



0730-7268(95)00060-7

CONCENTRATIONS, TRANSPORT AND BIOLOGICAL EFFECTS OF DORMANT SPRAY PESTICIDES IN THE SAN FRANCISCO ESTUARY, CALIFORNIA

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(Received 7 July 1994; Accepted 28 December 1994)

Abstract—The transport and biological effects of dormant spray pesticides were examined in the San Francisco Estuary, California, by measuring dissolved-pesticide concentrations and estimating toxicity using bioassays at a series of sites in January and February 1993. Distinct pulses of pesticides, including diazinon, methidathion, and chlorpyrifos, were detected in the San Joaquin River in January and February and in the Sacramento River in February following rainfall. The higher pesticide loads in the Sacramento River compared with those in the San Joaquin River can be attributed to the greater amount of rainfall in the Sacramento Valley. The use patterns and water solubility of the pesticides can account for the observed temporal and spatial distributions in the two rivers. The pesticide pulses detected at Sacramento were followed through the northern embayment of San Francisco Estuary. In contrast, the pesticide distribution in the Sacramento–San Joaquin Delta changed from distinct pulses to steady increases in concentration over time. Seven-day bioassays indicated that Sacramento River water at Rio Vista was acutely toxic to *Ceriodaphnia dubia* (water flea) for 3 consecutive d and San Joaquin River water at Vernalis for 12 consecutive d. These water samples all had the highest diazinon concentrations. Examination of 96-h LC50 values (lethal concentration that kills 50% of test organisms in 96 h) indicates that measured diazinon concentrations could account for most but not all the observed toxicity. Other pesticides present could contribute to the toxicity.

Keywords—Pesticides San Francisco Estuary Toxicity Diazinon Methidathion

INTRODUCTION

The biological effects of dormant spray pesticides used on orchards in California's Central Valley are of environmental concern; bioassay surveys indicate that San Joaquin River water with elevated concentrations of dormant spray pesticides is often toxic to *Ceriodaphnia dubia* (water flea) [1,2]. Results of previous studies of pesticide concentrations in the Sacramento and San Joaquin rivers in 1991 and 1992 indicate that rainfall is a major mechanism for transporting pesticides from orchards and fields into the river (K. M. Kuivila, unpublished data). Because of the extensive use of dormant spray pesticides in the Central Valley during the wettest times of the year (i.e., winter), there is a need for an understanding of inputs and transport of dormant spray pesticides to the San Francisco Estuary.

Dormant spray pesticides, including diazinon, methidathion, chlorpyrifos, and malathion, are typically applied to stone-fruit orchards in the Central Valley during January and February [3,4]. Diazinon, methidathion, and malathion are relatively hydrophilic with water solubilities ranging from 40 mg/L to 250 mg/L, whereas chlorpyrifos is more hydrophobic with a water solubility of 2.0 mg/L (Table 1). These organophosphate insecticides are acetylcholinesterase inhibitors and are most toxic to zooplankton [5,6].

The objectives of this study were to determine the concentrations, transport, and possible biological effects of dor-

mant spray pesticides in the rivers and estuary following rainfall in January and February 1993. Dissolved-pesticide concentrations were measured in the Sacramento and San Joaquin rivers, and the transport of these pesticides was tracked through the Sacramento–San Joaquin Delta and into San Francisco Bay (Fig. 1). Possible biological effects were estimated using bioassay surveys concurrently with the pesticide sampling. This study was a collaborative effort by the U.S. Geological Survey (USGS) and the California Regional Water Quality Control Board (RWQCB) and is part of a larger research effort by the USGS Toxic Contaminants Hydrology Program to assess quantitatively the transport and fate of pesticides in the San Francisco Estuary.

