Title

Pyrethroid pesticide transport into Monterey Bay through riverine suspended solids

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Abstract

The three largest coastal rivers discharging to Monterey Bay, the Salinas, Pajaro, and San Lorenzo Rivers potentially serve as a route of transport of pyrethroids and other pesticides into the shelf waters of Monterey Bay and deeper areas within Monterey Canyon. Suspended sediment samples from the lower reaches of the rivers were collected over several rain events in the winters of 2007/2008 and 2008/2009, and analyzed for pyrethroids and one organophosphate pesticide. Bed sediments from Elkhorn Slough, Monterey Bay, and Monterey Canyon were also analyzed for these same substances. Nearly all suspended sediments contained measurable pyrethroids, with the pyrethroids bifenthrin and permethrin being the most commonly detected. The differences in pyrethroid composition between the rivers, some with predominantly an agricultural watershed and some with substantial urban influence, were relatively minor reflecting the broad uses for many of the insecticides within this class. While it is clear that all three coastal rivers are introducing substantial amounts of pyrethroids into coastal waters, there is sufficient degradation and/or dilution with uncontaminated material such that bed sediments in Monterey Bay and Monterey Canyon contained no quantifiable pyrethroids. Toxicity to sensitive invertebrates due to pyrethroids is likely in the bed sediments of the lower reaches of the Salinas River, and potentially the other rivers, but pyrethroid-related toxicity is not likely in Elkhorn Slough or adjacent coastal waters.

Introduction and Problem Statement

Pyrethroid pesticides are current use insecticides, applied for agricultural purposes, urban pesticide management, and landscaping. Due to the withdrawal of some of the most widely used organophosphate insectides, pyrethroid use has been on the rise, with 419,000 kg used by professional applicators in 2007 (http://www.cdpr.ca.gov). This figure does not include retail sales and private homeowner use, since such data are not publicly reported. However, it is assumed that household uses are quite significant, as pyrethroids dominate insecticide sale at retail stores.

Unlike organophosphates, pyrethroids are highly hydrophobic, with log K_{ow}s in the range of 5-7 (Laskowski, 2002). This hydrophobicity results in the quick adherance of the chemicals to the organic carbon in sediment. Once applied, the major forms of degradation are photodegradation and biodegradation. Depending on conditions, degradation may take weeks to years. Those pyrethroids that have not degraded are most often transported from land into water via suspended solids carried by irrigation or stormwater runoff. These pyrethroid-loaded sediment particles can then affect downstream aquatic communities.

The Salinas River watershed is one of the richest agricultural areas in California. Several major urban areas are in the watershed, over 65% of the area is rangeland and pastureland, and 20% is agricultural. However it is the intense agriculture found in the Salinas Valley and the wide variety of crops grown there that have earned it the name, "America's Salad Bowl." Previous work has highlighted the possibility that pyrethroids used in the area could cause toxicity to freshwater invertebrates and these insecticides have been found in river sediments (Anderson et al., 2003, Anderson et al., 2006). Pyrethroid pesticides have indeed been finding their way into the Salinas River tributaries and have been pinpointed as the cause for toxicity in 80% of samples taken in and around the city of Salinas (Ng et al., 2008). While transport from areas of application into the river was confirmed to occur over short distances, further transport downstream and possibly into the marine environment has not been studied.

The Salinas River is a coastal river, delivering approximately 1,955,625 m^3/yr of sediment to Monterey Bay (Eittreim et al., 2002). It is the largest of three major rivers that drain into the Monterey Bay. While the Salinas River is the largest and probably the cause for most concern with regards to pesticide use due to the amount of agriculture and urban development, two other rivers may also be of significance. The Pajaro River watershed, while much smaller than the Salinas River watershed and contributing only 297,500 m^3/yr of sediment to the Monterey Bay (Eittreim et al., 2002), is also known for it's agriculture, which comprises about 25% of the watershed area. The San Lorenzo watershed is mostly forested, with areas of urban development and residential use, including the city of Santa Cruz. This watershed contributes 212,000 m^3/yr of sediment to Monterey Bay (Eittreim et al., 2002), however, due to the concentrated urban area right on the coast, it makes for a good contrast to the previous two, more agricultural, watersheds.

