Pyrethroids in southern California coastal sediments

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Abstract

Several studies have documented the potential impacts of synthetic pyrethroid pesticides in freshwater systems; however, little is known about their fate and effects in estuarine and marine environments. The goal of this study was to assess the extent and magnitude of pyrethroids in coastal embayments of the southern California Bight (SCB), USA. Using a stratified probabilistic design, 155 sediment samples were collected from 4 embayment habitats (estuaries, marinas, open bays, and ports) and analyzed for 8 common-use pyrethroids. Total pyrethroid concentrations ranged from less than 0.5 to 230 µg/kg dry weight (area-weighted mean concentration = 5.1 ±3.1 µg/kg) and were detected in 35% of the total SCB embayment area. Estuaries and marinas had the greatest areal extent of detectable concentrations (up to 65%) and the greatest area-weighted mean concentrations (22.1 ±26.5µg/kg). Furthermore, sites with the greatest pyrethroid concentrations were located near sources of runoff from urban watersheds. Bifenthrin and cyfluthrin were detected in 32 and 15% of all samples, respectively, whereas the other 6 pyrethroids were detected in ≤5% of samples. Permethrin and bifenthrin had the highest concentrations at 132 and 65 µg/kg. Toxic units (TUs) estimated for the marine amphipod *Eohaustorius estuarius* ranged from 0 to 5.8, exceeding unity in 9 and 32% of the total and estuary habitat area, respectively. Although increased mortality of *E. estuarius* was most frequently observed in toxicity tests run on split samples from estuaries compared with other strata, there was no clear correlation between pyrethroid TUs and amphipod mortality. This suggests other mitigating factors may affect the predictive capability of the TU approach resulting from a single test species.

Introduction

Synthetic pyrethroids have become the dominant current-use pesticides in both agricultural and non-agricultural applications since the phase-out of organophosphates over the past 20 years (Amweg *et al*. 2006). Between 1999 to 2008 in five southern California coastal counties, total annual sales of pyrethroid pesticides for professional (i.e., licensed) application increased from 65 to 153 metric tons (www.cdpr.ca.gov). However, these usage figures underestimate total pyrethroid sales as they do not include direct over-the-counter sales to consumers for residential use. In southern California, with over 17 million residents and 6 million housing units (http://quickfacts.census.gov), approximately 73% of pyrethroids have non-agricultural applications, such as structural pest control and landscape maintenance (http://www.cdpr.ca.gov).

Due to their hydrophobicity (log K_{ow} = 5 - 6) and particle reactive nature (Laskowski 2002, Gan *et al*. 2005), sediments in urban and agricultural runoff are the predominant sink of pyrethroids in California receiving waters (Ahn *et al*. 2005, Weston and Lydy 2010). Pyrethroids have been measured in sediments from California, Texas, and Illinois, and stormwater runoff has been implicated as a primary source (Amweg *et al*. 2005, Amweg *et al*. 2006, Hintzen *et al*. 2009, Domagalski *et al*. 2010, Weston and Lydy 2010). In much of urbanized California, stormwater and wastewater treatment systems are separate, so wet and dry weather runoff receive no treatment

before discharging to the coastal ocean. Moreover, the flood control system has been highly modified to reduce flooding (Tiefenthaler *et al*. 2008). As a result, storm flows can change by orders of magnitude in a matter of minutes and carry large quantities of sediment. For example, approximately 700,000 metric tons of suspended solids, with 89% carried by storm flow, were discharged to the coastal ocean of southern California Bight (SCB) in 1994-1995 (Schiff *et al*. 2000).

Pyrethroids can be highly toxic to non-target aquatic species (Amweg *et al*. 2006). In several California urban creeks, bifenthrin concentrations ranged from 2.19 to 219 ng/g dry weight, and most samples with greater than 0.5 toxic units (TUs) exhibited substantial toxicity to the freshwater amphipod *Hyalella azteca* (Holmes *et al*. 2008). In central Texas, pyrethroids were reported as the likely cause of toxicity to *H. azteca* in the sediments of urban streams (Hintzen *et al*. 2009). In Illinois, pyrethroids occurred up to 56 µg/kg with up to 2.9 TUs and were toxic to *H. azteca* in sediments of urban waterways (Ding *et al*. 2010).

Although pyrethroid use in California is widespread, and the potential for environmental impact is substantial, there is a limited number of comprehensive studies evaluating the occurrence, extent, or magnitude of pyrethroids in the coastal environment. Two relatively small-scale, site-specific studies indicating that concern over pyrethroid impacts in marine systems is warranted (Anderson *et al*. 2010, Lao *et al*. 2010) have been conducted in southern California marine habitats . One study in Ballona Creek (Los Angeles, CA), an intensely urbanized coastal estuary, reported pyrethroid concentrations up to 473 µg/kg dry weight and corresponding toxicity to a standard invertebrate toxicity test species *Eohaustorius estuarius*.

The first objective of the current study was to assess the extent and magnitude of pyrethroid concentrations in marine embayments across the entire SCB. The second objective was to assess the influence of discharge sources by comparing pyrethroid concentrations among different habitats, including estuaries, marinas, ports, and open bays. The third objective was to determine if a toxic-unit approach was predictive of toxicity observed for *E. estuarius* in sediment toxicity tests utilizing splits of the same samples to quantify pyrethroid concentrations.

