



# Ventura Countywide Stormwater Quality Management Program

## **PYRETHROID INSECTICIDES STUDY**

### **2015 FINAL REPORT**

**PREPARED BY THE:**

**VENTURA COUNTY WATERSHED PROTECTION DISTRICT**

**SUBMITTED ON BEHALF OF:**

**VENTURA COUNTY WATERSHED PROTECTION DISTRICT**

**COUNTY OF VENTURA**

**CITY OF CAMARILLO**

**CITY OF FILLMORE**

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**CITY OF PORT HUENEME**

**CITY OF SANTA PAULA**

**CITY OF SIMI VALLEY**

**CITY OF THOUSAND OAKS**

**CITY OF VENTURA**

**December 15, 2015**



## **EXECUTIVE SUMMARY**

Pyrethroid insecticide monitoring of sediments is required by Monitoring Program No. CI 7388, as part of the Ventura County Municipal Separate Storm Sewer System National Pollutant Discharge Elimination System Permit, Order No. R4-2010-0108 (Permit). A first round of pyrethroid sediment monitoring was performed in 2012 and repeated in 2015.

For 2015, the District elected to add Calleguas Creek Watershed sites to the Study to increase comparability and avoid issues with different detection levels, sampling strategies, and reporting cycles. The second round of the Study was conducted in April 2015 by the District at two sites each in the Ventura River, Santa Clara River, and Calleguas Creek watersheds. Of the eight Permit-required pyrethroid pesticides, two were detected: bifenthrin (three sites) and permethrin (one site). One non-required pyrethroid (fenpropathrin at one site) and two non-pyrethroid pesticides (dichloran at one site and pendimethalin at three sites) were also detected. Hypothetical toxicity units (TU) based on *H. azteca* LC50s (as for 2012) were also calculated for pyrethroids detected in 2015 samples. All samples had hypothetical TUs below one with the exception of bifenthrin in only the CC Down duplicate, however there was not significant toxicity in the measured sample. Hypothetical TU could not be calculated for detected analytes without LC50s (the non-pyrethroids - pendimethalin and dichloran) and so their hypothetical contribution to toxicity is unknown. Similarly, if a pyrethroid is not detected, there is the possibility that it is present in concentrations below the method detection limit and so its contribution to sample toxicity is unknown. Pollutants other than those detected may also be contributing to toxicity, however this study was focused on pyrethroid pollutants.

All samples were subjected to a 10-day survival sediment bioassay using *Hyalella azteca*. Some toxicity was observed in 2015 at VR Down and SCR Up. None of the Permit required pyrethroids were detected at SCR up. Bifenthrin was detected in VR Down, however other sites with higher concentrations exhibited no toxicity, and the calculated hypothetical toxicity for VR Down based on the bifenthrin concentration was not toxic. No significant toxicity was observed in the 2012 study samples.

Due to the increased detection of pyrethroids and the presence of significant toxicity in some of the samples that may or may not be attributable to urban contributions of pyrethroids, the recommendation to mitigate urban contributions of pyrethroids in the three sampled watersheds is to target pesticide use in the Ventura Countywide Stormwater Management Program's (Program) upcoming education and outreach campaign.

## **INTRODUCTION**

Pyrethroid insecticide monitoring of sediments is required by Monitoring Program No. CI 7388, as part of the Ventura County Municipal Separate Storm Sewer System National Pollutant Discharge Elimination System Permit, Order No. R4-2010-0108 (Permit). The Permit specifies that the Principal Permittee (Ventura County Watershed Protection District (District)) shall perform a pyrethroid insecticides study to accomplish the following objectives:

- i. Establish baseline data for major watersheds;
- ii. Evaluate whether pyrethroid insecticide concentrations are at or approaching levels known to be toxic to sediment-dwelling aquatic organisms;
- iii. Determine if pyrethroids discovered are from urban sources; and
- iv. Assess any trends over the permit term.

The first round of sediment monitoring for the Pyrethroid Insecticides Study (Study) was conducted in April 2012 by the Ventura County Watershed Protection District (District) at two locations in both the Ventura River and Santa Clara River watersheds. Data from the Calleguas Creek Watershed (CCW) Toxicity Total Maximum Daily Load (TMDL) monitoring program was used to meet the requirements for that watershed, as allowed by the Permit. The 2012 TMDL data were unavailable in time for the 2012 report, so 2008-2010 data were included in that report and the 2011 and 2012 data are included in this report.

In 2012, two pyrethroids were detected in the Study samples: bifenthrin (three sites) and permethrin (one site); and one pyrethroid (bifenthrin) was detected in the TMDL samples (two sites). No pyrethroids were detected in the 2011 TMDL samples. Hypothetical toxicity units were calculated based on the concentration of the pyrethroid (normalized for total organic carbon) and the known *Hyalella azteca* LC50, if available. All hypothetical toxicity units were less than one indicating the samples were non-toxic. This was supported by the lack of toxicity seen in the analysis of the sediment samples, with the exception of the two TMDL sites, which had significant toxicity. Two non-pyrethroid pesticides were also detected in the Study samples: pendimethalin (two sites) and dichloran (one site) but were not tested in the TMDL.

This study was repeated in 2015 with the addition of the Calleguas Creek Watershed to increase comparability and avoid issues with different detection levels, sampling strategies, and reporting cycles. The second round of the Study was conducted in April 2015 by the District at two sites each in the Ventura River, Santa Clara River, and Calleguas Creek watersheds.

## **METHOD**

In-stream sediment samples for chemical analysis and toxicity testing were collected using stainless steel scoops according to methods developed by the USGS and outlined in *Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants for the National Water Quality Assessment Program (1994)*. When possible, sediment sampling stations encompassed a section of the reach approximately 100 meters in length upstream from water-column sampling stations but this varied depending on site conditions. Five to ten wadeable depositional zones (low energy areas where fine-grained particles can accumulate) within the reach were targeted to obtain a sample representative of the site.

All sediment samples were analyzed for total organic carbon (TOC) by EPA 9060, pyrethroids by GC/MS NCI-SIM, and toxicity to 7 to 10 day old *Hyalella azteca*, as described in *Aquatic Toxicity Due to Residential use of Pyrethroid Insecticides*<sup>1</sup>. Water quality field measurements were taken with hand-held probes.