These three major watersheds surrounding Monterey Bay are of specific interest due to their direct influence on the Monterey Bay National Marine Sanctuary. The National Marine Sanctuary is a federally protected marine area just offshore of the California central coast, boasting one of the world's most diverse ecosystems. The land uses adjacent to the Marine Sanctuary are closely monitored and regulated. However, in 2007, Santa Cruz County used 836,000 kg of pesticides and Monterey County used 3,937,000 kg, both increases in use over 2006, while most counties in California reported a decrease. The very fertile lands and favorable weather conditions also mean that year-round farming is possible in the Monterey Bay area. The combination of increased pesticide use with year-round farming and pesticide applications could be a cause for concern about the possibility of transport of pesticides into the marine environment. Some of the most heavily pyrethroid sprayed crops, such as strawberries, broccoli, spinach, lettuce, celery, and artichokes, are commonly grown in the area.

Urban areas are an additional source of pyrethroids. Pyrethroids are heavily used in urban areas, for landscape management or protection of structures. Landscape applications are done mainly in the spring and summer months when people spend the most time outdoors, though structural use occurs year-around. For both urban and agricultural applications, summer irrigation can transport pyrethroids into creeks and rivers. However, the major transport probably occurs with runoff events during winter rains.

During a major runoff event, the major routes for sediment transport are the three major rivers: the San Lorenzo, Pajaro, and Salinas Rivers. As stated, the sediment loads from each river are considerable, and potentially that sediment carries with it highly hydrophobic pyrethroid pesticides. Sediment from the rivers first enters the Bay and then deposits on the continental shelf. The major accummulation of the most organic rich sediments are found at the 80 meter isobath on the continental shelf, after which there is a steep drop into the Monterey Canyon. If any pyrethroids were to be found in the marine environment, it would be in these most recently deposited surface sediments, and those with the highest organic carbon content. These sediments can be found at the 80 meter isobath, and then further in the marine environment, in the deep sea Monterey Canyon. Testing the sediments from all these areas, from the rivers to the continental shelf and to the deep sea canyon is important, since the quality of recently deposited riverine sediment is of great importance to the benthic community of Monterey Bay.

Objectives

The objectives of this study were two-fold:

1. To determine the concentrations of pyrethroids in suspended solids in three major rivers in the Monterey Bay.
2. To determine the concentrations of pyrethroids in bed sediments in depositional areas extending from coastal estuaries to the deep sea.

Procedure

Samples collected

River water samples were taken at bridges on the the San Lorenzo (36°58'32.41"N, 122° 1'23.32"W), Pajaro (36°52'47.68"N, 121°47'35.40"W), and Salinas (36°43'53.56"N, 121°46'56.95"W) Rivers during the major winter rain events in 2008 and 2009 to test suspended solids for pyrethroid pesticides. It was thought that these major storms would transport the highest amounts of pyrethroids via suspended solids into the Monterey Bay. All bridges were about 3 km away from the Bay. These three sites were chosen for easy bridge access and close proximity to the mouth of the river to allow for an integration of the whole watershed right before entrance of water and riverine sediments into the Bay, but without major tidal influences. Water samples were taken using a solvent cleaned stainless steel metal bailer, and then transferred into stainless steel kegs for transport. The heaviest rain events for the 2007-2008 rain year and the bulk of the sampling occurred on January 4 and January 26-28, 2008 at all three rivers. On Febuary 27 only the San Lorenzo and Pajaro Rivers were sampled due to low rainfall in the Salinas River watershed. Winter runoff events for the 2008-09 rain year were sampled on November 2, 2008 (San Lorenzo); February 15-17, 2009 (San Lorenzo and Pajaro); and March 3-5, 2009 (all three rivers). Most of the samples represented a single time point, though a few samples were composited from water samples obtained at two time points within a given runoff event (up to 48 h between samples). Water temperature was recorded and a subsample of water for total suspended solid analysis was taken for each sample event. Water samples were brought into the laboratory and stored at 4° C. Within 24 h, the suspended solids were extracted from the water samples using a continuous flow-through centrifuge (at 10000 rpm) processing water at 0.75 L/min. Water was discarded, the sediment was recovered from the centrifuge and stored at -20° C.

