Occurrence and Toxicity of Three Classes of Insecticides in Water and Sediment in Two Southern California Coastal Watersheds

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Ⓢ *Supporting Information*

ABSTRACT: The occurrence of chlorpyrifos, diazinon, pyrethroids, and fipronil was investigated in two watersheds along the southern California coast. Paired surface water and sediment samples were collected under dry and wet (after significant rain events) weather conditions. Insecticide concentrations in water and sediment were higher following rain events than during the dry season. Chlorpyrifos was the most frequently detected compound (>88%). Pyrethroids were detected in 74 and 100% of the water and sediment samples, respectively, with bifenthrin detected most frequently. *Trans*-permethrin was detected at the highest concentration followed by bifenthrin. Bifenthrin and *trans*-permethrin water concentrations were significantly correlated ($P < 0.01$) with the suspended solid level, suggesting transport facilitated by suspended particles. In 80% of the wet season samples with 100% of *Ceriodaphnia dubia* mortality, chlorpyrifos concentrations were >100 ng L^{-1}. Sediment pyrethroid levels (0.5–1100 ng g^{-1}) were frequently higher than the respective *Hyalella azteca* LC$_{50}$ values, with bifenthrin as the primary contributor of *H. azteca* toxicity.

KEYWORDS: nonpoint source pollution, pyrethroids, organophosphate pesticides, fipronil, stormwater runoff

■ INTRODUCTION

Over the past two decades, the dominance of organophosphate compounds (OPs) among the agricultural insecticides has led to some intensive monitoring studies of agricultural watersheds in regions such as California.[1−5] For example, diazinon and chlorpyrifos have been detected routinely in surface water of the Sacramento River, San Joaquin River, and Imperial Valley watersheds[2,3,6,7] and along the north-central coast of California.[1,2] Within these watersheds, chlorpyrifos and diazinon have been further implicated as causes of the observed toxicity to aquatic invertebrates.[1−3,8] With the use of OPs becoming more restricted, application of other classes of highly effective insecticides, including pyrethroids and fipronil, is increasing in both agricultural and urban areas.[7,9] More recently, monitoring efforts have been expanded to assess the occurrence and potential toxicity of pyrethroids and fipronil in water and bed sediments.[4,9−12] Studies show that contamination by bifenthrin and permethrin is widespread and is likely a primary cause of toxicity to native and indicator invertebrates.[9,11,13] A few other pyrethroids, including cyhalothrin,[15] cypermethrin,[9] and fenpropathrin,[14] have also been detected and, in some cases, were responsible for the observed aquatic toxicity.[15] Fipronil is a phenylpyrazole insecticide newly registered for use in California. Studies show that fipronil is readily transformed to three degradates, that is, fipronil desulfinyl, fipronil sulfone, and fipronil sulfide.[16] Fipronil degradates are equally as or more toxic than fipronil itself to nontarget organisms, including particularly aquatic crustaceans.[17]

The potential toxicity of OPs and replacement insecticides to aquatic organisms at trace levels warrants more research into the patterns (e.g., seasonality) and causes (irrigation vs rain-induced runoff) of contamination. In addition, monitoring of pesticide contamination in California so far has been limited mostly to the Sacramento—San Francisco Bay area in the north and the Central Valley.[5,10,15] Although watersheds along the southern and central California coast represent some of the most agriculture-intensive areas in the United States, and there are also many sensitive ecosystems, including wildlife habitats, at present relatively little information exists on the occurrence and potential ecotoxicological effects of current-use insecticides in these watersheds. This study surveyed the levels of OPs and their replacement insecticides, pyrethroids and fipronil, in water and sediment phases of two major watersheds within the agriculture-dominated Ventura County adjacent to Los Angeles County. Pesticide concentration data from 14 sites and 4 sampling cycles were considered to decipher seasonal trends.

■ MATERIALS AND METHODS

Study Area and Sample Collection. The study area consisted of two major watersheds, the Santa Clara River watershed (4232 km^2) and the Callegaus Creek watershed (883 km^2), which are located in Ventura County along the Pacific Ocean west coast (Figure 1). This region represents one of the most important agricultural areas in the United States, ranked among the top 10 counties in the total value of agricultural product sale (http://www.agcensus.usda.gov). These watersheds have a characteristic Mediterranean climate with distinctive wet and dry seasons, with almost all rainfall occurring in the months between December and March each year.