Methods

Study Region and Sample Collection

The SCB is delineated by a 400 km length of recessed coastline between Point Conception to the north and the United States-Mexico international border to the south. A stratified-random probability-based design (Stevens 1997) was used to conduct an unbiased survey of SCB embayments encompassing a total area of 94.1 km^2 and characterized by salinities greater than 30‰ during the sampling events. Samples were collected at 155 sites in 19 different geographic embayments (see Table SI-1 and Figure SI-1 in Supplemental Information (SI)). Sites were classified as belonging to one of four major strata (estuaries, marinas, ports, and open bays; Bergen 1996) , with more than 30 sites for each strata.

Sediment samples were collected during the regional dry season (July through September) in 2008 using a 0.1 m^2 modified Van Veen grab. The top 5 cm were composited. Subsamples for analysis of pyrethroids, total organic carbon (TOC), and total nitrogen (TN) were placed in pre-cleaned 250 ml amber glass containers with Teflon-lined lids and delivered to the laboratory on dry ice to be frozen at -20ºC until analysis. Subsamples for grain size analysis and toxicity testing were placed in 100 ml and 1 L pre-cleaned plastic containers, respectively, delivered to the laboratory on wet ice, and stored at ~4ºC until analysis and testing.

Sample Analysis

Bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, λ-cyhalothrin and permethrin were targeted for analysis in this study. Sediment samples for pyrethroid measurement were extracted with dichloromethane using a microwave extraction system according to EPA method 3546. Elemental sulfur was removed from extracts using acid-activated copper powder. The extracts were further cleaned using silica gel/alumina column chromatography and analyzed using an Agilent 6890 gas chromatograph coupled to a 5973 quadrupole mass spectrometer (GC-MS) with a DB-5MS column (60 m × 0.25 mm × 0.25 µm; Agilent Technologies, Palo Alto CA). The carrier gas was helium at a flow rate of 1.5 ml/minute. The oven temperature programmed 45°C for 5 minutes, then ramped at 25°C/minute to 150°C, then ramped at 2.5°C/minute to 285°C and held for 16.8 minutes. The MS was operated in full-scan (m/z 45 - 500) negative chemical ionization

mode at 1.67 scans/second. Quantitation was based on a 5-point internal standard calibration curve (with the lowest concentration at the reporting limit) with 2,2',5,5'-tetrabromobiphenyl as the internal standard (the quantitation and confirmation ions are listed in Table SI-2). Procedural blanks, matrix spikes, matrix spike duplicates, and replicate samples were analyzed to validate the analytical protocol. Mean recovery of target pyrethroids in matrix spikes/duplicates were 98.6 ±11.0% (n = 14, 95% confidence interval), and 97.6 ±5.5% (n = 14), respectively. The relative percent difference (mean ± standard deviation) for target pyrethroids in sample duplicates was 8.74 ±2.95% (n = 14). The method detection and reporting limits were 0.5 and 2.0 µg/kg for individual target pyrethroids with the exception of permethrin (5.0 and 25 µg/kg). Total organic carbon and TN were determined using a Carlo Erba 1108 CHN Elemental Analyzer, while grain size analyses were conducted using a Horiba LA900 instrument (Maruya and Schiff 2009).

Bulk sediment toxicity was measured by exposing the estuarine amphipod *E. estuarius* to split samples from SCB embayment sediments following previously published protocols (USEPA 1994). The amphipods were collected from a non-contaminated estuarine location (Beaver Creek, OR). Sediments were passed through a 2 mm sieve prior to testing to remove debris and any indigenous organisms. The exposures were conducted in 1 L glass chambers containing ~2 cm of sediment and 800 ml of filtered (≤20 µm) seawater at a salinity of 32‰. Twenty amphipods were added to each lightly aerated beaker and exposed for 10 days under constant light and 15ºC. Five replicates were tested for each station. At the end of the test, the surviving amphipods were counted to determine percentage mortality relative to control exposures. A negative control (amphipod collection site sediment) was included with each testing batch of samples (Bay *et al*. 2011a).

Data Analysis

Data analysis was comprised of four general steps: 1) spatial extent of detectable pyrethroids; 2) magnitude of concentrations; 3) mass inventories; and 4) toxicity potential. Pyrethroid concentration in sediment was expressed on a dry weight basis. For individual pyrethroids that were detected at estimated concentrations below the reporting limit but above the method detection limit, 1/2 of the reporting limit was used for calculation. A value of zero was used for individual pyrethroids that were not detected (i.e., below the method detection limit). Total pyrethroid concentration was the sum of the eight target compounds.

The extent of pyrethroid concentration was described using a cumulative distribution function (CDF), the total detectable area, percent of total area, and percent of detectable areas for individual pyrethroid. The CDF of concentration by area was calculated according to Equation 1:

$$CDF_j = \frac{\sum_{i=1}^{j} AW_i}{\sum_{i=1}^{n} AW_i} \qquad \text{Eq. 1}$$

where CDF_j is the cumulative distribution frequency for station j in ascending order, AW_i is the area weight (km^2) for station i, and n denotes the total number of the stations (Zeng *et al*. 2005).