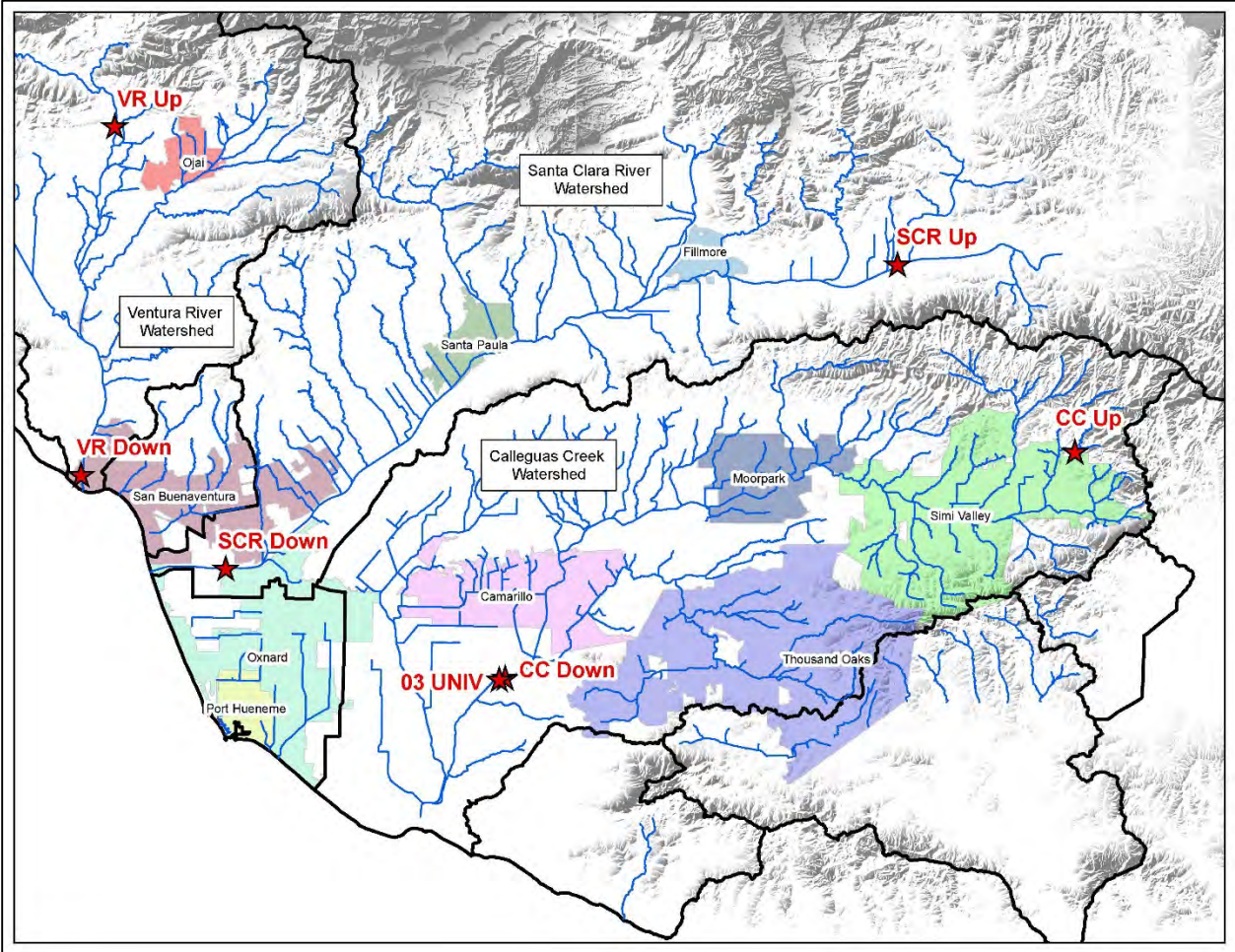
The stainless steel trowels used by the Study were cleaned prior to sample collection with Citranox laboratory detergent and tap water, rinsed with distilled water, and air dried. They were then sealed individually in Ziploc bags until arrival at the site. An equipment blank was collected by the laboratory from one clean, unused stainless steel trowel by rinsing with one liter of laboratory grade de-ionized water and analyzing the rinsate for TOC by SM 5310C and pyrethroids by GC/MS NCI-SIM. A second equipment blank was submitted and underwent the same procedure.

The Permit specifies that monitoring is to be conducted every three years, after sediment has settled within the water body and safe access can be assured. Ventura County has been experiencing unusually low rainfall for the past several years, which has dried out many waterways that were previously perennial. The number and size of storms in Ventura County during the 2014/2015 water year was exceptionally low, and in some areas including several Study sites, the rainfall was insufficient to cause a change in the hydrograph, and/or flow to resume. The District waited until April to conduct the sampling in the hope that there would be some late season storms that might cause some of the dry areas to flow, however only small amounts of rain fell so sampling was conducted at the end of the calendar wet season, April 15 and 16, 2015, approximately one week after a small storm (<0.3" precipitation) and one and a half months after a larger storm (0.2-0.75" rainfall). VR Down, SCR Up, and CC Down were flowing, however VR Up and SCR Down were damp with small remnant ponds and CC Up was dry, although there were some sediment deposits from earlier flows.

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<sup>1</sup> *Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides*; Weston, D., Holmes, R., You, J., Lydy, M.J (2005). Environ. Sci. Technol.; (Article); 2005; 39(24); 9780 pp.

Figure 1. Pyrethroid Sampling Locations 2015



## **2015 Pyrethroid Study**

For the Study, an upstream and a downstream site were selected on the main stems in the Ventura River, Santa Clara River, and Calleguas Creek watersheds (Figure 1). The upstream site was located higher in the watershed to reduce the influence of urban sources and the downstream site was located low in the watershed to include urban contributions. It was not possible to exclude upstream sources of agriculture or urban runoff from outside Ventura County in all cases. For the Ventura River watershed, the upstream site is on the Ventura River above the Casitas Municipal Water District's diversion structure near the north end of Rice Road in Meiners Oaks (VR Up, Figure 2). The downstream site is on the Ventura River near the Main Street Bridge in Ventura (VR Down, Figure 3). For the Santa Clara River watershed, the upstream site is on the Santa Clara River east of Torrey Road near the Los Angeles/Ventura County Line<sup>2</sup> (SCR Up, Figure 4) and the downstream site is on the Santa Clara River near the Victoria Avenue Bridge in Ventura (SCR Down, Figure 5). For the Calleguas Creek watershed, the upstream site (CC Up, Figure 6) is in Las Lajas Canyon above Las Lajas Dam, north of Simi Valley and the downstream site (CC Down, Figure 7) is on Calleguas Creek at the Camarillo Street (formerly University Drive) Bridge. Factors such as safety, ease of entry, upstream land use, hydrology, and long term accessibility including landowner permission were considered in site selection.

As described in the Ventura County MS4 Pyrethroid Insecticides Monitoring Quality Assurance Project Plan (QAPP), the top layer (~1 cm) of the most recently deposited sediment was collected with a pre-cleaned stainless steel scoop as specified in the permit. The quantity of sediment required for the tests precluded sampling directly into glass jars, so the sediment was deposited in a 24" by 36" 2mm polyethylene bag per site. The bag was closed and the sediment was manually homogenized onsite by squeezing and rotating the bag. Homogenized sediment was placed in two 8 oz wide-mouth glass jars and placed on ice for TOC and pyrethroid analysis. The jars were placed in the freezer at the end of the sampling day so that they could be frozen for pickup by the chemistry lab courier the following day. The remaining sediment (~ 3 liters) was double-bagged and put on ice for (same day) delivery to the toxicity lab.

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<sup>2</sup> Note that urban and agricultural areas are present upstream beyond the Ventura County boundary.

Figure 2. VR Up



Figure 3. VR Down



Figure 4. SCR Up



Figure 5. SCR Down



Figure 6. CC Up



Figure 7. CC Down





### **TMDL: 2011 and 2012 Data**

The Calleguas Creek Watershed is unusual because most of its developed areas are in the upper portions of the watershed with the lower portions heavily influenced by agriculture. The monitoring plan for the TMDL does not include sites without urban influence but includes two sites that are monitored for both sediment pyrethroids and sediment toxicity, 03\_UNIV and 04\_WOOD. The TMDL site that best represented the urban contribution of the watershed is 03\_UNIV, which is co-located with CC Down (Figure 1). Site 04\_WOOD is located on Revolon Slough on the east side of Wood Road in a predominantly agricultural area, although there are urban inputs upstream. These sites have been monitored for total organic carbon, pyrethroids in sediment, and toxicity to *Hyalella azteca* since August 2008.

As described in the Calleguas Creek Watershed Management Plan Quality Assurance Project Plan Monitoring and Reporting Program Plan for the Nitrogen, OC and PCBs, Toxicity, and Metals and Selenium Total Maximum Daily Loads (TMDL QAPP), sediment samples were collected from the top two to three centimeters (cm) of sediment using pre-cleaned stainless steel trowels. Collecting a thicker layer of sediments is a common approach to conducting sediment sampling for the purpose of sediment toxicity testing and is the approach used in sediment toxicity studies conducted by the Southern California Coastal Water Research Project (SCCWRP) Bight Program and the State Water Resources Control Board Bay Protection and Toxic Cleanup Program (BPTCP). The sediment samples were collected directly into a clean polyethylene bag and mixed. Subsamples from the bag were placed into glass jars for pyrethroid and TOC analysis and the remaining sediment was kept in the bag for toxicity analysis. All samples were stored at 4°C until arrival at the contract laboratory.

## **RESULTS**

### **Study Equipment Blanks**

The initial equipment blank analysis detected a small amount of TOC and a quantifiable amount of the pyrethroid bifenthrin (Table 1). A second trowel was analyzed to confirm the contamination, and bifenthrin was detected but not in a quantifiable amount. To collect each equipment blank sample, the laboratory rinsed the trowel with one liter of deionized water and analyzed the rinsate for pyrethroids and TOC. Several non-pyrethroid constituents were also analyzed by this method but were not detected.