A total of 14 sites were selected on the basis of their representation of the respective watersheds, accessibility, and water flow conditions (Figure 1). All of the sampling sites received mainly agricultural runoff
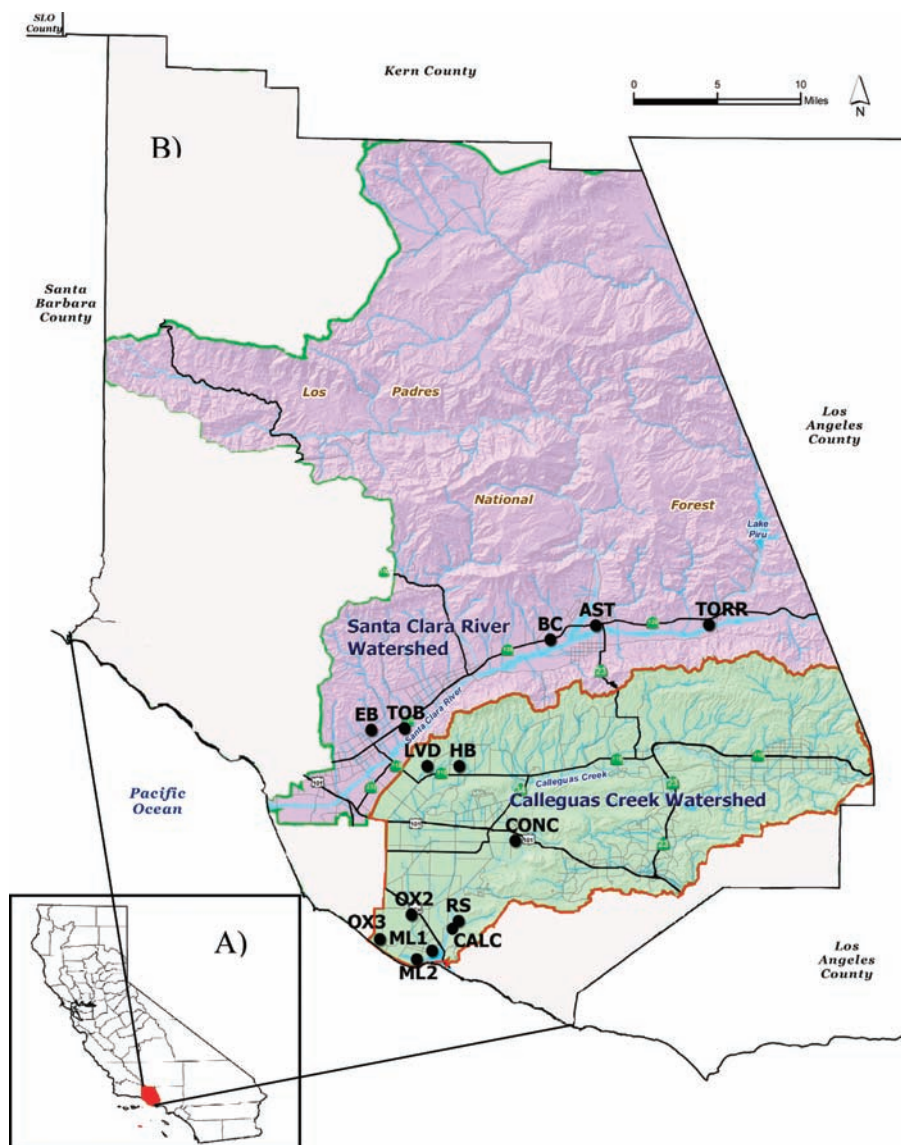
Figure 1. (A) Location of Ventura County in California. (B) Sampling locations within the Santa Clara River and Calleguas Creek watersheds in Ventura County along the southern California coast.

water. AST, TORR, and TOB sites within the Santa Clara River watershed and the CONC site within the Calleguas Creek watershed were located in water channels that flow close to urban areas. Thus, these sites may have some input from urban runoff. At each site, paired surface water and sediment samples were collected at the same sampling time. Water samples were collected manually at about 5 cm below the water surface and near midstream by filling 1 L precleaned amber glass bottles. Sediment samples were collected using a hand scoop into a 200 mL glass jar. Only the top layer of sediment (about 5 cm) was collected to represent the most recent sediment depositions. Surface water and sediment samples were stored on ice and transported to the laboratory within 24 h of sampling. All samples were kept at 4 °C until analysis. All samples were analyzed within 24 h after receipt.

Sampling spanned the course of the year 2009. Two sets of samples (wet-season samples) were collected after a major winter rain event in December (wet 1, mean precipitation of 11 mm h^{-1}) and February (wet 2, mean precipitation of 15 mm h^{-1}). The wet 1 sampling took place after the first major rain event of the year following the dry season. The two sets of dry-season samples were collected in May

(dry 1) and September (dry 2) during periods with no measurable precipitation.

Sample Characterization and Toxicity Assay. Surface water samples were measured for total suspended solid (TSS) content by weighing the solids collected on the membrane after filtration through a 1 μm glass fiber filter (Whatman, Maidstone, U.K.). The total organic carbon (TOC) content of sediment samples was measured using an elemental analyzer (Flash EA 1112 Soil Combustion Nitrogen/Carbon Analyzer System, Thermo Finnigan, Woods Hole, MA).[18]

The water samples were evaluated for their acute toxicity to the water flea *Ceriodaphnia dubia* using an EPA method.[19] Briefly, five *C. dubia* neonates were added to 10 mL of surface water samples in 20 mL scintillation vials. Organisms were fed with YCT daphnid feed mixture and *Selenastrum capricornutum* (Aquatic Biosystems, Fort Collins, CO) 2 h prior to the test. After 48 h of exposure, the organisms were fed and the water was renewed with the same water sample. After 96 h, the number of surviving organisms was determined, and the percent mortality was compared to the control prepared with hard water. Four replicates were used for each water sample.

Chemical Analysis. Water and sediment samples were solvent extracted and analyzed for the levels of diazinon, chlorpyrifos, fipronil and its degradates (fipronil desulfinyl, fipronil sulfone, and fipronil sulfide), and eight pyrethroids (bifenthrin, λ-cyhalothrin, esfenvalerate, permethrin, cyfluthrin, cypermethrin, deltamethrin, and fenpropathrin). Chemical standards were purchased from Chem Service (West Chester, PA). Duplicate analyses were carried out for each water or sediment sample. Pesticides in surface water samples were extracted using a modified version of EPA method 3510.[20] Briefly, each surface water sample (1 L) was transferred to a 2 L separatory funnel and extracted with 70 mL of methylene chloride. The methylene chloride fraction was passed through a Whatman no. 41 filter (Whatman, Maidstone, U.K.) filled with 20 g of anhydrous Na_2SO_4 to remove the residue water. The remaining aqueous phase was extracted with fresh methylene chloride two additional times. The solvent phase from the same sample was combined and concentrated to 5 mL on a vacuum rotary evaporator at 40 °C. The extract was transferred to a concentration tube, dried with a stream of nitrogen gas, and reconstituted to 1.0 mL with hexane.