HYDROLOGIC SETTING AND SAMPLING STRATEGY

Agriculture in the Central Valley of California accounts for 10 percent of the total pesticide usage in the United States. Two major rivers, the Sacramento and San Joaquin, drain this region, converging in a complex delta at the head of San Francisco Estuary (Fig. 1). The average flow of the Sacramento and San Joaquin rivers is 680 and 130 m³/s, respectively. Within the delta, the flows and flow patterns are controlled extensively by a variety of management strategies. State and federal projects (Fig. 1) export water from the delta to the San Joaquin Valley and the southern part of the state. The entire delta is tidally influenced and the net flow pattern is complex. Water from the Sacramento River primarily flows down the main river channel and out to Suisun Bay, although some of the water is diverted through the delta cross chan-

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Table 1. Dormant spray pesticides: Water solubility and amounts applied to orchards in January and February 1990 in the Sacramento and San Joaquin valleys

Pesticide name	Water solubility ^b at given temp. (mg/L)	Amount applied ^a	
		Sacramento Valley (kg)	San Joaquin Valley (kg)
Ethyl parathion	24 (25°C)	52,764	37,858
Diazinon	40 (20°C)	21,369	26,906
Methidathion	250 (20°C)	15,544	9,676
Chlorpyrifos	2 (25°C)	3,663	17,524
Malathion	145 (20°C)	4,472	6,130

^aCalifornia Department of Pesticide Regulation, 1990 [3].

^bWorthing and Walker, 1987 [27].

nel and Georgiana Slough to the state and federal export pumps. The San Joaquin River splits downstream from Mossdale, with some of the water flowing toward the export pumps via lower Old River and Grant Line Canal and the remainder flowing toward Stockton. Northwest from Stockton, the channel deepens and widens, resulting in an increase in water residence time. Water from the San Joaquin River mixes with water from the Mokelumne, Consumes, and Sacramento rivers, and the net flow is toward the pumps via Old and Middle rivers. Little, if any, of the San Joaquin River water gets out into San Francisco Bay. The USGS is currently collecting data on flows and flow patterns to be used to calibrate and validate a hydrodynamic model of the delta [7].

Pesticide concentrations were measured at a series of sites along two major flow paths: the Sacramento River from Sac-

