

Dissolved Pesticides in the Alamo River and the Salton Sea, California, 1996–97

Open-File Report 02-232

**Prepared in cooperation with the
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD**

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CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

Sacramento, California
2002

U.S. DEPARTMENT OF THE INTERIOR

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ABSTRACT

Water samples were collected from the Alamo River and the Salton Sea, California, in autumn 1996 and late winter/early spring 1997 and analyzed for dissolved pesticides. The two seasons chosen for sampling were during pesticide application periods in the Imperial Valley. Pesticide concentrations were measured in filtered water samples using solid-phase extraction and analyzed by gas chromatography/mass spectrometry. Generally, the highest concentrations were measured in the Alamo River. The concentrations of carbaryl, chlorpyrifos, cycloate, dacthal, diazinon, and eptam were highest in samples collected in autumn 1996. In contrast, the concentrations of atrazine, carbofuran, and malathion were highest in samples collected in late winter/early spring 1997. The highest concentrations measured of atrazine, carbofuran, dacthal, eptam, and malathion all exceeded 1,000 nanograms per liter.

INTRODUCTION

The Salton Sea in Imperial County, California, has been designated as a sensitive ecosystem by the Federal and State governments because it contains productive fisheries and provides important habitat for migratory birds. However, more than 6 million pounds (3 million kilograms) of pesticide-active ingredients are applied annually to vegetable crops grown year-round in the Imperial Valley (California Department of Pesticide Regulation, 1994). The Alamo River drains the Imperial Valley, and its flow consists of almost 100

percent irrigation runoff, which is discharged into the southeast end of the Salton Sea (fig. 1). Insecticide and herbicide concentrations in the Alamo River and Salton Sea are high enough to be toxic to aquatic life during autumn and late winter/early spring when these compounds are applied (de Vlaming and others, 1998; de Vlaming and others, 2000). DeVlaming and others showed that for a species of water flea, *Ceriodaphia dubia*, the toxicity was caused primarily by chlorpyrifos and diazinon during three months in the autumn, and primarily by carbofuran and diazinon during two months in the spring.

This report presents the results of pesticide sampling of the Alamo River and Salton Sea from late August to November 1996 and late February to mid April 1997. Surface-water samples were analyzed for 11 pesticides from seven sites. The first site, in the Alamo River, was chosen as representative of agricultural runoff from the Imperial Valley. The six Salton Sea sites were chosen to assess the change in pesticide concentration as Alamo River water became mixed and interacted with Salton Sea water. The sampling was done to determine the pesticides and concentrations present in the Alamo River and Salton Sea during periods when deVlaming and others showed the waters to be toxic to aquatic life.

The authors thank Lucian Baker II of the U.S. Geological Survey, and Kristy Cortright, Linda Deanovic, Melenee Emanuel, and Karen Larsen of the Aquatic Toxicology Laboratory at University of California, Davis, for processing the samples; and Ray Lukens of the California Regional Water Quality Control Board, Colorado River Basin Region, for collecting the water samples.