The total detectable area was the sum of area weight of stations from which any targeted pyrethroid was detected. The percent of total area was the ratio of the total detectable area to the total area. Percent of detectable area for individual pyrethroid was the ratio of its detectable area to the total detectable area. Permethrin was excluded in the CDF calculation due to its substantially higher reporting limit. The area and stratum calculations for total pyrethroids were not affected by the exclusion of permethrin because the other targeted pyrethroids were also detected at relatively high levels (>15 µg/kg) in the same sediments.

Area weighted mean (AWM) concentration and associated 95% confidence interval (95% CI) were computed according to Equations 2 and 3, respectively (Thompson 2000):

$$AWM = \frac{\sum_{i=1}^{n}(p_i \times AW_i)}{\sum_{i=1}^{n} AW_i} \qquad \text{Eq. 2}$$

$$95\%\ \text{CI} = 1.96 \times \sqrt{\frac{\sum_{i=1}^{n}[(p_i - AWM) \times AW_i)]^2}{(\sum_{i=1}^{n} AW_i)^2}} \qquad \text{Eq. 3}$$

where p_i is pyrethroid concentration at station i; AWM were calculated by stratum.

The total mass inventory of pyrethroids in surficial sediments by embayment stratum was calculated according to Equation 4:

$$Mass = AWM \times \delta \times A \times T \quad \text{Eq. 4}$$

where δ is dry density of sediment (estimated 1.5 g/ml; Maruya and Schiff, 2009), *A* is total area of stratum represented by the samples, and *T* is the thickness of sediment (2 cm here).

A disproportionate accumulation factor (DAF) of pyrethroids for each stratum was estimated by Equation 5:

$$\text{DAF} = \frac{\%Mass}{\%Area} \quad \text{Eq. 5}$$

DAF = 1 indicates mass accumulation in direct proportion with the stratum area.

Toxicity potential was calculated using a toxic-unit approach (Amweg *et al*. 2005). Pyrethroid-specific TUs were calculated for a given sample by dividing the organic carbon normalized pyrethroid concentration by its organic carbon normalized median lethal concentration (LC_{50}). Total pyrethroid TU was the sum of individual TU. Ten-day sediment organic carbon normalized LC_{50} values for *E. estuarius* were bifenthrin = 1.03 µg/g OC, cypermethrin = 1.41 µg/g OC, permethrin = 17.9 µg/g (Anderson *et al*. 2008), and cyfluthrin = 0.33 µg/g OC (Bay *et al*. 2011b). No LC_{50} values are currently available for the remaining target pyrethroids. AWM and 95% CI TUs were calculated by substituting TU for pyrethroid concentration in Equations 2 and 3. Associations among pyrethroid concentration, TOC, TN and grain size, percentage mortality and TU were assessed using Spearman's rank correlational analyses (SigmaState; V2.03, SPSS).

Results and Discussion

Total pyrethroid concentrations were correlated with TOC (r_s = 0.59; p <0.01; n=52) and weakly correlated with TN (r_s = 0.30; p <0.05; Table SI-3). This is not unexpected because pyrethroids are hydrophobic and have a strong affinity for organic phase (Laskowski 2002, Gan *et al*. 2005). There was no significant relationship between pyrethroid sediment concentrations and percent fine grained sediments (<63 µm), in contrast to a previous study (Lao *et al*. 2010) that observed targeted stations located a short distance from the mouth of Ballona Creek. This inconsistency could be the result of proximity to runoff sources and/or rapid transformation of many pyrethroids under estuarine/marine conditions, where hydrolysis rates are orders of magnitude greater than in freshwater systems (Laskowski 2002). For example, the eight target pyrethroids were stable (mortality >600 days) at a pH of ~5, while their half-lives ranged from ~4 to ~35 days in seawater with a pH of ~8 (W. Lao, unpublished data).

Extent by Area and Stratum

Pyrethroids were detected in 34.5% (32.5 km^2) of the sediments in SCB embayments (Figure 1). Approximately 9% of the sediments in SCB embayments had concentrations >10 µg/kg. While pyrethroids were detected in all 19 of the embayments sampled, the extent of detectable pyrethroid concentrations was dissimilar among strata (Table 1). The areal extent of detectable sediment pyrethroid concentrations was greatest in the marina stratum (65.0%), followed by estuaries (49.4%), open bays (35.8%), and ports (16.2%).