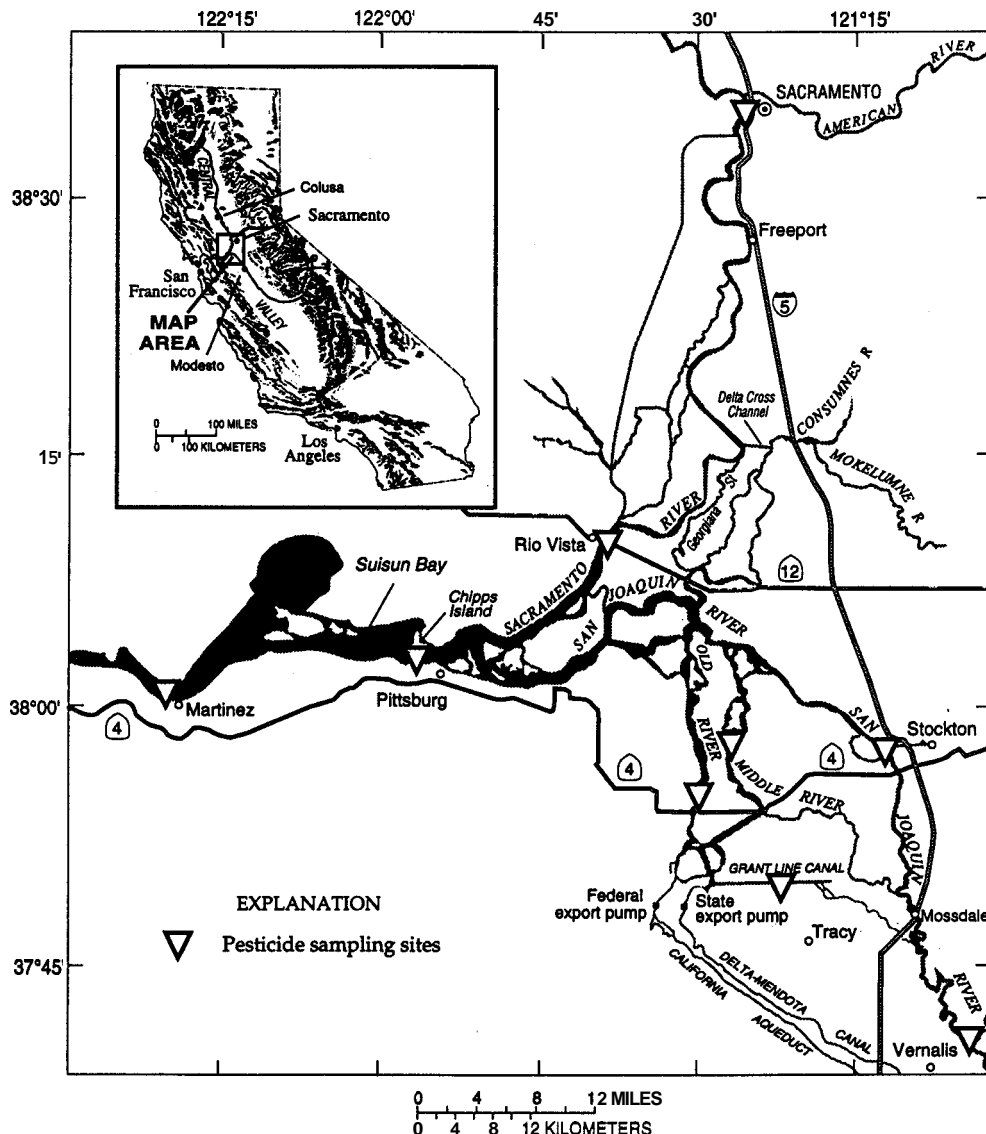


Fig. 1. Location of study area.

ramento to the western boundary of Suisun Bay and the San Joaquin River from Vernalis through Stockton to the export pumps (Fig. 1). Water samples for pesticide analysis were collected daily at all sampling locations (twice a day at Vernalis) using a depth-integrating, discharge-weighted sampler at either one or three verticals, depending on the site. Flow at the Sacramento and Vernalis sites is unidirectional, and sampling studies indicate that the composition and concentrations of dissolved constituents at a single vertical mid-channel are representative of the cross section under most flow conditions (data not shown). Discharge for the Sacramento River was recorded at Freeport (11 river miles downstream from Sacramento) with an ultrasonic velocity meter. Because the site at Freeport is affected by the tide, the discharge was tidally filtered to calculate a daily mean discharge [8]. For the San Joaquin River, discharge also was recorded at Vernalis, a streamflow-gaging station.

In contrast to the Sacramento and Vernalis sites, the flow at the other sites reverses during the tidal cycle. Samples were collected routinely at the tidally affected sites (Fig. 1) during slack after ebb tide, except at the Old and Middle River sites where samples were collected at slack after flood tide. This sampling scheme estimated the most seaward movement of solutes along the flow path through the delta or through Suisun Bay and created a consistency for comparison of daily concentrations.

ANALYTICAL METHODS

Dissolved pesticides were extracted from filtered 1-L (liter) samples onto C₈ solid-phase-extraction cartridges and eluted with three 2-ml aliquots of hexane:diethyl ether (1:1). The eluant was concentrated and analyzed using a capillary gas chromatograph/ion-trap mass spectrometer in full-scan mode [9,10]. Field blanks using organic-free water were processed every 20 samples; no contamination was detected throughout this study. A minimum of 10% of the samples were collected in duplicate and all analytes agreed within 25% or less. Replicate samples were also routinely sent to the USGS National Water Quality Laboratory for comparison. Although 19 pesticides are included routinely in the analysis, the focus of this study was diazinon, methidathion, chlorpyrifos, and malathion, with method detection limits of 30, 35, 40, and 35 ng/L, respectively. During matrix spike experiments, recovery of these four pesticides in Sacramento and San Joaquin River water was greater than or equal to 83%. For more details on the analytical method and quality-assurance practices, see Crepeau et al. [10].

Seven-day *C. dubia* bioassays [11] were done at Sierra Foothill Laboratory using mortality as an end point. Reproduction was not assessed. Tests were set up in batches 1 to 5 d after water collection with neonates less than 24 h old. All U.S. Environmental Protection Agency (EPA)-recommended water quality parameters, with the exception of alkalinity, were measured and found to be within acceptable limits to support aquatic life. Water from a local spring was used as a control. No mortality within 7 d was ever observed in the control.

