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Concentrations of Organic Contaminants Detected during Managed Flow Conditions, San Joaquin River and Old River, California, 2001

Data Series Report DS 120

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

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By James L. Orlando and Kathryn M. Kuivila

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Conversion Factors

Multiply	By	To obtain
cubic meter (m^3)	264.2	gallon (gal)
kilogram (kg)	2.205	pound avoirdupois (lb)
kilometer (km)	0.6214	mile (mi)
liter (L)	33.82	ounce, fluid (fl oz)

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

$$°F = (1.8 \times °C) + 32$$

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).

Acronyms and Abbreviations

BML	Bodega Marine Laboratory (UCD)
Delta	San Francisco Bay Delta
GC/MS	gas chromatography/mass spectrometry
MDL	method detection limit
NWQL	National Water Quality Laboratory (USGS)
OCL	organic chemistry laboratory (USGS)
SL	Sediment Laboratory (USGS)
UCD	University of California at Davis
USGS	U.S. Geological Survey
VAMP	Vernalis Adaptive Management Plan

ng/L	nanogram per liter
ft^3/s	cubic foot per second
mL	milliliter
μL	microliter

Concentrations of Organic Contaminants Detected during Managed Flow Conditions, San Joaquin River and Old River, California, 2001

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Abstract

Concentrations of organic contaminants were determined in water samples collected at six surface-water sites located along the San Joaquin and Old Rivers during April through June 2001. Water samples were collected, coincident with salmon smolt caging studies conducted by researchers from the Bodega Marine Laboratory at the University of California at Davis to characterize exposure of the salmon smolt to organic contaminants. Sampling occurred prior to, during, and following the implementation of managed streamflow conditions on the San Joaquin and Old Rivers as part of the Vernalis Adaptive Management Plan. Thirteen pesticides were detected in water samples collected during this study, and at least five pesticides were detected in each sample. The total number of pesticide detections varied little between river systems and between sites, but the maximum concentrations of most pesticides occurred in San Joaquin River samples. The total number of pesticides detected varied little over the three time periods. However, during the period of managed streamflow, the fewest number of pesticides were detected at their absolute maximum concentration. Nine wastewater compounds were detected during this study. Suspended-sediment concentrations were similar for the San Joaquin and Old Rivers except during the period of managed streamflow conditions, when suspended-sediment concentration was higher at sites on the San Joaquin River than at sites on the Old River. Values for water parameters (pH, specific conductance, and hardness) were lowest during the period of managed flows.

Introduction

Water flow and water quality are thought to be the primary factors affecting the survival of juvenile fall-run Chinook salmon in the San Joaquin River and the San Francisco Bay Delta (Delta) (San Joaquin River Group Authority, 2002). A marked decline in the number of adult salmon in the San Joaquin River Basin has led to the creation of numerous multistakeholder programs designed to stabilize and restore salmon populations in this region of California. One of these programs, the San Joaquin River Group Authority, has developed and implemented the Vernalis Adaptive Management Plan (VAMP), which is designed to support salmon population restoration by improving salmon smolt survival during emigration through the San Joaquin River Delta.

A critical component of the VAMP is the management of San Joaquin River and Delta flows during April and May to meet established flow targets. This is accomplished by (1) constructing flow barriers on key Delta waterways, (2) carefully timing the release of water from reservoirs within the upper San Joaquin River Basin to augment San Joaquin River flows, and (3) reducing Central Valley Water Project water exports from the Delta (San Joaquin River Group Authority, 2002).

Another key element of the VAMP is its support of multiple scientific studies designed to investigate the effects of San Joaquin River and Delta flow modifications on salmon smolt survival. Previous studies have shown that the survival of fall-run Chinook salmon (*Oncorhynchus tshawytscha*) smolt is much greater in the San Joaquin River than in the Old River (Herbold and others, 1992; Brandes and Pierce, 1998). The overall survival of salmon smolt in the Delta improves during high San Joaquin River flows and when the barrier at the head of Old River is in place to prevent salmon from entering Old River (Brandes and Pierce, 1998; Pierce and Brandes, 1999); however, the causes of lower survival rates of salmon smolt in Old River are unknown.

One subject of concern is the presence of organic contaminants and their potential effects on salmon smolt survival. Pesticides are used throughout the Delta and San Joaquin River Basin, and approximately 5.2 million kg were applied throughout the area in 2001 (California Department of Pesticide Regulation, 2001). Numerous studies have detected many of these pesticides in surface waters of the region (Kuivila and Foe, 1995; MacCoy and others, 1995; Kratzer, 1997; Dubrovsky, and others, 1998; Kuivila and others, 1999; Kuivila and Moon, 2004); however, little is known concerning the effects of these pesticides on the health and survival of juvenile Chinook salmon in the San Joaquin River and the Delta. Additionally, this region supports a number of large urban centers that discharge treated wastewater and associated contaminants to the San Joaquin River and its tributaries.

The effect of streamflow modifications, implemented as part of the VAMP, on the transport of organic contaminants from agricultural runoff and urban sources in both the San Joaquin and Old Rivers is unknown. It is possible that modifications in flow might lead to conditions detrimental to salmon smolt survival. As a result, one focus of the VAMP has been to study the effects of San Joaquin River flow modifications on water quality and related effects on Chinook salmon smolt survival.

