

Provided below is an overview of the study to follow on page 5, Appendix D.

Toxic Synthetic Pyrethroid Pesticide Levels Found in Stream Sediments

(*Beyond Pesticides*, May 10, 2004) A family of pesticides, synthetic pyrethroids, used increasingly nationwide in place of more heavily restricted organophosphate pesticides has accumulated in many creek sediments to levels that are toxic to freshwater bottom dwellers, according to a new study. The study, "Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies of California's Central Valley," Weston, D. P.; You, J. C.; Lydy, M. J.; Environ. Sci. Technol. (April, 2004), is available on line to members/subscribers of the American Chemical Society.

This study is believed to be the first to evaluate the effect of synthetic pyrethroids on sediment-dwelling organisms, such as midge larvae or shrimp-like amphipods, according to University of California, Berkeley, biologist Donald P. Weston, adjunct associate professor of integrative biology and lead author. Ironically, the two organisms studied, are used by the U.S. Environmental Protection Agency (EPA) as indicators of the health of fresh water sediment, according to the author.

Dr. Weston and colleague Michael J. Lydy of Southern Illinois University (SIU) in Carbondale collected sediment samples from 42 rivers, creeks, sloughs and drainage ditches in California's Central Valley and exposed amphipods and midge larvae to the sediments for 10 days. Twenty-eight percent of the sediment samples (20 of 71) killed amphipods at an elevated rate, and in 68 percent of these sediments, the pyrethroids were at levels high enough to account for the deaths. Thus, while other pesticides may well have contributed to the amphipod deaths in some sediment samples, pyrethroids alone explain the toxicity in the vast majority of the sediment samples, Dr. Weston said.

"About one-fifth of our Central Valley sediment samples are toxic to a standard testing species due to a class of pesticides no one has tested for before, for which there are little data on their toxicology when sediment-bound, and which are being promoted as an alternative to the increasingly restricted organophosphate insecticides," Dr. Weston said.

In the tests, the midge larvae died at higher rates when exposed to sediment from 13 percent of 39 collection sites, and 40 percent of these sediment samples contained enough pyrethroids to account for the deaths. Weston notes that these midges (*Chironomus tentans*) are known to be about three times less sensitive to pyrethroids than are the amphipods (*Hyalella azteca*), which explains the difference between the species results.

"Since the levels are high enough to be toxic to the standard 'lab rat' species, the next question is: What's happening with the resident species?" Dr. Weston said. "The concern is that invertebrates, particularly crustaceans, could have reduced populations, and these organisms are an important food for a variety of bottom-feeding fish."

Alternatively, the amphipods and midge larvae from areas of intensive agricultural or urban pesticide use may have adapted to live with normally toxic levels of the pesticide. Dr. Weston and his colleagues now are sampling these organisms from the rivers, creeks, sloughs and ditches to determine if they respond the same way as lab-raised organisms. Pyrethroids are a class of compounds represented by permethrin, first marketed in 1973, and various other chemicals usually ending in the suffix -thrin. Permethrin is found in home and garden pesticides ranging from RAID to flea killers and head lice creams, but permethrin and its kin find broad use in agriculture, such as on cotton, fruit and nut orchards, and on lettuce and rice. California's Central Valley produces more than half the nation's fruits, vegetables and nuts.

Though pyrethroids are used far less than organophosphates like diazinon and chlorpyrifos, their use in California has risen rapidly in recent years because of increased regulation of the spraying of organophosphates, due to health threats to farm workers and increased toxic runoff from fields. According to Weston, pyrethroid use in California increased 58 percent from 2001 to 2002, if account is taken of the increased potency of newer pyrethroids such as cypermethrin. Over a quarter of a million pounds of pyrethroids were spread on California farm fields in 2002, while about 500,000 pounds were used for structural and pest control and landscape maintenance.

Despite this increased use, environmental monitoring still concentrates on organophosphates, he said. Monitoring also tends to focus on concentrations in the water column, under the assumption that sediment-bound chemicals like pyrethroids are unavailable. The current study shows that to be untrue.

"It's amazing that, after 20 years of use, there is not one published study on pyrethroids in sediments in areas of intensive agriculture," Dr. Weston said.

Part of the reason for a lack of data is that analytical methods to detect pyrethroids in sediment have not been broadly available or standardized. Lydy, an environmental toxicologist with SIU-Carbondale's Illinois Fisheries and Aquaculture Center, developed such a method.

"Prior to our study, scientists in area water-monitoring programs were seeing that if they placed aquatic invertebrates in their sediment samples, the animals would die, but they didn't know why - they'd attribute it to organophosphates or organochlorines (two pesticide ingredients being phased out because of environmental concerns), or they'd put it down to 'unknown causes,'" Dr. Lydy said.

He continued: "Where our study is unique is that we looked at the toxicity and tried to figure out what was actually causing it. We detected organochlorines, such as DDT and chlordane, in the sediments, but at concentrations not high enough to cause the toxicity we noted, whereas concentrations of pyrethroids were high enough to account for that toxicity."

The samples, over 70 in all, were obtained from two major rivers - the San Joaquin and the Feather - and 19 creeks or sloughs, 17 irrigation ditches and two tailwater ponds in 10 Central Valley counties, including the ones with the greatest pyrethroid use: Fresno, Madera, Stanislaus and Sutter. Each sample was placed in a jar and left with 10 test organisms for 10 days, and the death rate compared with similar organisms raised with pristine sediment. The levels of pesticides in each sediment sample also were measured, and 75 percent contained pyrethroids.

Weston, who focuses on freshwater and marine pollution and how it gets from sediments into creatures living on the bottom, noted that another chemical sometimes applied with pyrethroids may be making the situation worse.

Piperonyl butoxide, or PBO, is a synergist that shuts down the enzymes that detoxify pyrethroids, making them last longer in an organism and increasing their killing potential.

He and his colleagues are now trying to measure the level of pyrethroid that kills amphipods, which is around 3 parts per billion in sediments, and whether levels of PBO need to be considered in order to estimate the true toxicity of pyrethroid pesticides. UC Berkeley post-doctoral researcher Erin Amweg is conducting the latter study.

"I don't want to give the impression that pyrethroids are destroying the streams, since that has not yet been shown, but if we are serious about maintaining stream health, we have to consider the sediments and not limit our sampling just to the water above," said Dr. Weston. "While pyrethroids may be preferable to the organophosphates that preceded them, our work shows that the environmental effects of pyrethroids can not be ignored and have had too little study for too long. We need to know more about pyrethroids, because if we don't, how can we regulate them?"