The greatest pyrethroid concentrations were observed at the mouths of urban watersheds, including: Ballona Creek near Marina del Rey in the Los Angeles metropolitan area; Dominguez Channel and the Los Angeles River, which both empty into the Los Angeles/Long Beach Harbor complex; and San Diego and Chollas Creeks, which empty into the San Diego Bay (Figures 2 and SI-2). Decreasing concentrations were often observed moving away from

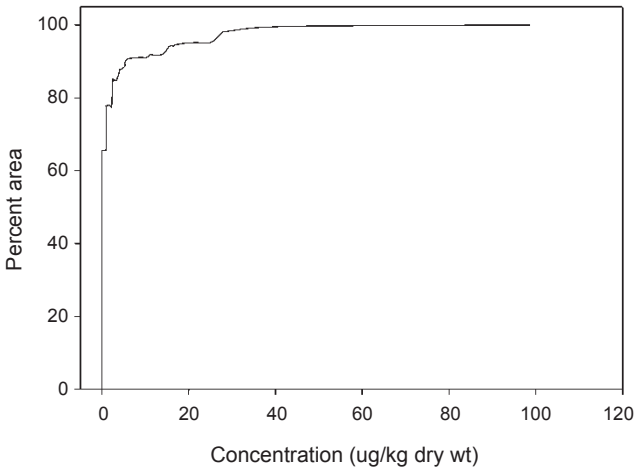

Figure 1. Cumulative distribution function of total pyrethroid concentration (excluding permethrin) versus area in Southern California Bight embayments (94.1 km^2).

Table 1. Extent of detectable pyrethroids in SCB embayment sediments.

Stratum	Sample Size	Total Area (km^2)	Pyrethroids Detectable Area[a]		(% of Detectable Area)		
			(km^2) [c]	(% of Total Area)	Bif [b]	Cyf	Cyp
Bay	29	51.7	18.5	35.8	100	33.1	22
Port	42	26.3	4.26	16.2	69.3	32.8	0
Marina	35	11.1	7.21	65.0	97.8	72.7	30.2
Estuary	49	4.99	2.47	49.4	100	63	51.8
Total	155	94.1	32.5	34.5	95.5	44.1	23.2

[a] Sum of the seven pyrethroids;

[b] Bif = bifenthrin, Cyf = cyfluthrin, Cpy = cypermethrin

[c] Used for calculating % of detectable area; Permethrin was excluded in this analysis due to its higher reporting limit

these creek mouths into their respective embayments. This is consistent with findings from a previous field survey at the Ballona Creek estuary (Lao *et al*. 2010) where pyrethroids discharged by the creek accumulated in the estuarine sediments during the dry season. In addition, the marinas contaminated by pyrethroid pesticides (e.g., Marina del Rey, Consolidated Slip in LA Harbor, Dana Point Marina, and San Diego South Bay Marina) were located adjacent to discharges from urban watersheds. Because of the absence of major point sources (e.g., industrial or municipal plants) in these watersheds,

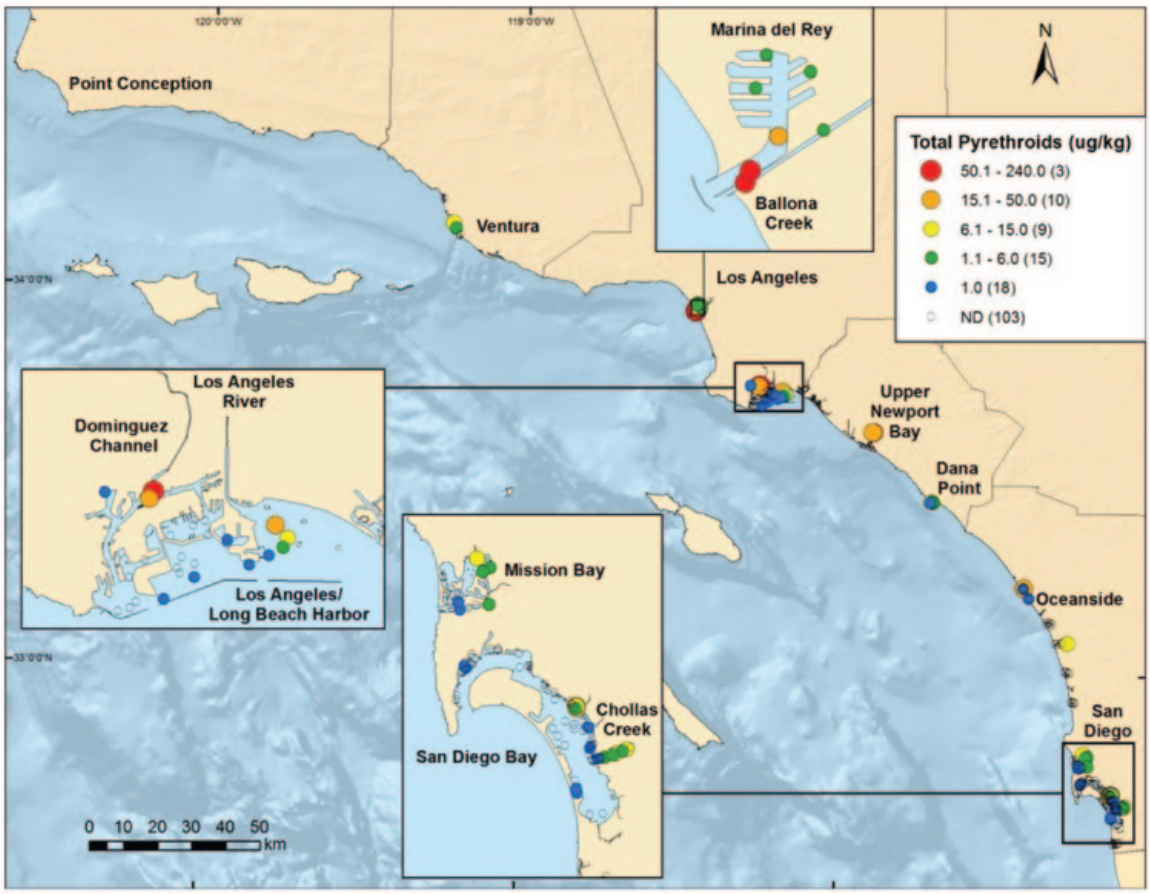

Figure 2. Geographical distribution of total pyrethroid concentrations in sediments from embayments of the Southern California Bight.

urban runoff is the most likely source of pyrethroids to SCB embayments.