Project Design

This project was designed to determine if exposure to organic contaminants contributes to varying survival rates of Chinook salmon smolt emigrating in the Old River and the San Joaquin River. To evaluate these potential effects, water samples were collected for the analysis of organic contaminants concurrently with salmon-smolt caging studies designed to measure smolt biological responses (DNA strand breakage, acetylcholinesterase activity, stress protein expression, and cytochrome P450 expression). Six sites were sampled: three located on the San Joaquin River and three on Old River (*fig. 1*, *table 1*). At each of these sites, sets of twelve, hatchery raised, salmon smolt were kept in cages for approximately 96 hours, during three time periods, before, during, and after the managed streamflow conditions of the VAMP (*fig. 2*). The discharge shown in *figure 2* was recorded at Vernalis, 29 km upstream from the head of the Old River. During the VAMP period, the mean daily flow measured in the Old River ranged from 75 to 692 ft^3/s (2.1 to 19.6 m^3/s) (San Joaquin River Group Authority, 2002).

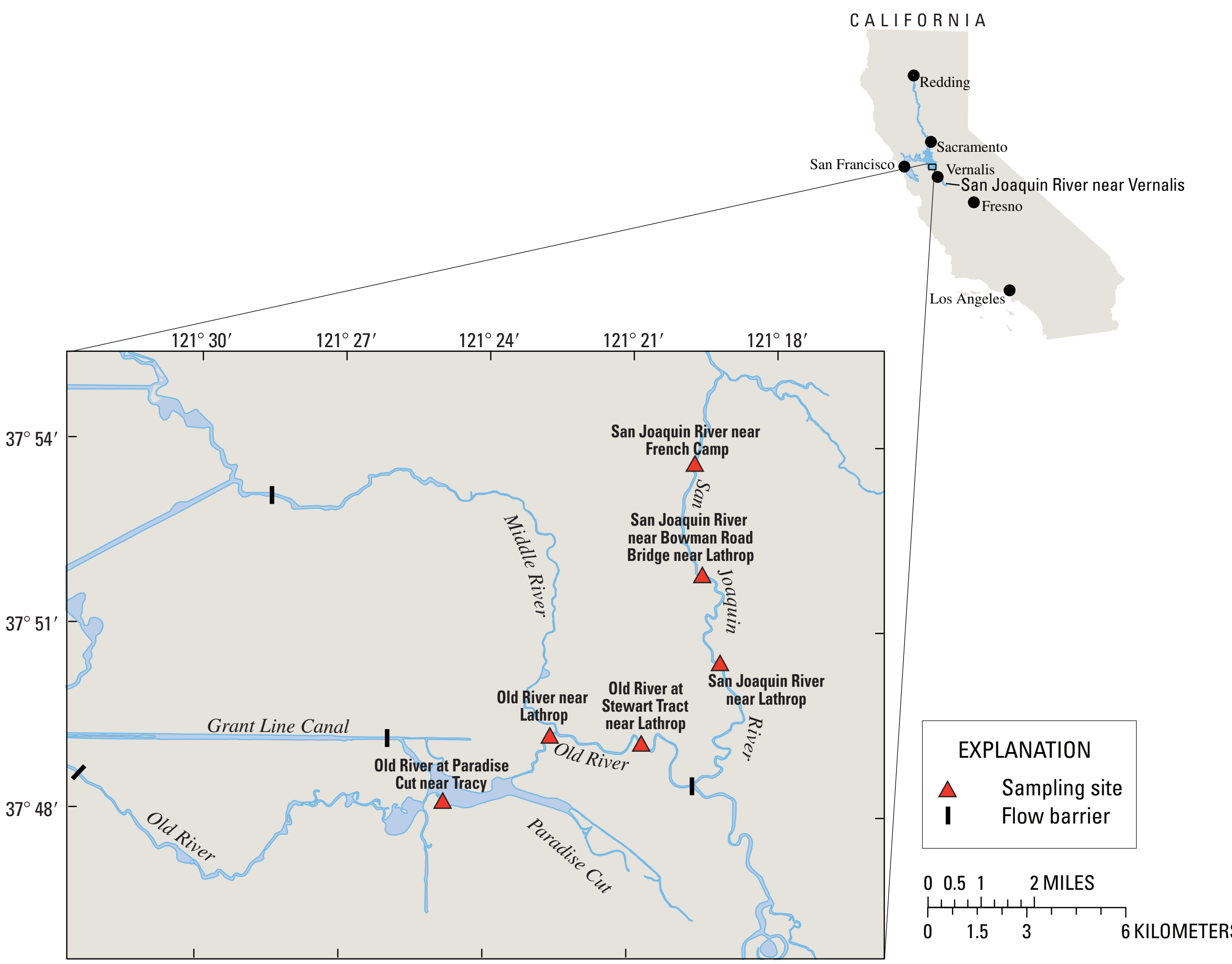

Figure 1. Map showing locations of sampling sites and flow barriers within the San Joaquin Delta, California.

Table 1. Water-quality sampling sites, Sacramento–San Joaquin Delta, California.

[Horizontal datum is NAD 83. USGS, U.S. Geological Survey]

Site name	USGS site identification no.	Latitude (degree/minute/second)	Longitude (degree/minute/second)
Old River at Stewart Tract near Lathrop	374910121204301	37°49′10.2″	121°20′43.4″
Old River near Lathrop	374916121223901	37°49′16.3″	121°22′39.4″
Old River at Paradise Cut near Tracy	374813121244901	37°48′13.0″	121°24′49.7″
San Joaquin River near Lathrop	375029121190601	37°50′29.0″	121°19′06.6″
San Joaquin River near Bowman Road Bridge near Lathrop	375154121193101	37°51′54.4″	121°19′31.1″
San Joaquin River near French Camp	375342121194301	37°53′42.4″	121°19′43.0″