Dr. Lydy said, "Best management practices,' such as introducing buffer strips and wetlands, may reduce pesticide loads in aquatic systems, which would reduce the risk to non-target species."

The study by Drs. Weston, Lydy and post-doctoral researcher Jing You in the Department of Zoology at SIU appeared in the April 8 online version of the American Chemical Society's journal *Environmental Science & Technology* and will be published later in hard copy.

For more information, contact Robert Sanders, rls@pa.urel.berkeley.edu, 510-643-6998, University of California – Berkeley, or find the study under:

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Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies of California's Central Valley

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The agricultural industry and urban pesticide users are increasingly relying upon pyrethroid insecticides and shifting to more potent members of the class, yet little information is available on residues of these substances in aquatic systems under conditions of actual use. Seventy sediment samples were collected over a 10-county area in the agriculture-dominated Central Valley of California, with most sites located in irrigation canals and small creeks dominated by agricultural effluent. The sediments were analyzed for 26 pesticides including five pyrethroids, 20 organochlorines, and one organophosphate. Ten-day sediment toxicity tests were conducted using the amphipod *Hyalella azteca* and, for some samples, the midge *Chironomus tentans*. Forty-two percent of the locations sampled caused significant mortality to one test species on at least one occasion. Fourteen percent of the sites (two creeks and four irrigation canals) showed extreme toxicity (> 80% mortality) on at least one occasion. Pyrethroid pesticides were detected in 75% of the sediment samples, with permethrin detected most frequently, followed by esfenvalerate > bifenthrin > lambda-cyhalothrin. Based on a toxicity unit analysis, measured pyrethroid concentrations were sufficiently high to have contributed to the toxicity in 40% of samples toxic to *C. tentans* and nearly 70% of samples toxic to *H. azteca*. Organochlorine compounds (endrin, endosulfan) may have contributed to the toxicity at a few other sites. This study provides one of the first geographically broad assessments of pyrethroids in areas highly affected by agriculture, and it suggests there is a greater need to examine sediment-associated pesticide residues and their potential for uptake by and toxicity to benthic organisms.

Introduction

The dominance of organophosphates (OPs) among agricultural insecticides over the past several decades has led environmental monitoring programs in California to focus on dissolved phase pesticides and their toxicity (1, 2). The

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FIGURE 1. Location of California's Central Valley (shaded area) and the counties in which sampling sites were located. The counties shown are as follows: BU = Butte, YU = Yuba, SU = Sutter, CO = Colusa, YO = Yolo, SO = Solano, SJ = San Joaquin, ST = Stanislaus, MA = Madera, and FR = Fresno.

emphasis on OPs has diverted attention from more hydrophobic pesticides associated with soils and sediments. Legacy pesticides such as some organochlorines and some currently used pesticides such as the pyrethroids are strongly hydrophobic, and monitoring suspended or bedded sediments would be more appropriate. First generation pyrethroids (e.g., permethrin) have been available since the 1970s, and many second generation pyrethroids (e.g., bifenthrin, cyfluthrin, lambda-cyhalothrin) became available in the 1980s, yet there are little data on their concentrations in aquatic sediments. There have been several mesocosm studies (e.g., refs 3 and 4), but published field data from agricultural areas are minimal. Given recent federal restrictions on residential and some agricultural applications of OPs, and a shift to pyrethroids as replacements, data are needed on realistic environmental concentrations of these compounds.

After gradual decline throughout the 1990s, agricultural use of pyrethroids in California increased 25% from 105 171 kg in 1999 to 131 422 kg in 2002 (data from California's Pesticide Use Reporting database; www.cdpr.ca.gov). In addition, the diversity of pyrethroids used is increasing, and the newer compounds have far greater toxicity to aquatic life. About half of agricultural pyrethroid use in California occurs in the Central Valley, a region lying within the watersheds of the Sacramento and San Joaquin Rivers (Figure 1) that produces more than half of the fruits, vegetables, and nuts grown in the United States. Our goal was to determine the concentrations of pyrethroids and other hydrophobic pesticides in sediments of agriculture-dominated water bodies of the Central Valley and to determine whether toxicity to aquatic life was associated with these residues.

TABLE 1. Patterns of Pyrethroid Use in Those Counties Selected for Sampling in the PUR-Guided Study^c

county	annual agricultural pyrethroid use (kg in 2001)	crops on which most pyrethroids used (% of total pyrethroid use in county)	primary pyrethroids used on specified crop (% of total annual pyrethroid use on crop)	months of greatest pyrethroid use on specified crop (% of total annual pyrethroid use on crop)
Fresno	14927	lettuce (32%) ^a	permethrin (87%) cypermethrin (6%)	Mar (31%) Oct (37%)
		cotton (12%) ^b	cyfluthrin (77%) bifenthrin (8%) (s)-cypermethrin (7%) lambda-cyhalothrin (5%)	July (51%) Aug (38%)
		alfalfa (7%)	lambda-cyhalothrin (44%) bifenthrin (38%) permethrin (16%)	Mar (32%) July (33%)
Madera	5224	pistachios (55%)	permethrin (100%)	May (38%) June (28%) July (22%)
Stanislaus	4809	almonds (46%)	permethrin (79%) esfenvalerate (21%)	July (59%)
Sutter	3305	peaches (51%)	permethrin (89%) esfenvalerate (11%)	May (41%) June (43%)

^a Head and leaf lettuce data combined. Use of pyrethroids on head lettuce comprises 88% of total use on lettuce. ^b Sampling site selection was based on pesticide use data from the year 2000, the most recent data available at the time. In that year, lettuce and alfalfa were the primary crops in Fresno County on which pyrethroids were used, and sample sites in the vicinity of these crops were selected. A 7-fold increase in cyfluthrin usage on cotton between 2000 and 2001 resulted in cotton moving to the second ranked crop in Fresno County in this table, based on 2001 data. ^c Data from the California Department of Pesticide Regulation's pesticide use reporting database, year 2001.