Riverine suspended solids ultimately are transported into the ocean, deposit to the bay sediments, and are incorporated into the bed material. The finest sediments and highest amounts of sediment deposition is known to occur around the 80 meter isobath of the continental shelf of the Monterey Bay (Eittreim et al., 2002), so a transect along the 80 meter isobath was sampled to make sure the most recently depositied sediment was sampled for the analysis. Another transect along the 40 meter isobath was taken as a halfway line between the coast and the area of deposition. Finally, to determine the influence of each river into the Monterey Bay, transects were taken coming out of the mouth of each river to show the influence of each river into the Monterey Bay (Figure 1). Benthic marine grab samples were taken with a modified Van Veen grab sampler on April 15-18, and May 16, 2008. Two centimeters were skimmed from the top of each grab using a stainless steel spatula, transferred into a solvent cleaned glass jar, and stored at 4° C. In the lab, the samples were homogenized by hand mixing and subsampled for chemical analysis. Sediment was transferred into amber glass jars and stored at -20° C.

Historic bed sediment samples were obtained from the CCLEAN program (CCLEAN, 2007). Their archived samples along the 80 meter isobath had been collected in the fall, spanned the years of 2000 to 2006, and had been stored at -20° C. Those chosen for chemical analysis were obtained from collections made in October 2005 and November 2006. Those two dates were after relatively high precipitation in the previous winters, and it was assumed that these two years would have the highest pyrethroid transport to the shelf. The 2007/2008 water year after which shelf sediments were collected for the present study, had half the precipitation as had occurred in early 2005 and 2006 as represented by the archived samples.

To determine if riverine pyrethroids were reaching the deep sea, 9 sediment samples from the Monterey Canyon were collected. Canyon samples were obtained at water depths typically from 1000-3000 m. Sediment cores were taken with plastic tubes about 40 cm long, and 8 cm in diameter using the ROVs Tiberon and Ventana during July to December, 2007. The push cores were pushed about 2/3 of the way into the sediment, locked and retrieved. On board ship, cores with minimal biotic disturbance were used for chemical analysis. Sediment was extruded from the cores, and the top 1-2 cm of sediment was used for pyrethroid analysis, assuming it to be the most recently deposited.

To test for estuarian influences of pyrethroids, samples were taken at sites at the Elkhorn Slough Research Reserve on June 5, 2008 (Figure 2). This slough is mainly influenced by the Salinas River. At most times the Salinas River flows into the Old Salinas River, then north to the south end of Elkhorn Slough. During high flow events, the Salinas River breaches the Salinas beach and bypasses the Slough. Samples were taken from places with the highest amount of freshwater influence, down to the mouth of the estuary. The top 1 cm of surface bed sediment was collected with a stainless steel spatula and stored in a solvent cleaned glass jar. In the laboratory, the sediment was homogenized by hand mixing and subsampled for chemical analysis.

Chemistry procedures

Frozen sediment samples were thawed, homogenized, and then freeze-dried to remove excess water (You et al., 2008). About 3-5 grams of dry sediment was mixed with 2 grams of treated copper, 5 grams of silica, and about 30 grams of diatomaceous earth in a stainless steel Accelerated Solvent Extractor cell. A 1:1 (v/v) methylene chloride-acetone mixture was run through a Dionex 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA) for the sediment extractions. Extracts were dried with about 12 g of anhydrous Na_2SO_4 and concentrated to 1 ml in a TurboVap II evaporator (Zymark, Hopkinton, MA) under a constant stream of N_2 gas, 50° C, and 15 psi. Further clean-up was performed by passing the extract through a Envi-Carb II/PSA Solid Phase Extraction column. After solvent exchange, the elutant was then concentrated to 1 ml under a gentle stream of N_2 using a Pierce Model 1878 Reactivap™ (Rockford, IL). Further clean-up with copper was necessary for a number of samples. Analysis of final extracts was done with an Agilent 6890 series gas chromatograph with an Agilent Technologies 7683 autosampler and micro-electron capture detector (GC-ECD, Agilent Technologies, Palo Alto, CA). Two Agilent columns were used to confirm analytical results: an HP-5MS and a DB-608. Samples were analyzed for the organophosphate chlorpyrifos and eight pyrethroids including bifenthrin, lambda-cyhalothrin, esfenvalerate, deltamethrin, permethrin, cyfluthrin, cypermethrin, and fenpropathrin. The quantification limit was 1 ng/g on a dry weight basis.

