L) [65090]	Napropamide (ng/L) [65092]	Pendimethalin (ng/L) [65098]	Propiconazole (ng/L) [66643]	Simazine (ng/L) [65105]	Trifluralin (ng/L) [65108]
Sacramento River above Point Sacramento near Antioch	03/27/2012	09:10	(1.3)	(3.7)	5.7	–	–	–	33.8	–
Sacramento River above Point Sacramento near Antioch	04/03/2012	11:35	(2.2)	–	8.6	–	–	–	44.8	–
Sacramento River above Point Sacramento near Antioch	04/10/2012	09:20	–	–	4.0	–	–	–	15.1	–
Sacramento River above Point Sacramento near Antioch	04/17/2012	11:30	(2.0)	–	7.6	–	12.0	20.2	95.8	–
Sacramento River above Point Sacramento near Antioch	04/24/2012	08:45	–	–	5.1	–	6.1	–	23.4	–
Sacramento River above Point Sacramento near Antioch	05/01/2012	11:30	–	–	29.3	–	–	–	126	–
Sacramento River above Point Sacramento near Antioch	05/08/2012	09:40	–	–	14.5	–	–	–	89.1	–
Sacramento River above Point Sacramento near Antioch	05/15/2012	11:55	–	–	18.7	–	–	–	97.5	–
Sacramento River above Point Sacramento near Antioch	05/22/2012	09:10	–	–	17.6	70.5	–	–	72.5	–
Sacramento River above Point Sacramento near Antioch	05/29/2012	11:05	–	–	29.1	–	–	–	83.5	–
San Joaquin River at Kimball Island near Antioch	03/27/2012	08:45	–	–	–	–	–	–	37.9	–
San Joaquin River at Kimball Island near Antioch	04/03/2012	11:05	–	–	8.9	–	–	–	42.3	–
San Joaquin River at Kimball Island near Antioch	04/10/2012	08:55	–	–	–	–	12.9	–	16.8	–
San Joaquin River at Kimball Island near Antioch	04/17/2012	11:00	–	–	7.3	–	15.8	–	54.6	3.2
San Joaquin River at Kimball Island near Antioch	04/24/2012	08:20	–	–	5.7	–	5.0	–	20.6	–
San Joaquin River at Kimball Island near Antioch	05/01/2012	11:00	–	–	21.0	–	–	–	140	–
San Joaquin River at Kimball Island near Antioch	05/08/2012	09:15	–	–	16.7	–	–	–	102	–
San Joaquin River at Kimball Island near Antioch	05/15/2012	11:15	–	–	22.0	–	–	–	118	–
San Joaquin River at Kimball Island near Antioch	05/22/2012	08:40	–	–	17.7	51.5	–	–	88.7	–
San Joaquin River at Kimball Island near Antioch	05/29/2012	10:40	–	–	31.1	–	–	–	84.8	–
Grizzly Bay near Suisun Slough	03/27/2012	10:35	(3.8)	–	–	–	–	–	39.8	–
Grizzly Bay near Suisun Slough	04/03/2012	13:45	–	–	5.3	–	–	–	29.7	–
Grizzly Bay near Suisun Slough	04/10/2012	11:00	–	–	9.1	–	8.0	–	35.3	–
Grizzly Bay near Suisun Slough	04/17/2012	13:15	–	–	8.7	–	11.8	21.1	32.2	–
Grizzly Bay near Suisun Slough	04/24/2012	10:10	–	–	13.2	–	12.9	–	55.5	2.6
Grizzly Bay near Suisun Slough	05/01/2012	13:20	–	–	23.4	–	–	–	139	–
Grizzly Bay near Suisun Slough	05/08/2012	11:05	–	–	22.6	–	–	–	101	–
Grizzly Bay near Suisun Slough	05/15/2012	13:30	–	–	17.8	–	–	–	94.6	–
Grizzly Bay near Suisun Slough	05/22/2012	11:10	–	–	16.1	–	–	–	97.0	–
Grizzly Bay near Suisun Slough	05/29/2012	12:40	–	–	16.8	–	–	–	88.4	–