Pesticides in the sediment samples were extracted using modified versions of EPA method 3550C[21] for extraction and EPA method 3660B[22] for removing sulfur interference. Briefly, a 5.0 g (dry weight) aliquot of sediment was mixed with anhydrous sodium sulfate in a beaker until the sample was dry. To each beaker was then added 70 mL of methylene chloride/acetone (1:1, v/v), and the slurry was sonicated for 10 min in an ultrasonic water bath (FS110H, Fisher Scientific, Pittsburgh, PA). The extract was decanted and filtered through a Whatman no. 41 filter paper (Whatman) filled with 20 g of anhydrous Na_2SO_4. The extraction was repeated two more times, and the extracts for the same sample were combined. The solvent phase was evaporated to <5 mL on a vacuum rotary evaporator at 40 °C. Activated copper (about 2 g) was added to the residue to remove sulfur. The extract was transferred to a concentration tube, dried with a stream of nitrogen, reconstituted to 1.0 mL with hexane/acetone (9:1, v/v), and then eluted through a silica cartridge (1.0 g) (Waters, Milford, MA). Prior to sample loading, the cartridge was conditioned with 5 mL of hexane/acetone (1:1, v/v). The sample was eluted with 10 mL of hexane/acetone (1:1, v/v) at 0.5 mL min^{-1}, followed by volume reduction to 1.0 mL in hexane/acetone (9:1, v/v).

Pesticide analysis was carried out on a Varian 3800 gas chromatograph (GC) (Varian Instruments, Sunnyvale, CA) coupled with a Varian 1200 triple-quadrupole mass spectrometer (MS/MS). Separation was achieved on a Factor Four-5 MS (Varian) capillary column (30 m × 0.25 mm i.d.) with 5% diphenyl—95% dimethylsiloxane liquid phase (0.25 μm film thickness). A 1.0 μL aliquot of the sample was injected at 260 °C in the splitless mode at a constant flow of 1 mL min^{-1}. Helium (99.999%) was used as the carrier gas in the pressure-pulse mode (45 psi for 0.8 min). The oven temperature program started at 80 °C (1.0 min), then increased at 25 °C min^{-1} to 160 °C, and further at 5 °C min^{-1} to 300 °C (7 min). The MS/MS electron ionization source was 70 eV (EI), and the transfer line, manifold, and ionization source temperatures were 270, 40, and 170 °C, respectively. Argon (99.999%) was used as the collision gas, with resolutions of quadrupoles equal to 1.2 and 2 for Q1 and Q3, respectively. The scan time was 0.25 s for all planned segments. Two calibration curves were used, for low-concentration (0.5—100 μg L^{-1}) and high-concentration (50—2000 μg L^{-1}) samples, respectively. Limit of detection (LOD) values were calculated by dividing the lowest detectable target analyte mass (minimum signal-to-noise ratio of 3) by the amount of water or sediment analyzed. LODs were 0.5—1 ng L^{-1} and 0.1—0.5 ng g^{-1} for water and sediment samples, respectively.

For quality control purposes, water and sediment samples were added prior to extraction with decachloridebiphenyl (Chem Service) as a recovery surrogate. The average recovery of the surrogate was 95 ± 10%. In addition, 10 μL of ^{13}C-labeled cis-permethrin and ^{13}C-labeled chlorpyrifos (Cambridge Isotope Laboratories, Andover, MA) at 1.2 mg L^{-1}

Table 1. Mean Recovery and Relative Standard Deviation (RSD) for the Pesticides Analyzed

pesticide	water samples		sediment samples	
	mean recovery (%)	RSD (%)	mean recovery (%)	RSD (%)
chlorpyrifos	79.8	2.9	97.8	12.0
diazinon	77.4	4.0	87.1	13.4
fipronil	96.3	4.8	71.3	10.8
fipronil desulfinyl	76.4	9.1	71.8	8.2
fipronil sulfide	75.2	1.8	81.9	10.9
fipronil sulfone	88.9	0.6	77.5	8.9
bifenthrin	93.6	3.2	91.4	12.0
fenpropathrin	87.2	9.2	86.5	11.3
λ-cyhalothrin	91.1	9.1	89.0	8.9
cis-permethrin	104.4	3.4	105.7	7.8
trans-permethrin	105.3	1.8	113.0	9.3
cyfluthrin	112.1	3.8	97.8	8.6
cypermethrin	112.2	3.8	100.6	7.1
esfenvalerate	100.9	5.2	95.5	9.1
deltamethrin	110.9	6.2	105.8	9.4

was added to each sample as internal standard before GC-MS/MS analysis. Matrix spikes, matrix spike duplicates, field duplicates, and method blanks were also processed for quality control purposes. Matrix spikes were sediment or water samples spiked with 50 ng of each compound. The matrix spike recoveries are shown in Table 1 for both water and sediment samples. The relative percent difference (RPD) values from field duplicates are shown in Tables 1 and 2 of the Supporting Information for water and sediment samples, respectively. The RPD between duplicates was <30% in 85% of the water and sediment samples. For five water samples and one sediment sample the RPD values were >75%, which is considered to be the acceptable limit for field duplicates.[23] No pesticides were detected in any of the blank samples.