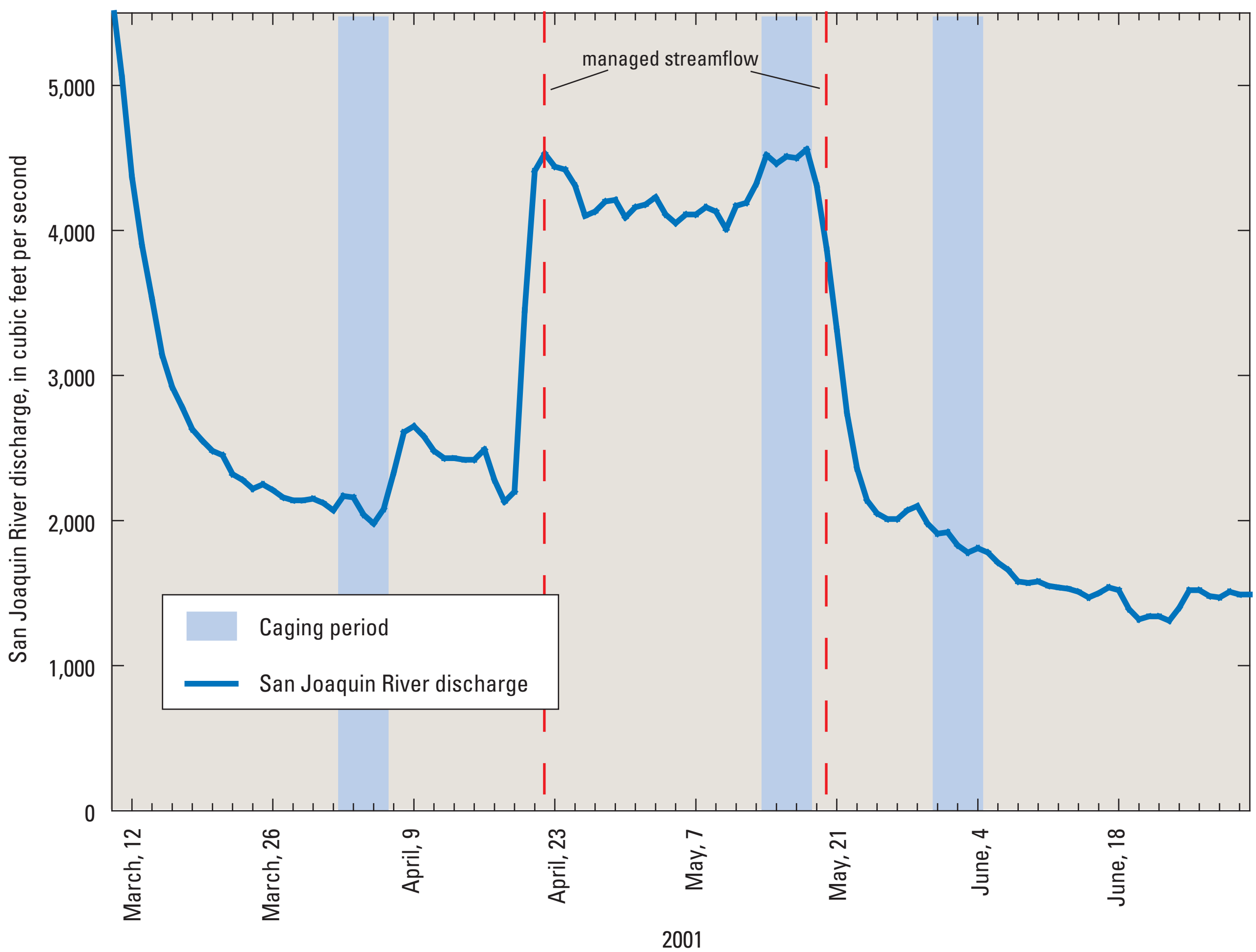

Figure 2. Graph showing San Joaquin River discharge measured at Vernalis, , California, and salmon smolt caging periods.

Water samples for the analysis of pesticides were collected at each of the sites, both when the smolt were emplaced (day 1) and when they were removed (day 5). Samples collected on days 1 and 5 were composited for each of the sites in an effort to approximate smolt exposure to pesticides during each 5-day caging period. Samples were analyzed for 32 current-use pesticides by gas chromatography/mass spectrometry (GC/MS) at the U.S. Geological Survey's (USGS) organic chemistry laboratory (OCL) in Sacramento, California. Additional samples were collected from two sites, once during each sampling period and sent to the USGS's National Water Quality Laboratory (NWQL) in Denver, Colorado, for analysis of wastewater compounds and pesticides.

Following exposure in the field, fish were dissected, and samples of blood and tissue were collected and analyzed for acetylcholinesterase activity, DNA strand breaks, cytochrome P450 expression, and stress protein expression. Analyses of these effects were conducted by researchers from the Bodega Marine Laboratory (BML) at the University California at Davis (UCD). Results of these analyses are beyond the scope of this report and are not included.

During this study, the USGS assisted UCD with the collection of water samples and conducted chemical analyses of all water samples. Water samples were analyzed for pesticides, wastewater compounds, suspended-sediment concentration, and standard water quality parameters (temperature, pH, conductivity, and hardness).

Purpose and Scope

This report describes the methods and procedures used during sample collection and analysis and presents water-quality data for samples collected during this study. Concentrations of 32 current-use pesticides analyzed in 18 composite water samples are presented in *table 2*. In addition, concentrations of select wastewater compounds and pesticides analyzed in six water samples by the NWQL are reported (in *table 3*) as well as suspended-sediment concentration and water quality parameters for the water samples (listed in *table 4*).

Acknowledgments

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Procedures and Methods

Description of Sampling Sites

Three sites were chosen on both the San Joaquin River and Old River near the southern end of the San Francisco Bay Delta, an area used by salmon smolt during migration (*fig. 1*, *table 1*). Because of the necessity of anchoring the fish cages, sites were selected near the river banks, in shallow water and often near stands of vegetation. All sites were accessible only by boat. Sampling sites were chosen by personnel from the U.S. Fish and Wildlife Service and BML.