Materials and Methods

Site Selection. We combined data from two studies with different site selection approaches. The first study used the California Department of Pesticide Regulation's Pesticide Use Reporting (PUR) database to identify Central Valley counties with the greatest agricultural use of pyrethroids. Three of the four counties with the greatest pyrethroid use in the San Joaquin River watershed (Fresno, Madera, Stanislaus) and the leading county in the Sacramento River watershed (Sutter) were selected for sampling. For ease of access to some water bodies, a few samples were taken across county lines into neighboring Butte, San Joaquin, and Yuba counties. We also used the PUR database to identify crops in each county on which the majority of pyrethroids were used, months of greatest pyrethroid use, and the compounds employed (Table 1). Sampling sites were located within the regions of each county where these crops were grown. A few additional sites were added in water bodies with anecdotal evidence of sediment toxicity. Sampling sites were located in two major rivers, 11 creeks or sloughs, eight irrigation canals, and two tailwater ponds.

Most stations were sampled twice, termed "peak use" and "winter". The peak use sampling occurred in the month immediately after the peak use of pyrethroids on the target crop(s) within each county. The time of peak use sampling ranged from July 2002 to November 2002, depending on the specific crop. We sampled all sites again in March 2003 following heavy rains ("winter" sampling).

In the second study, samples were obtained from an investigation of irrigation return flows. Farms in the region typically receive irrigation water through a network of canals, and excess irrigation water that flows off the soil surface (tailwater) is returned to the canal system. Sampling stations were located within these canals, termed "agricultural drains", or in creeks to which the canal systems discharged. The principal criteria for site selection was flow dominated by irrigation return water, with only minimal consideration of local pesticide use. Sites were sampled at the beginning (March/April 2003) and toward the end of the irrigation season (August 2003).

In total, the two studies sampled 42 locations, most twice, yielding 70 samples, or 81 including replicates (see Table S1 in Supporting Information).

Sampling Procedures. All sites were sampled from the bank, using a steel trowel to skim the upper 1 cm of the sediment column. In the PUR-guided study, two replicate samples were collected on each sampling occasion, with the second sample processed only if substantial toxicity was seen in the first replicate. In the irrigation return study, a second replicate was collected at only a few sites. All sediments were homogenized by hand mixing, then held at 4 °C (toxicity samples) or -20 °C (chemistry samples).

Analytical Procedures. Sediment samples were analyzed following the methods of You et al. (5) for five pyrethroids: *cis*- and *trans*-permethrin (summed in data presented), esfenvalerate, bifenthrin, and lambda-cyhalothrin. Organochlorine pesticides analyzed included alpha-, beta-, delta-, and gamma-BHC, heptachlor, heptachlor epoxide, alpha- and gamma-chlordane, alpha- and beta-endosulfan, endosulfan sulfate, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, and methoxychlor. Chlorpyrifos was the only organophosphate insecticide quantified. Briefly, analysis was performed on an Agilent 6890 series gas chromatograph with an Agilent 7683 autosampler and an electron capture detector (Agilent Technologies, Palo Alto, CA). Two columns from Agilent, a HP-5MS, and a DB-608 were used. Qualitative identity was established using a retention window of 1% with confirmation on a second column.

Grain size distribution was determined by wet sieving. Total organic carbon was determined on a CE-440 Elemental Analyzer from Exeter Analytical (Chelmsford, MA), following acid vapor treatment to remove inorganic carbon.

Toxicity Testing. In the PUR-guided study, bulk sediments were tested with 7-10-d old *Hyalella azteca* and 10-d old larvae of *Chironomus tentans*, generally following the protocols of the U.S. Environmental Protection Agency (6). The irrigation return study samples were tested with only *H. azteca*. Testing was done in 400 mL beakers containing 50-75 mL of sediment and 250 mL of overlying water, with continuous aeration at 23 °C and a 16 h light:8 h dark cycle. Water was 80% replaced every 48 h using Milli-Q purified water (Millipore Corp., Billerica, MA) made moderately hard by addition of salts (7). Temperature, dissolved oxygen, pH, alkalinity, hardness, and ammonia were measured at days 2 and 10 prior to water replacement. Both species were fed by adding a slurry of 10 mg of Tetrafin Goldfish Flakes to