Bifenthrin was the most widely distributed pyrethroid; it was present in over 95% of the samples that had detectable pyrethroid concentrations (Table 1). For samples with detectable pyrethroids, bifenthrin was present for 100% of the bay and estuary strata, 97.8% for marinas, and 69.3% for ports. Cyfluthrin was the next most prevalent pyrethroid (44% for the SCB embayment area). As with bifenthrin, cyfluthrin was most frequently detectable in estuaries and marinas. In contrast, cypermethrin was less prevalent in estuaries and marinas and not detected in the port stratum. Permethrin was detected in only 1.9% of the SCB embayment area; however, it should be noted that the 25 µg/kg reporting limit was 10 times higher than reporting limits for the other targeted pyrethroids. Still, this low detection percentage is in contrast with a recent study (Lao *et al*. 2010) suggesting that permethrin distribution can be wide with concentrations up to two times higher than those of the next most abundant pyrethroid. The remaining four pyrethroids (deltamethrin, esfenvalerate, fenpropathrin, and λ-cyhalothrin) were detected in <2% of the SCB embayment area.

Magnitude and Relative Abundance

Sediment pyrethroid concentrations ranged from not detectable to 230 µg/kg. The overall AWM concentration (±95% CI) for SCB embayments was 5.15 ±3.09 µg/kg. The greatest pyrethroid AWM concentrations were observed in the estuarine (22.1 ±26.5 µg/kg) and marina (20.1 ±17.5 µg/kg) strata; AWM concentrations in open bays (2.80 ±3.31 µg/kg) and ports (0.229 ±0.177 µg/kg) were one to two orders of magnitude lower (Figure 3). The spatial distribution of pyrethroids among embayment strata was dissimilar from the distribution of other persistent organic contaminants such as dichlorodiphenyl-trichloroethane (DDT) and its degradation products, polychlorinated biphenyl (PCB) congeners, and polycyclic aromatic hydrocarbons (PAHs). For example, significant differences in AWM concentrations of total DDTs, PCBs, or PAHs were observed between estuaries and marinas (Maruya and Schiff 2009).

Bifenthrin (37.5% of the pyrethroid AWM concentration) and permethrin (47.3%) were the most abundant compounds in SCB embayments (Table 2). Bifenthrin was the most abundant pyrethroid in open bays, ports and estuaries, but permethrin comprised

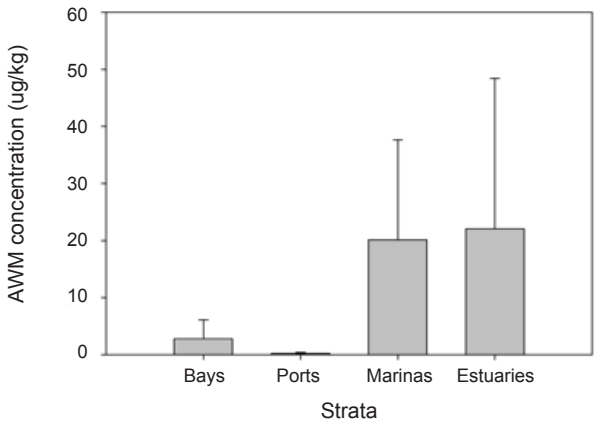

Figure 3. Area-weighted mean (AWM) concentrations of total pyrethroid concentration and associated 95% confidence intervals by stratum.

the majority of the total pyrethroid concentration in marinas. Cyfluthrin comprised a large portion (38%) of the pyrethroid AWM concentration in the port stratum. Contribution from each of the remaining four pyrethroids was <1% in the SCB embayment area.

The relative composition of the eight target pyrethroids did not correspond to the expected distribution based on application rates in SCB watersheds and assuming a 1:1 relationship between pyrethroid sales and usage (Table 2). California Department of Pesticide Regulation (CDPR) data on active ingredient application rates for agricultural and pest control applications indicate that bifenthrin comprised 9% of the eight target pyrethroids sales in the SCB region, yet this study found that bifenthrin comprised 38% of the estimated total pyrethroids in SCB sediments. This disparity between application and occurrence of bifenthrin was amplified within individual strata (i.e., ports). Cyfluthrin presented similar but less significant differences. Occurrence to application rate agreement was closest for permethrin (35 to 59% AWM vs. 62% usage), noting that occurrence was likely underestimated due to higher variability in its reporting limit. In contrast, the relative contribution of the remaining four pyrethroids in sediment was smaller than corresponding application rates.

