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Assessing the Occurrence and Distribution of Pyrethroids in Water and Suspended Sediments

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The distribution of pyrethroid insecticides in the environment was assessed by separately measuring concentrations in the dissolved and suspended sediment phases of surface water samples. Filtered water was extracted by HLB solid-phase extraction cartridges, while the sediment on the filter was sonicated and cleaned up using carbon and aluminum cartridges. Detection limits for the 13 pyrethroids analyzed by gas chromatography−tandem mass spectrometry were 0.5 to 1 ng L^{-1} for water and 2 to 6 ng g^{-1} for the suspended sediments. Seven pyrethroids were detected in six water samples collected from either urban or agricultural creeks, with bifenthrin detected the most frequently and at the highest concentrations. In spiked water samples and field samples, the majority of the pyrethroids were associated with the suspended sediments.

KEYWORDS: Pyrethroids; water; suspended sediment; GC-MS; GC-MS-MS

INTRODUCTION

Synthetic pyrethroid insecticide use in the United States has increased in recent years, primarily as alternatives to organophosphate insecticides. These compounds are applied in both agricultural and urban (commercial and residential) areas. Pyrethroids are hydrophobic (log K_{oc} ~5−6; (*1*)) and tend to sorb to suspended sediments present in natural water samples rather than remain in the dissolved phase (*2*, *3*). Highly toxic to fish and invertebrates in both fresh water and marine systems (*4*−*6*), the 10-day LC_{50} values for pyrethroids range from 2 to 140 ng L^{-1} in water (*Americamysis bahia* and *Ceriodaphnia dubia*) and 4 to 110 ng g^{-1} in sediment (*Hyalella azteca*) (*7*−*10*). With their increasing use and high toxicity, the partitioning of pyrethroids is critical to understanding their fate and effects in the environment.

Published methods for the routine analysis of pyrethroids in water typically take one of two approaches. One method is to analyze whole water (unfiltered) samples (*2*, *11*) and measure the combined concentrations in the dissolved and sediment-associated phases. Whole water methods are relatively easy to perform, but do not separate dissolved concentrations from those associated with suspended sediments. Most whole water methods employ the use of liquid/liquid extraction (LLE) (*2*, *11*, *12*), and in waters with high dissolved organic carbon (DOC) concentrations, emulsions can form that may interfere with extraction of the pyrethroids. The other method is to analyze filtered water samples (*12*) and measure just the dissolved fraction. Filtered water usually employs the use of solid-phase extraction (SPE) cartridges (the most common being C18 or C8) (*2*, *13*, *14*) and has the advantage of using less organic solvent than LLE. If partitioning in whole water samples is to be determined, the dissolved and sediment associated fractions must be measured separately.

Pyrethroids tend to associate with the walls of sample containers, further complicating their analysis in water samples. The size, material of the sample container, and time the sample is stored in the container affect the extent of association, which can vary from 5 to 75% of the total concentration (*2*, *15*−*18*). The smaller the sample container (volume-to-contact area ratio), the greater amount of pyrethroids lost (*15*, *16*, *18*). Amending containers by traditional methods such as silylating active sites on the bottle has resulted in minimal decreases in the amount of pyrethroids associated with the container (*16*). The association with the bottle wall is reversible, as the pyrethroids can easily be removed from the walls and returned into solution with shaking or vortexing (*16*, *18*). Analytical methods utilizing LLE account for pyrethroids associated with the container walls, but methods where water is pumped through an SPE cartridge present complications since the time to equilibrium with container walls is fairly rapid, < 24 h (*2*). Other researchers have added 30% methanol to their samples to increase pyrethroid recovery (*13*), but this may decrease the retention of other pesticides under investigation (data not shown) and may not be suitable for toxicity tests.

Quantitation of pyrethroids in water samples has been performed with gas chromatography−electron capture detection (GC-ECD; (*2*, *13*)), gas chromatography−mass spectrometry (GC-MS; (*2*, *11*, *13*)), and gas chromatography−negative chemical ionization−mass spectrometry (GC-NCI-MS; (*12*)). Pyrethroids have also been analyzed in other matrixes such as fruit/vegetables and soil using gas chromatography−tandem mass spectrometry to gain sensitivity and reduce background noise (GC-MS-MS; (*19*−*21*)). Detection limits for most water methods are in the 0.5−10 ng L^{-1} range (*11*−*13*). A published study (*21*) compared detection limits in soil samples using GC-MS, GC-MS-MS (in both electron impact and NCI modes), and GC-ECD and found the lowest detection limits with GC-MS-MS (operated in electron impact mode).