Results

Given the hydrophobicity of pyrethroids they will preferentially partition into sediments high in organic carbon, and therefore finer grained material is likely to contain higher concentrations and is most commonly used for monitoring purposes. Our samples along the 80 m isobath were specifically chosen because historical data had indicated it is the area of deposition for the finest grained material in Monterey Bay. As expected, these sediments were relatively muddy with relatively high levels of silt and clay (39-96% silt/clay; median =87%; Appendix 1). Shallower shelf sediments from 20-60 m depth and closer to the mouths of the rivers contained sandier material (2-65% silt/clay; median =33%). Most estuarine sediments were relatively muddy, though with a couple exceptions (3-97% silt/clay; median =46%), as were the deep canyon samples though quantitative data are lacking for this group of samples.

Chlorpyrifos was detected in all suspended solid samples (Table 1), while pyrethroids were found in all but one suspended sediment sample (Pajaro River sample from February 15, 2009). Bifenthrin was the most commonly detected pyrethroid, with concentrations up to 21.6 ng/g. Permethrin was the second most common pyrethroid, found in all but two suspended solid samples in 2008 and not at all in 2009. It was also the pyrethroid with the highest concentration, of 83.0 ng/g (Salinas River, Jan. 4, 2008). In fact, that sample also showed the highest amount of cypermethrin (23.4 ng/g) and esfenvalerate (42.0 ng/g). These data are from suspended sediments to which macrobenthic organisms would not be directly exposed prior to their deposition, but to help put these concentrations in a toxicological context, they can be compared to thresholds for toxicity to several amphipod species. Assuming an organic carbon content of about 1%, these concentrations are all well over the LC_{50} for both the freshwater amphipod, Hyalella azteca, which has 10-d LC_{50}s of 2-5 ng/g for several pyrethroids (Amweg et al., 2005) and the marine amiphod, Eohaustorius estuarius, which has LC_{50}s for several pyrethroids of about 10 ng/g (Anderson et al., 2008).

No pyrethroids were found in the Elkhorn Slough estuary. However, just upstream of the Slough, in the Old Salinas River, there were two sites that had detectable amounts of pyrethroids. Site ESP had all all pyrethroid analytes present except for cyfluthrin. The highest concentration of pyrethroid was 19.7 ng/g esfenvalerate, an indication of agriculture since this compound has little urban use. Site ESM contained chlorpyrifos, bifenthrin, and esfenvalerate, with the highest concentration being 35.6 ng/g of esfenvalerate. Given the pyrethroid sensitivity studies noted above, sediments at both these sites would be expected to be acutely toxic to at least H. azteca.

On the continental shelf, six archived bed sediment samples from 2005 and 2006 were analyzed from Monterey Bay at the 80 m isobath. There were no detectable pyrethroids in any of these samples. During the 2008 sampling year, 25 samples were taken throughout the Monterey Bay continental shelf, from the 80 m isobath and shallower. None of these samples showed detectable pyrethroids. Finally, all nine deep sea samples taken from Monterey Canyon also contained no detectable pyrethroids.

Conclusions

The Salinas, Pajaro, and San Lorenzo River all act as sources of pyrethroid pesticides to Monterey Bay. Nearly all suspended sediment samples from the rivers, extending over multiple rain events and multiple years, contained pyrethroids. The pyrethroid bifenthrin was of greatest concern, both because of its frequency of detection, and the frequency at which concentrations on suspended sediment exceeded toxicity thresholds for some benthic invertebrates were that material to be incorporated in bed sediments.

There were relatively minor differences in the pyrethroids associated with suspended sediment from the three rivers, despite the fact that two of the rivers have a predominantly agricultural watershed (Salinas and Pajaro) and one was primarily urban (San Lorenzo). Lambda-cyhalothrin, fenpropathrin and esfenvalerate are primarily agricultural pesticides with only minor urban use, and were entirely or largely absent in suspended sediments from the San Lorenzo River, draining urban areas surrounding Santa Cruz, CA. However, the other pyrethroids have broad uses, incorporating both agricultural and urban pest control. With such compounds it is often difficult to determine if they are of agricultural or urban origin (Ng et al., 2008), complicating efforts to control sources and mitigate environmental impact.

The three rivers surrounding Monterey Bay are clearly introducing pyrethroid pesticides into the Bay with each runoff event. Given that the three rivers combined provide approximately 2.5 million m^3/yr of sediment to Monterey Bay (Eittreim et al., 2002), and our data show this sediment commonly contained 10-50 ng/g pyrethroids, the amount of pesticides entering marine waters is considerable. Yet despite this input, no pyrethroids were measurable in the bed sediments on the shelf or in the deep canyon. The limited analysis of archived sediments from previous years with twice the annual rainfall suggests the absence of pyrethroid in shelf sediments is not limited only to the relatively dry sampling year of the present study.