■ RESULTS AND DISCUSSION

Pesticides in Surface Water. *Concentrations and Frequency of Detection.* Water concentrations of each pesticide at the different sampling sites are shown in Table 3 of the Supporting Information. In general, levels of pesticides in surface water were higher during the wet season than under dry weather conditions (Figure 2). The detection frequency of each pesticide was calculated as the number of samples with a pesticide concentration higher than the LOD expressed as a percentage of the total samples analyzed (Figure 3). Diazinon and chlorpyrifos were among the most frequently detected pesticides in the water samples during the wet season (Figure 3A). Chlorpyrifos was detected in about 90% of the water samples during both wet and dry seasons. Diazinon was detected in 82% of the samples collected during the wet season, and its detection frequency decreased to 44% during the dry season. For most of the sites, chlorpyrifos concentrations (0.5—729.5 ng L^{-1}) were much higher than those of diazinon (0.5—172.8 ng L^{-1}) during the wet season (Figure 2A; Table 3 of the Supporting Information). However, during the dry season, higher concentrations of diazinon (0.5—177.4 ng L^{-1}) than of chlorpyrifos (0.5—37.1 ng L^{-1}) were detected at some of the sites (Figure 2A; Table 3 of the Supporting Information).

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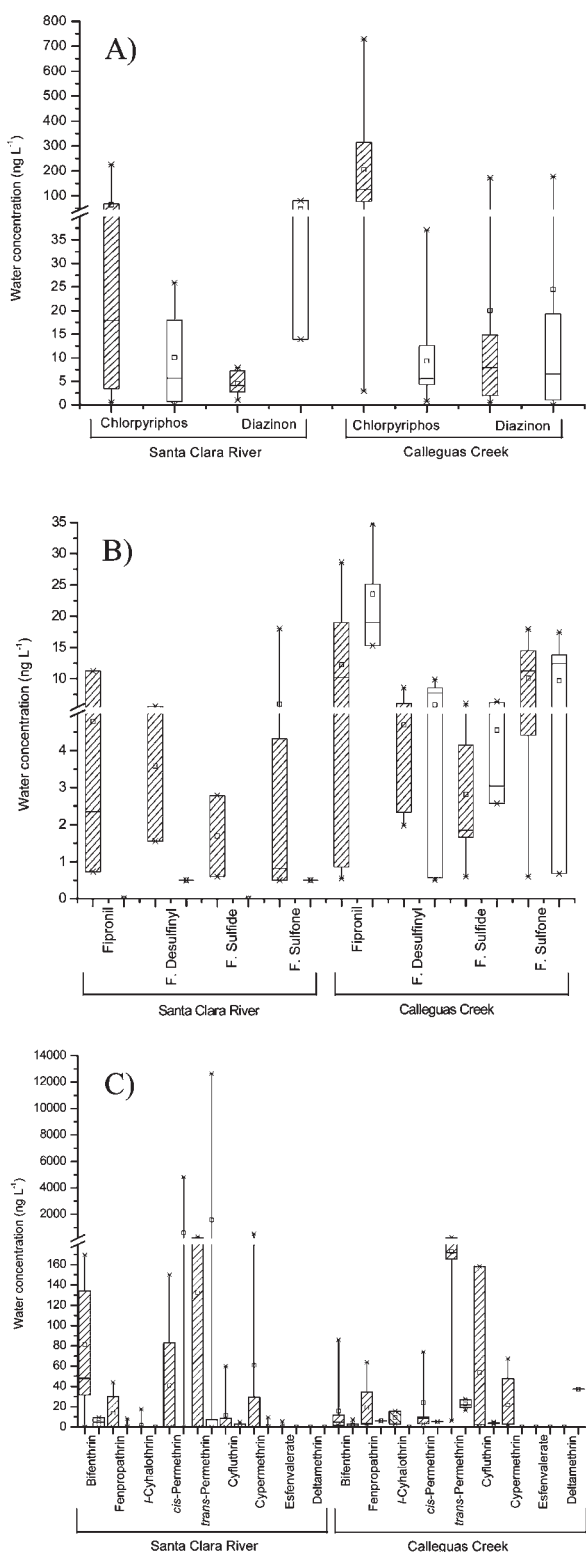dx.doi.org/10.1021/jf202049s |*J. Agric. Food Chem.* 2011, 59, 9448–9456

Figure 2. Box plots of pesticide concentrations in water samples from the Santa Clara River and Calleguas Creek watersheds taken under wet (shaded boxes) and dry (open boxes) weather conditions. The bottom and top of each box are the 25th and 75th percentiles, respectively. Median is shown within the box. The small square inside/outside the box represents the mean of the data. The whiskers are the 5th and 95th percentiles.

Fipronil was detected in 50% of the samples during the wet season and in 16% during the dry season (Figure 3A), with

concentrations ranging from 0.5 to 34.8 ng L^{-1} (Figure 2B; Table 3 of the Supporting Information). In the Santa Clara River watershed, water concentrations of fipronil varied from wet to dry seasons. However, in the Calleguas Creek watershed, the difference in fipronil levels between wet and dry seasons was not statistically significant ($P = 0.79$) (Figure 2B). Fipronil sulfone and fipronil desulfinyl were the most frequently detected fipronil degradates in water, whereas fipronil sulfide was detected less frequently (Figure 3A) and also at lower levels (Figure 2B; Table 3 of theSupporting Information). In general, the Calleguas Creek watershed showed higher water concentrations of fipronil and its degradates than the Santa Clara River watershed (Figure 2B).