This article presents a routine method for the direct analysis of 13 pyrethroids in a 1-L water sample in both the dissolved phase and those associated with suspended sediments. To measure the dissolved fraction, water samples were filtered prior to extraction.

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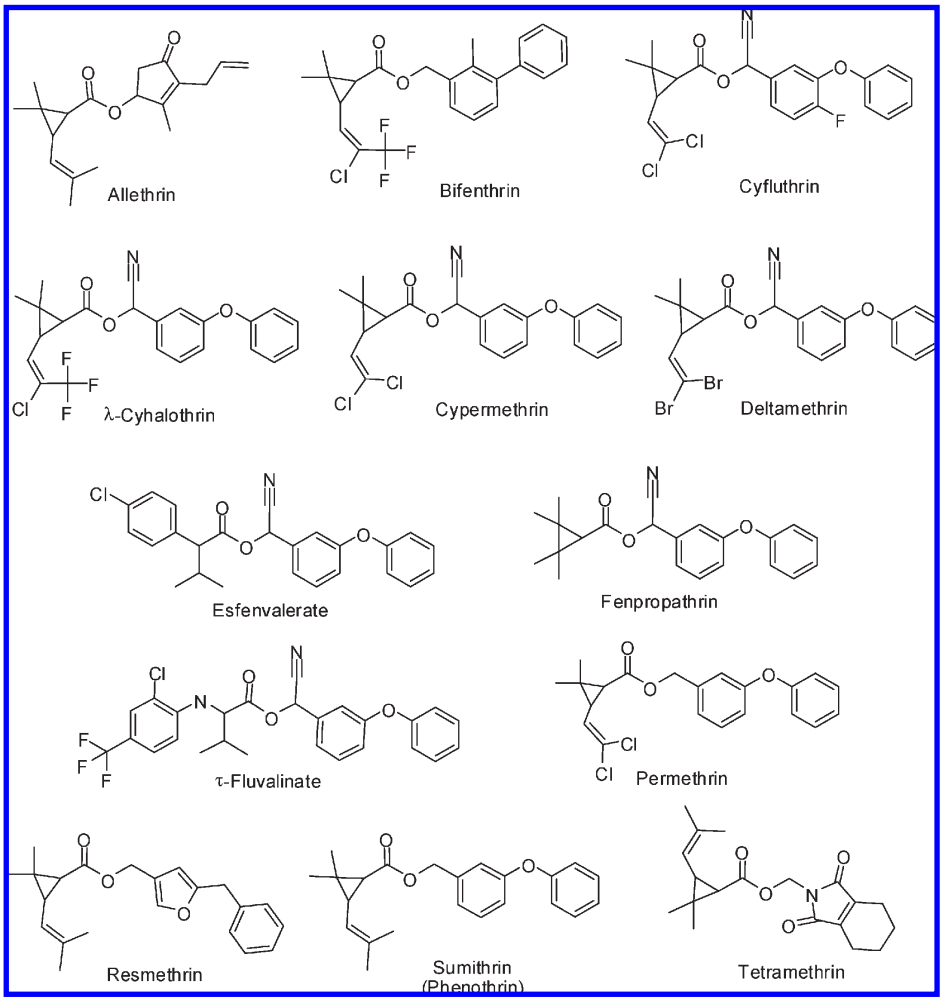

Figure 1. Structures of pyrethroid insecticides.

Any pyrethroids that associate with the sample container during storage were extracted with an organic solvent. The filter paper was extracted and analyzed separately to determine the amount of pyrethroids associated with particulate matter. The validated method was used to quantify pyrethroids in six surface water samples from California creeks and drains using GC-MS and GC-MS-MS in California. This method allows for a more complete assessment of pyrethroids, enabling a better understanding of their transport and fate in the environment.

MATERIALS AND METHODS

Chemicals. Allethrin (d-trans), bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, τ-fluvalinate, permethrin, resmethrin, sumithrin (phenothrin), and tetramethrin were purchased from Chem Service (West Chester, PA). Unless noted, all standards were a mixture of isomers. Purities ranged from 95% to 99%. Structures for the pyrethroids included in the method can be found in **Figure 1**. Internal standards, d_{10}-acenaphthene, d_{10}-phenanthrene, and d_{10}-pyrene were purchased from Cambridge Isotope Laboratories (Andover, MA). All solvents and other reagents used were of ACS grade or better. Neat pesticides were dissolved individually in acetone for an initial concentration of 1 mg mL^{-1}. Standard calibration curves were made with concentrations ranging from 0.002 to 2.5 ng μL^{-1} in ethyl acetate and stored in a freezer at −20 °C. All solvents and other reagents used were of ACS grade or better (Fisher Scientific, Pittsburgh, PA). The surrogate for the urban and agricultural creek samples was phenoxy-$^{13}C_6$-*cis*-permethrin (Cambridge Isotope Laboratories).