The presence of pyrethroids on suspended sediment entering Monterey Bay, but their absence in the bed sediment where this suspended material is ultimately deposited, is likely due to two factors. First, dilution probably plays a major role. While still in the water column, the riverine sediments are likely diluted with other suspended material moving into Monterey Bay from other coastal areas to the north and south, and potentially containing lower concentrations of pyrethroids. Upon deposition, these sediments are further diluted by biological and/or physical mixing with the bed material already in place. Our sampling procedures skimmed off the top 1-2 cm of the sediment column, but this procedure virtually assured that the material collected represented an integrated sample representing a lengthy period of deposition (i.e., years), rather than only the most recently deposited material that may have had greater pyrethroid content.

Second, pyrethroid degradation may have played a role. Bifenthrin, the pyrethroid most commonly found on the suspended material, has a half-life once adsorbed to sediment of 1-2 yr. Most other pyrethroids, however, have sediment half-lives in the range of 3-6 months (Gan et al., 2008). Most of our shelf samples were collected in April, immediately after the end of the rainy season (November to March) when most of the suspended sediment would be discharged from the rivers to the Bay. But even so, there could have been loss of half of most pyrethroids since the time of discharge. Even for bifenthrin, while residues from the just-ended rainy season would remain, there would be substantially reduced residues remaining from deposition in previous years. DDT originating from farmlands surrounding Monterey Bay is known to occur not only in shelf sediments but in the deep canyon (Paull et al., 2002), though this pesticide is far more persistent than the pyrethroids.

Suspended sediments containing pyrethroids do appear to be depositing in the lower reaches of the Salinas River just upstream of its entry into Elkhorn Slough. Sediment concentrations of pyrethroids in this area exceeded toxicity thresholds for H. azteca, a species commonly used for sediment toxicity testing. However, in Elkhorn Slough itself, and in adjacent coastal areas, bed sediments contained no measurable pyrethroids.

Potential toxicity to benthic organisms appears limited to bed sediments in the rivers themselves, rather than the marine waterbodies into which they discharge. Water column toxicity, though not addressed by the present study, is also a potential concern, as it has recently been shown pyrethroids can be in sufficient concentration in the water column to cause toxicity to sensitive invertebrates (Weston and Jackson, 2008; Weston and Lydy, in press). Such toxicity, if it occurs, would likely be limited to freshwater environments within the rivers, and diluted out upon mixing with marine waters.

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Publications arising from the present study

One publication is in preparation and will be submitted early 2010.

Table 1. Concentrations (ng/g dry weight) of pesticides in suspended sediments of the three rivers studied and bed sediments in Elkhorn Slough estuary and tributaries. Concentrations less than the reporting limit (1 ng/g) are shown as zero. LC_{50} values for several amphipod species widely used for sediment toxicity testing are shown to provide a frame of reference.[1]

		Chlor	Bifen	Fenpr	Cyhal	Perm	Cyflu	Cyper	Esfen	Delta
SUSPENDED SEDIMENT (2007/2008 rainy season)										
San Lorenzo	1/4/2008	7.4	1.7	0	0	0	0	0	0	0
San Lorenzo	1/26/2008	1.0	4.1	0	3.7	36.0	0	0	0	0
San Lorenzo	2/24/2008	4.7	10.6	0	0	30.1	0	0	0	
Pajaro	1/4/2008	5.9	5.3	3.6	0	30.4	0	6.8	0	0
Pajaro	1/28/2008	26.1	21.6	5.3	1.1	33.1	0	0	0	0
Pajaro	2/24/2008	14.0	12.1	0	4.6	0	0	0	0	0
Salinas	1/4/2008	17.8	14.0	0	7.6	83.0	0	23.4	42.0	0
Salinas	1/27/2008	23.4	1.1	0	0	24.9	0	0	0	0
SUSPENDED SEDIMENT (2008/2009 rainy season)										
San Lorenzo	11/2/2008	3.3	10.6	0	0	0	0	0	0	0
San Lorenzo	2/15-16/09	6.5	12.2	0	0	0	0	0	0	0
San Lorenzo	3/3-5/09	3.5	6.1	0	0	0	0	0	0	0
Pajaro	2/15-17/09	16.7	0	0	0	0	0	0	0	0
Pajaro	3/3-5/09	12.7	11.2	7.6	4.1	0	0	0	0	0
Salinas	3/5/2009	40.9	3.8	0	3.0	0	0	0	2.1	0
ELKHORN SLOUGH										
ESS	6/5/08	0	0	0	0	0	0	0	0	0
ESK	6/5/08	0.7	0	0	0	0	0	0	0	0
ESD	6/5/08	0	0	0	0	0	0	0	0	0
ESV	6/5/08	0	0	0	0	0	0	0	0	0
ESP	6/5/08	12.3	6.4	4.5	2.7	17.8	0	4.5	19.7	1.8
ESM	6/5/08	5.8	1.7	0	0	0	0	0	35.6	0
REPORTED 10-d SEDIMENT LC_{50} VALUES[2]										
Hyalella azteca		18-42	5.2	22	4.5	108	10.8	2-6	15.4	7.9
Eohaustorius estuarius			8			140		11		
Ampelisca abdita			948			8913		469		