RESULTS AND DISCUSSION

The results of this study consist of the following three parts: riverine pesticide concentrations, transport into the estuary, and biological effects of the observed pesticides. Measured concentrations of dissolved pesticides in the Sacramento and San Joaquin rivers were examined in the context of pesticide usage in the valley. Pesticide loads were calculated and the loads of the two rivers compared. Transport of these pesticides was followed through the Sacramento-San Joaquin Delta and into San Francisco Bay. Finally, the biological effects of these pesticides were estimated by using bioassays and by comparing the measured concentrations to regulatory limits.

Pesticide pulses following rainfall

Pulses of diazinon were detected following rainfall in the Sacramento and San Joaquin rivers in previous years (K.M. Kuivila, unpublished data); this phenomenon is similar to the spring flush of herbicides observed in surface-water runoff in the midwestern United States [12]. The riverine pulses of diazinon typically were narrow and well defined; elevated concentrations were measured for only a few days to weeks.

In the Sacramento and San Joaquin valleys, a series of rainstorms (cumulative rainfall greater than 2.5 cm) began on January 6 and continued through January 21 (Figs. 2A and 3A). Dormant spray pesticides were applied either before these rainstorms (late December and early January) or during 2 weeks of dry weather following these rainstorms (late January). Another series of rainstorms began in early February and continued through February 26.

Elevated concentrations of pesticides were detected in the Sacramento River at Sacramento in February but not in January; diazinon and methidathion were the only dormant spray pesticides detected. A few days after the rainfall on February 5, 7, and 8, streamflow at Freeport increased, reaching a maximum on February 14 (Fig. 2A). Similarly, diazinon concentrations increased on February 8 and reached a measured maximum of 393 ng/L on February 12 (Fig. 2B). Distribution of methidathion over time was similar to that of diazinon, but the peak shape was slightly broader, and the maximum concentration was 212 ng/L. It rained again February 17 to 19, and both discharge and pesticide concentrations increased. During this second pulse, the maximum concentrations of diazinon and methidathion were lower and the peaks were more spread out than during the first pulse. The maximum diazinon concentration was 193 ng/L on February 21, whereas methidathion concentration peaked at 71 ng/L on February 22. The discharge also reached a maximum 2 d later (February 24).

In contrast to the Sacramento River, elevated concentrations of pesticides were detected in the San Joaquin River at Vernalis in both January and February. Only diazinon was detected in January, whereas diazinon, methidathion, and chlorpyrifos were detected in February. In the San Joaquin Valley, three periods of rainfall (accumulations of greater than 2.5 cm) occurred, beginning on January 6, 12, and 17. Each rainfall was followed by a corresponding increase in

double pulse of diazinon in February after the February 7 to 8 rainfall period [13]. The concurrent distribution of methidathion showed only a single peak, which occurred between the two diazinon peaks. The relative timing of the methidathion and diazinon peaks indicates that the primary source of methidathion was at a location between the two sources of diazinon.

In 1990, more chlorpyrifos was applied in the San Joaquin Valley than in the Sacramento Valley (Table 1). The low concentrations of chlorpyrifos detected for only a few days in the San Joaquin River, despite a higher use than methidathion, can be explained by the hydrophobic nature of chlorpyrifos. With a water solubility of only 2.0 mg/L, chlorpyrifos has a tendency to sorb onto sediments and will be transported from the orchards primarily via sediment erosion rather than water runoff. In contrast, although malathion has a high water solubility (145 mg/L), it was not detected in any of the water samples during this study. The low use and rapid degradation of malathion in soil [14] can explain the absence of detectable malathion in the two rivers.

Calculation of pesticide loads

Pesticide loads for the Sacramento River were calculated by multiplying the instantaneous measured pesticide concentration by the tidally filtered, daily mean discharge (Fig. 4A). For diazinon, the integrated loads for each peak were 160 kg for February 8 to 16 and 130 kg for February 19 to 25. Although the maximum concentration during the second peak (193 ng/L) was only half that during the first peak (393 ng/L), the loads of diazinon in the river were similar. For methidathion, the integrated loads were 120 and 57 kg, respectively. In contrast to diazinon, the methidathion load was much lower following the second rainfall; the higher water solubility of methidathion as compared with diazinon may account for the higher percentage of the methidathion discharging from the watershed during the first rainfall.