Table 1. Equipment Blank Results

<b>Analyte</b>	<b>Trowel Blank I (Initial Analysis) (µg/L, MDL varies)</b>	<b>Trowel Blank II (2<sup>nd</sup> Trowel) (µg/L, MDL varies)</b>
Allethrin	ND (<0.00085)	ND (<0.00085)
<b>Bifenthrin</b>	<b>0.0026</b>	<b>0.00091 (DNQ)</b>
<b>Cyfluthrin</b>	ND (<0.00083)	ND (<0.00083)
<b>Cypermethrin</b>	ND (<0.00066)	ND (<0.00066)
<b>Deltamethrin/Tralomethrin</b>	ND (<0.0019)	ND (<0.0019)
Dichloran	ND (<0.00080)	ND (<0.00080)
<b>Esfenvalerate</b>	ND (<0.00098)	ND (<0.00098)
Fenpropathrin (Danitol)	ND (<0.0020)	ND (<0.0020)
Fenvalerate	ND (<0.00098)	ND (<0.00098)
<b>L-Cyhalothrin</b>	ND (<0.0012)	ND (<0.0012)
Pendimethalin	ND (<0.00050)	ND (<0.00050)
<b>Permethrin</b>	ND (<0.0050)	ND (<0.0050)
Prallethrin	ND (<0.00092)	ND (<0.00092)
Sumithrin	ND (<0.0024)	ND (<0.0024)
Tefluthrin	ND (<0.00093)	ND (<0.00093)
<b>TOC</b>	<b>0.18 mg/L (DNQ)</b>	<b>0.23 mg (DNQ)</b>

<b>Analyte listed in Permit</b>
<b>Detections</b>
ND = Not Detected
DNQ = Detected Not Quantified

## **Study Sites – Pyrethroids**

### 2015

The Permit specifies eight pyrethroids for analysis (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, I-cyhalothrin, permethrin, and tralomethrin), of which two were detected in the 2015 study: bifenthrin (VR Down, SCR Down, and CC Down) and permethrin (CC Down). One non-required pyrethroid was also detected: fenpropathrin (VR Down). A field duplicate sample was collected at CC Down and the detected pyrethroids were the same as the source sample, however there was some variation in quantities. The same five constituents were detected in the 2012 study, however there was some variation in the quantity and location of the detections between years.

All samples were subjected to a 10-day survival sediment bioassay using *Hyalella azteca*. Four of the six 2015 sites (VR Up, SCR Down, CC Up and CC Down) did not display significant toxicity, and the *H. azteca* survival rate at these sites was 82.5% or greater. However, some toxicity was observed in 2015 at VR Down (20.00%) and SCR Up (55.00%), and their corresponding toxicity units (TU) were greater than one, indicating that there was significant toxicity in the sample. No significant toxicity was observed in the 2012 study samples.

TOC amounts ranged from 8.27 g/kg in the downstream Calleguas Creek field duplicate (CC Down 2) to 33.8 g/kg in the upstream Ventura River site, with no clear reason for the differences. The distribution and differences in TOC between upstream/downstream samples and between watersheds is different than that observed in the 2012 study, which had values of 5.4 g/kg (SCR Up) to 26 g/kg (VR Down).

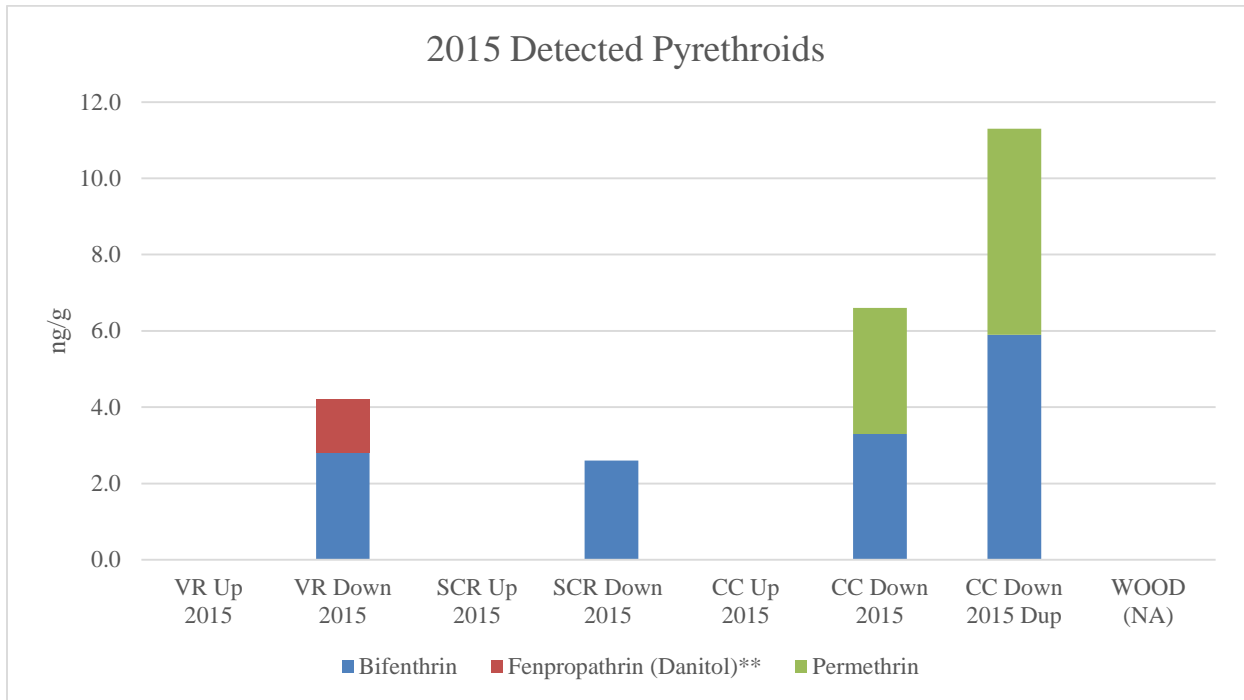
The results are provided in Table 2. The constituents (pyrethroid and non-pyrethroid) that were not required by the Permit are also included in this table.

Table 2. Study Results 2015 - as reported by laboratory

Analyte	VR Up	VR Down	SCR Up	SCR Down	CC Up	CC Down 1	CC Down 2	MRL	Units
Allethrin	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>Bifenthrin</b>	ND	<b>2.8</b>	ND	<b>2.6</b>	ND	<b>3.3</b>	<b>5.9</b>	Varies	ng/g
<b>Cyfluthrin</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>Cypermethrin</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>Deltamethrin</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
Dichloran	ND	ND	ND	<b>1.1</b>	ND	ND	ND	Varies	ng/g
<b>Esfenvalerate</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
Fenpropathrin (Danitol)	ND	<b>1.4</b>	ND	ND	ND	ND	ND	Varies	ng/g
Fenvalerate	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>L-Cyhalothrin</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
Pendimethalin	ND	ND	<b>1.4</b>	<b>8.8</b>	ND	<b>3.8</b>	<b>2.5</b>	Varies	ng/g
<b>Permethrin</b>	ND	ND	ND	ND	ND	<b>3.3</b>	<b>5.4</b>	Varies	ng/g
Prallethrin	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
Sumithrin	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
Tefluthrin	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>Tralomethrin</b>	ND	ND	ND	ND	ND	ND	ND	Varies	ng/g
<b>TOC</b>	<b>33.8</b>	<b>18.8</b>	<b>17</b>	<b>11.4</b>	<b>12.2</b>	<b>12.3</b>	<b>8.27</b>	Varies	g/kg
<b>Toxicity</b>	<b>95.00</b>	<b>20.00</b>	<b>55.00</b>	<b>90.00</b>	<b>95.00</b>	<b>82.50</b>	<b>87.50</b>		% Survival
<b>Toxicity Units (t two-sample test)</b>	<b>1</b>	<b>&gt;1</b>	<b>&gt;1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>		TU Survival
<b>Toxicity Units (Linear Interpolation EC50)</b>	<b>&lt;1</b>	<b>1.6</b>	<b>&lt;1</b>	<b>&lt;1</b>	<b>&lt;1</b>	<b>&lt;1</b>	<b>&lt;1</b>		TU Survival

<b>Analyte listed in Permit</b>
<b>Detections</b>
ND = Not Detected
NA = Not Applicable