[1]Chlor=chlorpyrifos, Bifen=bifenthrin, Fenpr=fenpropathrin, Cyhal= Lambda-cyhalothrin, Perm=permethrin, Cyflu= cyfluthrin, Cyper=cypermethrin, Esfen=esfenvalerate, Delta=deltamethrin.
[2]Sediment LC_{50} data from Maund et al., 2002; Amweg et al., 2005; Amweg and Weston, 2007; Anderson et al., 2008; Weston et al., 2009. Some of these sources provide organic carbon normalized LC_{50}s, and these data have been converted to dry weight in the table assuming 1% organic carbon.

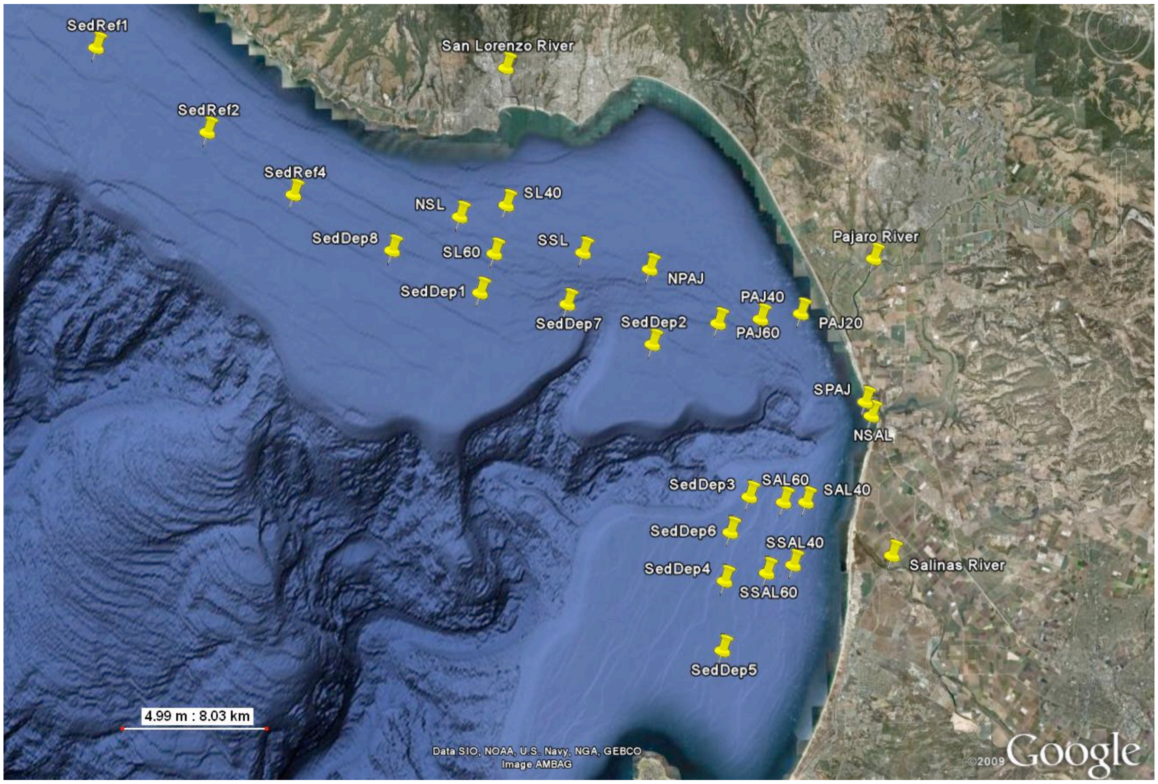

Figure 1. Location of sampling sites on the Monterey Bay continental shelf and near the mouths of the Salinas, Pajaro and San Lorenzo Rivers.