Pesticide loads for the San Joaquin River were calculated by multiplying the instantaneous measured pesticide concentration by the daily mean discharge at Vernalis (Fig. 4B). For diazinon, the integrated load for January 8 to 28 was 48 kg and for February 7 to 28 was 44 kg. Although the diazinon concentrations were much higher in February, the discharge was much lower than in January so that the resulting loads were similar. It is likely that additional diazinon was applied to orchards between the January and February rains, but the lack of detailed data on diazinon application at this time makes it impossible to verify. The load of methidathion was much lower, with only 12 kg of methidathion for February 8 to 19 in the San Joaquin River.

There is a striking contrast between the pesticide loads in the two rivers. The load of diazinon in the Sacramento River for January and February (340 kg) was 3.5 times the diazinon load in the San Joaquin River (98 kg), whereas the difference in methidathion loads (190 and 12 kg, respectively) was a factor of 17. The lack of current pesticide-use data precludes a quantitative comparison of the riverine load to use ratios in the two valleys. In 1990, 15 times as much ethyl parathion was applied in the Sacramento Valley as in the San Joaquin Valley and equal amounts of diazinon were applied

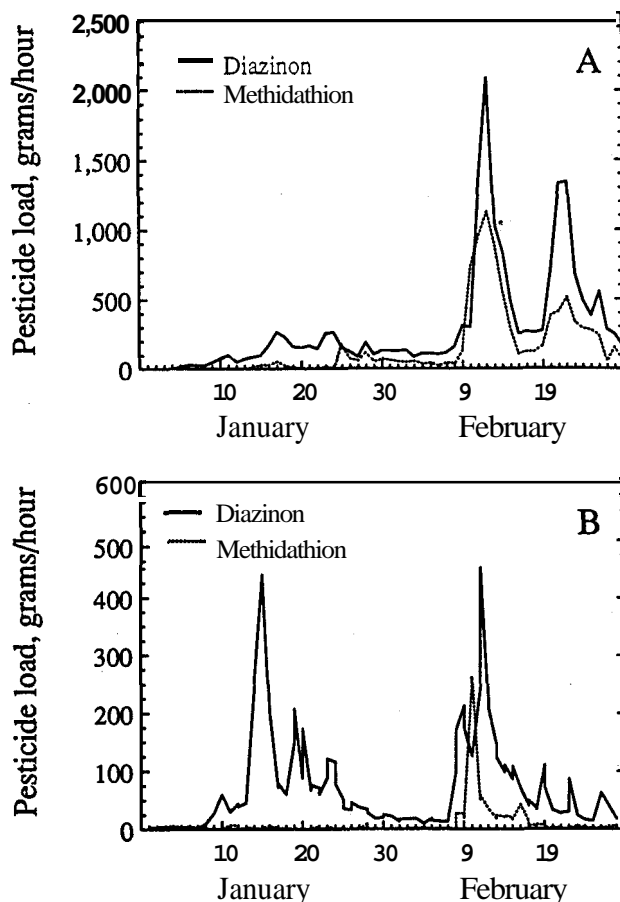


Fig. 4. Pesticide loads: (A) Sacramento River at Sacramento, and (B) San Joaquin River at Vernalis, January and February 1993.

(Table 1) If the entire amount of ethyl parathion used in 1990 was replaced by diazinon (1:1), approximately equal amounts of diazinon would have been applied to the two valleys. In addition, methidathion was probably applied in similar amounts to the two watersheds. These pesticide-use patterns cannot account for the higher load of both diazinon and methidathion in the Sacramento River.