Sample Collection

Water samples were collected for analysis of pesticide and suspended-sediment concentrations and water quality parameters (specific conductance, pH, and hardness) at all six sites, both at the time of fish emplacement and at retrieval. Water samples were collected by submerging a 3-L Teflon collection bottle in a weighted steel cage. A single Teflon bottle was used at all the sites and was prerinsed between sites three times with water from the site about to be sampled and (or) with deionized water. All samples were collected from the same depth as (0.5 to 1.0 m) and in proximity to the fish cages. Immediately after collection, the Teflon bottle was shaken for one minute to homogenize the sample, which was then poured into a 1-L baked, amber glass bottle containing 100 mL of methylene chloride, one 500-mL glass milk bottle for sediment analysis, and one 125-mL plastic bottle for analysis of water parameters. Additional 1-L water samples were collected only at the farthest downstream sites on both the San Joaquin River and Old River once for each caging event. These samples were collected for analysis of wastewater compounds and pesticides by the NWQL and required a second use of the Teflon bottle sampler at these sites. All samples were preserved on ice and transported to the OCL in Sacramento within 6 hours of collection.

Table 2. Pesticide concentrations in water samples collected in 2001.

[All sample types are composites. Samples were analyzed for the following pesticides that were not detected in any samples: Alachlor, Bifenthrin, Butylate, DCPA, Diethatyl-ethyl, Dimethoate, Esfenvalerate, Ethalfluralin, lambda-Cyhalothrin, Malathion, Methidathion, Methyl parathion, 2-keto-molinate, Napropamide, Pebulate, Permethrin, Phosmet, Piperonyl butoxide, and Thiobencarb. Concentrations are in nanograms per liter; m/d/y, month/day/year; nd, not detected; ( ), values are estimated because the compounds were detected at a concentration below the method detection limit]

Sampling site	Date (month/day/year)	Atrazine	Carbaryl	Carbofuran	Chlorpyrifos	Cycloate	Diazinon	EPTC	Metolachlor
Old River at Stewart Tract near Lathrop, California	4/2/01 and 4/6/01	nd	nd	(6.9)	nd	nd	17.0	nd	13.4
Old River at Stewart Tract near Lathrop, California	5/14/01 and 5/18/01	nd	12.6	nd	nd	nd	8.3	nd	30.9
Old River at Stewart Tract near Lathrop, California	5/31/01 and 6/4/01	nd	nd	nd	nd	11.6	6.7	51.5	27.5
Old River near Lathrop, California	4/2/01 and 4/6/01	13.5	nd	(10.8)	nd	nd	54.1	nd	20.2
Old River near Lathrop, California	5/14/01 and 5/18/01	nd	nd	nd	nd	nd	9.0	nd	24.6
Old River near Lathrop, California	5/31/01 and 6/4/01	nd	nd	nd	nd	9.6	5.5	42.3	27.3
Old River at Paradise Cut near Tracy, California	4/2/01 and 4/6/01	nd	nd	12.7	nd	nd	131	nd	16.9
Old River at Paradise Cut near Tracy, California	5/14/01 and 5/18/01	nd	nd	111	nd	nd	9.8	26.3	139
Old River at Paradise Cut near Tracy, California	5/31/01 and 6/4/01	nd	nd	17.3	nd	8.9	8.4	9.8	211
San Joaquin River near Lathrop, California	4/2/01 and 4/6/01	nd	21.4	13.9	nd	nd	241	nd	11.0
San Joaquin River near Lathrop, California	5/14/01 and 5/18/01	nd	9.8	nd	4.6	nd	10.0	nd	26.7
San Joaquin River near Lathrop, California	5/31/01 and 6/4/01	nd	nd	nd	nd	11.9	5.6	38.3	36.4
San Joaquin River near Bowman Road Bridge near Lathrop, California	4/2/01 and 4/6/01	nd	nd	(9.3)	nd	nd	13.9	nd	10.8
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/14/01 and 5/18/01	nd	9.9	nd	nd	nd	8.4	nd	24.7
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/31/01 and 6/4/01	nd	nd	nd	nd	13.5	6.8	18.8	41.2
San Joaquin River near French Camp, California	4/2/01 and 4/6/01	nd	11.8	13.3	nd	nd	11.3	nd	15.3
San Joaquin River near French Camp, California	5/14/01 and 5/18/01	nd	10.2	nd	5.3	(4.3)	9.1	9.1	28.9
San Joaquin River near French Camp, California	5/31/01 and 6/4/01	nd	nd	nd	nd	13.1	5.8	nd	42.0

Table 2. Pesticide concentrations in water samples collected in 2001—***Continued***.

[All sample types are composites. Samples were analyzed for the following pesticides that were not detected in any samples: Alachlor, Bifenthrin, Butylate, DCPA, Diethatyl-ethyl, Dimethoate, Esfenvalerate, Ethalfluralin, lambda-Cyhalothrin, Malathion, Methidathion, Methyl parathion, 2-keto-molinate, Napropamide, Pebulate, Permethrin, Phosmet, Piperonyl butoxide, and Thiobencarb. Concentrations are in nanograms per liter; m/d/y, month/day/year; nd, not detected; ( ), values are estimated because the compounds were detected at a concentration below the method detection limit]