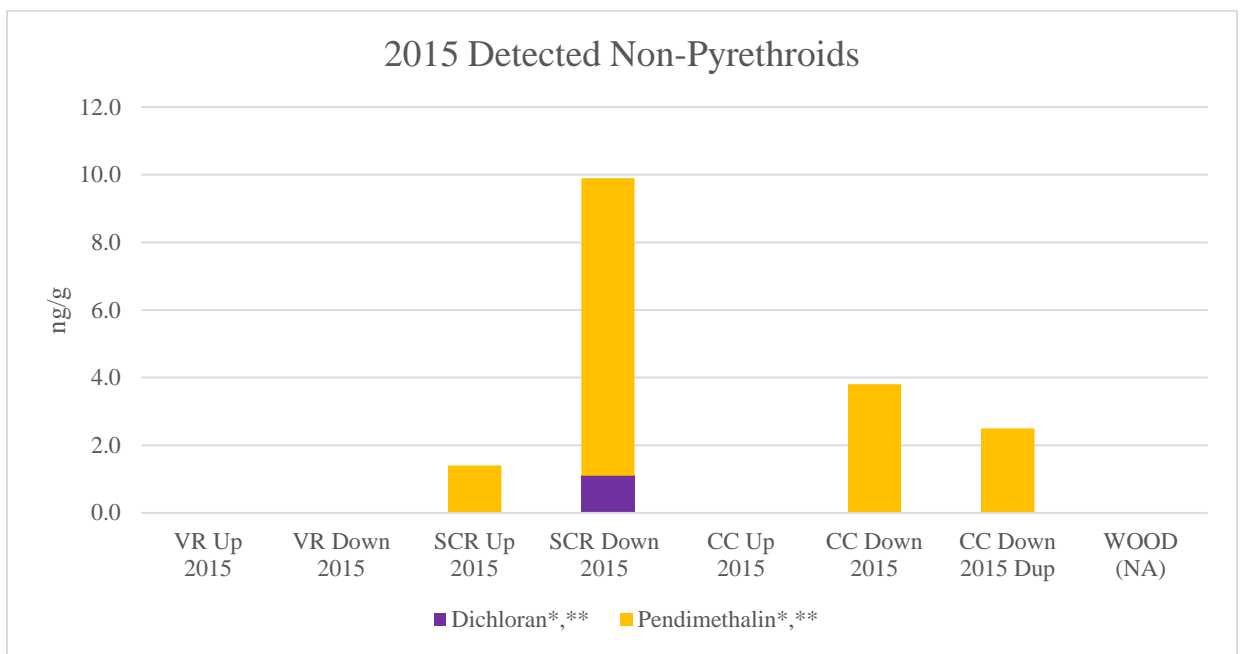
Figure 8. 2015 Detected Pyrethroids



\*\* Analyte not required by Permit

Two non-pyrethroids were also detected: dichloran at SCR Down and pendimethalin at SCR Up, SCR Down, and CC Down. These results are shown in Figure 9.

Figure 9. 2015 Detected Non-Pyrethroids



\* Analyte not analyzed by TMDL

\*\* Analyte not required by Permit

**TMDL 2011 - 2012**

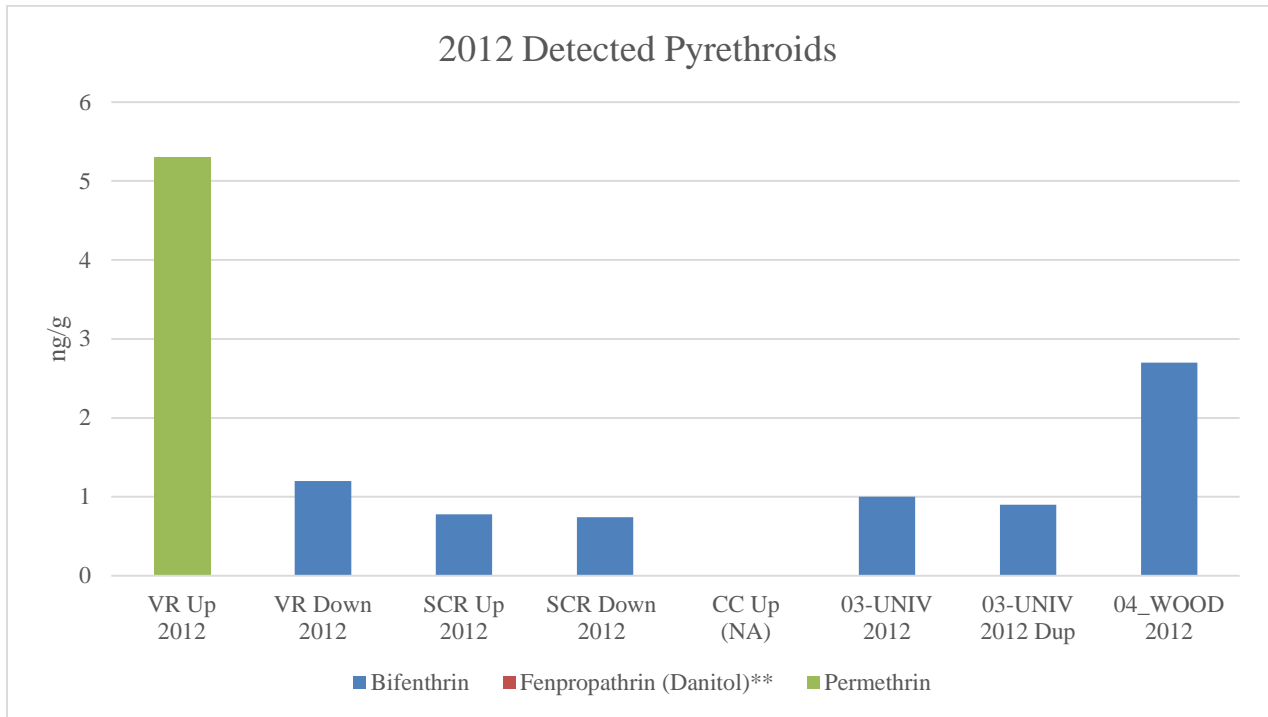
Since the 2012 TMDL data was not available at the time of the 2012 Pyrethroid Study, the data is being included here. TMDL site 03\_UNIV is co-located with CC Down, however 03\_UNIV is sampled with TMDL protocols which are different to the CC Down Study Protocols. Pyrethroids were not detected in either of the TMDL samples in 2011, however bifenthrin was detected at both sites (03\_UNIV and duplicate and 04\_WOOD) in 2012. Dichloran and pendimethalin were not part of the TMDL study. Significant toxicity to *Hyalella azteca* survival was observed in all sediment toxicity samples. The percent survival ranged from 0% at 04\_WOOD in 2011 to 88.3% at 03\_UNIV in 2011. TOC amounts were between 3.3 g/kg (2012) and 6.2 g/kg (2011). The 2011-2012 TMDL results are shown in Table 3. The TMDL and Study results from 2012 are included in Figure 10 and Figure 11.

Table 3. TMDL Results 2011-2012 - as reported by laboratory

Analyte	03_UNIV			04_WOOD		MDL	Units
	8/4/2011	8/29/2012	8/29/2012 Duplicate	8/4/2011	8/29/2012		
Allethrin	ND	ND	ND	ND	ND	0.5	ng/g
<b>Bifenthrin</b>	ND	<b>1 (DNQ)</b>	<b>0.9 (DNQ)</b>	ND	<b>2.7</b>	0.5	ng/g
<b>Cyfluthrin, total</b>	ND	ND	ND	ND	ND	0.5	ng/g
<b>Cypermethrin, total</b>	ND	ND	ND	ND	ND	0.5	ng/g
<b>Deltamethrin</b>	ND	ND	ND	ND	ND	0.5	ng/g
<b>Esfenvalerate</b>	ND	ND	ND	ND	ND	0.5	ng/g
Fenpropathrin (Danitol)	ND	ND	ND	ND	ND	0.5	ng/g
Fenvalerate	ND	ND	ND	ND	ND	0.5	ng/g
Fluvalinate	ND	ND	ND	ND	ND	0.5	ng/g
<b>L-Cyhalothrin</b>	ND	ND	ND	ND	ND	0.5	ng/g
<b>Permethrin, cis-</b>	ND	ND	ND	ND	ND	5	ng/g
<b>Permethrin, trans-</b>	ND	ND	ND	ND	ND	5	ng/g
Prallethrin	ND	ND	ND	ND	ND	0.5	ng/g
Resmethrin	ND	ND	ND	ND	ND	5	ng/g
<b>Total Organic Carbon (TOC)</b>	<b>6.2</b>	<b>4.4</b>	<b>3.3</b>	<b>4.5</b>	<b>5.6</b>	0.1	g/kg
<b><i>H. azteca</i> Toxicity</b>	88.8 SG	75.0 SG	NS	0.0 SG	66.3 SG	-	% Survival