TABLE 2. Physical Properties and Pesticide Residues in the Sediments Sampled^a

station	sampling time	% silt and clay	% organic carbon	Bif	Esf	Lam	Per	total BHC	total DDT	Diel	total Endr	total Endo	Met
AD2	Apr 2003	33.1	0.53	U	U	1.0	7.2	U	9.2	U	U	U	U
AD2, rep. 1	Aug 2003	67.2	2.35	U	9.7	U	15.1	2.2	20.1	U	U	U	U
AD2, rep. 2	Aug 2003	75.7	2.38	U	12.2	U	18.7	3.1	23.6	U	U	U	1.1
AD5	Aug 2003	68.0	1.65	U	10.9	U	129	1.3	14.3	1.1	U	U	U
AD6	Apr 2003	87.6	1.80	U	5.1	U	20.7	U	15.4	1.2	962	U	2.0
AD6	Aug 2003	91.2	1.49	U	27.5	U	U	1.3	13.5	1.2	U	U	U
AD8	Aug 2003	32.3	1.06	U	30.0	U	U	U	34.9	1.8	1.2	1.3	U
AD10	Mar 2003	14.0	0.47	U	U	U	1.3	U	1.4	U	345	U	U
AD11	Mar 2003	78.7	1.25	U	U	U	1.4	U	17.5	U	9.2	U	1.4
AD13	Aug 2003	56.0	1.81	U	U	U	U	8.5	2.1	U	U	U	1.1
AD16	Aug 2003	81.5	2.20	U	U	U	1.1	3.4	5.9	U	U	U	U
AD18	Apr 2003	69.1	0.85	U	U	U	U	U	13.8	374	U	U	190
AD19	Apr 2003	56.8	1.67	U	U	U	13.8	U	8.8	U	399	U	U
AD19	Aug 2003	66.3	0.86	U	U	U	U	U	16.2	U	U	1.1	9.0
AD21	Apr 2003	52.8	0.44	U	U	U	U	U	3.8	U	1.9	U	U
AD24	Apr 2003	69.6	0.97	U	U	U	U	U	23.6	U	1.0	U	117
AD24	Aug 2003	54.4	1.30	U	U	U	U	U	20.1	1.3	U	2.3	8.1
DC	July 2002	17.2	3.16	1.1	1.4	U	7.3	2.3	3.1	U	2.5	U	1.6
DP	Aug 2002	83.7	1.09	21.0	17.9	2.6	46.9	15.8	78.5	2.6	10.1	17.7	22.7
DP, rep. 1	Mar 2003	58.9	1.40	2.8	1.9	1.0	7.4	U	48.4	1.4	U	U	U
DP, rep. 2	Mar 2003	35.0	0.50	U	1.4	U	3.7	U	33.2	1.3	1.4	U	1.1
FA	Aug 2002	48.4	1.01	U	U	U	1.5	4.3	5.8	U	U	U	U
FL, rep. 1	Nov 2002	54.7	0.48	U	U	U	224	1.1	85.6	1.9	9.8	22.3	1.7
FL, rep. 2	Nov 2002	56.5	0.65	2.6	1.3	U	133	1.3	97.4	1.7	10.3	23.2	4.3
FL	Mar 2003	72.6	0.88	U	U	U	14.1	U	76.1	1.2	1.2	12.6	U
FR, rep 2	July 2002	16.0	0.61	U	U	U	4.0	U	U	U	U	U	4.6
FS, rep. 1	Aug 2002	58.1	0.59	3.6	U	2.6	10.1	1.1	408	11.3	9.3	11.6	2.2
FS, rep. 2	Aug 2002	55.8	0.55	2.0	U	2.3	5.8	U	60.0	5.7	6.3	10.7	1.6
GS	Mar 2003	36.9	1.72	U	U	U	5.3	U	8.0	U	U	U	U
IC, rep.1	Mar 2003	77.9	0.80	1.4	2.2	1.6	6.8	U	228	2.7	3.5	1.7	U
IC, rep. 2	Mar 2003	49.8	1.25	U	7.3	1.5	14.1	U	155	5.3	9.2	2.3	U
JS	Mar 2003	55.8	2.05	U	U	U	3.2	U	4.8	4.7	U	2.7	U
LL, rep 1	Nov 2002	70.2	1.00	6.5	7.0	16.8	459	11.4	371	2.9	27.7	81.5	16.4
LL, rep. 2	Nov 2002	75.1	0.76	28.8	11.6	8.3	290	7.1	257	2.3	18.1	62.5	14.7
LL	Mar 2003	56.0	0.32	7.2	U	1.0	70.5	U	384	3.3	24.4	571	1.6
MA	Mar 2003	60.8	1.30	8.8	U	7.8	6.0	U	61.2	1.9	U	11.3	U
MS	July 2002	34.3	1.26	U	1.3	U	5.9	6.9	61.4	U	U	U	U
MS	Mar 2003	41.6	1.84	U	10.7	U	7.8	U	67.4	U	U	U	U
RC	July 2002	45.4	1.05	U	1.1	U	55.4	U	U	U	U	U	2.8
RC	Mar 2003	64.8	1.40	7.7	U	U	120	U	4.8	U	U	U	U
SJ, rep. 1	July 2002	57.4	0.78	1.2	2.7	1	U	U	54.5	U	2.2	2.2	6.3
SJ, rep. 2	July 2002	55.3	U	U	1.8	U	U	U	35.2	U	1.0	1.2	U
SS, rep. 2	July 2002	21.2	0.48	U	U	U	U	1.4	3.1	U	U	U	1.2
TL, rep. 1	Mar 20 03	57.6	1.36	10.4	U	U	U	U	7.5	U	U	1.0	U

^a Pesticide concentrations as ng/g, dry weight basis, with <1 ng/g indicated by "U". The samples listed were in the highest 10th percentile for the concentrations of one or more analytes and/or were found to show toxicity to one or both test species. A analytical chemistry data for all samples is available in Table S2 of the Supporting Information. Bif = bifenthrin, Esf = esfenvalerate, Lam = lambda-cyhalothrin, Per = permethrin, Diel = dieldrin, Endr = endrin, Endo = endosulfan, and Met = methoxychlor. Total BHC = sum of alpha-, beta-, delta-, and gamma-BHC. Total DDT = sum of p,p'-DDT, p,p'-DDE, and p,p'-DDD. Total endrin = sum of endrin, endrin aldehyde, and endrin ketone. Total endosulfan = sum of alpha- and beta-endosulfan, and endosulfan sulfate.

each beaker daily. Survival was determined after a 10-d exposure period. Five to eight replicates per sample were tested. Sediment from San Pablo Dam Reservoir, El Sobrante, CA was used as a control. Control survival averaged 91% for *H. azteca* and 82% for *C. tentans*. Due to difficulties with *H. azteca* culturing, there was a significant delay in testing many of the PUR peak use sample set (18% of total samples) with this species. Testing could not be done for 5 months, with the sediment samples maintained in the dark at 4 °C during this time. This delay is noted below where it affects interpretation of results.

Spiked sediment tests were done with *H. azteca* and/or *C. tentans* to determine 10-d LC₅₀ values for methoxychlor, endrin, and endosulfan. Control sediment containing 1% organic carbon was spiked with each pesticide and stored at 10 °C for 7 days before testing.

Data were analyzed using ToxCalc Version 5.0 (Tidepool Scientific Software, McKinleyville, CA). Dunnett's Multiple Comparison test was used to identify stations with signifi-

cantly greater mortality than the control. Arcsine square root transformation was used when necessary to meet assumptions of normality and homogeneity of variance. Maximum likelihood regression using probit transformation was used when determining LC₅₀ by dilution of test sediments.

Results

Sediment Chemistry. The tailwater ponds (stations FL and LL; Table 2) were the most contaminated of all sites, with sediments containing a wide variety of pesticides. These sediments had the highest observed concentrations of bifenthrin (28.8 ng/g), lambda-cyhalothrin (16.8 ng/g), permethrin (459 ng/g), and total endosulfan (571 ng/g), and the second highest concentrations of total BHC (11.4 ng/g) and total DDT (384 ng/g). The ponds received tailwater from adjacent lettuce fields, and their contents were recycled back onto the fields with no discharge to public waters. Many farms do not have tailwater ponds, and irrigation return flow reaches public waters either directly or indirectly via canals.

Nevertheless, since the lettuce tailwater ponds do not discharge to public waters and since sediment quality in the ponds was not typical of Central Valley surface waters in general, their data are excluded from the remainder of these sediment chemistry results.