Sampling Site	Date (month/day/year)	Molinate	4-keto-molinate	Prometryn	Simazine	Trifluralin
Old River at Stewart Tract near Lathrop, California	4/2/01 and 4/6/01	nd	nd	86.5	22.9	6.3
Old River at Stewart Tract near Lathrop, California	5/14/01 and 5/18/01	(4.0)	nd	nd	17.4	6.6
Old River at Stewart Tract near Lathrop, California	5/31/01 and 6/4/01	16.7	12.5	nd	12.6	(4.3)
Old River near Lathrop, California	4/2/01 and 4/6/01	nd	nd	114	29.5	5.8
Old River near Lathrop, California	5/14/01 and 5/18/01	(6.1)	nd	nd	15.3	6.5
Old River near Lathrop, California	5/31/01 and 6/4/01	11.5	(9.5)	nd	14.9	(3.4)
Old River at Paradise Cut near Tracy, California	4/2/01 and 4/6/01	nd	nd	107	27.3	(4.4)
Old River at Paradise Cut near Tracy, California	5/14/01 and 5/18/01	(6.2)	nd	nd	19.3	(5.0)
Old River at Paradise Cut near Tracy, California	5/31/01 and 6/4/01	18.4	12.5	nd	15.6	7.7
San Joaquin River near Lathrop, California	4/2/01 and 4/6/01	nd	nd	122	26.7	(4.0)
San Joaquin River near Lathrop, California	5/14/01 and 5/18/01	8.7	nd	nd	19.1	9.4
San Joaquin River near Lathrop, California	5/31/01 and 6/4/01	17.6	(11.5)	nd	15.5	(4.0)
San Joaquin River near Bowman Road Bridge near Lathrop, California	4/2/01 and 4/6/01	nd	nd	108	31.0	(4.9)
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/14/01 and 5/18/01	(4.4)	nd	nd	17.8	8.3
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/31/01 and 6/4/01	12.5	(11.2)	nd	15.3	(4.2)
San Joaquin River near French Camp, California	4/2/01 and 4/6/01	nd	nd	82.4	64.9	(4.4)
San Joaquin River near French Camp, California	5/14/01 and 5/18/01	(7.0)	nd	nd	14.6	10.1
San Joaquin River near French Camp, California	5/31/01 and 6/4/01	35.2	24.4	nd	16.9	(3.8)

Table 3. Concentrations of pesticide and wastewater compounds detected in samples analyzed by the U.S. Geological Survey's National Water Quality Laboratory.

[Samples were analyzed for the following compounds that were not detected in any samples: 1,4-Dichlorobenzene, 1-Methylnapthalene, 2,6-Dimethylnapthalene, 2-Methylnapthalene, 3-beta-Coprostanol, 3-Methyl-1(H)-indole, 3-tert-Butyl-4hydroxyanisole, 4-Cumylphenol, 4-n-Octylphenol, 5-Methyl-1H-benzotriazle, Acetophenone, Anthracene, Anthraquinone, Benzo(a)pyrene, Benzophenone, beta-Stigmastanol, Bisphenol A, Bromoform, Camphor, Carbaryl, Carbazole, Chlorpyrifos, Cotinine, DEET, Dichlorvos, d-Limonene, Ethanol, 2-butoxy-,phosphate, Fluoranthene, Hexahydrohexamethyl cyclopentabenzopyran, Indole, Isoborneol, Isophorone, Isopropylbenzene, Isoquinoline, Menthol, Methyl salicylate, Naphthalene, Nonylphenol,diethoxy-(total), Octyphenol,monoethoxy-, Octylphenol,diethoxy-, p-Cresol, para-Nonylphenol-total, Pentachlorophenol, Phenanthrene, Prometon, Pyrene, Skatol, Tetrachloroethylene, Tri(2-chloroethyl)phosphate, Tri(dichlorisopropyl)phosphate, Tributyl phosphate, Triclosan, Triethyl citrate, Triphenyl phosphate, and Tris(2-butoxyethyl)phosphate. Concentrations are in nanograms per liter; m/d/y, month/day/year; h, hours; m, minutes; E, estimated; * denotes pesticide; <, less than]

Compound	Location	Old River at Paradise Cut near Tracy, CA			San Joaquin River near French Camp, CA		
	Date (m/d/y)	4/6/01	5/14/01	6/4/01	4/6/01	5/14/01	6/4/01
	Time (hhmm)	1130	1545	1040	0920	1415	0833
4-tert-Octylphenol		< 1,000	E110	< 1,000	< 1,000	E120	< 1,000
Acetyl hexamethyl tetrahydro naphthalene		< 500	E61	< 500	< 500	< 500	< 500
beta-Sitosterol		E800	E1,300	< 2,000	E700	E1,400	< 2,000
Bromacil*		E77	<500	< 500	E59	< 500	< 500
Caffeine		< 500	E80	E130	< 500	< 500	< 500
Cholesterol		E880	E1,800	< 2,000	E830	E1,400	< 2,000
Diazinon*		E12	<500	< 500	E16	< 500	< 500
Metalaxyl*		E19	<500	< 500	E11	< 500	< 500
Metolachlor*		E35	E160	E72	E26	E51	E48
Phenol		E490	<500	E310	E340	< 500	E620

Table 4. Suspended-sediment concentrations and water parameters in water samples collected in 2001.

[µg/L, milligram per liter; NA, parameter not available; µS/cm, microsiemens per centimeter; m/d/y, month/day/year; h, hours; m, minutes]