There were several potential reasons for the differences between reported application rates and occurrence in SCB embayment sediments (Table 2). First, pyrethroids are highly hydrophobic and have a strong affinity for solid phases (i.e., soils, sediments, and concrete), which may result in retention in the upper parts of the watershed. Only a small fraction of the total sediment-associated pyrethroid pool is available to be mobilized and subsequently

Table 2. Relative percentage contributions of targeted pyrethroids to the total average weighted mean (AWM) concentration and toxic units (TUs) in SCB embayments sediments.

	Total Pyrethroids (%)										
	Bay		Port		Marina		Estuary		Entire area		Usage [a]
	AWM	TUs	AWM	TUs	AWM	TUs	AWM	TUs	AWM	TUs	
Bifenthrin	46	55	62	40	28	47	45	86	38	57	9.2 ± 2.5
Cyfluthrin	9.7	36	38	60	7.9	44	3.7	10	7.8	38	4.9 ± 1.7
Cypermethrin	9	8.1	0	0	4.2	4.7	5	2.4	5.8	3.8	16 ± 5.0
Permethrin [b]	35	1.9	0	0	59	4.6	42	1.5	47	2	62 ± 4.4
Other pyrethroids [c]	0		0		1.4		4.4		1.7		8.4 ± 3.4

[a] Average annual (1999-2008) use (± standard deviation) in five coastal counties (Santa Barbara, Ventura, Los Angeles, Orange, and San Diego) of southern California (USA) (www.cdpr.ca.gov)

[b] Reporting limit for permethrin was ten times higher than for the other targeted pyrethroids

[c] Sum of deltamethrin, esfenvalerate, fenpropathrin, λ-cyhalothrin.

transported out of the watershed via stormwater runoff (Gan *et al*. 2005, Ortiz-Pérez *et al*. 2005, Jiang *et al*. 2011). Further, the sediment-associated pyrethroids could be retained in detention ponds, storm drains, or other catchments in the watershed (Budd *et al*. 2009). Second, the individual pyrethroids targeted in this study exhibit differential persistence in aquatic systems, have different hydrolysis and photolysis rates (Laskowski 2002), and undergo rapid hydrolysis in alkaline aqueous media, such as seawater, at different rates (Camilleri 1984;Takahashi *et al*. 1985a,b). For example, the half-lives for bifenthrin and cyfluthrin have been estimated at 35.0 ±0.08 and 4.44 ±1.7 days in seawater, respectively (W. Lao, unpublished data). Third, the reported commercial sales rates may not reflect actual usage, because direct over-the-counter sales of pyrethroids to consumers are not reported.

Bifenthrin and permethrin concentrations from this study were similar to concentrations in marine sediments, but lower than concentrations measured in freshwater sediments reported previously. The highest concentrations of bifenthrin (64.8 µg/kg) and permethrin (132 µg/kg) in sediments from the Ballona Creek estuary (this study) were comparable to those reported for the same estuary by Lao *et al.* (2010). Estuarine sediments from Switzer Creek in San Diego Bay had bifenthrin and permethrin concentrations of 23.9 µg/kg and 135 µg/kg, respectively (Anderson *et al*. 2010). In contrast, higher bifenthrin concentrations were reported in freshwater sediments, for instance, an urban wetland in Los Angeles (Sims Pond, 610 µg/kg; Brown *et al*. 2010), San Diego Creek in Orange county (542 µg/kg; Budd *et al*. 2007), and California's Central Valley (Clover Creek, 219 µg/kg; Holmes *et al*. 2008). In addition, sediment from a residential runoff drain near Sacramento, CA, contained 744 µg/kg bifenthrin and 539 µg/kg permethrin (Weston *et al*. 2009). Relative to freshwater sediments, the lower pyrethroid concentrations in marine sediments are partly due to localized differences in loading and persistence, losses during transport, and dilution and flushing due to tidal exchange (Camilleri 1984, Takahashi *et al*. 1985b, Gan *et al*. 2005, Lao *et al*. 2010, Weston and Lydy 2010).

Mass Inventories

The total mass of the eight target pyrethroids in SCB embayment sediments was estimated to be 36 kg, assuming identical conditions of surface sediment deposition and conservation in the embayment. This mass represents a miniscule fraction (0.036% ±0.003%) of the quantity of pyrethroid sales in the SCB region, which were estimated to be 101 ±10 mt in 2007-08 (www.cdpr.ca.gov). To estimate pyrethroid loading to SCB embayments via stormwater runoff, annual stormwater runoff volumes were multiplied by average stormwater pyrethroid concentrations determined by a regional consortium of stormwater agencies (Table SI-4). The mass of pyrethroids estimated to reside in SCB embayment sediments was only 27% of the total annual loading estimated from stormwater runoff, assuming no

previous accumulation of pyrethroids in the sediments. Even without assuming degradation, a large fraction of pyrethroids likely resides in freshwater sediments upstream of SCB embayments, which is consistent with previous reports of higher concentrations in freshwater sediments (Brown *et al*. 2010, Jiang *et al*. 2011). Another explanation for the lack of mass balance in SCB embayments is the advection of stormwater inputs out of estuaries and bays, as evidenced by the presence of particulate-laden freshwater plumes extending as far as 30 km offshore (Ahn *et al*. 2005).