Water Collection and Preparation. Surface water from the American River was used for determining initial recoveries and method detection limits (MDLs); seven 1-L filtered water samples were spiked with pyrethroids at a concentration of 10 ng L^{-1}. The water for the partitioning study was a mixture of water from the American River and Colusa Basin Drain; the waters were mixed to achieve the desired dissolved organic carbon (DOC) concentration (5 mg L^{-1}) and suspended sediment concentration (SSC; 14 mg L^{-1}) which would lead to partitioning in both phases. The partitioning experiment water was separated into three 1-L water samples and spiked with pyrethroids for a whole water concentration of 400 ng L^{-1} for each pyrethroid. The samples were allowed to sit at 4 °C for three days to equilibrate. Both American River and Colusa Basin Drain water was analyzed for background pyrethroid concentrations before spiking for MDLs or the partitioning study.

The final method was validated using six surface water samples from urban and agricultural areas in northern and central California. Five samples were collected from urban drains and creeks in the greater Sacramento, California metropolitan area. Two of the urban drains, Elk Grove and Roseville, have been sampled in a published study (*22*) and had pyrethroid detections in both the water and sediment (suspended and bed). An additional drain, Rancho Cordova, was chosen for its proximity to a new suburban housing development (similar to those of Elk Grove and Roseville). One of the creeks near El Dorado Hills had previous detections of pyrethroids in the bed sediments (*23*). The other creek, Arcade Creek, has been monitored by the USGS National Water-Quality Assessment (NAWQA) program and has no known pyrethroid detections in filtered water samples but has had detections in bed sediments (*24*). For the five urban sites, water samples were collected after a recent rain event in the fall of 2008. A sixth site, an agricultural drain in Central California receiving runoff from lettuce and strawberry fields, was sampled during the fall of 2007 during nonstorm conditions.

All water samples were filtered through a prebaked 0.7 μm GF/F filter (Whatman; Florham Park, NJ) and separated into the dissolved (including

Table 1. Retention Times, Number of GC Peaks, Selected Ion Storage (SIS) Levels and Quantitation Ions for Pyrethroids Analyzed by GC-MS (Ion-Trap)[a]

compound	retention time (min)	GC peaks	SIS storage levels	quantitation ions (*m*/*z*)	confirmation ions (*m*/*z*)
allethrin	15.0	2	89−95, 121−125	123	79, 91
resmethrin	17.9	2	95−146, 163−179	143 + 171	123
bifenthrin	18.4	1		181	165, 166
tetramethrin	18.4	2		164	123
fenpropathrin	18.5	1	93−100, 119−143, 158−186, 195−201, 262−269	181 + 265	125
sumithrin	18.9	1		123 + 183	81
λ-cyhalothrin	19.3	1		181	197, 225
permethrin	20.2	2		183	127, 163
cyfluthrin	20.7	4	89−95, 149−170, 178−201, 224−229	127 + 163 + 199	
cypermethrin	21.0	4		127 + 163 + 181	
τ-fluvalinate	22.0	2		250	167, 181
esfenvalerate	22.0	1	123−129, 149−156,165−184, 223−228, 248−257	225	181, 252
deltamethrin	22.5	1		253	172, 181

[a] Multiple quantitation ions are used for some pyrethroids to gain greater sensitivity.

pyrethroids associated with the glass container) and suspended-sediment associated phases. Each fraction (dissolved and suspended) was spiked with the surrogate (phenoxy-$^{13}C_6$-*cis*-permethrin) at a mass of 50 ng (recoveries were 90−103% for all samples). A separate sample was also collected for DOC analysis (*25*). The SSC were low for the urban areas, 20 to 72 mg L^{-1}, and the agricultural drain had a much higher SSC of 700 mg L^{-1}. In contrast, the DOC concentrations were higher for the urban areas (7.3 to 15 mg L^{-1}) than that for the agricultural drain (5.3 mg L^{-1}).