Sampling site	Date (m/d/y)	Time (hhmm)	Suspended sediment concentration (mg/L)	Temperature (C°)	pH	Specific conductance (µS/cm)	Hardness (mg/L as $CaCO_3$)
Old River at Stewart Tract near Lathrop, California	4/2/01	1515	32	17.0	8.10	1015	270
Old River at Stewart Tract near Lathrop, California	4/6/01	1230	35	15.5	7.96	900	240
Old River at Stewart Tract near Lathrop, California	5/14/01	1645	13	20.5	7.74	316	90
Old River at Stewart Tract near Lathrop, California	5/18/01	1128	21	22.1	7.61	338	90
Old River at Stewart Tract near Lathrop, California	5/31/01	1210	64	24.5	8.50	646	150
Old River at Stewart Tract near Lathrop, California	6/4/01	1130	61	22.0	8.81	730	190
Old River near Lathrop, California	4/2/01	1450	39	17.0	8.02	1014	270
Old River near Lathrop, California	4/6/01	1200	36	15.5	8.00	902	260
Old River near Lathrop, California	5/14/01	1615	16	21.5	7.53	325	100
Old River near Lathrop, California	5/18/01	1154	19	22.0	7.66	345	90
Old River near Lathrop, California	5/31/01	1229	40	24.0	8.51	649	150
Old River near Lathrop, California	6/4/01	1109	48	21.7	8.69	719	170
Old River at Paradise Cut near Tracy, California	4/2/01	1415	21	17.0	8.08	962	260
Old River at Paradise Cut near Tracy, California	4/6/01	1130	28	15.5	7.99	921	270
Old River at Paradise Cut near Tracy, California	5/14/01	1545	20	23.0	7.49	578	150
Old River at Paradise Cut near Tracy, California	5/18/01	1225	17	22.6	7.58	526	140
Old River at Paradise Cut near Tracy, California	5/31/01	1251	NA	24.5	8.22	842	210
Old River at Paradise Cut near Tracy, California	6/4/01	1040	60	21.7	8.32	712	170
San Joaquin River near Lathrop, California	4/2/01	1330	20	17.5	8.07	970	260
San Joaquin River near Lathrop, California	4/6/01	1030	30	15.5	7.91	916	240
San Joaquin River near Lathrop, California	5/14/01	1315	48	19.8	7.52	310	90
San Joaquin River near Lathrop, California	5/18/01	0930	48	20.7	7.67	320	90
San Joaquin River near Lathrop, California	5/31/01	1018	53	24.0	8.26	645	150
San Joaquin River near Lathrop, California	6/4/01	0937	55	21.1	8.78	713	170
San Joaquin River near Bowman Road Bridge near Lathrop, California	4/2/01	1300	25	17.5	8.00	983	270
San Joaquin River near Bowman Road Bridge near Lathrop, California	4/6/01	1000	47	15.5	7.96	925	260
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/14/01	1345	75	20.5	7.52	316	90
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/18/01	0904	63	20.5	7.68	326	90
San Joaquin River near Bowman Road Bridge near Lathrop, California	5/31/01	1052	NA	25.0	8.48	653	150
San Joaquin River near Bowman Road Bridge near Lathrop, California	6/4/01	0905	45	21.1	8.70	697	170
San Joaquin River near French Camp, California	4/2/01	1220	40	17.5	7.95	918	240
San Joaquin River near French Camp, California	4/6/01	0920	39	15.5	7.97	913	260
San Joaquin River near French Camp, California	5/14/01	1415	85	21.5	7.74	313	100
San Joaquin River near French Camp, California	5/18/01	0833	61	20.1	7.62	325	100
San Joaquin River near French Camp, California	5/31/01	1112	39	24.5	8.62	667	150
San Joaquin River near French Camp, California	6/4/01	0833	54	21.4	8.73	665	170

Analysis of Pesticides

Water samples collected for the analysis of pesticides by the OCL were processed by liquid-liquid extraction. Each 900-mL water sample was preserved immediately upon collection by pouring the sample into a 1-L amber glass bottle containing 100 mL of methylene chloride. Within 24 hours of sample collection, the water sample and solvent were transferred to a separatory funnel. The sample bottle was rinsed three times with methylene chloride and the rinsate added to the separatory funnel, along with 200 µL of terbuthylazine surrogate. The entire sample was then extracted three times using 100 mL of methylene chloride each time. The methylene chloride extract was then dried with sodium sulfate, reduced to 0.5 mL, and solvent-exchanged into ethyl acetate. The extract from day 1 was stored in the freezer until the day 5 sample was extracted; then the two extracts from each site were combined.

For analysis, extracts were amended with internal standards and reduced to 200 µL. The extracts were analyzed using a Saturn 2000 GC/MS ion trap system (Varian, Inc., Walnut Creek, California), for 32 current-use pesticides. The details of the instrumental method used for analysis and quality assurance procedures are described in Crepeau and others (2000). The major differences between the overall method in this study and the previous method (Crepeau and others, 2000) are the use of liquid–liquid extraction of whole water samples instead of solid-phase extraction of filtered samples, changes in some analytes, and an overall improvement in method detection limits. As liquid–liquid extraction was used rather than solid-phase extraction, 12 new analytes were added to the method and quantified using calibration standards. Other analytical details are recorded in a standard operating document on file at the laboratory.

The analytical method was validated by spiking eight replicates of a natural water sample with a mixture of pesticides at a concentration of 20 ng/L to estimate accuracy and precision and to determine the method detection limits (MDLs). Two unspiked replicate samples were used to determine the background concentrations of the pesticides. The water was collected from the Colusa Basin Drain, which has a similar water chemistry to the sites sampled in this study.

The MDL was calculated for each pesticide using the equation

$$MDL = S \times t(n-1, 1-\alpha = 0.99)$$

where

MDL	=	method detection limit
S	=	standard deviation of replicate analyses (nanogram per liter)
n	=	number of replicate analyses, and
$t(n-1, 1-\alpha = 0.99)$	=	2.998, the Student's t value for 99 percent confidence level with 7 degrees of freedom (Eichelberger and others, 1988).

MDLs ranged from 2.1 to 11.8 ng/L (*table 5*). Analytes can be identified at concentrations less than the method detection limit, but there is lower confidence in the actual value; therefore, these concentrations are reported as estimated values.

