Summary of Pyrethroid Monitoring Data, Exceedances of Criteria and Environmental Properties

Summary of Exceedances

Staff evaluated water quality data for exceedances from monitoring sites and surface waters in the Santa Maria valley (Figure 2 and Table 6) and determined that the following surface waters are impaired for pyrethroids pesticides based exceedances of pyrethroid criteria in sediment and in water and therefore included them along with other exceedances found in Table 1 and Table 3 in the TMDL Technical Report.

- <u>Bradley Channel</u>: Criteria for **bifenthrin** were exceeded in two separate sediment samples one at 312BRO and one at 312BCJ.
- <u>Main Street Channel</u>: Criteria for **lambda-cyhalothrin** and **permethrin** were exceeded in two separate sediment samples one at 312MSS and one at 312MSD.
- <u>Orcutt Creek:</u> Criteria for **cyfluthrin** were exceeded in three separate samples, one in the sediment and one in the water column at 312ORC and one in the water at 312GVT.
- <u>Santa Maria River</u>: Criteria for **lambda-cyhalothrin** were exceeded in two separate samples, one in the sediment and one in the water column at 312SMA.
- <u>Blosser Channel:</u> Criteria for **bifenthrin** were exceeded in two separate samples, one in the sediment and one in the water column at 312BCD.

Pyrethroid Sediment Monitoring Data and Exceedances

Staff evaluated pyrethroid sediment monitoring data for exceedances of the Central Coast Basin, Water Quality Control Plan (Basin Plan) narrative objectives for pesticides and toxicity based on numeric sediment targets developed for the TMDL. The Basin Plan does not contain numeric objectives/criteria for pyrethroids. Therefore staff evaluated the sediment monitoring data based on two studies of pyrethroid toxicity to invertebrates in sediment (Amweg et al, 2005) (Maund et al, 2003). The assessment values are found in Table 2 and the pyrethroid sediment monitoring data and assessments are found in Table 1. The organic carbon normalized pyrethroid LC50 values were used as evaluation guidelines for the 303(d) listings in the 2010 Integrated Report (Water Boards, 2011).

Table 1 Pyrethroid concentrations in sediment. Shading indicates concentration greater than criteria (Table 2). Underlined sites and waterbodies had more than one exceedance in either sediment of water phase.

Site and waterbody	Analysis Date	Project ID	Bifenthrin ng/g (ppb)	Cyfluthrin ng/g (ppb)	Cypermethrin ng/g (ppb)	Lambda- Cyhalothrin ng/g (ppb)	Permethrin ng/g (ppb)
312SOL	6/19/2009	Oso_Orcutt	ND	ND	2.3	1.4	ND
312ORC	12/9/2008	Oso_Orcutt	ND	ND	3.5	2.9	ND

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Pyrethroid Analysis

Site and waterbody	Analysis Date	Project ID	Bifenthrin ng/g (ppb)	Cyfluthrin ng/g (ppb)	Cypermethrin ng/g (ppb)	Lambda- Cyhalothrin ng/g (ppb)	Permethrin ng/g (ppb)
Orcutt							
312SMA Santa Maria	12/9/2008	Oso_Orcutt	ND	ND	6.2	14.1	ND
312SMA Santa Maria	6/19/2009	Oso_Orcutt	ND	ND	11	2.4	ND
312GVS Green	6/19/2009	Oso_Orcutt	ND	1.4	3	0.9	ND
312GVT Green	6/19/2009	Oso_Orcutt	ND	0.7	1	1.7	157.5
312OFC Oso Flaco Creek	6/19/2009	Oso_Orcutt	ND	ND	ND	ND	19.8
312OFL Oso Flaco Lake	12/9/2008	Oso_Orcutt	ND	ND	ND	ND	ND
312OFL (Oso Flaco Lake	6/19/2009	Oso_Orcutt	ND	ND	ND	ND	ND
<u>312BRO</u> Bradley	6/19/2009	Oso_Orcutt	83.1	ND	35.8	1.5	122.7
<u>312BCD</u> <u>Blosser</u>	6/19/2009	Oso_Orcutt	375	37.2	58.2	15	1279
<u>312MSS</u> <u>Main</u>	6/19/2009	Oso_Orcutt	21	214	499	125	540
312BCC Bradley	5/25/2010	RWB3_CC WQP	8.5	-0.5	ND	0.7	24.1
<u>312BCJ</u> Bradley	5/25/2010	RWB3_CC WQP	216.4	1.4	5.2	17.9	286.4
312GVS Green	5/25/2010	RWB3_CC WQP	2.9	1.1	0.7	11.1	15.7
<u>312MSD</u> <u>Main</u>	5/25/2010	RWB3_CC WQP	9.4	9.2	4.6	6.7	266.7
312OFC Oso Flaco Creek	5/25/2010	RWB3_CC WQP	15.4	ND	0.6	3	16.5
312OFN Little Oso Flaco Creek	5/25/2010	RWB3_CC WQP	28.2	ND	1.1	1.4	21.4
<u>312ORC</u> <u>Orcutt</u>	5/25/2010	RWB3_CC WQP	0.7	13.8	1.8	2.7	5.1
312ORI Orcutt	5/25/2010	RWB3_CC WQP	3.1	0.7	1.4	3.1	75.5
312SMA Santa M.	5/25/2010	RWB3_CC WQP	ND	0.9	ND	ND	ND