Sample Extraction and Cleanup. One liter of water (prefiltered) was pumped through an Oasis HLB extraction cartridge (6 cc, 500 mg; Waters Corporation, Milford, MA), dried, and eluted with ethyl acetate. After the extraction, sodium sulfate was added to the sample bottle to remove residual water, and the bottle was rinsed with dichloromethane (DCM). The DCM fraction was blown down under a gentle stream of nitrogen (N-evap; Organomation Associates, Berlin, MA) and then added to the SPE fraction; for the container association studies, the dichloromethane fraction was blown down separately from the SPE fraction and exchanged into ethyl acetate. The ethyl acetate was reduced to 0.2 mL under nitrogen, and 0.02 mL of internal standard was added. More details of the water method can be found elsewhere (*26*)

The filter paper containing the suspended sediments was dried at room temperature overnight (in the dark) and then cut up and placed in an Erlenmeyer flask and extracted twice with 75 mL of 1:1 dichloromethane/acetone in a sonicator (Branson 5200; Danbury, CT) for 30 min. The solvent was filtered (GF/F, 0.7 μm) and reduced using a Zymark Turbovap II (Hopinkton, MD) to 0.5 mL. The coextracted matrix was removed using a Carboprep 90 graphitized carbon cartridge (500 mg; Restek, Bellafonte, PA) stacked onto a Sep-Pak Plus alumina A cartridge (Waters Corporation). The cartridges were conditioned with 15 mL of dichloromethane. The sample was loaded onto the cartridges, and the pyrethroids were eluted with 10 mL of dichloromethane. The sample was reduced to 0.5 mL, exchanged into ethyl acetate, and further reduced to 0.2 mL with N-evap. If solid sulfur was present in the extract, it was removed using a gel permeation chromatography (GPC) system using a Lab Alliance (State College, PA) Series I isocratic pump and UV detector. The analytical column was a PL-Gel (300 × 7.5 mm with 10 μm, 50 Å pore size) from Polymer Laboratories (Amherst, MA). Ethyl acetate (which was used as the mobile phase in the procedure) was pumped through the column at a rate of 1.0 mL min^{-1}. The size of the collection window was verified daily using pesticide standards and monitoring at a wavelength of 254 nm. The extract was reduced to 0.2 mL using the N-evap, and 0.02 mL of internal standard was added (fixed internal standard concentration of 1 ng μL^{-1}).

Instrumental Analysis. Extracts were analyzed on a Varian CP-3800 gas chromatograph coupled to a Saturn 2000 ion-trap mass spectrometer (Walnut Creek, CA). The injector was held at 275 °C, and 1 μL injections were made in splitless mode with a 50 psi pressure pulse for 1 min. The flow of He through a GC column was constant and set at 1.2 mL min^{-1}. The oven program was 80 °C for 1 min, ramped at 10 °C min^{-1} until 300 °C, and then held for 5 min. A DB-5 ms (Agilent, Santa Clara, CA) 30 m length × 0.25 mm ID × 0.25 μm phase thickness column was used. The transfer line from the GC to the MS was set at 280 °C, and the ion trap of the MS was set at 220 °C. The MS was operated in electron ionization (EI) mode with an emission current of 45 μA with a multiplier offset of 300 V (emission current was reduced to 15 μA, and no offset for the internal standards). Data were collected in the selected ion storage (SIS) mode; details of the SIS windows are given in **Table 1**. Pyrethroids that gave multiple peaks (allethrin, cyfluthrin, cypermethrin, τ-fluvalinate, permethrin, resmethrin, and tetramethrin) were added together for quantification.

Table 2. Analysis and Quantitation Parameters for Pyrethroids Analyzed by GC-MS-MS (Ion-Trap)

compound	parent ion (*m*/*z*)	excitation storage level (*m*/*z*)	excitation amplitude (V)	quantitation ions (*m*/*z*)
allethrin	123	54.0	41	67 + 81 + 95
bifenthrin	181	79.7	67	153 + 165 + 166
cyfluthrin	163	71.7	58	91 + 127 + 167
λ-cyhalothrin	181	79.7	87	151 + 152 + 153
cypermethrin	181	79.7	86	151 + 152 + 153
deltamethrin	253	111.5	62	172 + 174
esfenvalerate	225	99.1	82	119 + 142 + 169
fenpropathrin	265	116.8	85	172 + 210 + 236
τ-fluvalinate	250	110.2	100	180 + 194 + 200
permethrin	183	80.5	74	153 + 165 + 168
resmethrin	143	62.9	53	128 + 141
sumithrin	183	80.5	75	153 + 168 + 181
tetramethrin	164	72.1	61	77 + 91 + 107

GC-MS-MS was used to further reduce the background noise of the samples and lower the method detection limit. The instrument was operated in EI mode with an emission current of 50 μA with no multiplier offset. The isolation window was 3.0 *m*/*z*. Automated method development was used to determine the excitation amplitude for nonresonant ionization of the parent ion. The excitation amplitude was optimized to a voltage (0−100 V) which gave almost complete disassociation of the parent ion; the details are given in **Table 2**.