The accuracy or the mean recovery was calculated as the measured concentration divided by the actual spike added, expressed as a percentage, and the precision was expressed in terms of the percent relative standard deviation of the eight replicate water samples. The percent relative standard deviation equals the standard deviation (ng/L) divided by the mean observed concentration (ng/L) multiplied by 100. Carbofuran, dimethoate, 4-keto molinate, molinate, and thiobencarb were detected in the blank sample at concentrations of 9.4 to 211 ng/L, so the background concentrations were added to the matrix spike concentration to determine the mean recovery for these compounds. Mean recoveries for the method ranged from 79 to 176 percent (*table 5*). Five of the seven compounds with mean recoveries greater than 120 percent were not detected in the environmental samples, but carbaryl and carbofuran, which had the highest mean recoveries, were detected (*table 2*).

Because of the limited number of samples collected during this study, no field or laboratory blanks were analyzed. Another study conducted during this same time period, involving the same equipment, collection procedures, and personnel, included the analysis of ten field blanks and no pesticides were detected (Orlando and others, 2004).

Table 5. Method detection limit, accuracy, and precision data from eight determinations of the method analytes spiked using 20.0 nanograms-per-liter concentrations in Colusa Basin Drain water.

[ng/L, nanogram per liter]

Pesticide	Method detection limit (ng/L)	Mean accuracy (percentage of true concentration)	Mean observed concentration (ng/L)	Matrix plus background (ng/L)	Standard deviation (ng/L)	Relative standard deviation (percent)
Alachlor	6.5	113	22.6	20.0	2.2	10
Atrazine	2.1	83	16.6	20.0	0.7	4
Bifenthrin	3.2	91	18.3	20.0	1.1	6
Butylate	3.1	89	17.7	20.0	1.0	6
Carbaryl	8.8	176	35.1	20.0	2.9	8
Carbofuran	11.5	150	44.0	29.4	3.8	9
Chlorpyrifos	3.6	101	20.2	20.0	1.2	6
Cycloate	4.4	105	21.0	20.0	1.5	7
DCPA	2.7	104	20.9	20.0	0.9	4
Diazinon	2.7	90	18.0	20.0	0.9	5
Diethatyl-ethyl	2.4	127	25.4	20.0	0.8	3
Dimethoate	7.1	108	115.0	107.0	2.4	2
EPTC	5.1	96	19.2	20.0	1.7	9
Esfenvalerate	2.3	79	15.9	20.0	0.8	5
Ethalfluralin	5.2	99	19.8	20.0	1.7	9
Lambda-cyhalothrin	3.9	95	19.0	20.0	1.3	7
Malathion	6.3	128	25.6	20.0	2.1	8
Methidathion	4.8	101	20.2	20.0	1.6	8
Methylparathion	4.9	144	28.8	20.0	1.6	6
Metolachlor	4.2	99	19.7	20.0	1.4	7
Molinate	8.0	103	156.0	152.0	2.7	2
2-keto-molinate	7.6	119	23.8	20.0	2.5	11
4-keto-molinate	11.7	98	227.0	231.0	3.9	2
Napropamide	11.8	137	27.4	20.0	3.9	14
Pebulate	5.3	109	21.7	20.0	1.8	8
Permethrin	9.9	111	22.3	20.0	3.3	15
Phosmet	4.6	102	20.4	20.0	1.5	8
Piperonyl butoxide	4.4	126	25.2	20.0	1.5	6
Prometryn	5.1	101	20.1	20.0	1.7	8
Simazine	6.4	120	24.0	20.0	2.1	9
Thiobencarb	5.9	102	92.4	90.2	2.0	2
Trifluralin	5.8	111	22.2	20.0	1.9	9

Analysis of Wastewater Compounds

Water samples collected for analysis of wastewater compounds by the NWQL were filtered through baked 0.7-µm glass fiber filters within 24 hours of collection and shipped on ice to the NWQL for analysis. Samples were analyzed for more than 60 compounds using polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry as reported in Zaugg and others (2002).

Analysis of Suspended-Sediment Concentration and Parameters

Whole water samples were analyzed for suspended-sediment concentration at the USGS's Sediment Laboratory (SL) in Marina, California. Details of the analytical method can be found in Guy (1969). Analytical results of single-blind quality control samples provided by SL's quality assurance project showed that laboratory performance during the period of this study was satisfactory (U.S. Geological Survey, 2005).

Water parameters (specific conductance, pH, and hardness) were measured in whole water samples at the OCL within 24 hours of sample collection. Specific conductance and pH were measured using two handheld instruments, (Cole Parmer Model 141-61 and Orion Model 250A, respectively), as described in the USGS's national field manual (Wilde and Radtke, 1998). Hardness, reported as mg/L of $CaCO_3$, was determined using a Hach Model 5-EP titration kit following the manufacturer's guidelines (Hach, 2005). Water temperature was measured in the field at the time of collection using a digital thermometer.

Results

Pesticide Concentrations

During this study, 13 current-use pesticides were detected in samples collected from six sites along the San Joaquin and Old Rivers (*table 2*). A minimum of five pesticides were detected in each sample. One insecticide (diazinon) and three herbicides (metolachlor, simazine, and trifluralin) were detected in every sample. Maximum concentrations of each of the pesticides detected ranged from 5.3 ng/L (chlorpyrifos) to 241 ng/L (diazinon). In addition to diazinon, three other compounds—carbofuran, metolachlor, and prometryn—were detected at high concentrations, with maximum values of 111 ng/L, 211 ng/L, and 122 ng/L, respectively.

In general, the number of detections varied little between rivers—62 detections in Old River samples as compared with 65 in San Joaquin River samples. A breakdown of pesticide detections by site shows that the number of detections per site varied by less than 3 percent of the total number of detections. In contrast, the maximum concentrations for nine pesticides were detected in San Joaquin River samples as compared with four in Old River samples.