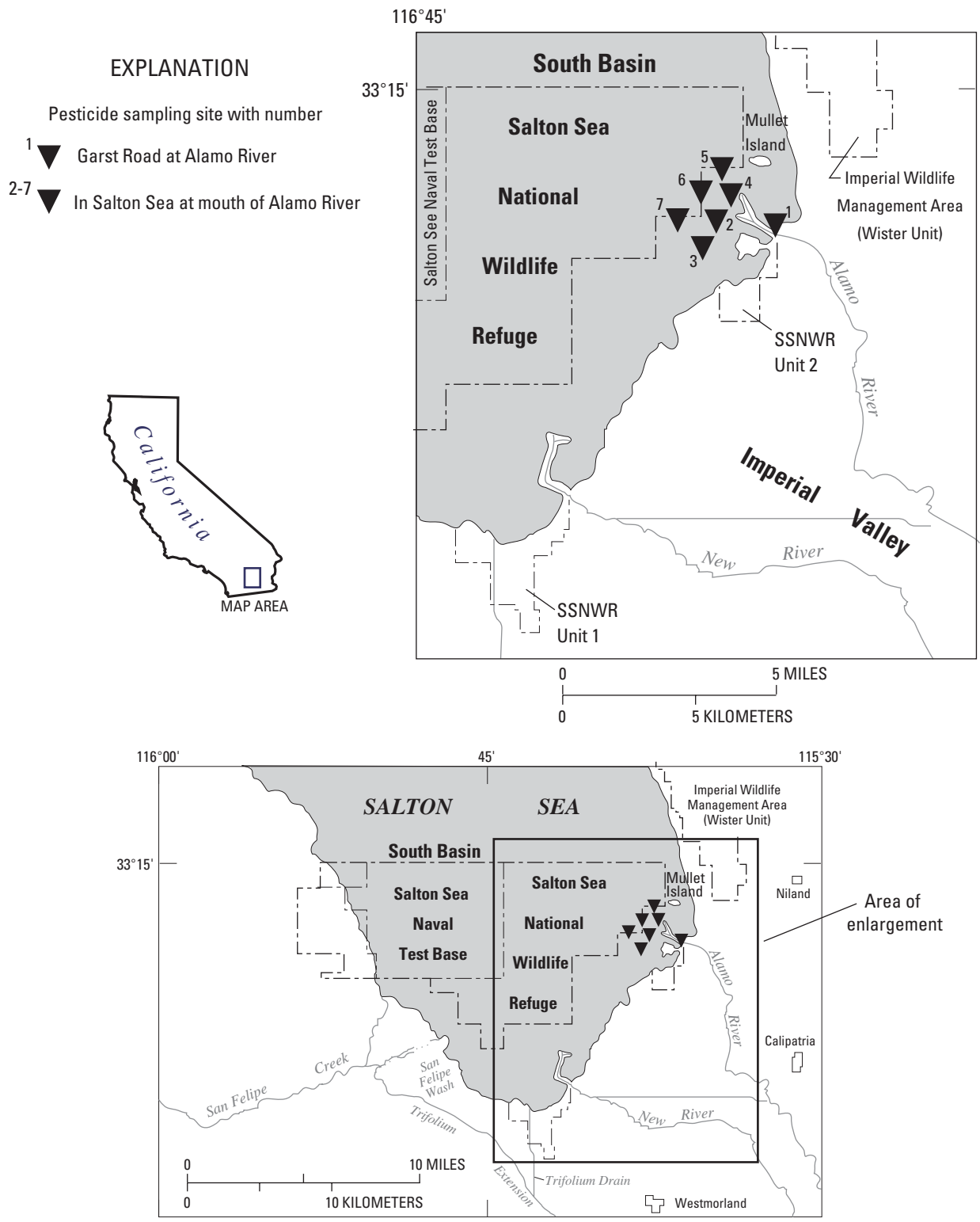


Figure 1. Map showing Alamo River and Salton Sea, California, showing pesticide sampling sites.

SAMPLE COLLECTION, PROCESSING, AND ANALYSIS

Water samples were collected from one site on the Alamo River and six near-shore sites in the Salton Sea southeast of the Salton Sea National Wildlife Refuge (fig. 1). The samples were collected every few weeks from August through November and from February through April to coincide with the pesticide application periods in the Imperial Valley (autumn and late winter/early spring). The samples were not collected through integrated sampling methods as normally required by USGS methodology, but the river is well mixed and the analyses are limited to dissolved constituents and, therefore, are considered reliable indicators of the water quality of the Alamo River. Subsurface grab samples were taken from the Alamo River at the Garst Road bridge, and using a boat in the Salton Sea.

The water samples were shipped on ice to the Aquatic Toxicology Laboratory at the University of California at Davis, where they were filtered through a

0.7-micron glass-fiber filter and extracted using a C-8 solid-phase extraction cartridge. The cartridges were then packed on ice and delivered to the USGS California District Organic Chemistry Laboratory in Sacramento, California, for analysis.

The percent recovery and method detection limits (MDL) of the pesticides were determined using surface water from Suisun Bay, which has a similar specific conductivity as that of the study sites; the conductivity affects the extraction efficiency of the solid-phase cartridge. The pesticides were analyzed by gas chromatography/mass spectrometry (GC/MS). The mean recoveries for the pesticides were between 78 and 114 percent and relative standard deviations were below 10 percent; the detection limits were between 3 and 15 ng/L (nanograms per liter)(table 1). However, the pesticide recoveries and detection limits for Salton Sea samples may be different than those given here; although the specific conductivities of Salton Sea samples were similar to Suisun Bay, the water matrix was different. Additional details of the method are described by Crepeau and others (2000).