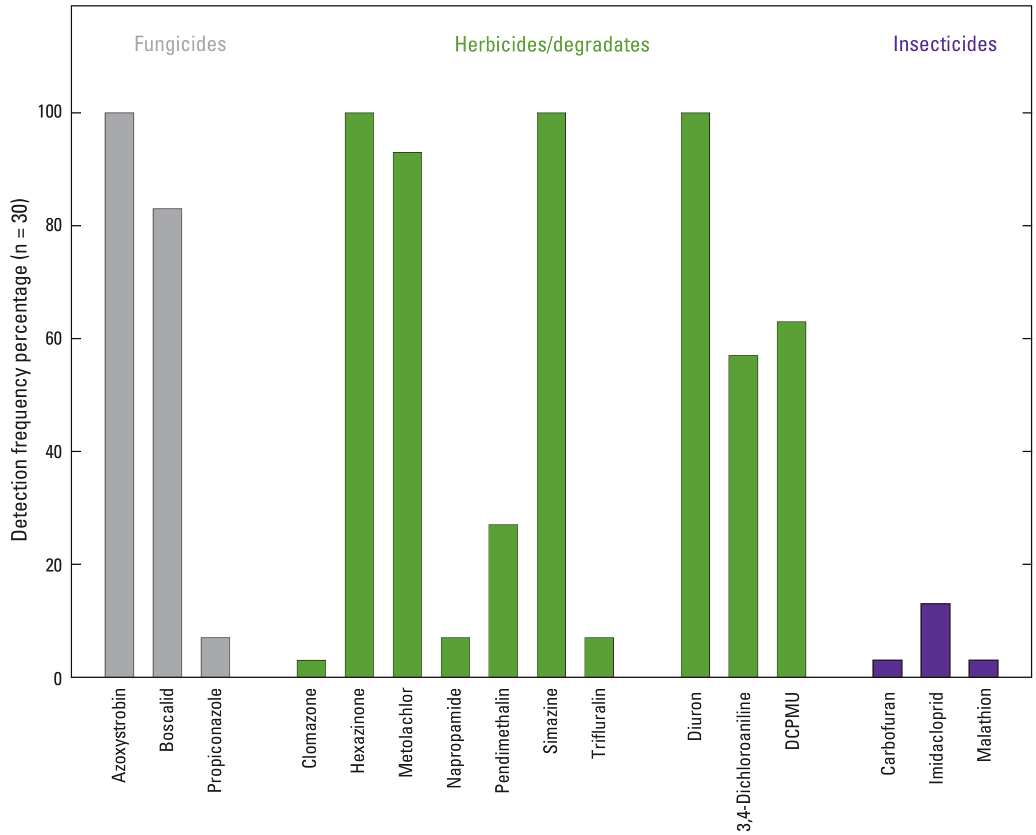

Figure 7. Pesticide detection frequencies from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2012.

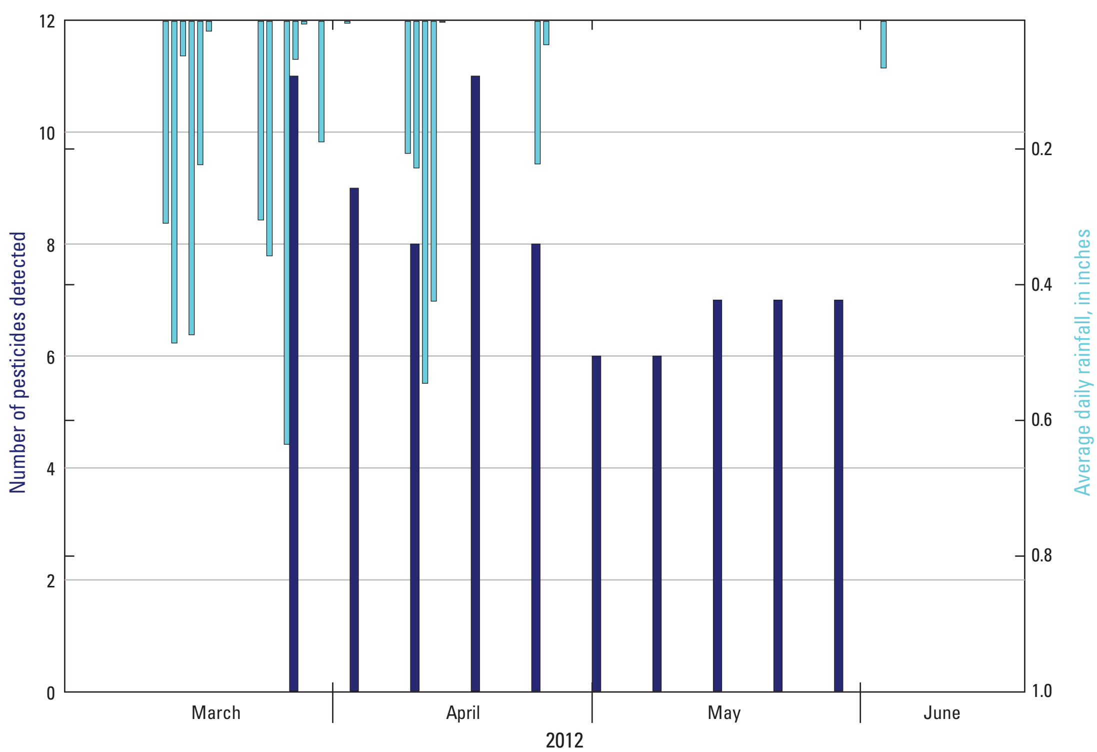

Figure 8. Pesticide detections at Sacramento River above Point Sacramento, California, by sampling event during spring 2012.