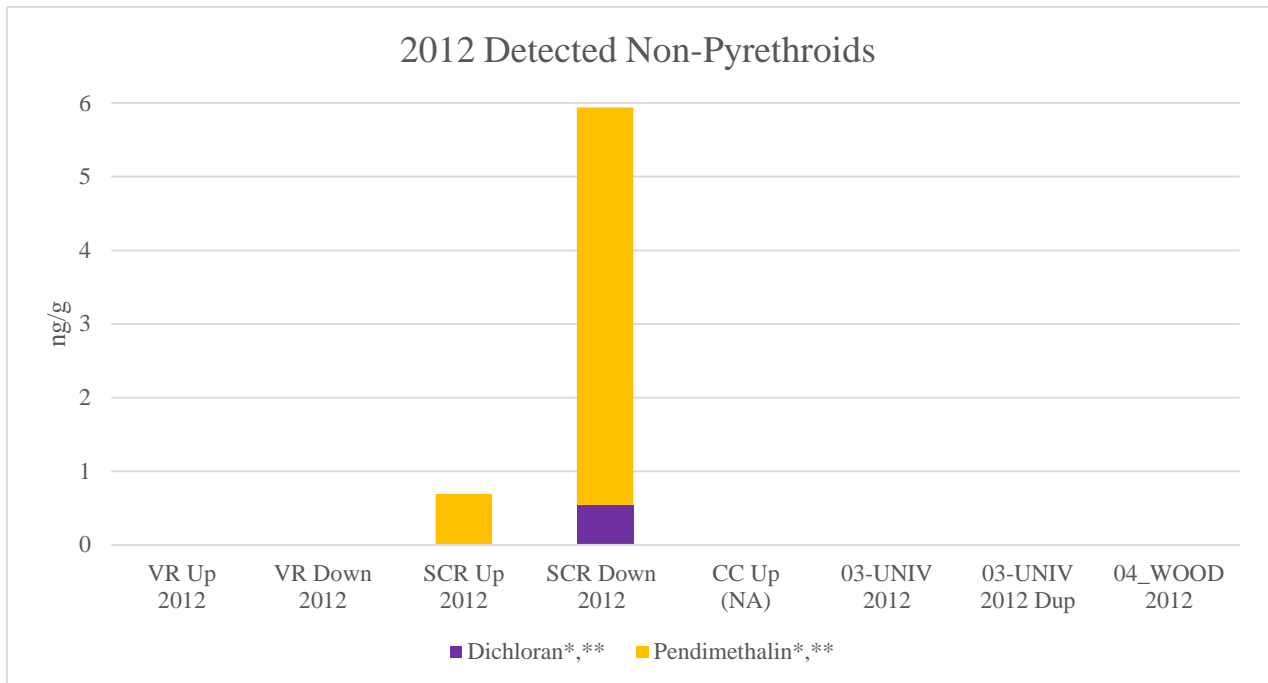
<b>Analyte listed in Permit</b>	DNQ = Detected Not Quantified	NS = Not Sampled
<b>Analyte Detected</b>	ND = Not Detected	SG = Significant Effect

Figure 10. 2012 Detected Pyrethroids



\*\* Analyte not required by Permit

Figure 11. 2012 Detected Non-Pyrethroids



\* Analyte not analyzed by TMDL

\*\* Analyte not required by Permit

## **DISCUSSION OF RESULTS**

### **Equipment Blank**

The source of the detected bifenthrin in the Study's original equipment blank is uncertain. The equipment blank is collected by rinsing the trowel with one liter of laboratory grade deionized water and collecting the rinsate for analysis. One liter is used as it is the volume required for the analytical method and collecting extra for a potential re-analysis may dilute the sample. Since one liter of rinsate is insufficient to re-analyze for pyrethroids, the re-analysis required analyzing a second trowel. A smaller amount of bifenthrin was detected in the second analysis. The source of the contamination is undetermined. The laboratory QC was within limits for both equipment blank batches, i.e. bifenthrin was not detected above the reporting limit of 0.0020 µg/L in either of the laboratory method blanks, and the laboratory control samples and duplicates were all within acceptance limits. The equipment blank may have been contaminated during rinsate collection and/or analysis at the laboratory, or Citranox may have been insufficient to remove all bifenthrin contamination from the trowels. Citranox is formulated to remove scale, metals, trace inorganics, soil, grease, fats, oils, particulates, deposits, chemical and solvents." A different detergent, such as Alconox, may be more effective at removing pyrethroid contamination.

Regardless of whether the pyrethroid contamination occurred at the laboratory or was present on the trowel, the amount of contamination is insignificant in comparison to the amounts detected in the environmental samples. The total mass of each pyrethroid detected in the one liter of equipment blank rinsate is equal to the concentration per liter, since the total rinsate volume was one liter. This amount is at least two orders of magnitude below the concentrations detected in the environmental samples. The amounts of bifenthrin detected in the environmental samples could be considered to be upper limits due to the equipment blank detections.

Cleanup instructions for bifenthrin-containing products vary depending on manufacturer/formulation. The instructions for accidental release measures in the MSDS for Bifen (a bifenthrin containing insecticide/termiticide) are to "wash with a suitable solution of caustic or soda ash, and an appropriate alcohol (i.e. methanol, ethanol, or isopropanol). Follow this by washing with a strong soap and water solution." The MSDS for HomeshieldXP is similar, with bleach named instead of caustic. Other MSDS's for bifenthrin-containing products only designate water and detergents for cleanup.

The amount of TOC measured in the equipment blank was at least four orders of magnitude below the environmental samples and so can be considered insignificant.