Oso_Orcutt Project ID samples from the UC Davis Santa Maria River Watershed and Oso Flaco Creek Watershed TMDL Monitoring Study RWB3_CCWQP samples from a Central Coast Water Quality Preservation for Irrigated Agriculture Study

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Table 2 Sediment chemistry targets and evaluation guidelines. LC50 indicates median lethal concentration.

Chemical	Concentration ng/g (ppb)	Concentration ug/g OC*(ppm)	Endpoint	Reference
Bifenthrin	12.9	0.52	LC50	(Amweg et al., 2005)
Cyfluthrin	13.7	1.08	LC50	(Amweg et al., 2005)
Cypermethrin	14.87	0.38	LC50	(Maund et al., 2002) mean value
Esfenvalerate	41.8	1.54	LC50	(Amweg et al., 2005)
Lambda Cyhalothrin	5.6	0.45	LC50	(Amweg et al., 2005)
Permethrin	200.7	10.83	LC50	(Amweg et al., 2005)

*Median lethal concentration (LC50) for amphipods (Hyalella azteca) organic carbon normalized concentrations (ug/g OC)

Pyrethroid Water Column Monitoring Data and Exceedances

The Basin Plan contains narrative objectives for pesticides and toxicity and does not contain numeric objectives for pyrethroids in water. Therefore staff evaluated water concentrations of pyrethroid using the TMDL targets as guidelines. The targets are based on criteria developed by UC Davis (Table 4). Pyrethroid water column monitoring data and assessments are found in Table 1. In addition to evaluating the monitoring data based on the guidelines, staff compared the data to EPA aquatic benchmarks for pyrethroids. The monitoring data water column concentrations were measured from whole water samples, which may include concentrations bound to dissolved particles in the water that are less available and toxic. In the criteria reports, UC Davis noted that the freely dissolved concentrations in water only samples maybe the best indicator of toxicity. Staff chose to use the criteria to evaluate whole water samples because the concentrations are many times above the criteria and due to the high concentrations of pyrethroids in sediment, particularly for bifenthrin in Blosser Channel.

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Table 3 Pyrethroid water column concentrations. Shading indicates concentrations greater than UC Davis chronic criteria (Table 4). Underlined values indicate concentrations greater than the EPA Aquatic Life Benchmarks (Table 5). Bold values are below the reporting limit, but above the detection limit.