At a detection limit of 1 ng/g, pyrethroids were detected in 75% of the samples. Permethrin was the most frequently reported pyrethroid, found in 66% of the samples. The median concentration was 1.5 ng/g, with highs of 129 ng/g in an irrigation canal (AD5); 55.4 and 120 ng/g in Root Creek adjacent to pistachio groves; and 46.9 ng/g in Del Puerto Creek, a small creek passing through orchards and diverse row crops. Bifenthrin was detectable in 18% of the samples, with a maximum of 21.0 ng/g in Del Puerto Creek. Two irrigation canals, sites MA and TL, also contained substantial amounts of bifenthrin (8.8 and 10.4 ng/g, respectively). Esfenvalerate was detectable in 32% of the samples. Highest concentrations were found in Little John Creek (30.0 ng/g), three irrigation canals (AD2, AD5, AD6; 9.7–27.5 ng/g), Del Puerto Creek (17.9 ng/g), and in Morisson Slough (10.7 ng/g) in an area of peach and plum orchards. Lambda-cyhalothrin was detectable in 12% of the samples. Maximum concentration was 7.8 ng/g in irrigation canal sediments from an alfalfa-growing area.

Total DDT was quantifiable in almost all samples. Median concentration was 6.9 ng/g and reached a maximum of 408 ng/g in an irrigation canal. DDE was the principal degradation product found, typically comprising about two-thirds of the total DDT. Dieldrin was rarely found at concentrations more than a few ng/g but reached 374 ng/g in one creek used for irrigation return. Endrin also had several atypically high concentrations (345–962 ng/g) in water bodies dominated by irrigation return flow. Total BHC reached 15.8 ng/g. Concentrations of the most toxic gamma isomer of BHC never exceeded 2 ng/g.

Endosulfan and methoxychlor are currently used organochlorines. Peak endosulfan concentrations were largely limited to the ponds adjacent to lettuce fields, but 17.7 ng/g was found in Del Puerto Creek. The most toxic form, alpha-endosulfan, typically comprised about 10% of the total endosulfan but reached 50% in some tailwater pond samples. Methoxychlor concentrations were usually low but reached 117 and 190 ng/g in two water bodies with high inputs of irrigation return flow.

Data are not presented for aldrin, alpha- and gamma-chlordane, chlorpyrifos, heptachlor, and heptachlor epoxide as they were rarely detected and were at low concentrations when measurable (<7 ng/g).

Toxicity Testing. Sediments of the tailwater ponds not only had the highest concentrations of many pesticides but also proved to be highly toxic. They were the only samples that caused statistically significant mortality in both *C. tentans* and *H. azteca*, with total or near total mortality in both species. A dilution series using sediments from LL (replicate 2, Nov 2002) and varying amounts of control sediments indicated a 10-d LC₅₀ to *C. tentans* of 13% LL sediment (95% confidence interval = 10–16%). Dilution series with sediments from FL (replicate 2, Nov. 2002) indicated a *C. tentans* 10-d LC₅₀ of 92% (c.i. = 89–94%) and a *H. azteca* 10-d LC₅₀ of 69% (c.i. = 60–80%).

Excluding the tailwater ponds, toxicity to one of the test species was seen in 32% of the 77 samples tested (see Table S3 in Supporting Information). Five of the 39 samples tested with *C. tentans* showed toxicity, and 20 of 71 samples were toxic to *H. azteca*. No stations other than tailwater ponds were toxic to both species. Sites with particularly high or persistent mortality to *H. azteca* included Del Puerto and Ingram Creeks and 4 irrigation canals (AD2, AD6, MA, TL). A dilution series with the August AD6 sample provided a

10-d LC₅₀ to *H. azteca* of 36% (c.i. = 25–49%), and the March MA sample indicated a 10-d LC₅₀ of 26% (c.i. = 18–34%).

Investigating Causes of Sediment Toxicity. A toxicity unit (TU) approach was used to identify pesticides potentially responsible for observed toxicity. TU was calculated as the actual concentration divided by the LC₅₀, both on an organic carbon (oc) normalized basis. Sediment LC₅₀ values (Tables 3 and 4) for both species were estimated as follows:

Pyrethroids. Cypermethrin 10-d LC₅₀ values average 1.3 μg/g oc (range = 0.48–2.20) and 0.38 μg/g oc (range = 0.18–0.60) for *C. tentans* and *H. azteca*, respectively (8). Cypermethrin is not one of the major pyrethroids used in our study area and thus not among our analytes, but it is possible to use these data to estimate sediment LC₅₀s for other pyrethroids. Solomon et al. (9) plotted all water toxicity data for a wide variety of pyrethroids and noted that the 10th percentile of the toxicity distributions is a convenient criterion for characterizing relative toxicity. The 10th percentile LC₅₀s for cypermethrin = 10 ng/L, lambda-cyhalothrin = 10 ng/L, bifenthrin = 15 ng/L, esfenvalerate/fenvalerate = 37 ng/L, and permethrin = 180 ng/L. Given the sediment toxicity of cypermethrin and the relative toxicity of other pyrethroids, sediment LC₅₀ values for the other pyrethroids were estimated. This approach assumes that the other pyrethroids are comparable to cypermethrin in the bioavailability of particle-adsorbed residues. This assumption is reasonable, since the toxicity of pyrethroids to benthic organisms is predictable by the equilibrium partitioning-derived pore water concentration (8), and the pyrethroids in this study have *K_{oc}*'s comparable to cypermethrin (10).

Two published LC₅₀s are available as an independent check on the estimated LC₅₀ values. The permethrin 10-d sediment LC₅₀ for *C. riparius* is 21.9 μg/g oc (11), a value very close to our estimated permethrin 10-d LC₅₀ for *C. tentans* (23 μg/g oc). The lambda-cyhalothrin 28-d EC₅₀ for emergence of *C. riparius* is 6.8 μg/g oc (12) given an oc content of the test sediment of 3.7% provided by J. Warinton (personal communication), a value five times greater than our estimate of 1.3 μg/g oc.

DDE, DDD, DDT. 10-d LC₅₀s of DDT to *H. azteca* range from 100 to 470 μg/g oc and average 260 μg/g oc (13, 14). DDD and DDE are 5.2 and 32 times less toxic to *H. azteca*, respectively, in water exposures (averaging results of refs 15 and 16), suggesting the sediment LC₅₀s for these organochlorine compounds are approximately 1300 and 8300 μg/g oc, respectively.

No sediment toxicity data are available for *C. tentans*, but in water exposures the species is 12 times less sensitive to DDT than *H. azteca* and 4.3 and 1.3 times more sensitive to DDD and DDE, respectively (16). These factors, when applied to *H. azteca* sediment LC₅₀ values, yield the *C. tentans* sediment LC₅₀ estimates of Table 3.

Dieldrin. Ten-day sediment LC₅₀ values for *C. tentans* have been measured at 35 and 78 μg/g oc, averaging 57 μg/g oc. Values have ranged from 1100 to 3700 μg/g oc for *H. azteca* and average 2000 μg/g oc (17).