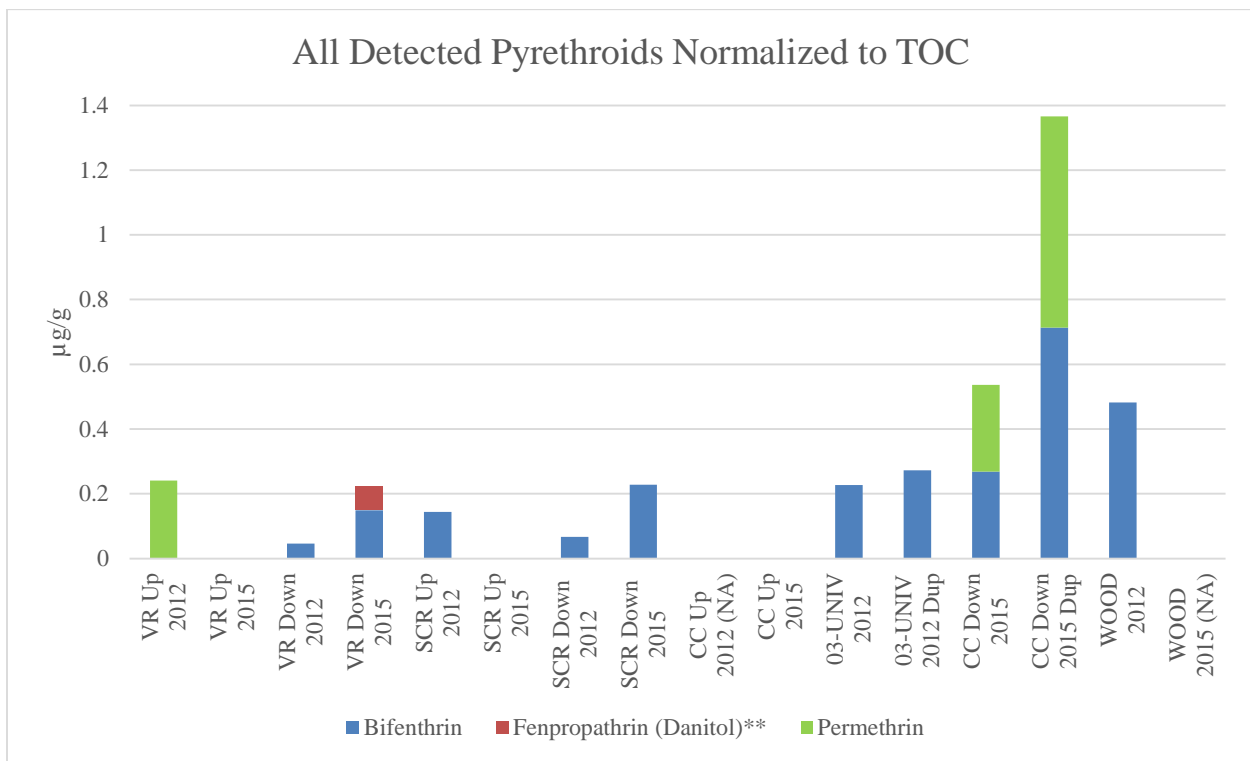
### **Toxicity**

Toxicity levels vary between pyrethroids. Hypothetical toxicity units (TU<sub>H</sub>) can be calculated to compare the relative toxicity of different samples and pyrethroids. This is done by normalizing the sediment pyrethroid concentrations to TOC concentration to account for hydrophobicity (Figure 12 and Table 4)



and then dividing by the *Hyalella azteca* ten day median lethal concentration (LC50) for each detected pyrethroid, if available (Table 5). LC50s for the detected analytes bifenthrin and permethrin were obtained from the study referenced in the Permit, "Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides (2005) by Weston *et al.* The Study did not include an LC50 for the pyrethroid fenpropathrin or the non-pyrethroids dichloran and pendimethalin. To complete this Pyrethroid Study, an LC50 for fenpropathrin was obtained from the Los Angeles Regional Water Quality Control Boards study, "Occurrence and Toxicity of Three Classes of Insecticides in Water and Sediment in Two Southern California Coastal Watersheds (2011) by Delgado-Moreno *et al.* The overall hypothetical pyrethroid toxicity of a particular sample can be calculated by summing the calculated pyrethroid TU<sub>H</sub> for that sample. TU<sub>H</sub> greater than one indicate significant hypothetical toxicity. The non-pyrethroids were also normalized to TOC (Figure 13) but TU<sub>H</sub> were not calculated since they are not pyrethroids and do not have LC50s in the Permit-referenced study.

Figure 12. All Detected Pyrethroids Normalized to TOC



\*\* Analyte not required by Permit

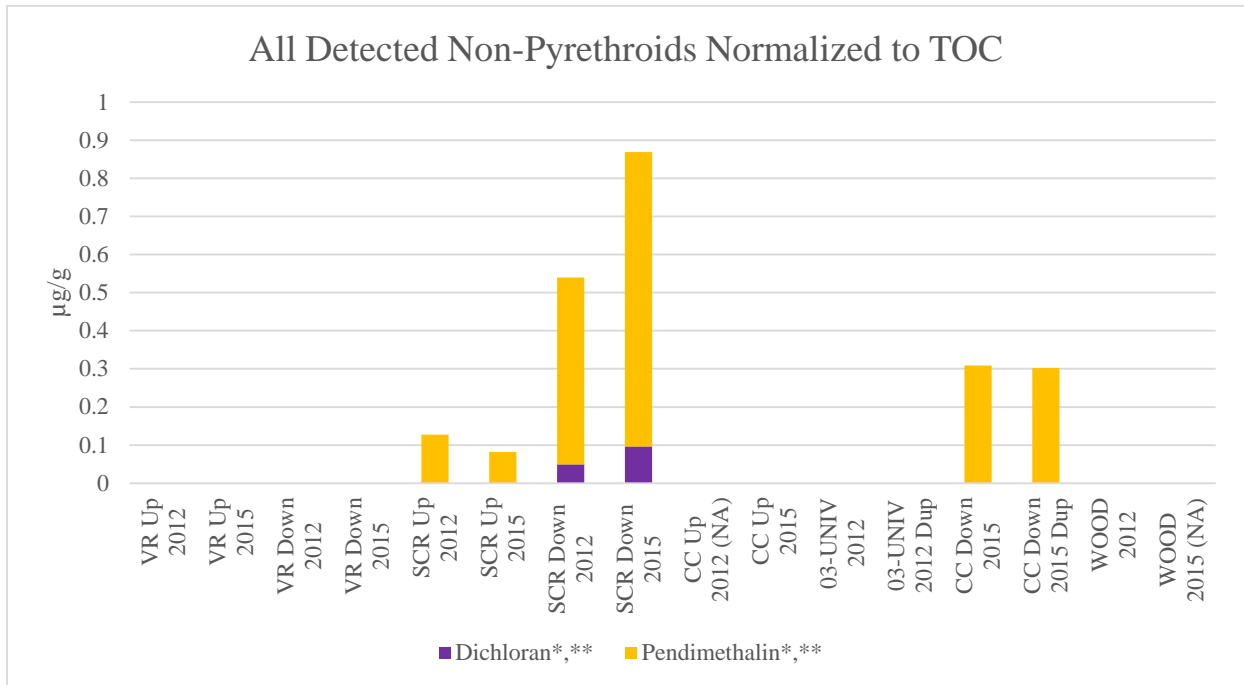
Table 4. Detected Analytes Normalized to TOC

Analyte	2012								2015							Units
	VR Up 2012	VR Down 2012	SCR Up 2012	SCR Down 2012	CC Up 2012 (NA)	03_UNIV 2012	03_UNIV 2012 Dup	04_WOOD 2012	VR Up 2015	VR Down 2015	SCR Up 2015	SCR Down 2015	CC Up 2015	CC Down 2015	CC Down 2015 Dup	
Bifenthrin	ND	0.05	0.14	0.07	NA	0.23(DNQ)	0.27(DNQ)	0.48	ND	0.15	ND	0.23	ND	0.27	0.71	µg/g
Dichloran*,**	ND	ND	ND	0.05	NA	ND	ND	ND	ND	ND	ND	0.10	ND	ND	ND	µg/g
Fenpropathrin (Danitol)**	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	µg/g
Pendimethalin*,**	ND	ND	0.13	0.49	NA	ND	ND	ND	ND	ND	0.08	0.77	ND	0.31	0.30	µg/g
Permethrin	0.24	ND	ND	ND	NA	ND	ND	ND	ND	ND	ND	ND	ND	0.27	0.65	µg/g
Analyte listed in Permit	Detections				ND = Not Detected				NA = Not Applicable							
Note: CC Up was not part of the 2012 study and 03_UNIV is co-located with CC Down, however the TMDL and Study have different sediment collection methods.																
* Not analyzed by TMDL																
** Analytes not required by Permit																

Table 5. Comparison of Toxicity Units (TOC normalized results)

Analyte	2012									2015							Units			
	LC <sub>50</sub> <i>H. azteca</i> *** (µg/g TOC)	VR Up 2012	VR Down 2012	SCR Up 2012	SCR Down 2012	CC Up 2012 (NA)	03-UNIV 2012	03-UNIV 2012 Dup	04_WOOD 2012	VR Up 2015	VR Down 2015	SCR Up 2015	SCR Down 2015	CC Up 2015	CC Down 2015	CC Down 2015 Dup				
Bifenthrin	0.52	ND	0.09	0.28	0.13	NA	0.44(DNQ)	0.52(DNQ)	0.93	ND	0.29	ND	0.44	ND	0.52	1.37	TU			
Dichloran*,**	NA	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	TU			
Fenpropathrin (Danitol)**	1.1	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	TU			
Pendimethalin*,**	NA	ND	ND	NA	NA	NA	ND	ND	ND	ND	ND	NA	NA	ND	NA	NA	TU			
Permethrin	10.83	0.02	ND	ND	ND	NA	ND	ND	ND	ND	ND	ND	ND	ND	0.02	0.06	TU			
Summed Hypothetical TU		0.02	0.09	0.28	0.13	NA	0.44	0.52	0.93	-	0.36	-	0.44	-	0.54	1.43	TU			
Measured TU		≤1	≤1	≤1	≤1	NA	>1	NA	>1	≤1	>1	>1	≤1	≤1	≤1	≤1	TU (survival)			
Measured Toxicity to <i>H. azteca</i>		83.75%	88.75%	98.75%	96.25%	NA	75.00%	NA	66.30%	95.00%	20.00%	55.00%	90.00%	95.00%	82.50%	87.50%	% Survival			
Measured Significant Effect		NSG	NSG	NSG	NSG	NA	SG	NA	SG	NSG	SG	SG	NSG	NSG	NSG	NSG	Sig Effect			
Analyte listed in Permit	Detections				ND = Not Detected				NA = Not Applicable				SG = Significant Effect				NSG = Non-significant Effect			
Note: CC Up was not part of the 2012 study and 03_UNIV is co-located with CC Down, however the TMDL and Study have different sediment collection methods.																				
* Not analyzed by TMDL																				
** Analytes not required by Permit																				
*** LC50 values from "Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides", Weston et al (2005), except fenpropathrin which is from "Occurrence and Toxicity of Three Classes of Insecticides in Water and Sediment in Two Southern California Coastal Watersheds", Delgado-Moreno et al (2011)																				