Table 1. Method detection limits, mean recovery, and relative standard deviation from seven determinations of pesticides spiked at a concentration of 50 nanograms per liter

[ng/L, nanograms per liter]

Pesticide	Method detection limit (ng/L)	Mean recovery (percent)	Relative standard deviation (percent)
Atrazine	5	78	3
Carbaryl	10	90	6
Carbofuran	8	92	5
Chlorpyrifos	8	96	4
Cycloate	11	85	3
Dacthal	3	85	2
Diazinon	3	87	1
Eptam	5	88	3
Fonofos	5	96	3
Malathion	15	114	7
Simazine	5	84	3

SAMPLING RESULTS

Insecticide and herbicide data from 52 water samples collected from the Alamo River and Salton Sea are presented in [table 2](#). For most compounds the highest concentrations were detected in the Alamo River and lower concentrations in the Salton Sea. The concentrations of carbaryl, chlorpyrifos, cycloate, dacthal, diazinon, and eptam were highest in the samples collected in the autumn, ranging from 5 to 10 times the concentrations measured in the late winter/early spring. In contrast, the concentrations of atrazine, carbofuran, and malathion were highest in the samples collected in the late winter/early spring, ranging from 5 to 200 times the concentrations measured in the autumn. The highest concentrations of atrazine, carbofuran, dacthal, eptam, and malathion all exceeded 1,000 ng/L. The total pesticide concentration for all the samples ranged from 166 ng/L to 16,100 ng/L.

Some of the pesticide concentrations are reported as estimates because the concentrations exceed 1,000 ng/L, the highest calibration standard. These estimates are based on a linear extension of the calibration curve and may underestimate actual pesticide concentrations owing to saturation of the ion trap detector at high concentrations (Eichelberger and Budde, 1987). All estimated concentrations are designated with an “E” in [table 2](#). The lowest calibration standard was 1 ng/L. Pesticide concentrations that were present but below the method detection limit are reported in parentheses.

The data in [table 2](#) are rounded using a model that plots the standard deviation versus the concentration to determine the number of significant figures for each compound. This method of rounding is based on the Phoenix Project for National Water Quality Laboratory data and the American Society for Testing Materials E29-93a (Phoenix Project, 2002; American Society for Testing and Materials, 1993).

QUALITY ASSURANCE

Quality assurance samples analyzed to determine contamination and variability included equipment blanks and replicates. Matrix spikes were not included in this study.

Equipment blanks were organic-free water filtered into a 1-liter glass bottle then extracted and analyzed in the same way as the samples. A total of six blanks were analyzed on the GC/MS. Cycloate was detected in only one blank, at 3 ng/L, which indicates that there was no systematic contamination from processing and analyzing the samples.

Replicate samples were collected to assess variability, including matching both the nondetections and numerical values of pesticides detected. Seven pairs of replicates were analyzed at the USGS California District Organic Chemistry Laboratory. For 88 percent of the analyses, the nondetections were paired. Two pesticides were detected in the environmental sample but not in the replicate. If the pesticide is detected in both the sample and the replicate, the difference in the measured concentration gives an assessment of the variability. The percent difference is defined as the absolute value of the difference in the concentration between replicates divided by their mean and then multiplied by 100. The mean percent difference is 3 percent (n=53).

To further assess variability, 13 pairs of replicates were analyzed at two different laboratories. One of the replicates was analyzed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, and the other by the USGS California District Organic Chemistry Laboratory. The mean percent difference when the pesticides were detected in both replicates is 13 percent (n=104). This is a reasonable difference for pesticides analyzed at two different laboratories and indicates the concentrations of the pesticides in the environmental samples and the replicates are within a factor of 1.14 of each other.

Terbutylazine was added as a surrogate to all samples, including equipment blanks, to quantify the extraction efficiency of the solid-phase cartridge and GC/MS analysis. The average percent recovery for terbutylazine was 85 percent and the standard deviation was 15 percent. Sample data were excluded from this report if the recovery of terbutylazine was ± 1.5 standard deviations from the mean recovery for all samples. A total of four samples were excluded.