Endrin. Sediment 10-d LC₅₀ for *C. tentans* was measured as part of this study and found to be 4.22 μg/g oc (c.i. = 0.70–8.11). Ten-day sediment LC₅₀s to *H. azteca* range from 54 to 257 μg/g oc and average 140 μg/g oc (13, 14). Information on the relative aquatic toxicities of endrin and its aldehyde and ketone degradation products was lacking, but all three compounds were summed when determining the TUs of endrin present. While the validity of this assumption is unclear, it is of little consequence since at those stations with the highest total endrin concentrations, endrin itself comprised >85% of the total.

Methoxychlor. Methoxychlor 10-d LC₅₀ values were measured for this study and found to be 36.7 (c.i. = 27.2–46.8)

TABLE 3. *C. tentans* Toxicity Units (TU) of the Pesticide Analytes at All Stations Exhibiting Significant Toxicity to *C. tentans*^a

sample	Mort	toxicity units of individual pesticides										ΣTUs
		Bif	Esf	Lam	Per	DDT	Diel	Endr	Met	Endo	BHC	
LL, Nov 2002, rep. 1	100 ± 0	0.3	0.2	1.3	2.0	<i>b</i>	<i>b</i>	0.7	<i>b</i>	4.7	<i>b</i>	9.2
LL, Nov 2002, rep. 2	100 ± 0	1.9	0.3	0.8	1.7	<i>b</i>	<i>b</i>	0.6	0.05	3.3	<i>b</i>	8.7
LL, Mar 2003	100 ± 0	1.1	<i>b</i>	0.2	1.0	<i>b</i>	<i>b</i>	1.8	<i>b</i>	74.6	<i>b</i>	78.7
FL, Nov 2002, rep. 1	98 ± 4	<i>b</i>	<i>b</i>	<i>b</i>	2.0	<i>b</i>	<i>b</i>	0.5	<i>b</i>	1.3	<i>b</i>	3.8
GS, Mar 2003	62 ± 8	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
FL, Nov 2002, rep. 2	60 ± 17	0.2	<i>b</i>	<i>b</i>	0.9	<i>b</i>	<i>b</i>	0.4	<i>b</i>	1.0	<i>b</i>	2.5
FR, July 2002, rep. 2	58 ± 36	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
FS, Aug 2002, rep. 2	54 ± 11	0.2	<i>b</i>	0.3	0.05	<i>b</i>	<i>b</i>	0.3	<i>b</i>	0.5	<i>b</i>	1.4
DC, July 2002	50 ± 28	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
FS, Aug 2002, rep. 1	44 ± 24	0.3	<i>b</i>	0.3	0.07	<i>b</i>	<i>b</i>	0.4	<i>b</i>	0.6	<i>b</i>	1.7
# nontoxic samples with ≥0.5 TU (n=31)		1	0	1	0	0	0	1	0	0	0	
LC ₅₀ used to derive TUs (μg/g o.c.)		2.0	4.8	1.3	23	DDT = 3100 DDD = 300 DDE = 6400	57	4.2	36.7	α = 0.96 β = 3.2 sulf = 5.2	0.73	

^a Mort = % mortality; Bif = bifenthrin; Esf = esfenvalerate; Lam = lambda-cyhalothrin; Per = permethrin; DDT = sum TU of DDT, DDD, DDE; Diel = dieldrin; Endr = endrin; Met = methoxychlor; Endo = sum TU of alpha- and beta-endosulfan and endosulfan sulfate; BHC = gamma-BHC.
^b <0.05 TU.

and 85.8 μg/g oc (c.i. = 72.1–102.6) for *C. tentans* and *H. azteca*, respectively.

Endosulfan. *C. tentans* 10-d LC₅₀ values were measured for this study and found to be 0.96 (c.i. = 0.41–1.46), 3.24 (c.i. = 1.46–4.27), and 5.22 μg/g oc (c.i. = 3.23–5.82) for alpha- and beta-endosulfan and endosulfan sulfate, respectively. *H. azteca* 10-d LC₅₀ values were measured as 51.7 (c.i. = 38.6–61.6), >1000, and 873 μg/g oc (c.i. = 660–1139) for the same compounds.

BHC. The 24-h sediment EC₅₀ of gamma-BHC to *C. riparius* is 0.73 μg/g oc (18). This estimate is shown in Table 3 as the best available data, although the actual 10-d LC₅₀ for *C. tentans* is likely to be less considering our 10-d exposure and the fact that *C. tentans* is more sensitive to gamma-BHC than is *C. riparius* (19). No sediment LC₅₀ data were available for *H. azteca*, but in 10-d water exposures, the LC₅₀ of the species is 75% of that of *C. riparius* (20), and that conversion factor was used to derive an estimated sediment LC₅₀ for *H. azteca* of 0.55 μg/g oc. In calculating TUs present at the sampling sites, only the sediment concentration of the gamma-isomer was used since other isomers of BHC have much lower aquatic toxicities (21).

In most of the 10 samples toxic to *C. tentans*, the TU approach suggests that several of the measured analytes were present in concentrations that could account for the observed mortality (Table 3). In the tailwater pond samples (FL and LL) where near total mortality was observed, bifenthrin, lambda-cyhalothrin, permethrin, endrin, and endosulfan were all in sufficient concentrations in most of the samples so that any one of these pesticides alone could account for the toxicity. One sample (LL, March 2003) contained 78 TU of endosulfan.

To account for cumulative effects of multiple pesticides, the TUs of individual pesticides were summed to determine a total TU in each sample. This approach implicitly presumes additivity of toxicity as is common among pesticides (22), though the data do not exist to demonstrate whether specific combinations of our analytes are greater or less than additive. The default presumption of additivity is made more defensible by the fact that since the organochlorines only had appreciable TUs at a few sites, the sum TU is largely a summation of TUs of the individual pyrethroids for which a common mode of toxic action is more likely.

Outside of the tailwater ponds, the combined effects of bifenthrin, lambda-cyhalothrin, and endosulfan may have contributed to the mortality in both replicates of station FS,

since they together contribute nearly 1 TU. The combined concentrations of endrin and endosulfan account for about another TU at this site. DDT, dieldrin, and BHC most likely did not contribute to the observed toxicity to *C. tentans* in any sample. In 3 of the 10 toxic samples (GS, FR, DC) the measured analytes could not account for the toxicity.