Of the estimated 36 kg of pyrethroids that reside in SCB embayment sediments, the greatest mass (46%) occurred in marinas and the least mass (1%) in ports (Table 3). However, a disproportionately greater accumulation of pyrethroids was observed in both the marina and estuary strata relative to their areas. The DAF values indicated that four times the mass resides in marina and estuary strata relative to their area. In contrast, bays accumulated approximately half of the mass expected based on an equal distribution according to area.

Toxicity Potential

Toxic units based on individual pyrethroid LC_{50}s derived for *E. estuarius* ranged from 0 to 5.8 (Figure 4), and 14 of the 155 samples had TUs greater than unity. The maximum TU was calculated for a sample from the Ballona Creek estuary. In a sediment sample from a previous study in San Diego Bay (Anderson *et al*. 2010), calculated pyrethroid TU (sum of bifenthrin, permethrin and cyfluthrin) based on *E. estuarius* was 21.7. In another pilot study of sediments from Ballona Creek (Lao *et al*. 2010), the calculated pyrethroid TU (sum of bifenthrin, permethrin, cyfluthrin and cypermethrin) based on *H. azteca* ranged from 1.1 to 29.8 and exhibited high spatial and temporal variations. Thus, using these

Table 3. Disproportionate accumulation factors (DAF) for total pyrethroid mass in sediments from embayments in the Southern California Bight.

	Area %	Mass %	DAF
Bay	55.0	29.9	0.54
Port	27.9	1.2	0.04
Marina	11.8	46.1	3.91
Estuary	5.3	22.8	4.29

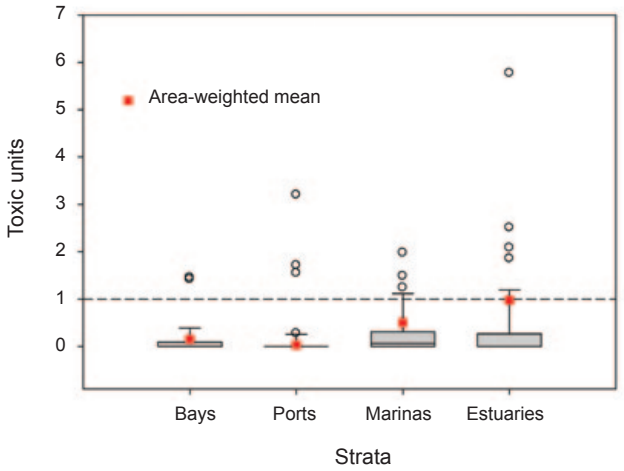

Figure 4. Box plots of toxic units (TUs) for total pyrethroid concentrations (sum of bifenthrin, cyfluthrin, cypermethrin and permethrin) by stratum based on the estuarine amphipod *E. estuarius*. Boxes represent the median, 25th and 75th percentiles, 10th and 90th percentiles, and individual sites beyond the 10th and 90th percentile of TUs. Also shown in square symbols is the area-weighted mean TU of total pyrethroid concentration for each stratum. The dashed reference line represents TU = 1.

TUs and *H. azteca* LC_{50} data, the pyrethroid TU based on *E. estuarius* could be estimated ranging from 0.59 to 31.2. Notably, the maximum TU for the current study was lower than that for the two earlier site-specific studies, reflecting spatial and temporal variability in coastal environments.

Approximately 9% of the total SCB embayment area, and a relatively large extent of the estuarine (32.2%) and marina (26.2%) strata compared to port (0.3%) and open bay (7.9%) strata, had a TU greater than unity. Furthermore, TUs exceeding unity were in 26.7% total pyrethroid detectable-area. Similarly, within the pyrethroid-detectable area of each stratum, TUs exceeding unity were in 64.4, 40.3, 22.1, and 2.1% for estuary, marina, bay, and port strata, respectively. The estuary stratum had the greatest AWM TU (0.98 ±0.82) of the four strata (Figure 4).

Bifenthrin was the dominant contributor to the pyrethroid TUs in SCB embayment sediments (Table 2). In contrast to being a dominant component in total pyrethroid concentration, permethrin had negligible contribution to the TUs due to its relative low toxicity (17 and 54 times less toxic than bifenthrin and cyfluthrin, respectively, based on LC_{50} values for *E. estuarius*). Cyfluthrin was the second highest contributor to TUs and approximately three times more toxic than bifenthrin.

The Ballona Creek estuary sediment sample with the highest TU also exhibited a high degree of toxicity based on *E. estuarius* 10-day mortality (97%) of. However, the overall predicted toxicity based on TUs did not correlate to observed sediment toxicity (% mortality) for *E. estuarius* (r_s = 0.129; p = 0.110; n = 155, Figure 5). Amphipod mortality was ≤25% relative to controls for 13 sediments with TUs that ranged from 1.0 to 3.2 with no clear relationship between total pyrethroid TUs and *E. estuarius* toxicity. In contrast, *E. estuarius* mortality ranged from 0 to 41% relative to controls when pyrethroids were not detectable (TU = 0).