Table 2 Pesticide concentrations in water samples from the Alamo River and Salton Sea, California, August 1996 through April 1997

[μ S/cm, microSiemens per centimeter at 25° Celsius; ng/L, nanograms per liter; nd, not detected; (), pesticide is present but below the detection limit; E, Estimate of pesticide concentration; determined value is greater than highest standard calibration of 1,000 ng/L and therefore, this value is probably an underestimate of the pesticide concentration; --, not recorded. Water samples were collected and pH, specific conductance, and temperature were measured by California Regional Water Quality Control Board]

Sampling site	Date	Time	pH	Specific conductance (uS/cm)	Temperature (°C)	Atrazine (ng/L)	Carbaryl (ng/L)	Carbofuran (ng/L)	Chlorpyrifos (ng/L)	Cycloate (ng/L)	Dacthal (ng/L)	Diazinon (ng/L)	E-ptam (ng/L)	Fonofos (ng/L)	Malathion (ng/L)	Simazine (ng/L)	
1	08/28/96	1125	7.8	3,440	31	86	nd	nd	36.1	(3)	10.0	10.4	44.6	nd	nd	nd	
	09/10/96	1200	7.6	4,000	30	54.8	nd	11.2	34.3	153	E1,290	36.7	252	nd	nd	nd	
	10/01/96	1640	8.0	3,000	26	32.0	160	nd	107	601	1,000	553	E1,560	101	169	nd	
	10/21/96	1500	7.8	3,400	19	42.3	135	35.5	152	193	E1,350	355	E9,100	30.7	114	nd	
	10/31/96	--	18.1	13,380	125	48.4	230	83	102	91	E1,040	417	E6,410	16.5	178	nd	
	11/12/96	1030	7.7	3,400	18	38.1	78	58	76	111	E1,030	165.2	E13,000	25.2	35	nd	
	11/18/96	1230	8.0	3,600	16.5	31.0	53	nd	57	30.5	E1,330	144.0	E12,300	19.6	98	nd	
	02/27/97	--	7.9	2,500	18.4	E3,180	(8)	E3,010	18.9	(7)	334	334	29.1	252	5.6	750	15.9
	03/05/97	1200	7.6	2,400	17	840	(6)	E2,450	26.3	13.6	151	151	16.6	127	14.8	E1,340	11.0
	03/25/97	1630	7.3	3,200	22	358	27.5	740	10.8	(3)	46.6	46.6	109.9	E1,190	(2)	195	5.0
2	08/28/96	1015	7.8	3,700	31	81	nd	nd	37.8	(6)	nd	8.4	38.8	nd	nd	nd	
	09/10/96	1000	7.6	5,000	30	58.8	nd	nd	35.0	130	E1,160	34.0	525	7.7	13.8	16.8	
	10/01/96	1540	8.0	17,000	28	37.8	120	nd	110	416	E1,030	414	E2,030	80	134	nd	
	10/31/96	--	18.1	110,300	125	61.8	322	32.5	93	81	974	411	E10,000	27.5	173	nd	
	11/12/96	1200	7.7	5,000	19	39.3	79	58	77	115	E1,020	156.8	E12,400	23.3	35	nd	
	03/25/97	1515	7.3	3,600	20.5	315	28.3	870	13.9	(3)	44.4	48.6	E1,090	nd	261	6.8	
	04/15/97	--	7.6	3,600	22	213	nd	133	(4)	nd	25.2	5.5	104	nd	65	(1)	
	08/28/96	1049	7.9	6,000	31	82	nd	nd	42.5	(2)	nd	11.1	42.4	nd	(9)	nd	
	09/10/96	1100	7.6	5,000	30	55.9	nd	nd	34.7	127	E1,200	32.8	401	9.9	(2)	nd	
	10/01/96	1500	7.9	15,000	28	39.7	111	nd	111	501	912	468	E3,350	77	119	nd	
3	10/31/96	--	18.1	110,500	125	64.7	360	26.6	96	84	E1,010	437	E13,800	27.8	179	nd	
	11/12/96	1310	8.2	5,000	21	56.8	82	33.2	71	105	961	155.2	E10,600	24.0	37	nd	
	04/15/97	1400	7.2	4,000	21	224	nd	179	(3)	nd	24.9	5.6	98	nd	59	(2)	
	08/28/96	1005	7.8	8,000	31	82	nd	nd	35.0	(3)	10.6	9.7	42.0	nd	nd	nd	
	09/10/96	1115	7.7	17,000	30	70	nd	nd	31.3	112	E1,020	29.1	326	nd	nd	18.5	
	10/01/96	1510	8.0	33,000	28	59.8	60	nd	73	306	507	285	E1,310	54.4	90	nd	