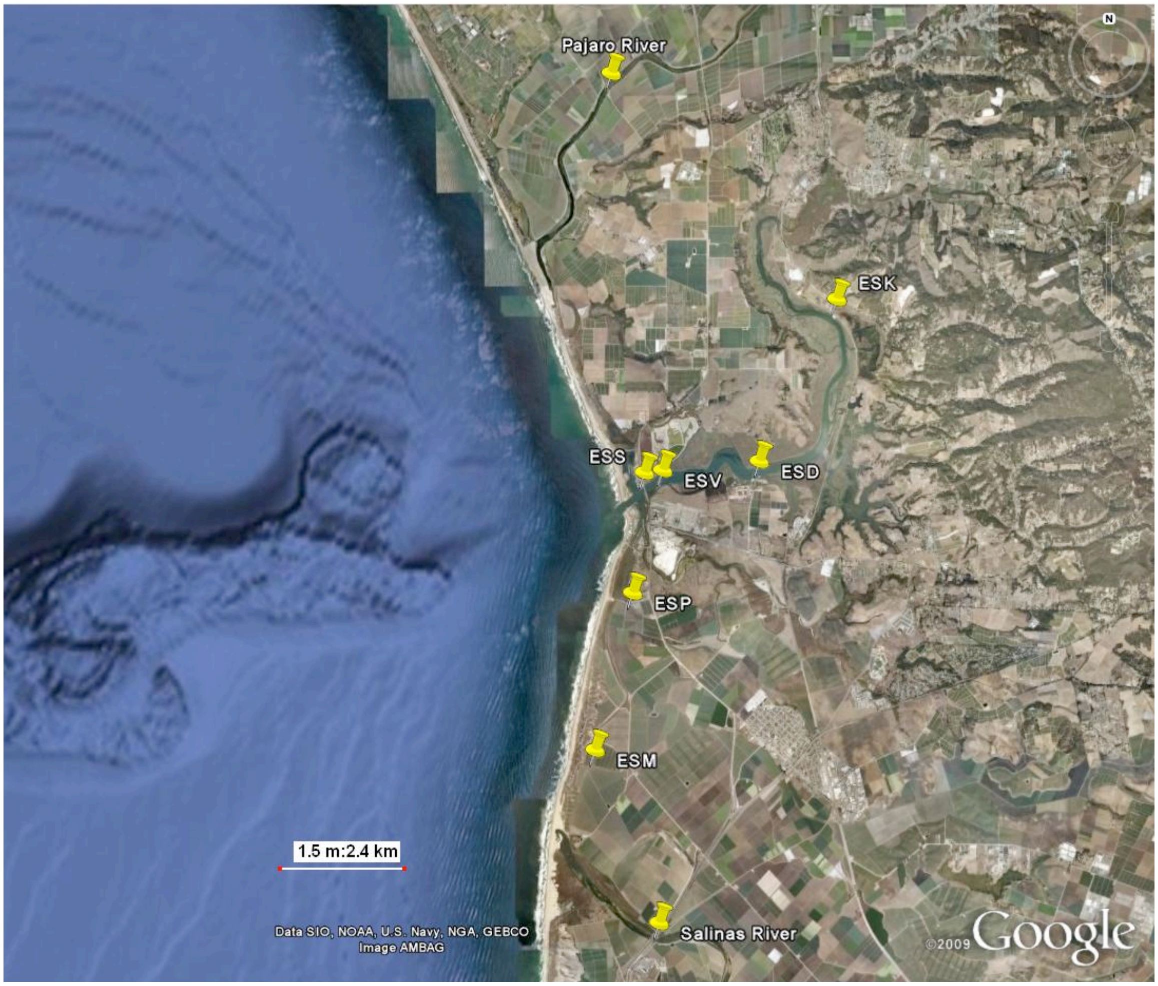

Figure 2. Location of sampling sites in the Old Salinas River (ESM, ESP) and the Elkhorn Slough estuary. The single sites in each of the Salinas and Pajaro Rivers are the same as on Figure 1.