During the wet season, total concentrations of pyrethroids ranged between 1.8 and 901 ng L^{-1}. During the dry season, excluding the TOB site for the dry 1 sampling cycle, total concentrations of pyrethroids ranged between 0.5 and 41 ng L^{-1}. In the water sample from the TOB site (dry 1), *trans*- and *cis*-permethrin were found at 13000 and 4800 ng L^{-1}, respectively (Table 3 of the Supporting Information). The unusually high concentrations were a single-time episode and may be due to application drift, cleaning of spray equipment, or improper disposal of spray waste. Bifenthrin was the most frequently detected pyrethroid with a frequency of detection of about 61 and 48% during the wet and dry seasons, respectively (Figure 3A). Other studies evaluating urban or agricultural streams in northern and central California also showed that bifenthrin was the most ubiquitous pyrethroid.[5,15,24] During the wet season, *trans*-permethrin (54%) and fenpropathrin (50%) were the second most frequently detected pesticides (Figure 3A), whereas cypermethrin (36%), *cis*-permethrin (32%), and cyfluthrin (29%) were less frequently detected among the pyrethroids (Figure 3A). During the dry season, *trans*-permethrin (44%) and cyfluthrin (44%) were the second most frequently detected pesticides (Figure 3A). Fenpropathrin, *cis*-permethrin, and cypermethrin were detected in <10% of the samples (Figure 3A). λ-Cyhalothrin, esfenvalerate, and deltamethrin were infrequently detected at $\leq 11\%$ (Figure 3A). In general, for both wet and dry seasons, *trans*-permethrin was present at higher concentrations than the other pyrethroids followed by bifenthrin (Figure 2C). The highest detection frequency and levels of pyrethroids occurred in the wet 2 samples, and the occurrence coincided with the presence of high TSS in the water samples (Table 3 of the Supporting Information). Concentrations of bifenthrin and *trans*-permethrin in surface water were significantly correlated with TSS ($P < 0.01$), clearly indicating that these compounds were sorbed to fine particles that were mobilized by rain-induced erosion of surface soil. The facilitation of pyrethroid transport by TSS was in agreement with previous studies.[24]

The Calleguas Creek watershed showed generally higher levels of OPs than the Santa Clara River watershed (Figure 2A). However, concentrations of pyrethroids were higher in the Santa Clara River watershed than in the Calleguas Creek watershed (Figure 2C). Some sample sites (AST, TOB, TORR) within the Santa Clara River watershed were close to urban areas, whereas water samples collected within the Calleguas Creek watershed were of agricultural origin. Pyrethroid products, especially bifenthrin, are commonly used in urban areas for management of structural and landscape pests.[11] Concentrations of bifenthrin were found to be higher from sites potentially receiving runoff from urban areas than from those with agricultural runoff as the sole input (Table 3 of the Supporting Information). In Ventura
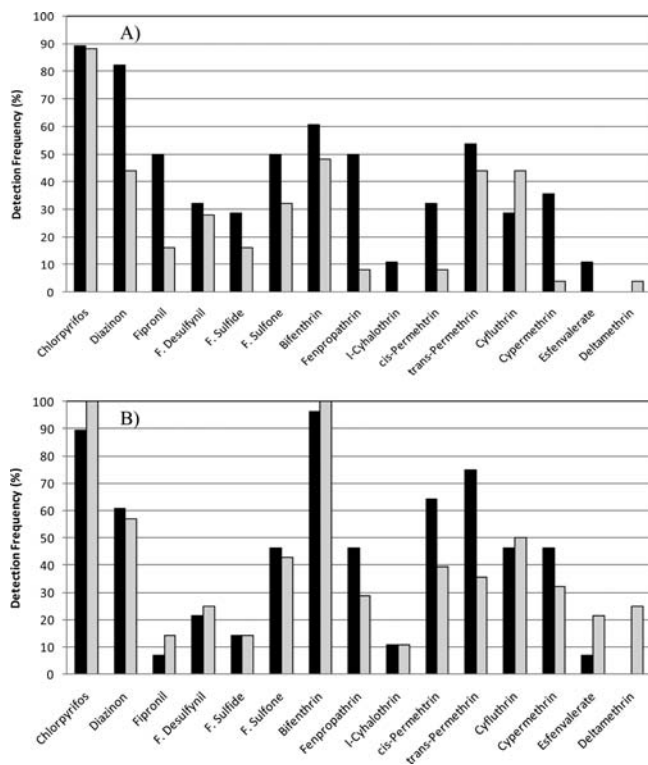
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Figure 3. Frequency of detection of individual pesticides in (A) water and (B) sediment samples.

County the use of bifenthrin for structural pest control represented around 30% of the total bifenthrin use in 2008 (http://www.cdpr.ca.gov/docs/pur/purmain.htm). Higher levels of bifenthrin were also found in urban streams in other areas than in agriculture-dominated waterways.[13]

Acute Aquatic Toxicity. Acute toxicity to *C. dubia* was detected in 54% of the samples analyzed. Significant toxicity to *C. dubia* was found in 71, 21, 42, and 69% of the wet 1, wet 2, dry 1, and dry 2 samples, respectively. With the exception of one site (CONC), water samples from the Calleguas Creek watershed taken during wet 1 showed 100% mortality to *C. dubia* (Table 2). The higher occurrence of toxicity in the wet 1 samples than in wet 2 samples reflected the accumulation of pesticides and other chemical stressors under dry weather conditions and the mobilization of such residues by the first rain events of the year. Among the wet 2 samples, RS and ML samples showed 100% mortality to *C. dubia* (Table 2). Under dry weather conditions, consistent mortality was observed in water samples from the ML sites (Table 2). Magu Lagoon, where the ML sites were located, is the final destination of runoff and drainage water of the Calleguas Creek watershed. Magu Lagoon is known for its historical contamination of organochlorine compounds and heavy metals, partly due also to its vicinity to a naval base.[25,26] The observed high mortality may be therefore a result of compounded factors, including sustained levels of stressors not evaluated in this study. Water samples from all other sites under dry weather conditions showed no or moderate toxicity (Table 2).