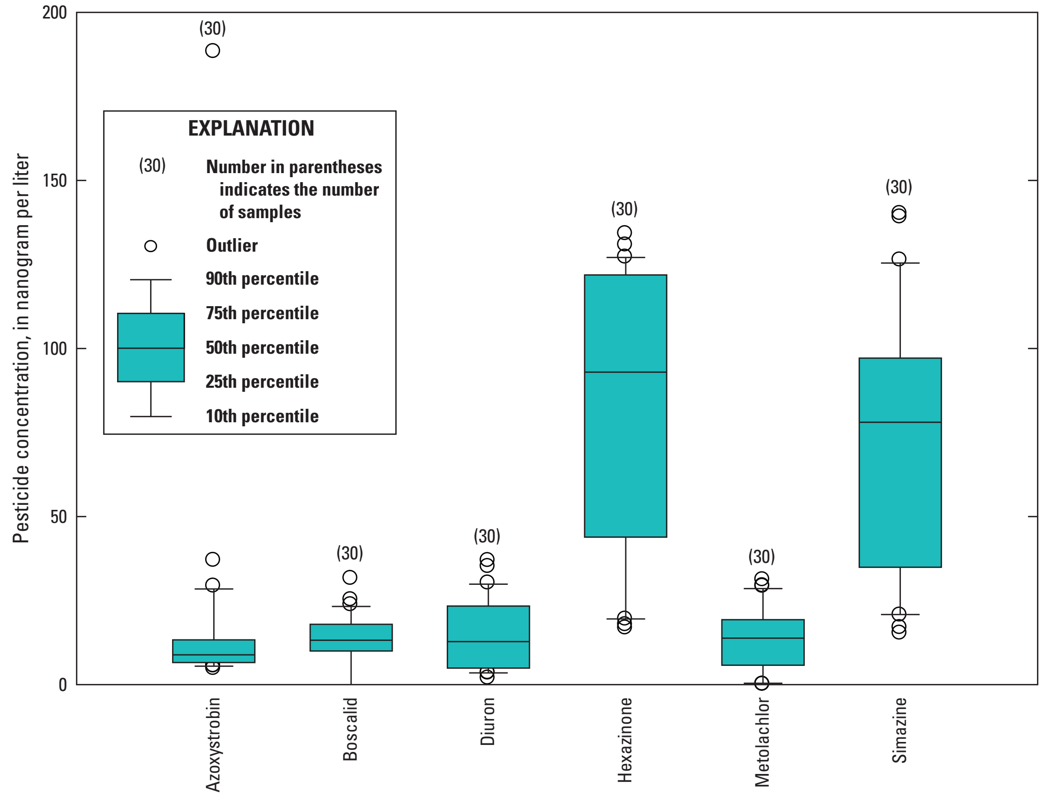

Figure 9. Concentrations of the most frequently detected pesticides from sites in the Sacramento-San Joaquin Delta and Grizzly Bay, California, during spring 2012.

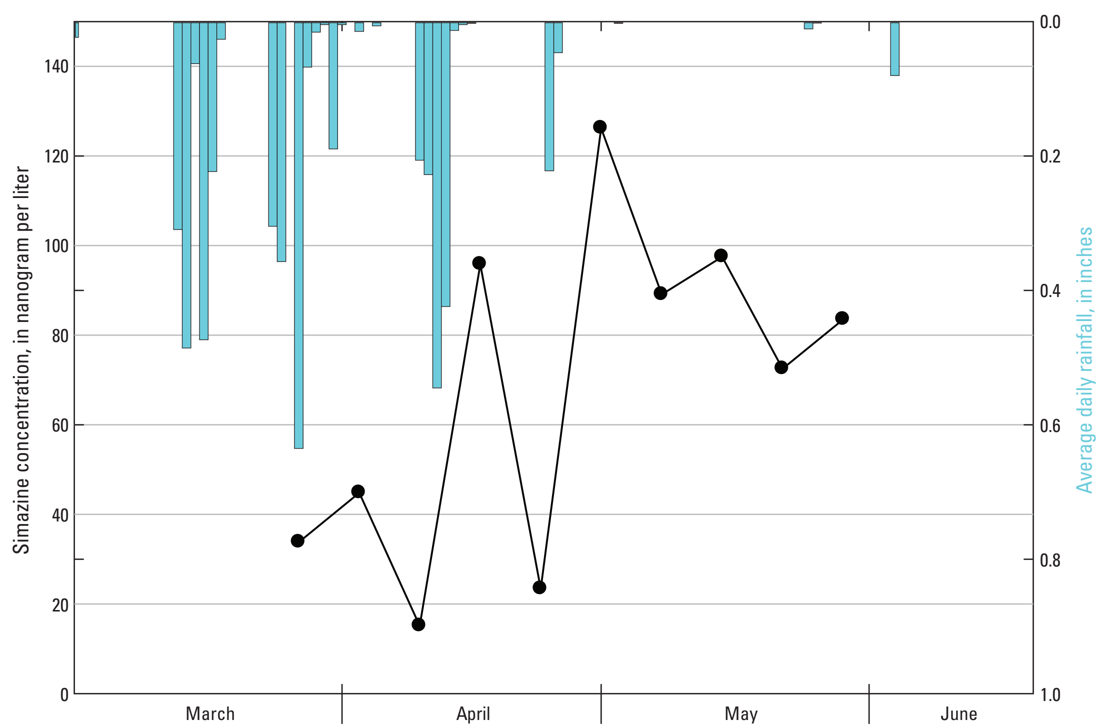

Figure 10. Simazine concentrations in samples from the Sacramento River above Point Sacramento, California, during spring 2012.

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