Other factors that influence runoff of pesticides include timing of application relative to rainfall, total amount of rainfall, and saturation of soil due to antecedent conditions. Details are not known about the exact timing of dormant spray application in 1993, but most of the application in both valleys was probably during the dry period at the end of January. The amount of rainfall before and after pesticide application varied greatly between the two valleys. The average rainfall in Sacramento Valley was 16.0 cm in December, 17.9 cm in January, and 18.3 cm in February. In comparison, the San Joaquin Valley was significantly drier with only 5.89, 9.96, and 9.96 cm of rain in December, January, and February, respectively. The differences in the amount of rainfall before and after pesticide application in the two basins could account for the observed differences in pesticide loads.

Table 2. Bioassay results and pesticide concentrations in Sacramento and San Joaquin River water

Sample date	Bioassay results (% mortality)	Dormant spray pesticides (ng/L)			Other pesticides (ng/L)		
		Diazinon	Methidathion	Chlorpyrifos	Atrazine	Carbaryl	Simazine
Sacramento River at Rio Vista							
Feb 7	0	67	tr ^a	nd	tr	nd	71
Feb 8	0	37	12	nd	18	nd	84
Feb 9	0	37	11	nd	nd	nd	65
Feb 10	0	46	tr	nd	30	nd	175
Feb 11	0	100	133	nd	31	nd	309
Feb 12	100 ^b	253	157	nd	50	nd	302
Feb 13	100 ^b	281	179	nd	45	nd	221
Feb 14	100 ^b	187	98	nd	30	nd	106
Feb 15	0	139	78	nd	19	nd	125
Feb 16	10	93	53	nd	tr	nd	90
Feb 17	0	75	29	nd	16	nd	178
Feb 18	0	60	29	nd	tr	nd	96
Feb 19	0	149	55	nd	51	nd	331
Feb 21	0	166	68	nd	37	nd	272
Feb 23	0	136	54	nd	22	nd	157
Feb 25	0	72	42	nd	nd	nd	93
San Joaquin River at Vernalis							
Feb 5	0	73	tr	nd	nd	tr	128
Feb 7	0	84	tr	nd	nd	tr	95
Feb 8	100 ^c	773	122	nd	nd	101	103
Feb 9	100 ^c	586	36	tr	nd	106	596
Feb 10	100 ^c	358	214	tr	nd	62	492
Feb 11	100 ^c	1,071	140	31	nd	41	844
Feb 12	100 ^c	554	92	42	nd	14	455
Feb 13	100 ^d	396	49	32	nd	10	393
Feb 14	100 ^d	331	70	tr	nd	nd	247
Feb 15	100 ^d	364	56	tr	nd	10	248
Feb 16	100 ^b	263	157	tr	nd	nd	180
Feb 17	100 ^b	195	22	tr	nd	nd	193
Feb 18	100 ^b	148	30	tr	nd	nd	160
Feb 19	100 ^d	350	23	nd	nd	nd	360
Feb 20	0	83	tr	nd	nd	nd	187
Feb 21	0	74	nd	nd	nd	tr	238
Feb 23	0	79	17	nd	nd	nd	137
Feb 24	20	49	10	nd	nd	nd	135
Feb 25	0	43	tr	nd	nd	nd	89

nd, not detected.

^aTrace means compound detected at concentration below method detection limit.

^bMortality occurred within 7 d.

^cMortality occurred within 24 h.

^dMortality occurred within 48 h.

response (Table 2). The comparative toxicities of these pesticides are (in order of toxicity) chlorpyrifos, diazinon, methidathion, carbaryl, atrazine, and simazine. Chlorpyrifos was the most toxic pesticide detected; the laboratory 96-h LC50 for *C. dubia* was between 80 and 130 ng/L of chlorpyrifos [2]. The other pesticides detected in these water samples are less toxic than diazinon. For methidathion and carbaryl, the laboratory 96-h LC50s for *C. dubia* were 2,000 and 8,300 ng/L [2,17]. Atrazine and simazine are much less toxic, with reported 48-h LC50s of 6.9×10^6 and 1.0×10^7 ng/L for *Daphnia magna* (also a water flea) [18,19]. Because the concentrations of methidathion, carbaryl, atrazine, and simazine were an order of magnitude or more lower than their respective LC50s, these compounds probably do not contribute to the observed toxicity. However, the additive or

synergistic effects of pesticides are not well understood. In addition, other compounds from agricultural and urban runoff, including trace metals and other organic compounds, could be present and could be contributing to the overall toxicity observed in the bioassay surveys.