Table 2. Pesticide concentrations in water samples from the Alamo River and Salton Sea, California, August 1996 through April 1997—Continued

Sampling site	Date	Time	pH	Specific conduc- tance (uS/cm)	Temper- ature (°C)	Atrazine (ng/L)	Carbaryl (ng/L)	Carbofu- ran (ng/L)	Chlor- pyrifos (ng/L)	Cycloate (ng/L)	Dacthal (ng/L)	Diazinon (ng/L)	Eptam (ng/L)	Fonofos (ng/L)	Malathion (ng/L)	Simazine (ng/L)
4	10/31/96	--	8.1	120,000	12.5	82	271	63	80	79	861	354	E13,100	22.9	150	38.5
	11/12/96	1300	8.1	20,000	18	96	51	nd	50	77	573	94.8	E6,590	nd	21.6	48.6
	03/25/97	1500	7.5	12,000	21	281	nd	500	14.8	(3)	41.2	44.8	E1,080	nd	174	7.7
	04/15/97	--	8.1	11,000	21.5	259	nd	195	(3)	nd	23.6	5.3	96	nd	62	(4)
5	08/28/96	1034	8.1	30,000	32	83	nd	26.9	31.6	(4)	5.5	9.5	24.4	nd	nd	nd
	09/10/96	1030	7.8	35,000	31	68	nd	nd	20.0	73	580	20.2	202	6.6	nd	nd
	10/01/96	1520	8.1	50,000	29	74	nd	nd	20.8	89	127	73.6	192	nd	nd	nd
	10/31/96	--	8.1	131,000	12.5	92	194	30.4	60	61.1	639	264	E7,400	nd	89	47.9
	11/12/96	1220	7.9	30,000	21	110	nd	nd	28.8	44.1	253	51.0	E2,650	nd	nd	57.7
	03/25/97	1445	7.9	40,000	21.5	158	nd	189	(6)	nd	13.1	32.0	277	nd	32	19.4
	04/15/97	--	8.2	23,000	23.5	193	nd	133	(2)	nd	17.9	4.2	72	nd	38	6.3
	08/28/96	1024	8.0	25,000	31	93	nd	nd	32.3	(4)	3.8	10.6	27.9	nd	nd	nd
09/10/96	1020	7.8	17,000	30	61.8	nd	nd	32.9	111	E1,030	30.1	403	nd	nd	32.4	
10/01/96	1530	8.1	40,000	30	75	(5)	nd	50	238	523	249	E2,030	39.7	117	nd	
10/31/96	--	8.0	126,300	12.5	95	249	29.7	61	66.2	669	296	296	E8,000	nd	110	48.1
11/12/96	1230	8.3	25,000	20	97	48	nd	47.0	76	579	96.1	E6,450	nd	17.8	94	
03/05/97	1045	7.8	22,000	16	665	(5)	E1,760	19.9	(8)	109	20.3	125	8.9	990	18.2	
03/25/97	1400	8.0	5,000	21	372	29.4	810	15.6	(3)	46.0	109.8	E1,380	(1)	197	6.6	
04/15/97	--	8.2	19,000	23	206	nd	124	(3)	nd	18.7	4.7	90	nd	44	(4)	
7	08/28/96	1041	8.1	23,900	33	94	nd	nd	34.7	(4)	7.1	9.7	30.6	nd	nd	41.8
	09/10/96	1130	7.6	20,000	31	68	nd	nd	26.9	106	908	28.2	317	nd	nd	31.5
	10/01/96	1430	8.0	42,000	29	71	(6)	nd	43.0	185	299	169.2	720	34.8	60	nd
	10/31/96	--	8.0	129,800	12.5	86	227	60	65	62.0	661	271	E3,250	nd	110	nd
	11/12/96	1250	8.3	25,000	20	103	42	nd	41.8	66.1	480	83.6	E5,060	nd	14.9	51.3
	03/05/97	1115	8.3	22,000	17	611	(4)	E1,540	20.4	(9)	109	19.6	128	5.9	910	15.8
04/15/97	--	8.3	22,000	23	192	nd	106	(1)	nd	17.2	4.4	72	(3)	17.2	6.2	

¹Laboratory value.

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