Site and waterbody	Analysis Date	Project ID	Bifenthrin ng/L (ppt)	Cyfluthrin ng/L (ppt)	Cypermethrin ng/L (ppt)	Lambda- Cyhalothrin ng/L (ppt)	Permethrin ng/L (ppt)
312SOL Orcutt Tributary	2/3/2009	Oso_Orcutt	ND	ND	5.2	1.9	ND
312ORC Orcutt	8/27/200 9	Oso_Orcutt	ND	2.1	ND	0.7	ND
312SMA Santa Maria	2/3/2009	Oso_Orcutt	ND	ND	3.5	<u>2.1</u>	ND
312GVS Green	6/12/200 9	Oso_Orcutt	ND	ND	ND	ND	ND
312GVT Orcutt	8/27/200 9	Oso_Orcutt	ND	2.9	7.2	1.6	7.9
312OFC Oso Flaco Creek	6/12/200 9	Oso_Orcutt	ND	ND	ND	ND	ND
312OFL Oso Flaco Lake	8/27/200 9	Oso_Orcutt	ND	0.9	ND	ND	ND
312BRO Bradley Channel at River Oaks	6/12/200 9	Oso_Orcutt	ND	ND	64.4	ND	ND
312BCD Blosser Channel	2/3/2009	Oso_Orcutt	<u>3.6</u>	ND	ND	ND	ND
312MSS Main Str.	8/27/200 9	Oso_Orcutt	1.4	5.5	18.3	<u>4.3</u>	14.6

Oso_Orcutt Project ID samples from the UC Davis Santa Maria River Watershed and Oso Flaco Creek Watershed TMDL Monitoring Study

Staff developed water column numeric targets and evaluation guidelines based on criteria developed by UC Davis. UC Davis defines numeric criteria as "science-based values, which are intended to protect aquatic life from adverse effects of pesticides, without considerations of defined water body use, societal values, economics or other non-scientific considerations." UC Davis developed a methodology for deriving criteria for pesticides that are not addressed by published EPA guidelines for criteria development (TenBrook et al. 2009). Criteria development was supported by the Central Valley Regional Water Quality Control Board and the goal of the UC Davis methodology is to derive a numeric criteria that meets the Central Valley Basin Plan narrative toxicity objective of maintaining water free of "toxic substances in concentrations that produce detrimental physiological responses in plant, animal, or aquatic life" (CVRWQCB 2004). The Central Valley narrative objective corresponds to the toxicity narrative objective in the Central Coast Basin Plan, which is the basis of the

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TMDL targets. The criteria are based on freely dissolved concentrations in pure water but whole water samples may be assessed for compliance for additional margin of safety for the targets.

Chemical	UC Davis Acute Criteria ng/L (ppt)	UC Davis Chronic Criteria ng/L (ppt)	Reference
Bifenthrin	4	0.6	(Palumbo et al., 2010)
Cyfluthrin	0.3	0.05	(Fojut et al., 2010)
Lambda- Cyhalothrin	1	0.5	(Fojut et al., 2010)

Table 4 Pyrethroid Water Column Numeric Criteria

Staff evaluated EPA Aquatic Life Benchmarks as a suitable toxicity values for the pyrethroid pesticide TMDL aquatic targets (USEPA, 2012). EPA has authority to register pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and EPA's Office of Pesticide Programs (OPP) evaluates the environmental risks of pesticides. OPP develops aquatic life bench marks for pesticides to assess environmental risk to aquatic invertebrates; the aquatic life benchmarks for pyrethroids are summarized in Table 5. The difference between aquatic life benchmarks and water quality criteria is that benchmarks are for specific taxa (e.g. invertebrates or fish) and aquatic criteria are more broadly protective of multiple organisms and the development process is much more complex.

Table 5 EPA Office of Pesticide Programs' freshwater aquatic life benchmarks for pyrethroid pesticides

	Invertebrates				
Pesticide	Acute ¹ ng/L (ppt)	Chronic ² ng/L (ppt)			
Bifenthrin	800	1.3			
Cyfluthrin	12.5	7			
Cypermethrin	210	69			
Esfenvalerate	25	17			
Lambda- Cyhalothrin	3.5	2			
Permethrin	10	1.4			

¹Benchmark = Toxicity value x LOC. For acute invertebrate, toxicity value is usually the lowest 48- or 96-hour EC50 or LC50 in a standardized test (usually with midge, scud, or daphnids), and the LOC is 0.5.

²Benchmark = Toxicity value x LOC. For chronic invertebrates, toxicity value is usually the lowest NOAEC from a lifecycle test with invertebrates (usually with midge, scud, or daphnids), and the LOC is 1.