The temporal distribution of pesticide detections varied little over the three time periods sampled, whereas the number of pesticides having their maximum concentration detected during the period of managed streamflows was least. For the three sampling periods, 39 detections occurred in the period prior to the managed flows, 40 during managed flows, and 48 after the managed flows. The highest concentrations of only three of the 13 pesticides were detected during the managed flow period, whereas the highest concentrations of five pesticides were detected in both the before and after periods.

Wastewater Compounds

Samples analyzed at the NWQL contained six wastewater compounds and four pesticides (*table 3*). Concentrations of these compounds ranged from 11 ng/L to 1,800 ng/L, but all results are uncertain because the values are below the normal laboratory minimum reporting levels. Compounds detected at concentrations above the MDL limit, but below the method reporting limit, are denoted by an "E" along with the value, because they are estimates (Zaugg and others, 2002). The pesticide metolachlor was the only compound detected in each of the samples. Diazinon and metolachlor were detected in both the wastewater and pesticide analyses and the paired results are consistent, though they are not directly comparable because of differences in sample type and method detection limits.

Suspended-Sediment Concentrations and Water Parameters

Suspended-sediment concentration was determined for 34 samples collected during this study (*table 4*). Suspended-sediment concentrations were similar between river systems except during the period of managed streamflow conditions, during which suspended-sediment concentrations were much higher at sites on the San Joaquin River than at sites on the Old River (*fig. 3*). In samples collected from sites on the Old River, suspended-sediment concentrations were generally highest in the period following the VAMP and lowest during the VAMP. Suspended-sediment concentrations in samples collected from the San Joaquin River were generally highest during managed flow conditions.

Water temperature, conductivity, pH, and hardness were also measured for all samples, and these values are presented in *table 4*. Values of conductivity, pH, and hardness were lowest at all sites during the managed flow period (*fig. 3*).

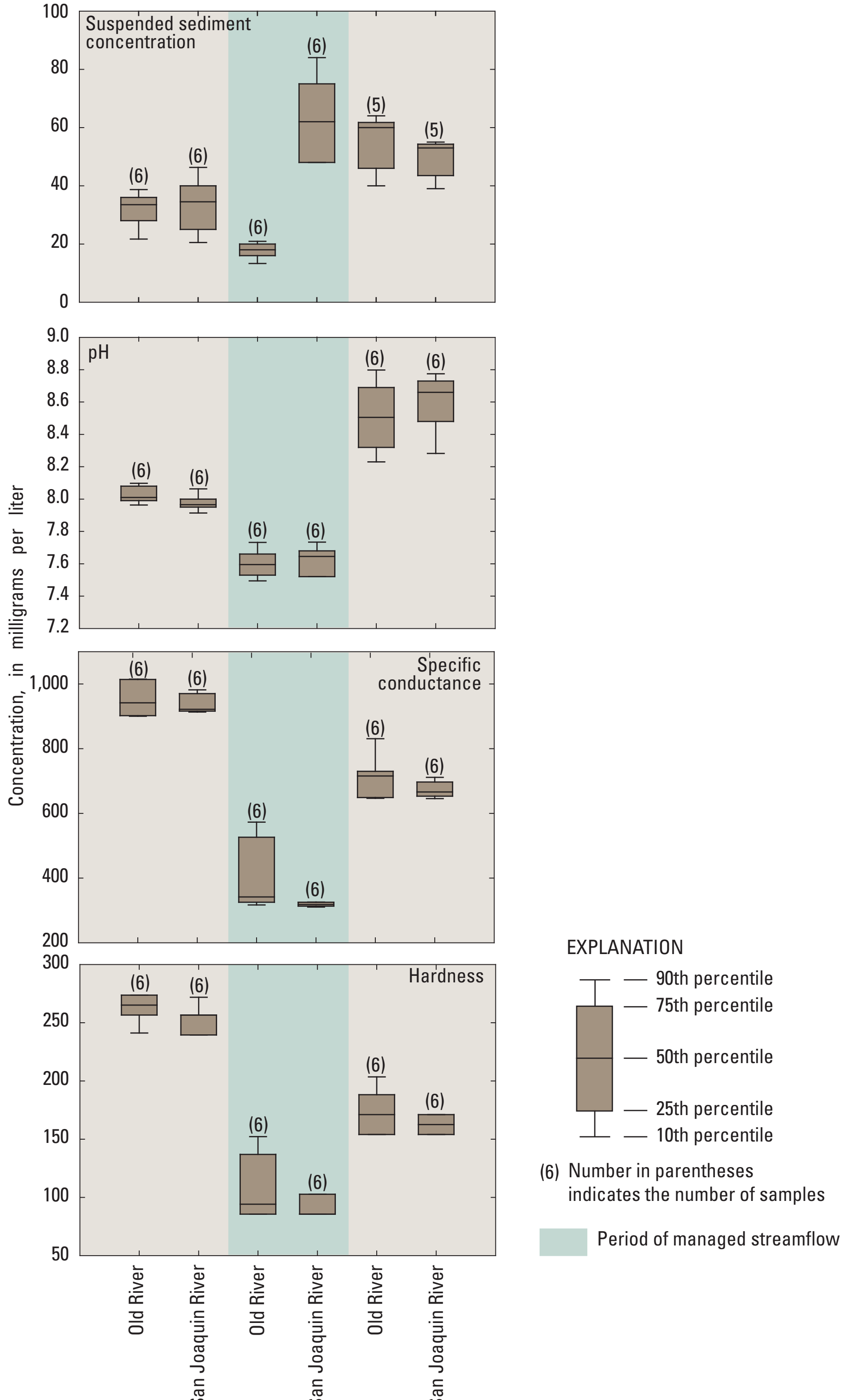

Figure 3. Box plots of water parameter values determined in this study.

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