The presence of chlorpyrifos and diazinon above the *C. dubia* LC$_{50}$ has been related to the observed toxicity in runoff water samples from agricultural areas.[1] In this study, diazinon concentrations in the surface water samples were below the *C. dubia*

Table 2. Acute Toxicity to *Ceriodaphnia dubia* in Water Samples in 96 h Static Exposure Test (Mean Mortality, Percent)

sample	wet 1	wet 2	dry 1	dry 2
Santa Clara River Watershed				
TORR	0	0	NSC[a]	20
AST	0	0	0	0
BC	40	0	47	0
TOB	0	0	100	20
EB	100	0	0	10
Calleguas Creek Watershed				
HB	100	0	NSC	NSC
CONC	0	0	0	15
LVD	100	0	0	0
RS	100	100	0	100
CALC	100	0	0	0
OX-2	100	0	0	10
OX-3	100	0	17	55
ML-1	100	75	100	100
ML-2	100	100	100	100

[a] NSC, no sample collected.

LC$_{50}$ (320 ng L^{-1}).[8] Chlorpyrifos concentrations exceeded the *C. dubia* LC$_{50}$ (55 ng L^{-1}),[8] by 1.2—13.3-fold in 26% of the samples in which chlorpyrifos was detected. Sites with chlorpyrifos concentrations higher than the *C. dubia* LC$_{50}$ included TOB and EB in the Santa Clara River watershed and HB, LVD, RS, CALC, OX-2, OX-3, and ML-1 in the Calleguas Creek watershed. All of the samples with chlorpyrifos concentrations higher than the LC$_{50}$ were from the wet season. However, no significant correlation ($P = 0.137$) was found between the levels of chlorpyrifos and the mortality of *C. dubia* if samples from both wet and dry seasons were pooled. About 60% of the wet 1 samples displayed 100% mortality to *C. dubia*, whereas concentrations of chlorpyrifos exceeded the *C. dubia* LC$_{50}$ in 47% of the samples. If only wet 1 samples were considered, a significant correlation ($P = 0.01$) between chlorpyrifos concentrations and *C. dubia* mortality was present.

In the wet 2 samples, levels of bifenthrin in water exceeded the *C. dubia* LC$_{50}$ (50 ng L^{-1})[27] by 1.7—3.4-fold at three sites within the Santa Clara River watershed (TOB, TORR, and EB) and at one site (LVD) within the Calleguas Creek watershed. In addition, cypermethrin was detected at a concentration 2.7-fold its *C. dubia* LC$_{50}$ (194 ng L^{-1})[27] at the TOB site. However, despite the relatively high levels of bifenthrin and cypermethrin, toxicity to *C. dubia* was not detected in these samples (Table 2). This may be due to the fact that bifenthrin and cypermethrin were mainly associated with suspended solids and dissolved organic matter,[24,28] whereas the truly dissolved concentrations[29] may be considerably lower than their respective LC$_{50}$ values. Yang et al.[27,30] studied the effect of suspended solids and natural DOM on the acute toxicity of different pyrethroids to *C. dubia*. They observed that the LC$_{50}$ values consistently increased with increasing suspended solids or DOM, demonstrating the inhibitory effects of suspended solids and DOM on pyrethroid toxicity.

Pesticides in Bed Sediments. *Concentration and Frequency of Detection.* Sediment concentrations of pesticides at the

different sampling sites are shown in Table 4 of the Supporting Information. The patterns of pesticide detection in the sediment samples were well related to those observed in the surface water. Similar to water samples, concentrations of pesticides in sediment were higher during the wet season than under dry conditions (Figure 4). This finding suggests that pesticides applied during the dry season may accumulate at the soil surface and then become mobilized by overland flow caused by winter rain events.

Chlorpyrifos was detected in about 90 and 100% of the sediment samples from the wet and dry seasons, respectively (Figure 3B). Chlorpyrifos median concentrations were 19 and 2 ng g^{-1} for the wet and dry seasons, respectively. Chlorpyrifos was also detected at the highest concentration (280 ng g^{-1}). Multiple sites (EB, LVD, ML-1, and RS) showed concentrations of chlorpyrifos >100 ng g^{-1} during the wet season (Table 4 of the Supporting Information). However, chlorpyrifos levels during the dry season were always <20 ng g^{-1} (Table 4 of the Supporting Information). Diazinon was detected in about 60% of the samples during the wet and dry seasons. Diazinon levels in sediments were much lower than those of chlorpyrifos, with median concentrations of about 1 ng g^{-1} during the wet season and <0.5 ng g^{-1} during the dry season (Figure 4A).

Fipronil was detected in 7 and 14% of the sediment samples from the wet and dry seasons, respectively (Figure 3B). Similar to water samples, the most frequently detected fipronil degradates were fipronil sulfone (around 45% for both dry and wet seasons), followed by fipronil desulfinyl (25 and 21% for dry and wet seasons, respectively). In the sediment samples, fipronil degradates were more frequently detected than fipronil (Figure 3B) and often also at higher levels (Figure 4B). The highest concentrations of fipronil desulfinyl and fipronil sulfone were observed during the wet season (Figure 4B; Table 4 of the Supporting Information). In general, concentrations of fipronil and its degradates were low even when detected, and the occurrence was unlikely to incite acute toxicity based on known LC$_{50}$ values to sensitive arthropods.[17] The low level of fipronil occurrence in the sediment samples from agricultural areas may be attributed to its exclusive urban use in this area (http://www.cdpr.ca.gov/docs/pur/purmain.htm).