LOC = Level of Concern

Pyrethroid Environmental Fate and Transport and Aquatic Bioavailability

Pyrethroid pesticides are not naturally occurring compounds and are present in the environment primarily due to applications to control insect pests on agricultural crops and to control insect pests around structures in the urban setting. Pesticides have properties that affect how they move through the environment and their availability and toxicity in the aquatic environment. A key environmental property of pyrethroids is that they are non-polar with a strong affinity to bind to soil particles and organic matter in soil and sediment (referred to as the K_{OC} , organic carbon – water adsorption coefficient) and have low water solubility (Palumbo et al., 2010). Due to its high K_{OC} , pyrethroids move from application areas in runoff attached to sediment and soil organic matter and wash into streams and channels. Once in streams pyrethroids are primarily found in sediment but they partition between sediment organic matter and the water phases. Pyrethroids eventually reach a partitioning equilibrium between the phases (Figure 1).

In the aquatic environment pyrethroids adsorption to sediments affects their bioavailability and toxicity. In stream sediments, pyrethroids degrade slowly and have a very long half-life (Amweg, et al. 2005). One study found bifenthrin to have a long halflife of 165 days in sediment (Lee et al., 2004). In the aquatic environment pyrethroids slowly reach equilibrium between dissolved and sediment-bound phases. Benthic organisms such Hyalella azteca live in close proximity to sediment and uptake freely dissolved pyrethroids that desorb from particles. Studies suggest that the freely dissolved fraction of pyrethroids is most available and toxic to benthic invertebrates and UC Davis recommends the use of the dissolved fraction of pyrethroids for compliance in the criteria reports (Palumbo et al., 2010).

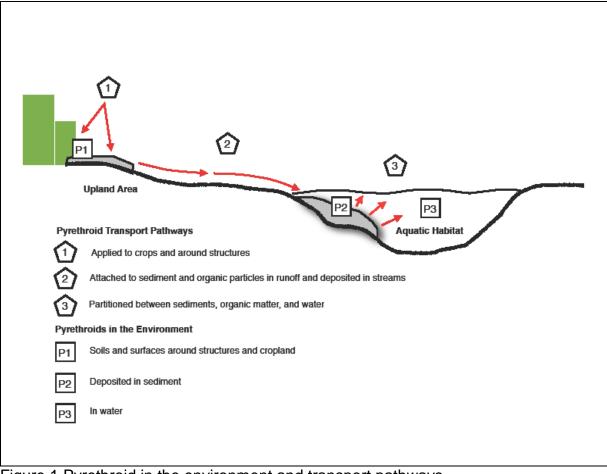


Figure 1 Pyrethroid in the environment and transport pathways

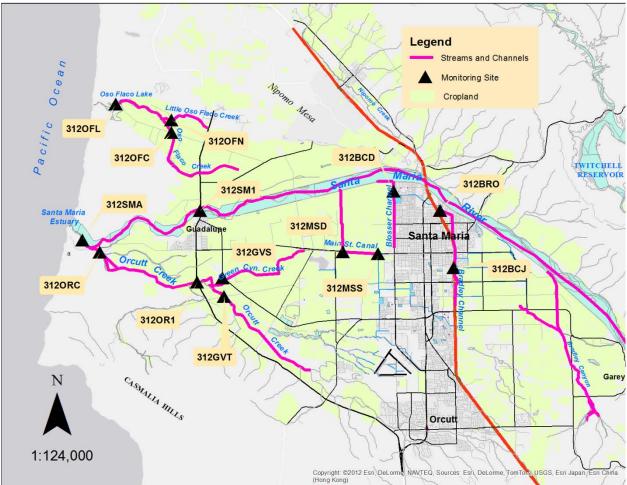


Figure 2 Map of monitoring sites, cropland and streams and channels in the Santa Maria Valley