TU calculations for samples not toxic to *C. tentans* are not shown in Table 3 to conserve space, but for each analyte the number of nontoxic samples that contained at least 0.5 TU is shown. The 0.5 TU threshold is arbitrary but suggests a strong likelihood that the analyte makes a substantial contribution to the observed mortality. Bifenthrin, lambda-cyhalothrin, and endrin were the only pesticides for which mortality was expected but not seen, with only one nontoxic sample for each compound having ≥0.5 TU.

A similar TU analysis for the *H. azteca* toxicity data (Table 4) indicates bifenthrin, lambda-cyhalothrin, and permethrin concentrations were sufficiently high (≥0.5 TU) that each compound individually could have had a substantial contribution to the mortality in six of the 23 toxic samples. Esfenvalerate concentrations were ≥0.5 TU in five samples. Cumulatively, pyrethroids were likely responsible for much of the toxicity in 17 of the 23 toxic samples. The most extreme cases were the tailwater ponds where the combined effect of all four pyrethroids created up to 12.9 TUs, and 98% mortality to *H. azteca* was observed.

As was the case for *C. tentans*, the TU calculations for *H. azteca* indicated that most of the legacy organochlorine compounds were present at concentrations far too low to account for the observed toxicity. The only exception to this generality was endrin, which was found at 0.4 TU in one irrigation canal toxic to *H. azteca* and at 0.5 TU in another nontoxic canal sample. Among the current use organochlorines, methoxychlor approached toxic thresholds in one creek (Stone Corral Creek, AD18), and endosulfan may have contributed to mortality in a tailwater pond. None of the measured analytes could explain toxicity at AD11 and AD21.

Among samples without significant *H. azteca* toxicity there were only rare instances of samples containing ≥0.5 TU of any pesticide (one sample for lambda-cyhalothrin and endrin, two for permethrin). The only exception was bifenthrin for which four samples contained ≥0.5 TU of the compound but were nontoxic. Nevertheless samples containing ≥0.5 TU bifenthrin were more than three times as likely to be toxic than nontoxic, suggesting our bifenthrin LC₅₀ estimate, while perhaps slightly low, is not grossly in error. Overall, the

TABLE 4. *H. azteca* Toxicity Units (TU) of the Pesticide Analytes at All Stations Exhibiting Significant Toxicity to *H. azteca*^a

sample	Mort	toxicity units of individual pesticides										ΣTUs
		Bif	Esf	Lam	Per	DDT	Diel	Endr	Met	Endo	BHC	
MA, Mar 2003	100 ± 0	1.2	<i>b</i>	1.6	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	2.9
LL, Nov 2002, rep. 1	98 ± 4	1.1	0.5	4.4	6.8	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.06	<i>b</i>	12.9
FL, Nov 2002, rep. 1	97 ± 5	<i>b</i>	<i>b</i>	<i>b</i>	6.9	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	6.9
AD2, Apr 2003	97 ± 7	<i>b</i>	<i>b</i>	0.5	0.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.7
DP, Mar 2003, rep. 1	90 ± 14	0.4	0.1	0.2	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.8
IC, Mar 2003, rep. 2	90 ± 14	<i>b</i>	0.4	0.3	0.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.9
IC, Mar 2003, rep. 1	85 ± 13	0.3	0.2	0.5	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.1
AD6, Aug 2003	85 ± 19	<i>b</i>	1.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.3
AD2, Aug 2003, rep. 2	84 ± 9	<i>b</i>	0.4	<i>b</i>	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.5
FL, Nov 2002, rep. 2	83 ± 6	0.7	0.1	<i>b</i>	3.0	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	3.8
TL, Mar 2003, rep. 1	82 ± 18	1.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.3
AD2, Aug 2003, rep. 1	81 ± 18	<i>b</i>	0.3	<i>b</i>	0.09	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.4
DP, Aug 2002	78 ± 16	3.4	1.2	0.6	0.6	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.2	6.0
LL, Mar 2003	76 ± 29	4.0	<i>b</i>	0.8	3.2	0.2	<i>b</i>	0.05	<i>b</i>	0.9	<i>b</i>	9.2
MS, Mar 2003	68 ± 33	<i>b</i>	0.4	<i>b</i>	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.5
AD8, Aug 2003	67 ± 18	<i>b</i>	2.0	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	2.0
DP, Mar 2003, rep. 2	58 ± 16	<i>b</i>	0.2	<i>b</i>	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.3
AD5, Aug 2003	47 ± 27	<i>b</i>	0.5	<i>b</i>	1.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.7
AD6, Apr 2003	39 ± 25	<i>b</i>	0.2	<i>b</i>	0.2	<i>b</i>	<i>b</i>	0.4	<i>b</i>	<i>b</i>	<i>b</i>	0.8
AD18, Apr 2003	36 ± 28	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.3	<i>b</i>	<i>b</i>	0.3
AD11, Mar 2003	34 ± 27	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
SJ, July 2002, rep. 2	34 ± 15	<i>b</i>	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.1
AD21, Apr 2003	31 ± 17	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
# nontoxic samples with ≥0.5 TU (n=51)		4	0	1	2	0	0	1	0	0	0	
LC ₅₀ used to derive TUs (μg/g o.c.)		0.57	1.4	0.38	6.8	DDT = 260	2000	140	85.8	α = 52	0.55	
						DDD = 1300				β = >1000		
						DDE = 8300				sulf = 870		

^a Mort = % mortality; Bif = bifenthrin; Esf = esfenvalerate; Lam = lambda-cyhalothrin; Per =permethrin; DDT = sum TU of DDT, DDD, DDE; Diel = dieldrin; Endr = endrin; Met = methoxychlor; Endo = sum TU of alpha- and beta-endosulfan and endosulfan sulfate; BHC = gamma-BHC. ^b <0.05 TU.

rarity of high TU values among nontoxic samples for all analytes suggests our LC₅₀ estimates are reasonable.

Discussion

There have been few measurements of pyrethroids in sediments of agriculture-influenced water bodies, and fewer still that have incorporated toxicity testing of these sediments. We found that pyrethroid residues can be widespread in sediments from regions of intensive agriculture, and in some locations are present in concentrations likely to cause toxicity to sensitive species. The tailwater ponds represented the most extreme instance, containing at least four pyrethroids that were present at concentrations that, even if considered individually, were capable of causing substantial mortality.