Figure 13. All Detected Non-Pyrethroids Normalized to TOC

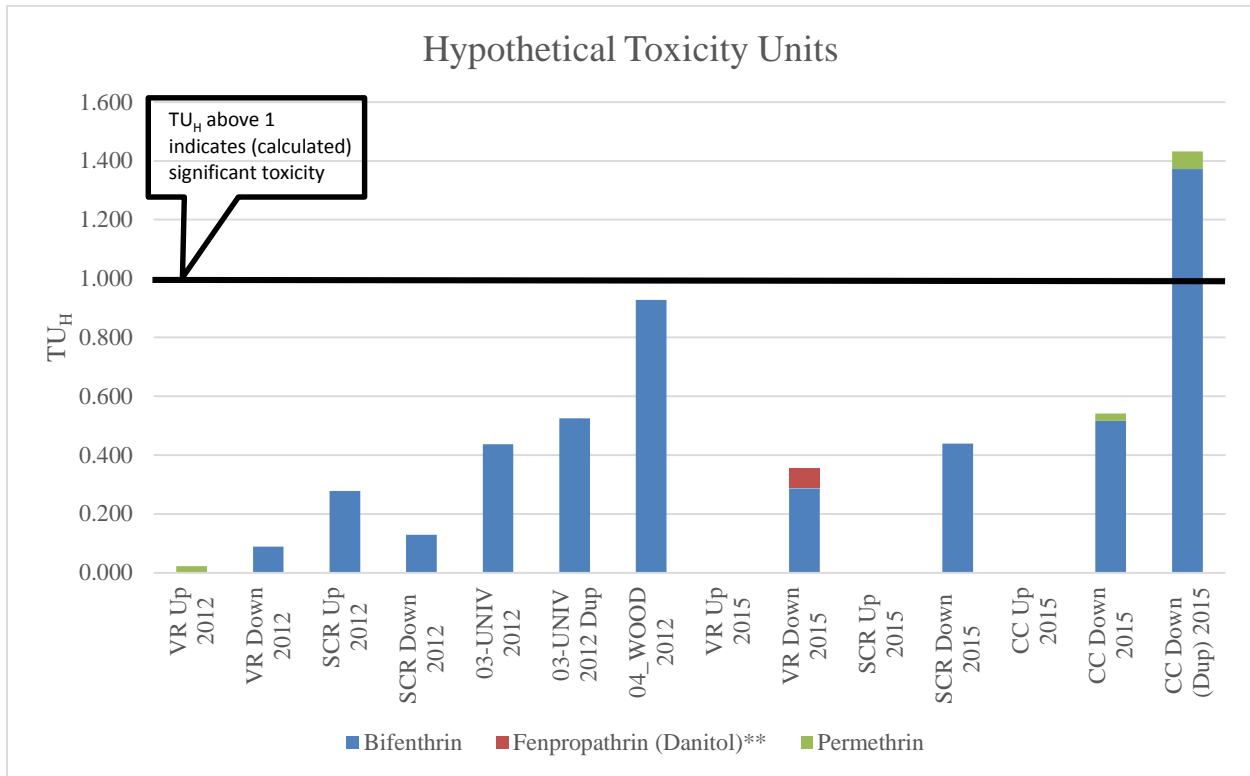


\* Analyte not analyzed by TMDL

\*\* Analyte not required by Permit

With the exception of the CC Down Duplicate, the calculated toxicity units from the Study samples were all less than one (Figure 14 and Table 5) and so these samples can be considered non-toxic by this evaluation method. For the CC Down Duplicate, even though the calculated  $TU_H$  was greater than one, the measured toxicity units were not above one, which means that significant toxicity was not observed in the *H. azteca* test. The study referenced in the Permit does not contain an LC50 for dichloran or pendimethalin, however the lack of toxicity in the environmental sample infers a calculated  $TU_H$  of less than one for these analytes. The calculated  $TU_H$  were not correlated with the observed toxicity, possibly due to the presence of unanalyzed constituents in the samples.

Figure 14. Hypothetical Toxicity Units for Detected Pyrethroids



\*\* Analyte not required by Permit

### Pyrethroids

Pyrethroids, with the exception of bifenthrin, were not detected in the sediment samples collected in 2011 and 2012 from TMDL sites 03\_UNIV and 04\_WOOD. The amount of bifenthrin detected at 04\_WOOD is approaching a hypothetical TU of 1, which indicates that pyrethroids may be contributing to the significant toxicity measured at this predominantly agricultural site in 2012. Given its location within the Oxnard Plain, an area notable for its large crops of strawberries, peppers, and leafy green vegetables, the source of this bifenthrin is likely agricultural, however there are some upstream discharge contributions from urban sources. The Permit requested that pyrethroid detection limits be as close to 1 ng/g (dry weight) as reasonably achievable and the TMDL monitoring effort was able to meet this level for all pyrethroids except for permethrin and resmethrin (not required by Permit), which had MDLs of 5 ng/g. The TMDL permethrin detection limit of 5 ng/g is above/near the quantities measured in the 2015 CC Down samples, so the higher TMDL detection limit may have obscured the presence of similar concentrations of permethrin in the TMDL samples.

Pyrethroid pesticides were more prevalent in the downstream samples for most analytes/watersheds, with the exception of both the Ventura River Watershed and Santa Clara River Watershed in 2012. Non-pyrethroid pesticide detections were limited to the Santa Clara River Watershed and the downstream Calleguas Creek 2015 Samples. Trends are inconclusive for this Permit term.

## **POTENTIAL PESTICIDE SOURCES**

The pounds of pesticides applied annually for agriculture and structural pest control is tracked by the California Department of Pesticide Regulation (CDPR). The *Annual Pesticide Use Report Indexed by Chemical* (Use Report) for Ventura County in 2012 and 2013 (the two latest reports available at the time of this report) summarize the reported pesticide use for agriculture (including food and ornamental), structural pest control, and landscape maintenance. The application of pesticides for residential, industrial, and commercial use is not tracked, with the exception of structural pest control by certified applicators. Many pesticides have both general use (lower concentrations and/or small areas) and restricted use (higher concentrations and/or large scale applications) formulations. General use pesticides can be applied by anyone however restricted use pesticides applications require CDPR Certified Pesticide Applicators.

Bifenthrin and permethrin are insecticides that have both agricultural and urban and general and restricted use applications. Bifenthrin is used as a restricted use pesticide in orchards, nurseries, and homes (structural pest control). Some products with lower concentrations are available for unrestricted residential use for indoor and outdoor insect control. Permethrin is a restricted use pesticide for crop and wide area applications (e.g. nurseries, sod farms) but is also a general use pesticide for residential (e.g. indoor and outdoor spaces, pets) and industrial applications. The 2012 and 2013 Use Reports show large amounts of bifenthrin and permethrin used in both agricultural and structural pest control applications within Ventura County. However, according to the United States Environmental Protection Agency's "Reregistration Eligibility Decision (RED) for Permethrin (December 2007)", approximately 70% of permethrin is used in non-agricultural settings and approximately 30% is used on food/feed crops in agricultural settings. The RED states that approximately 55% of the non-agricultural applications are made by professionals, 41% by homeowners on residential areas, and 4% on mosquito abatement areas. This suggests that the detected permethrin may have come from urban and/or agricultural sources.