Deltamethrin cannot be differentiated from tralomethrin when analyzing via GC. Tralomethrin degrades to deltamethrin in the GC injector (*27*); therefore, what is measured can only be stated as the sum of deltamethrin and tralomethrin. Absolute identification requires the use of LC-MS to confirm which of the two pyrethroids is present.

Method Detection Limits. MDLs for the water samples using GC-MS were determined previously (*25*). MDLs for both the GC-MS and GC-MS-MS were calculated using the EPA method (*27*). The method detection limits for each compound in water are listed in **Table 3**. SSC can vary greatly; therefore, the limit of detection (LOD) was determined as the amount of analyte in the spiked sample that produced a signal greater than three times the background signal (*28*) for a given SSC. LODs for a suspended sediment concentration of 500 mg L^{-1} are listed in **Table 3**.

RESULTS AND DISCUSSION

This method provides for the analysis of pyrethroids in both the dissolved and the suspended-sediment-associated fractions to

Table 3. Compound Recoveries along with Relative Standard Deviations (RSD) and Method Detection Limits (MDL) for Water Samples and Limits of Detection (LOD) for Suspended Sediments for Pyrethroids Analyzed via GC-MS and GC-MS-MS[a]

		water			suspended sediment (assuming 500 mg L^{-1})		
compound	log K_{oc}[b]	% recovery (% RSD)	MDL GC/MS (ng L^{-1})	MDL GC/MS/MS (ng L^{-1})	% recovery (% RSD)	LOD GC/MS (ng g^{-1})	LOD GC/MS/MS (ng g^{-1})
allethrin	3.1	107 (7)	6.0	1.2	82 (7)	15	2
bifenthrin	5.4	94 (6)	4.7	0.7	97 (8)	22	2
cyfluthrin	5.1	89 (9)	5.2	1.1	82 (6)	20	5
λ-cyhalothrin	5.5	85 (9)	2.0	0.5	89 (9)	18	2
cypermethrin	5.0	85 (8)	5.6	1.1	87 (8)	26	4
deltamethrin	6.0	96 (9)	3.5	0.6	82 (9)	25	2
esfenvalerate	3.7	89 (8)	3.9	0.5	83 (8)	21	2
fenpropathrin	4.6	88 (7)	4.1	0.6	90 (6)	21	2
τ-fluvalinate	5.9	83 (9)	5.3	0.7	99 (9)	26	2
permethrin	4.9	98 (8)	3.4	0.6	93 (3)	10	2
resmethrin	5.0	92 (8)	5.7	1.1	89 (6)	19	5
sumithrin	5.3	99 (8)	5.1	1.0	101 (3)	13	3
tetramethrin	3.2	95 (5)	2.9	0.5	83 (4)	14	2

[a] Water samples were fortified at 10 ng L^{-1}, and sediment samples were fortified at 10 ng g^{-1}. [b] log K_{oc} was taken from refs *1* and *39*.

better understand their transport and partitioning in the environment. A laboratory study was conducted to validate the method, address laboratory artifacts such as association of the pyrethroids to sampling containers, and quantify partitioning between water and sediments. Finally, the method was used to quantify pyrethroids in surface water samples.

Method Validation. The method for both dissolved and suspended-sediment-associated fractions was tested for analyte recovery, and MDLs or LODs were determined. The association of the pyrethroids to the sample container and the filter paper are also examined.

The HLB SPE cartridges quantitatively recovered the dissolved pyrethroids (spiked, filtered water). Recoveries ranged from 83 to 107% at a concentration of 10 ng L^{-1} (**Table 3**). The MDLs for the water samples analyzed via GC-MS were 2 to 6 ng L^{-1} but were lowered to 0.5 to 1.2 ng L^{-1} by using GC-MS-MS (**Table 3**). The GC-MS MDLs are near toxicity LC_{50} values of 2 to 140 ng L^{-1}, but the GC-MS-MS MDL values are below the LC_{50} values. MDLs are higher for the compounds that chromatograph as multiple peaks and can be further reduced by obtaining individual isomers.