Results of this pesticide study are useful to estimate the possible effects of dormant spray pesticides on the ecology of the delta and bay. The National Academy of Sciences and National Academy of Engineering [20] has recommended a guideline of 9 ng/L diazinon as a maximum concentration in surface water for protection of aquatic life, and the International Joint Commission [21] suggests a similar guideline of 8 ng/L diazinon for the Great Lakes. Currently (1995), there is no EPA aquatic-life criterion for diazinon. For chlorpyrifos, the EPA water quality criteria for protection of

freshwater aquatic organisms is 41 and 83 ng/L for chronic and acute exposures, respectively [22]. In all the samples collected during this study, concentrations of diazinon always exceeded the National Academy of Sciences and National Academy of Engineering recommended guidelines, whereas the dissolved concentrations of chlorpyrifos were less than the recommended EPA criteria on all dates except for February 12 on the San Joaquin River.

Bioassay results demonstrate that diazinon and possibly other compounds present in storm runoff were biologically available. Although there is not an extensive toxicological database for diazinon, what is available suggests that other invertebrates are more sensitive to diazinon. For example, the 96-h LC50 for *Daphnia magna*, *Gammarusfaciatus*, and *Chironomus tentans*, two of which are present in the estuary, are 210,200, and 30 ng/L diazinon, respectively [23–25]. These organisms are 2 to 18 times more sensitive than *C. dubia*. Reproduction was not measured in this study. However, the IC25 for *C. dubia* (concentration that produces a 25% reduction in reproduction) is 125 ng/L diazinon. As with mortality, reproductive impacts for other organisms probably occur at still lower concentrations. Therefore, the pesticide field data suggest that sensitive organisms in the San Francisco Estuary may experience short periods of acutely toxic conditions and longer periods with potentially chronic impacts in the winter.

Ecological effects of pesticides on aquatic biota in the delta have not yet been studied; however, most freshwater zooplankton (copepods, rotifers, and cladocerans) in the delta are in decline [26]; the cause is unknown. More studies need to be conducted to ascertain the impact of pesticides in controlling the abundance and distribution of organisms in the San Francisco Estuary.

SUMMARY AND CONCLUSIONS

Results of this and previous studies indicate that rainfall runoff is an important mechanism for transporting dormant spray pesticides from orchards into rivers. Elevated concentrations of diazinon, methidathion, and chlorpyrifos were detected after rainfall in January and February in the Sacramento and San Joaquin rivers. Timing of pesticide application, amounts of pesticides applied, water solubility, and soil half-life explain most of the observed temporal and geographic differences in riverine pesticide concentrations. Differences in riverine pesticide loads in the Sacramento and San Joaquin rivers are likely due, in part, to variations in amount of rainfall to the basins before and after pesticide application.

Under high-flow conditions in February 1993, diazinon and methidathion were transported in distinct pulses down the Sacramento River and into San Francisco Bay. These pesticides also were transported from the San Joaquin River through the Sacramento–San Joaquin Delta; within the delta, distribution of pesticides was a steady increase in concentration over time, rather than distinct pulses.

Results of 7-d bioassays indicate that Sacramento River water at Rio Vista was acutely toxic to *C. dubia* for 3 consecutive d and San Joaquin River water at Vernalis for 12 consecutive d (Table 2). Bioassay mortality corresponded

with the highest diazinon concentrations at both sites, and diazinon does explain a good deal of the observed *C. dubia* toxicity. In addition, other pesticides were present that could have contributed to the toxicity of the water samples.

Concentrations of diazinon in all water samples collected in this study exceeded the water quality guidelines recommended by NAS/NAE for protection of aquatic life [20]; concentrations of all other pesticides were below any recommended or regulatory limits. More extensive chemical and toxicological testing needs to be done to ascertain the chemicals responsible for causing toxicity, to determine their distribution and fate within the delta, and to evaluate their effect on native organisms.

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