The maximum levels of pyrethroids observed in this study were similar to or higher than what was previously reported for several agricultural[5,15] and urban[9,31] creeks in California. All of the target pyrethroids were detected in the sediment samples (Figure 4C; Table 4 of the Supporting Information). The frequency of detection and concentrations varied greatly among the pyrethroids. Bifenthrin was detected in 96 and 100% of the sediment samples during the wet and dry season, respectively (Figure 3B). Bifenthrin median concentrations were 4 and 2 ng g^{-1} for the wet and dry seasons, respectively. The highest concentrations of bifenthrin were found at LVD (91 ng g^{-1}) and RS (66 ng g^{-1}) sites within the Calleguas Creek watershed following the rain event in December (wet 1) (Table 4 of the Supporting Information). *cis-* and *trans-*permethrin were detected in about 65 and 75% of the sediment samples, respectively, during the wet season. Their frequency of detection decreased during the dry season to about 40% (Figure 3B). *Cis-* and *trans-*permethrin median concentrations were 9 and 27 ng g^{-1}, respectively, during the wet season. The respective values for the dry season were 8 and 7 ng g^{-1}. These results are in good agreement with the 2008 and 2009 annual pesticide use reported for Ventura County. The use of bifenthrin and permethrin
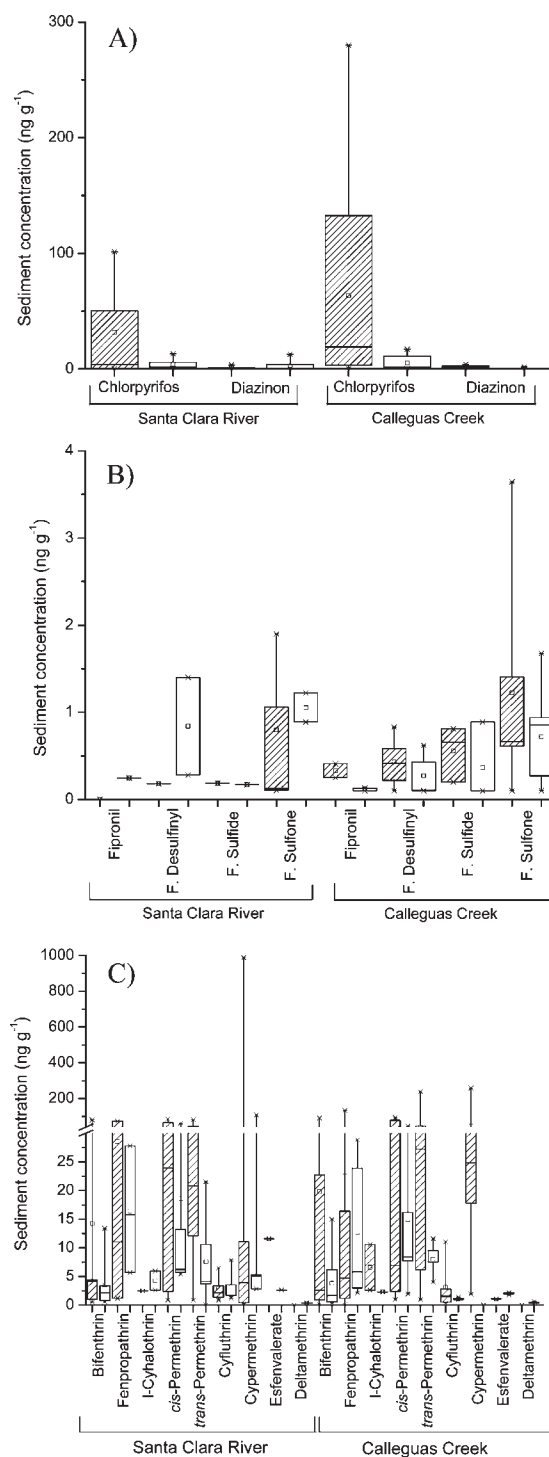

Figure 4. Box plots of pesticide concentrations in sediment samples from the Santa Clara River and Calleguas Creek watersheds taken under wet (shaded boxes) and dry (open boxes) weather conditions. The bottom and top of each box are the 25th and 75th percentiles, respectively. Median is shown within the box. The small square inside/outside the box represents the mean of the data. The whiskers are the 5th and 95th percentiles.

accounted for 75% of the total pyrethroid use in agriculture (http://www.cdpr.ca.gov/docs/pur/purmain.htm). Several previous studies from California have also consistently shown bifenthrin and permethrin as the most ubiquitous pyrethroids

Table 3. Toxicity Unit (TU) Values Higher than Unity Calculated from LC$_{50}$ Thresholds for Chlorpyrifos and Pyrethroids