When water samples are allowed to sit for a period as short as an hour, the pyrethroids start to associate with the glass container walls (*16*, *18*). When the water was removed slowly from the 1-L bottles by pumping at 10 mL min^{-1} for SPE, 20 to 27% of the pyrethroids (initial concentration = 400 ng L^{-1}) remained associated with the walls (**Figure 2**). But the association with the container is reversible, indicating that the compounds are not degrading. Either shaking the bottles and immediately pouring them out or just pouring out the water quickly from the bottles decreased association of the pyrethroids with the container wall to1 to 4% for 1-L bottles (**Figure 2**). Even when water is pumped out of the bottle, the amount of the pyrethroids associated with the 1-L bottle wall can vary from 5 to 40%, depending on the filtered water composition (*18*). Waters with higher dissolved organic carbon concentrations (that have already been filtered to remove suspended sediments) tended to have lower amounts of pyrethroids associated with the bottle: 5 to 12% for water with 8 mg L^{-1} of DOC, 16−27% water with 1 mg L^{-1} DOC, and up to 40% for deionized water (*18*). Because the association of pyrethroids with containers can vary with water composition and because it is reversible with simple shaking, the amount lost cannot be easily predicted.

Following SPE extraction of the dissolved phase, the empty bottle was rinsed with dichloromethane to remove any pyrethroids

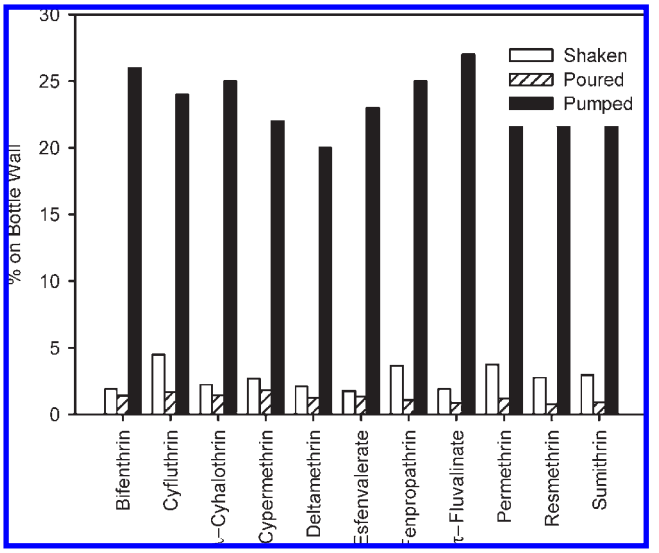

Figure 2. Percentage of pyrethroids associated with the 1-L glass bottle was calculated after shaking the bottle before pouring out the water, pouring out the water gently, and pumping the water through an SPE cartridge at 10 mL min^{-1}. Water was spiked at 400 ng L^{-1} and allowed to equilibrate for 24 h.

associated with the bottle walls. This bottle rinse was then added to the SPE eluent to account for any loss to the sample container; these fractions can be combined for natural water samples as this is a laboratory artifact and is not related to the environmental partitioning.

To ensure the pyrethroids on the filter paper were associated with the suspended sediments and were not dissolved pyrethroids sticking to the filter, a filtered water sample spiked with pyrethroids was passed through an additional filter. This filter was then extracted in the same manner as the filters with suspended sediments. Pyrethroid loss to the filter paper was minimal (< 5% (*18*)).

The extracts of the suspended sediment collected on the filter paper can have coextracted matrix interferences. Use of carbon/alumina SPE columns along with GPC cleanup has been shown to be effective at removing the matrix from the bed and suspended sediment samples in a previously developed method (*29*). The suspended sediment extraction resulted in recoveries of 83 to 101% at a fortified concentration of 10 ng g^{-1}. LODs, calculated

for water samples containing 500 mg/L of suspended sediment (**Table 3**), were 10−26 ng g^{-1} for GC-MS and 2−5 ng g^{-1} for GC-MS-MS. These detection limits would have to be adjusted higher or lower if the amount of suspended sediment was different, and the detection limits would be lower if there was a larger amount of suspended sediment present. An additional advantage when using MS-MS for sediment samples is the decrease in background noise. Other researchers (*21*) have found that MS-MS is more advantageous (lower detection limits for more compounds) over other detectors such as ECD or NCI for soil samples.

Laboratory Partitioning Study. After the method was tested in separate parts, a mass balance was undertaken to test the method as a whole. After spiking the test water with pyrethroids (400 ng L^{-1}), the water was filtered and analyzed in three separate fractions: the dissolved, bottle rinse, and filter. Total recoveries summed from all three phases ranged from 88 to 95% (**Figure 3**). Variability for the samples was low in all three fractions, and the percent relative standard deviation was less than 4%.