Several factors may have contributed to the lack of correlation between predicted and observed toxicity in this study. Where toxicity was observed, but not predicted based on pyrethroid TUs, the presence of other contaminants may have acted as toxicants. Estuarine and marina sediments in the SCB are known to have a complex mixture of organic and inorganic toxicants, including petroleum, chlorinated hydrocarbons, and trace metals (Tiefenthaler *et al*. 2008). Anderson *et al*. (2010) reported that pyrethroids only partially contributed to the sediment toxicity observed for *E. estuarius* in San Diego Bay based on toxicity identification evaluation procedures. Other investigators have found toxicity in SCB embayments prior to the onset of widespread pyrethroid applications (Fairey *et al*. 1998).

Both chemical and toxicological factors may have contributed to instances where toxicity was predicted but not observed. Uncertainties in both the chemical and toxicological test methods may have contributed to variability as great as ±30%. Although a comprehensive quality assurance and quality control approach that included analysis of blanks and matrix spikes was instituted, the lack of an appropriate standard or certified reference sediment material makes it difficult to fully validate any pyrethroid method, particularly at low (µg/kg) concentrations. The LC_{50} values used to generate TUs may also contribute uncertainty due to the limited scope of sediments utilized. For example, LC_{50} values of bifenthrin, permethrin and cypermethrin for *E. estuarius* were determined in formulated sediment (salinity = 20‰; TOC = 0.78%) that may not accurately represent chemical partitioning among dissolved and particulate phases (Anderson *et al*. 2010) or the diversity of natural sediment encountered in this study. While this is somewhat accounted for by TOC normalization, there may be other ameliorating factors in natural sediment (i.e., presence of pore water dissolved organic carbon) that were not present during the initial dosing experiments with *E. estuarius*. Furthermore, calculating LC_{50} values from freely dissolved porewater concentration estimates has been shown to yield results with lower variability (Hawthorne *et al*. 2005, Xu *et al*. 2007). Another complicating factor in using laboratory-derived LC_{50}s for predicting *in situ E. estuarius* toxicity may be temperature or the presence of antagonistic/synergistic compounds (i.e., piperonyl butoxide) that are known to alter the toxicity of pyrethroids (Weston *et al*. 2006). Moreover, variability could be increased based on differences in potency for chiral enantiomers of the same parent pyrethroid compound (Liu *et al*. 2005).

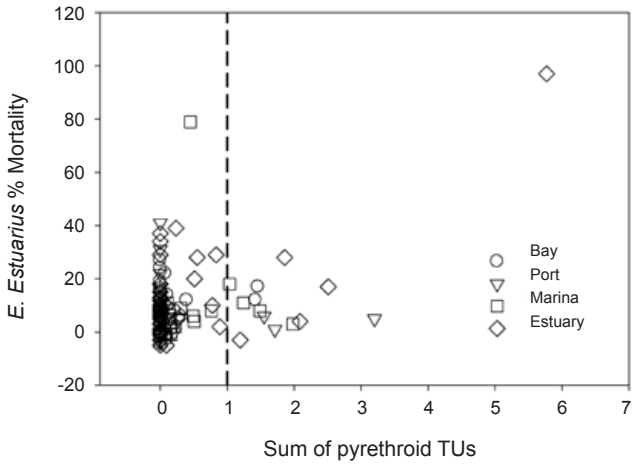

Figure 5. Percent mortality of *E. estuarius* in 10-day whole sediment toxicity tests versus TUs for total pyrethroid concentration (sum of TUs for bifenthrin, cyfluthrin, cypermethrin and permethrin) from sediments collected in embayments of the Southern California Bight.

One final confounding factor may be the bioavailability of pyrethroids in urban sediments (You *et al*. 2008, Hunter *et al*. 2009). Bondarenko *et al*. (2007) reported that the freely dissolved (or "bioavailable") concentration of pyrethroids using solid-phase microextraction (SPME) was only a small fraction of the total pore-water concentration determined by liquid–liquid extraction in a marine sediment. Slightly negative correlations between pyrethroid availability and black carbon content in sediment have also been observed (Yang *et al*. 2009). In general, little is currently known of the true pyrethroid bioavailability across aquatic sediments, particularly sediments that have been profoundly impacted by human activity.

The inconsistencies observed in the current study's attempts to correlate predicted pyrethroid toxicity to laboratory-measured toxicity have also been observed by other investigators. For example, earlier studies observed poor relationships between toxicity to the freshwater amphipod, *H. azteca* and predicted sediment toxicity with pyrethroid TUs between 1 and 5 (Amweg *et al*. 2005, 2006; Weston and Lydy 2010). Further, in Hintzen *et al*. (2009) <30% *H. azteca* mortality was observed after exposure to sediments from an urban stream in central Texas with pyrethroid TUs ranging between 1 and 3. On the other hand, most studies to date have found that sediments with pyrethroid TUs >5 are nearly always highly toxic to amphipods (Weston *et al*. 2005; Amweg *et al*. 2005, 2006; Hintzen *et al*. 2009; Domagalski *et al*. 2010; Lao *et al*. 2010;).

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Supplemental Information

Supplemental info available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2011AnnualReport/ar11_SupplementalInfo_Pyrethroids.pdf