		TU[a]						
		CLR[b]	BF	FNP	λ-CYH	PM	CYPM	ΣTU PYRs
LC$_{50}$ H. azteca (μg g^{-1} OC)		2.9	0.5	1.1	0.5	10.8	0.4	
Santa Clara River Watershed								
TORR	wet 1	<LOD[c]	1.7	<0.1	0.2	<0.1	0.9	2.8
BC	wet 1	<LOD	1.2	1.4	ND[d]	<0.1	ND	2.5
BC	wet 2	0.1	16.2	6.9	ND	1.0	ND	24.0
TOB	wet 1	0.5	<LOD	ND	ND	0.4	28.3	28.7
TOB	wet 2	1.3	0.2	ND	ND	0.7	198.4	199.3
EB	wet 1	2.0	0.1	ND	ND	ND	0.9	1.0
EB	wet 2	1.9	0.5	ND	ND	0.2	0.6	1.3
BC	dry 1	0.1	2.0	1.1	ND	0.1	ND	3.2
TOB	dry 1	0.2	0.4	ND	ND	0.1	15.4	15.9
TOB	dry 2	0.2	0.1	0.4	0.9	0.6	ND	1.9
Calleguas Creek Watershed								
HB	wet 1	1.7	0.6	ND	ND	ND	ND	0.6
CONC	wet 2	0.2	3.7	ND	ND	0.7	0.8	5.2
LVD	wet 1	4.8	16.9	0.4	ND	ND	65.4	82.5
LVD	wet 2	4.3	0.7	0.3	ND	0.3	ND	1.3
RS	wet 1	2.6	7.3	0.9	1.4	0.8	2.7	13.0
RS	wet 2	4.7	3.4	4.1	ND	0.6	5.1	13.2
OX2	wet 1	5.3	4.0	1.5	ND	0.1	ND	5.6
OX2	wet 2	5.5	4.2	9.8	ND	0.5	ND	14.5
OX3	wet 2	0.6	1.4	0.2	ND	1.3	ND	2.8
ML1	wet 1	1.7	3.9	0.4	ND	0.3	ND	4.4
ML1	wet 2	4.0	5.3	5.0	ND	1.3	3.6	15.2
LVD	dry 1	1.0	0.4	ND	ND	ND	ND	0.4
RS	dry 1	0.9	2.2	0.2	ND	0.2	ND	2.7
RS	dry 2	0.6	1.6	0.4	ND	0.2	ND	2.1
OX2	dry 1	1.3	2.9	1.1	ND	0.5	ND	4.5
OX2	dry 2	0.2	1.3	1.1	ND	0.3	ND	2.7
ML1	dry 2	0.2	1.4	1.3	ND	0.1	ND	2.7

[a] TU was calculated as the sediment pesticide concentration divided by the *H. azteca* 10 day sediment LC$_{50}$, both on an organic carbon (OC) normalized basis. [b] CLR, chlorpyrifos; BF, bifenthrin; FNP, fenpropathrin; λ-CYH, λ-cyhalothrin; PM, sum of *cis*- and *trans*-permethrin; CYPM, cypermethrin; PYRs, sum of pyrethroids. [c] <LOD, concentration below the detection limit. [d] ND, pesticide not detected.

in bed sediments.[9,15,32] The detection frequencies of fenpropathrin, cyfluthrin, and cypermethrin ranged from about 30 to 50% (Figure 3B). Esfenvalerate, deltamethrin, and λ-cyhalothrin were less frequently detected (≤11%) during the wet season (Figure 3B). However, during the dry season esfenvalerate and deltamethrin detection frequencies increased to 21 and 25%, respectively (Figure 3B). The median concentrations of fenpropathrin and cypermethrin were 27 and 11 ng g^{-1}, respectively for the wet-season samples and 9 and 5 ng g^{-1}, respectively, for samples taken under dry weather conditions. Cyfluthrin, esfenvalerate, λ-cyhalothrin, and deltamethrin were detected at median concentrations of <7 ng g^{-1}.

Pesticide Sediment Toxicity. The potential toxicity of sediment-borne pesticide residues was estimated by converting the detected concentrations to toxicity units (TU) using known toxicity thresholds for the benthic invertebrate *Hyalella azteca*. The number of TUs was calculated as the actual concentration divided by the *H. azteca* 10 day sediment LC$_{50}$,[13,33] both on an organic carbon (OC) normalized basis (Table 4 of the

Supporting Information). The estimated TU values for chlorpyrifos and individual and total pyrethroids are summarized in Table 3. Chlorpyrifos concentrations were higher than the *H. azteca* LC$_{50}$ at two sites (TOB and EB) within the Santa Clara River watershed and at five sites (HB, LVD, RS, OX2, and ML1) within the Calleguas Creek watershed. Total pyrethroid TU values were higher than unity in 50% of the samples analyzed, indicating that these sediments may present significant toxicity to *H. azteca*. Of the different pyrethroid compounds, bifenthrin consistently contributed the most to the total TU values from pyrethroids, suggesting that bifenthrin was likely responsible for the potential toxicity in most samples. In streambed sediments of central California, Illinois, and Texas, bifenthrin was also detected as the dominant cause of *H. azteca* toxicity.[5,13,15,32,33] In the present study, cypermethrin was the main component responsible for *H. azteca* toxicity at the TOB and LVD sites. At these sites cypermethrin concentrations (normalized by OC content) were between 15- and 200-fold the *H. azteca* LC$_{50}$ (normalized by OC content). Total pyrethroid TU values ranged from 0.1 to 24 with

the exception of LVD and TOB sites, which had total pyrethroid TU values of >25 for some sampling events (Table 3). Similar total pyrethroid TU values were reported by Holmes et al.[11] in a targeted survey of sediments from California urban creeks.

Results from this study demonstrate that rainfall-induced runoff is an important mechanism for the transport of both OP and pyrethroids pesticides and that pesticide accumulation under dry weather conditions may contribute to elevated levels of contamination in the wet season. Chlorpyrifos, despite its use having been restricted in the past decade, was detected in water samples often at levels sufficient to cause acute toxicity to aquatic invertebrates. The source of chlorpyrifos is unknown and merits further investigation. The switch to the use of more hydrophobic insecticides such as pyrethroids, although possibly leading to a decrease in the toxicity to water-column invertebrates, may result in increased pesticide accumulation in the sediment and toxicity to benthic organisms. As the occurrence of pyrethroids in water was closely related with the presence of suspended solids, management practices aiming at preventing erosion of organic materials from soil surfaces should be generally effective at reducing offsite runoff of pyrethroids.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Relative percent difference (RPD) values between field duplicates for water and sediment samples and water and sediment concentrations of pesticides at the different sampling sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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