For most pyrethroids (except allethrin and tetramethrin), a large portion of the mass was found associated with the suspended sediments (**Figure 3**). Between 48% and 65% was associated with the suspended sediments even though the SSC was relatively low at 14 mg L^{-1}. Only 20 to 38% of the pyrethroids were in the dissolved phase and 5 to 9% associated with the bottle walls. This illustrates that the pyrethroids have a greater affinity for the suspended sediments rather than water; this is to be expected from their relatively high partitioning coefficients (log K_{oc} ~5−6) and has been demonstrated by other researchers (*3*).

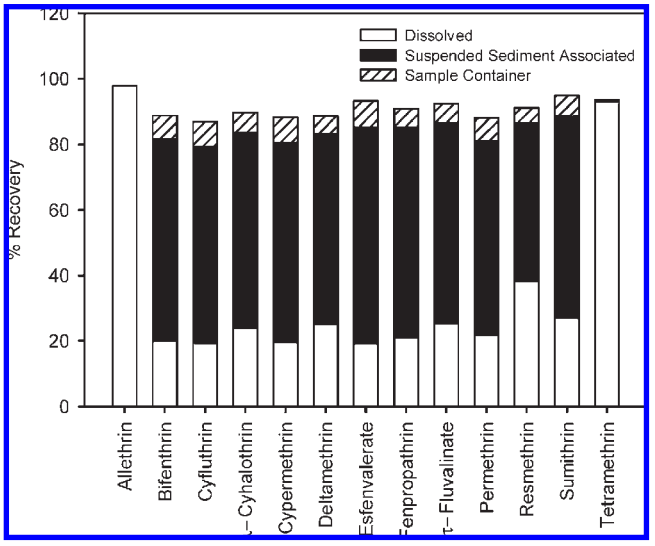

Figure 3. Mass balance of water samples ($n = 3$) spiked at 400 ng L^{-1} into natural water (SSC = 14 mg L^{-1} and DOC = 5 mg L^{-1}). The sample sat for 3 days at 4 °C before extraction. The sample was divided into that which was associated with the suspended sediments, what was extracted in the dissolved phase with the SPE cartridge, and what was associated with the bottle wall after pumping the water through the extraction cartridge.

Two of the pyrethroids, allethrin and tetramethrin, did not appear to sorb appreciably to the sediment or bottle walls. These compounds are structurally different from the other pyrethroids (**Figure 1**); they have lower organic carbon partition coefficients (log K_{oc} values; **Table 3**). The dissolved fraction represented 98 and 93% for allethrin and tetramethrin, respectively, and little or none was associated with the bottle walls.

Field Samples. In the urban samples, four pyrethroids (bifenthrin, cyfluthrin, cypermethrin, and permethrin) were detected (**Table 4**). Bifenthrin was detected the most frequently and at the highest concentrations. For all pyrethroids, concentrations ranged from 5.4 to 15 ng L^{-1} in the dissolved phase and 1.8 to 870 ng L^{-1} in the suspended-sediment-associated phase. Four pyrethroids were also detected in the agricultural drain sample (all associated with the suspended sediments), but permethrin was the only pyrethroid detected in common with the urban samples; pyrethroid concentrations were λ-cyhalothrin (17 ng L^{-1}), esfenvalerate (25 ng L^{-1}), τ-fluvalinate (7 ng L^{-1}), and permethrin (19 ng L^{-1}).

Two of the drains, Elk Grove and Roseville, had been sampled in a previously published study (*22*). During the wet season (fall and winter), whole water samples were analyzed for pyrethroids, and median and maximum concentrations were reported. The two drains had frequent detections of the same four pyrethroids found in the current study (the previous study also infrequently detected deltamethrin and esfenvalerate); median concentrations of the whole water samples ranged from 3 to 22 ng L^{-1}. The studies were similar in that the same pyrethroids were detected most frequently and at the highest concentrations; however, there are considerable variations in the data which are likely due to rainfall amount and timing of sampling.

The samples from concrete-lined urban drains (Elk Grove, Rancho Cordova, and Roseville) contained at least one pyrethroid detected in both the dissolved and suspended-sediment-associated phases. In contrast, the other three water samples had detectable pyrethroids only with the suspended-sediment-associated fraction. By calculating the mass of pyrethroids in a 1-L sample for the dissolved versus suspended phases, the pyrethroids associated with the suspended sediments ranged from 68 to 98%