Sediments collected from creeks, rivers, and the irrigation canals that discharge to them did not show the extreme pesticide concentrations found in the tailwater ponds but nevertheless frequently showed toxicity to the test species. Statistically significant mortality to *C. tentans* or *H. azteca* was observed in 32% of the 77 sediment samples tested, and 42% of the locations sampled were toxic to at least one species on at least one occasion. Toxicity was seen on occasion in both major rivers sampled, eight of the 19 creeks and sloughs sampled, and seven of the 17 irrigation canals. Six sites (14% of those tested) showed >80% mortality in a test species on at least one occasion.

It appears the analytes we measured were at sufficient concentrations to explain the vast majority of observed mortality. Pyrethroids were likely to have contributed to the toxicity in 40% of samples toxic to *C. tentans* and nearly 70% of samples toxic to *H. azteca* (excluding tailwater ponds). Endrin, endosulfan, and methoxychlor may have been important in a few instances, but for the remaining toxic samples, it was not possible to determine if pesticides or other substances were responsible for the toxicity. There are

over 130 pesticides used in the Central Valley, and since the concentrations of most are not measured in any monitoring program, their contribution to toxicity is unknown.

Our toxicity data are supported by an independent study that overlapped with two sampling locations. California's Central Valley Regional Water Quality Control Board sampled the Del Puerto Creek site three times from June to October of 2002 and found 39–100% mortality to *H. azteca* (J. Rowan, personal communication), compared to our observation of 78% mortality in August 2002. The same agency sampled the Orestimba Creek site in September 2002 and found 59% mortality to *H. azteca*, compared to our determination of 60% mortality in March, 2003.

In considering the frequency of toxicity and the sediment concentrations of pesticides, it should be recognized that sampling for the PUR-guided study was focused on areas of high pyrethroid use or water bodies where water quality degradation was likely. However, the irrigation return study, which made up half the total samples, targeted water bodies dominated by irrigation return flow with only minimal consideration of pesticide use or crops grown. There was a greater frequency of toxicity in the PUR-guided study (34% vs 27% in irrigation return study) and in the frequency of pyrethroid detection (85% vs 65%), but the results are still quite striking even for the return flow study with minimal site selection bias.

While our work focused on smaller tributaries, there is some indication of sediment quality impacts in the larger rivers. One sample (of three) in the Feather River proved toxic to *C. tentans* with the responsible agent unknown. Three locations were sampled on the San Joaquin River: one in July 2002 and all three in March 2003, with the July sample showing *H. azteca* mortality due to unknown causes. Further

sampling in the major rivers would be desirable to better characterize regional impacts.

An important conclusion from these data is that legacy organochlorines, while widely distributed in Central Valley sediments, were far below acutely toxic concentrations to sensitive aquatic invertebrates. The only exception to this generalization was endrin, which was found at concentrations of approximately half its LC₅₀ in a few irrigation canals. Current-use organochlorine compounds (endosulfan, methoxychlor) were below acutely toxic thresholds in the majority of samples, though they may have contributed to toxicity in the tailwater ponds or a few irrigation canals where concentrations exceeded several hundred ng/g.

The extreme toxicity of sediment-associated pyrethroids indicates the need to improve the detection limits achieved in this study. The sediments tested had organic carbon contents typically about 1%, and in such sediments the *H. azteca* 10-d LC₅₀ of cypermethrin is 3.6 ng/g (8). Based on relative toxicity among the pyrethroids, in the same sediment the LC₅₀s for bifenthrin, cyfluthrin, and deltamethrin would be on the order of 3–6 ng/g, the LC₅₀s for esfenvalerate or fenvalerate would be about 10–15 ng/g, and the LC₅₀s for permethrin and fenprothrin would be about 60–90 ng/g. Excluding permethrin and fenprothrin, these estimates of LC₅₀ are only slightly above the one ng/g detection limit. Thus, mere detection of any of the more toxic pyrethroids at least raises the possibility of acute toxicity, even without considering that other species may be more sensitive than *H. azteca* or that chronic toxicity may occur at concentrations less than the 10-d LC₅₀ used in these estimates.

The data suggest that pyrethroid concentrations in aquatic habitats of the Central Valley tend to be greater shortly after their use rather than after heavy winter rains. Though there is some dormant spraying of pyrethroids on orchard crops during winter months, most Central Valley crops treated with pyrethroids receive the greatest amounts in the summer. During this period, the mechanisms for transport of residues to aquatic systems would be irrigation return and spray drift from aerial application. Potentially pesticide-bearing soils are washed into aquatic systems by heavy rains, largely confined to December through March. However, pyrethroids typically have half-lives on the order of 1–2 months in aerobic soils (10), providing opportunity for substantial degradation between summer application and winter rains. In this study, 65% of the sites with measurable pyrethroids had the highest concentrations in the late summer and fall near the end of the irrigation season. At only 35% of the sites were concentrations greatest in March and April at the conclusion of the rainy season.

The prevalence of sediment toxicity in this study, and evidence that pyrethroids were likely to be responsible for much of it, clearly shows the need for greater awareness of the risks of particle-associated pyrethroids. There are considerable data on the toxicity of dissolved-phase pyrethroids to aquatic life that have been used in developing risk assessments for the compounds (9, 12, 23, 24), but these risk assessments have generally focused more on the water column than on sediments. The bioavailability and toxicity of sediment-bound residues have received little attention, as indicated by the difficulty in locating direct sediment LC₅₀ measurements for the compounds of interest in this study. The log *K*_{oc} for most pyrethroids ranges from 5 to 6 (10), and they rapidly partition on to soils or sediments (8). Except in close proximity to and shortly after application, pyrethroids will largely be sediment associated (26). It has been argued that the hydrophobicity of these compounds lessens their bioavailability (12, 25), which may be the case for organisms living within the water column (e.g., daphnids widely used for toxicity testing). However, results from our study indicate a substantial risk remains to benthic organisms under realistic

conditions of agricultural use. Our study did not differentiate whether the primary route of toxicity was exposure to dissolved phase pyrethroids within the pore water or ingestion and digestive desorption of particle-associated residues. Digestive routes of contaminant uptake often take on increasing importance for strongly hydrophobic compounds (26), and deposit-feeder digestive fluids are usually far more effective extractants of hydrophobic organics than is water (27). Regardless of the route of uptake, our findings of widespread sediment toxicity indicate pyrethroid uptake by and toxicity to benthic organisms, and particularly deposit-feeding species, deserves closer study.

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Supporting Information Available

Sampling location details (Table S1), analytical chemistry results for all samples (Table S2), and toxicity testing results for all samples (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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