Appendix 1. Bed sediment samples used for pyrethroid analysis.

Site	Collection date	Water depth (m)	Latitude	Longitude	silt and clay (%)
ELKHORN SLOUGH					
40 ESK	6/5/08	intertidal	36° 50.430'	-121° 44.636'	92.1
41 ESD	6/5/08	intertidal	36° 48.730'	-121° 45.648'	66.3
44 ESV	6/5/08	intertidal	36° 48.635'	-121° 46.911'	2.7
39 ESS	6/5/08	intertidal	36° 48.610'	-121° 47.150'	15.1
47 ESP	6/5/08	intertidal	36° 47.427'	-121° 47.485'	97.4
53 ESM	6/5/08	intertidal	36° 45.703'	-121° 47.789'	25.7
CONTINENTAL SHELF					
SedDep05	4/17/08	83	36° 41.063'	-121° 53.372'	39.1
SedDep06	4/17/08	81	36° 44.437'	-121° 52.882'	86.7
SedDep07	4/15/08	83	36° 51.449'	-121° 59.047'	75.7
SedDep08	4/16/08	81	36° 53.084'	-122° 05.438'	91.9
SAL30	4/16/08	33	36° 46.263'	-121° 50.004'	2.2
SAL50	4/16/08	52	36° 45.503'	-121° 51.039'	13.4
SSAL40	4/17/08	41	36° 43.616'	-121° 50.632'	3.8
SSAL60	4/17/08	61	36° 43.371'	-121° 51.496'	33.4
PAJ20	4/16/08	20	36° 51.156'	-121° 50.316'	2.6
PAJ40	4/16/08	41	36° 50.979'	-121° 51.810'	18.2
PAJ60	4/15/08	61	36° 50.872'	-121° 53.489'	62.3
SL40	4/16/08	42	36° 54.457'	-122° 01.357'	39.2
SL60	4/16/08	59	36° 52.968'	-122° 01.801'	65.2
NSAL	4/17/08	27	36° 48.084'	-121° 47.756'	1.6
SPAJ	4/15/08	30	36° 48.52'	-121° 48.151'	No data
NPAJ	4/15/08	49	36° 52.504'	-121° 55.860'	50.1
SSL	4/16/08	51	36° 52.770'	-121° 58.472'	46.1
NSL	4/16/08	54	36° 54.090'	-122° 03.117'	54.1
SedRef1	4/18/08	82	36° 59.155'	-122° 16.800'	39.4
SedRef2	4/18/08	81	36° 59.155'	-122° 12.610'	81.1
SedRef4	5/16/08	83	36° 54.746'	-122° 09.380'	88.8
SedDep1	4/18/08	81	36° 59.155'	-122° 02.366'	88.0
SedDep2	5/16/08	80	36° 50.245'	-121° 55.871'	95.5
SedDep3	5/16/08	80	36° 45.670'	-121° 52.283'	82.8
SedDep4	4/17/08	80	36° 43.251'	-121° 53.214'	94.0
PREVIOUSLY ARCHIVED SHELF SAMPLES					
SedDep1	10/30/05	81	36° 59.155'	-122° 02.366'	32
SedDep2	10/30/05	80	36° 50.245'	-121° 55.910'	89
SedDep3	10/30/05	80	36° 45.670'	-121° 52.290'	92
SedDep4	10/30/05	80	36° 43.145'	-121° 53.225'	94
SedDep1	10/24/06	81	36° 59.155'	-122° 02.366'	93
SedDep3	10/24/06	80	36° 45.670'	-121° 52.290'	90

Appendix 1 (continued)

MONTEREY CANYON[1]					
22-1	9/12/07				No data
35-1	8/2/07				No data
2-1	8/2/07				No data
1126	9/5/07	3165	36° 14.381’	122° 55.152’	No data
1133	9/9/07	1133	36° 06.663’	121° 52.789’	No data
62-1	9/10/07	1856	36° 42.135’	122° 06.226’	No data
3047-2					No data
14-1					No data
62-2	9/10/07	1856	36° 42.135’	122° 06.226’	No data
67-1	9/9/07	3165	36° 14.380’	122° 55.150’	No data

[1]For some of the canyon samples we are currently awaiting date, depth or coordinate data from the Monterey Bay Aquarium and Research Institute. Data are not yet available for inclusion in this report.