Table 4. Locations, Suspended Sediment Concentrations (SSC), and Dissolved Organic Carbon (DOC) Concentrations along with Pyrethroids Detected in Water and Suspended Sediment Associated Phases of Five Urban Creeks in California after a Recent Rain Event in the Fall of 2008[a]

				bifenthrin		cyfluthrin		cypermethrin		permethrin	
site	location (latitude, longitude)	SSC (mg L^{-1})	DOC (mg L^{-1})	water (ng L^{-1})	suspended sediment (ng L^{-1})	water (ng L^{-1})	suspended sediment (ng L^{-1})	water (ng L^{-1})	suspended sediment (ng L^{-1})	water (ng L^{-1})	suspended sediment (ng L^{-1})
Arcade Creek	38.64194, −121.38167	72	9.5	nd	6.8	nd	nd	nd	nd	nd	3.1
El Dorado Hills	38.64307, −121.07858	30	8.2	nd	3.0	nd	2.6	nd	nd	nd	4.8
Elk Grove	38.40765, −121.35062	20	7.7	nd	2.0	5.4	17	nd	8.0	nd	1.8
Rancho Cordova	38.54348, −121.23478	40	7.3	9.0	49	nd	nd	nd	nd	nd	nd
Roseville	38.8027, −121.33855	32	15	15	870	7.0	38	nd	6.2	nd	9.6

[a] Suspended sediment concentrations are presented in terms of ng L^{-1} for whole water comparisons but are greater than the LOD on a ng g^{-1} basis. nd = not detected.

of the total. For those samples with no detectable pyrethroids in the dissolved fraction, an aqueous concentration of 1/2 the MDL was assumed for the calculations. In these samples, the results were similar, with at least 86 to 98% of the pyrethroids associated with the suspended sediments. The majority of the pyrethroids sorbed to suspended sediments even though the SSC was relatively low (20 to 72 mg L^{-1}).

Prior research has found that pyrethroids preferentially sorb to suspended particles, but the extent can vary. Liu et al. (*3*) compared LLE of centrifuged and noncentrifuged water samples (another method of removing particulates) and found that the amount of bifenthrin and permethrin associated with the suspended sediment phase was 97% in streamwater and 73 to 90% in runoff effluent from an agricultural area. Other studies found lesser amounts sorbed to suspended particles; one study of river runoff after a storm detected from 3 to 87% of the total permethrin on the suspended solids (*30*), while another study found that 30 to 60% of bifenthrin and permethrin was associated with the suspended phase in a laboratory-created solution (*31*). The amount of variability could depend on time; solutions created in the laboratory may sit for hours to days (*31*), but the pyrethroids may need a month to reach equilibrium (*32*). The composition of the particulate phase is also an important aspect for pyrethroid partitioning (*17*). Other researchers have noted that the partitioning of pesticides associated with suspended sediments differ from depositional bed sediments; the suspended-sediment-associated pesticides are not at equilibrium with the aqueous phase because of a relatively short re-equilibration time during transport (*33*). Since it is hard to predict the extent of pyrethroid partitioning between water and suspended sediments, it is important to directly measure all fractions, even in waters with low suspended sediment concentrations.

The number of samples in this study that would be considered to exceed aqueous LC_{50} toxicity values is lower when the dissolved water concentrations are used instead of whole water concentrations. Some research suggests that the bioavailability of pyrethroids is limited to the dissolved phase for organisms that live in the water column (*34*, *35*), but others have found that benthic organisms may be also exposed to pyrethroids within the water column (*36*). None of the field samples in this study (dissolved or whole water concentrations) ever exceeded the reported permethrin LC_{50} value of 68 ng L^{-1} (5th percentile of all organisms as reported in ref *22*; data taken from ref *37*). The other pyrethroids detected (bifenthrin, λ-cyhalothrin, cyfluthrin, cypermethrin, and esfenvalerate) would have exceeded their respective LC_{50} values (3.8, 4, 4, 4, and 17 ng L^{-1}) if whole water concentrations were used. However, if only the dissolved concentrations were used, then only 2 of 5 bifenthrin detections and 2 of 3 cyfluthrin detections would have exceeded the LC_{50} value. The toxicity of sediment-associated pesticides in the water column is still unknown, but it is important to assess the pyrethroid partitioning to determine their bioavailability to organisms.

Measuring the occurrence and distribution of pyrethroids in different environmental compartments is important to understanding their behavior in the environment. Partitioning influences both the transport and persistence of pyrethroids. Pyrethroids deposited with bed sediments may be resuspended during high flow events, and sediment-associated pyrethroids are susceptible to different degradation processes than dissolved pyrethroids (*38*). Being able to measure both the dissolved and suspended-sediment-associated pyrethroid concentrations in a water samples, rather than measuring whole water or just the dissolved phase, allows for greater characterization of pyrethroids in the environment.

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