Table 6 List of monitoring sites and geographic locations

Site	Site Name	Latitude	Longitude
312BCD	Blosser Channel	34.9792	-120.4529
312BRO	Bradley Channel at River Oaks	34.9742	-120.4245
312MSS	Main Street Channel	34.9531	-120.4633
312MSD	Main Street Channel	34.9527	-120.4614
312GVS	Green Valley Ck. at Simas	34.9422	-120.5564
312GVT	Orcutt Ck. at Brown Road	34.9340	-120.5579
312OFC	Oso Flaco Ck. at OFC Road	35.0164	-120.5875
312OFL	Oso Flaco Lake	35.0304	-120.6211
312SOL	Solomon Ck. at Sand Plant	34.9573	-120.6317
312ORC	Orcutt Ck. at Sand Plant	34.9575	-120.6323
312SMA	Santa Maria River	34.9611	-120.6414

Pyrethroid Analysis

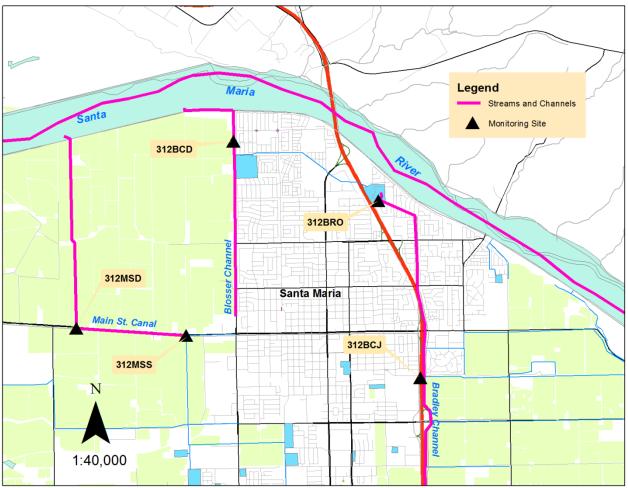


Figure 3 Monitoring sites and streams and channels in the Santa Maria City subwatershed area

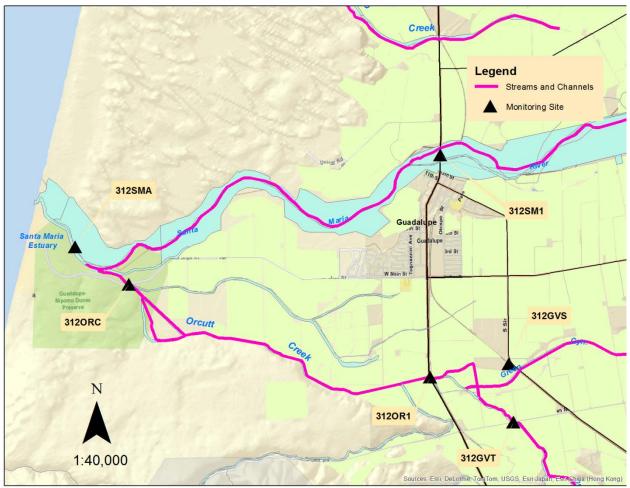


Figure 4 Monitoring sites and streams in the lower Orcutt Creek and Santa Maria River subwatershed area

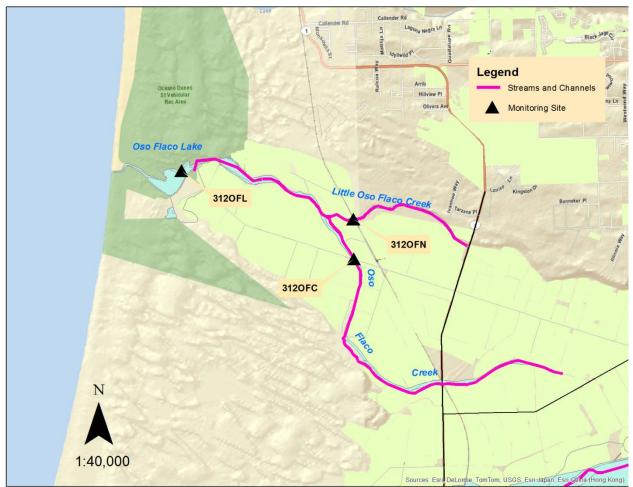


Figure 5 Monitoring sites and streams in the Oso Flaco subwatershed area

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