Fenpropathrin is a pyrethroid insecticide that is registered for multiple crops but its restricted use designation makes it unlikely to have an urban source, however it can be used to treat Asian citrus psyllid infestations (as can cyfluthrin, which was not detected), which have become a problem in Ventura County. It is not used for structural pest control in Ventura County. Dichloran is a (non-pyrethroid) general use fungicide with no residential uses [DCNA (Dicloran) Reregistration Eligibility Decision (RED) Fact Sheet (EPA 738-F-06-013, July 2006)], therefore the detected dichloran is unlikely to be from an urban source. Pendimethalin is a (non-pyrethroid) general use selective herbicide used to control broadleaf weeds and grassy seed species in agricultural and non-agricultural settings. It was primarily used on strawberries in Ventura County according to the 2012 and 2013 Use Reports. It is unknown if the detection of this non-pyrethroid is related to an urban source.

Table 6. Ventura County Pesticide Use Reported to CDPR

	2012					2013 <sup>^</sup>				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
<b>Bifenthrin</b>	2911.63	1673.06	1211.49	27.08	Strawberry 1364	3350.01	1635.33	1684.09	30.59	Strawberry 1253
<b>Permethrin</b>	4625.02	2060.4	2515.73	48.89	Celery 873, Lettuce 335	4678.32	2408.77	2201.2	68.35	Celery 1142
Fenpropathrin (Danitol)**	788.71	788.08	0	0.63	Strawberry 595	1668.9	1668.9	0	0	Strawberry 1307
Dichloran*,**	15545.81	15545.81	0	0	Celery 14854	19557.51	19557.51	0	0	Celery 18984
Pendimethalin*,**	5983.35	5739.14	0	244.21	Strawberry 5140	11899.69	11862.37	0	37.32	Strawberry 10855
<sup>^</sup> 2014 and 2015 unavailable at time of report		* Not analyzed by TMDL		** Analytes not required by Permit		Other - E.g. landscape maintenance, rights of way, vertebrate control, etc.				

## **PESTICIDE REDUCTION EFFORTS**

### **Integrated Pest Management Programs**

A model integrated pest management (IPM) program was drafted through the Public Agencies Activities Subcommittee and used as a template by the Permittees to develop their own plans by November 2009. This standardized protocol was amended in February 2014 at the amended version is posted on Program's website at: <http://www.vcstormwater.org/index.php/publications/manuals/pesticide-application-protocol>.

The prevention of pesticides from harming non-target organisms is the primary goal of the Permittees IPM program. The intent is to focus on preventing pesticides, fertilizers, and herbicides from entering the storm drain system and discharging to receiving waters. This protocol is applicable to 1) the outdoor use of pesticides, herbicides, and fertilizers; 2) the use of pesticides and fertilizers where the materials may come into contact with precipitation; 3) the use of pesticides, herbicides, and fertilizers where these materials may come into contact with runoff (natural or induces); and 4) the use of pesticides, herbicides, or fertilizers anywhere where they may be directly or indirectly discharged to a storm drainage system.

An effective IPM program includes the following elements:

- Pesticides are used only if monitoring indicates they are needed according to established guidelines.
- Treatment is made with the goal of removing only the target organism.
- Pest controls are selected and applied in a manner that minimizes risks to human health, beneficial, non-target organisms, and the environment.
- Its use of pesticides, including Organophosphates and Pyrethroids do not threaten water quality.
- Partner with other agencies and organizations to encourage the use of IPM.
- Adopt and verifiably implement policies, procedures, and/or ordinances requiring the minimization of pesticide use and encouraging the use of IPM techniques (including beneficial insects) in the Permittees' overall operations and on municipal property.
- Policies, procedures, and ordinances shall include commitments and timelines to reduce the use of pesticides that cause impairment of surface waters by implementing the following procedures:
  - Quantify pesticide use by its staff and hired contractors.
  - Prepare and annually update an inventory of pesticides used by all internal departments, divisions, and other operational units.
  - Demonstrate reductions in pesticide use.

The protocol is applicable to any Permittee staff and contracted services that apply pesticides, fertilizers, or herbicides. Such staff commonly include, park, public works, purchasing, building/grounds maintenance, hazardous materials, and pesticide application staff. It is not applicable to the indoor use of pesticides, herbicides or fertilizers, but is applicable to the consequential outdoor handling, mixing, transport, or disposal of materials related to indoor use. This protocol also does not apply when another NPDES permit and/or abatement orders are in effect at the selected site. Furthermore, this protocol is not intended to replace federal or state requirements or provide complete directions for applying, handling, transporting, mixing, or storing pesticides, fertilizers, or herbicides.

### **Public Outreach and Education on Pesticide Use**

Timed to coincide with the spring planting season, the Program's outreach effort (Community for a Clean Watershed) ran a five-week pesticide campaign in 2010 utilizing television and radio campaign elements from past years' creative arsenal. Another campaign is planned for Spring 2016. The animated "More, Better" television commercial graphically demonstrates how using too much pesticide runs into the storm drains, eventually making it into the Watershed, adversely affecting plants and animals. The radio spot was a humorous adaptation of the television ad, featuring the two animated characters as they defend their house against garden pests and inadvertently poison the watershed. An animated web banner corresponded with both broadcast media while the transit shelters took a more direct approach showing a snail and telling residents "Don't kill an ocean just to keep pests out of your garden."



*Spanish Language Pesticide Outreach*



*Newspaper Advertisement*

### **Retail Partnership Brochures: Nurseries and Gardeners,**

Watershed Protection Tip pamphlets aimed at residents were created to encourage best practices in their homes. These brochures were distributed to targeted retail stores to reach the population that is



likely involved in the activities. The colorful pamphlet defines the Watershed, explains the storm drain system, how polluted water is damaging and gives both overall and topic-specific tips for how to keep the Watershed clean. In this case the one aimed at gardeners talks about plant selection, irrigation, fertilizer and pesticide practices, integrated pest management and proper yard maintenance.

**How Can You Help Keep the Watershed Clean?**  
 Whether your home is one mile or many miles from the Pacific Ocean, what starts in your garden can end up as toxic stormwater runoff and contribute to coastal pollution.  
 You can do the right thing and keep preventable pollutants out of the storm drain system. Unlike sewer systems, storm drain systems direct runoff, untreated, straight into local waterways.  
 Preventable pollutants include both seen and unseen materials that accumulate in our yards, driveways, gutters and streets and that damage our watersheds.  
 Simple changes in the way we care for our gardens can make a big difference in keeping our watersheds clean.

**The Watershed Should Only Shed Water**  
 The storm drain system is a vast network of gutters, pipes and open channels designed for flood control, which directs runoff – untreated – from the watershed straight into the waterways.  
 Polluted stormwater contaminates streams, rivers and lakes. It can kill or damage plants, fish and wildlife, and can degrade the quality of our water.  
 The Community for a Clean Watershed program was established to protect Ventura County's watershed by preventing stormwater pollution.  
 For more information on how to keep our watersheds clean, go to [cleanwatershed.org](http://cleanwatershed.org).

**What Is Our Watershed?**  
 Our watershed is the total land area, including your yard, from which stormwater drains into streams, rivers or other bodies of water. In Ventura County our primary watersheds drain into the Ventura and Santa Clara Rivers, Malibu and Calleguas Creeks and the marinas and estuaries that flow into the Pacific Ocean.

COMMUNITY FOR A CLEAN WATERSHED  
[cleanwatershed.org](http://cleanwatershed.org)

COMMUNITY FOR A CLEAN WATERSHED  
[cleanwatershed.org](http://cleanwatershed.org)

Printed on recycled paper

**Clean Gardening Practices**

**Plant Selection**  
 Select pest-resistant and drought-resistant native plants for your garden to reduce the need for pesticides, fertilizers and water. Create landscaped areas next to sidewalks and driveways to naturally collect and filter any potentially polluted runoff from paved surfaces. Go to [bewaterwise.com](http://bewaterwise.com) for a California-Friendly Gardening Guide.

**Irrigation**  
 Save water and money by automating your sprinkler system. Irrigate after dusk or early in the morning when less water is lost to wind and evaporation. Even during the hot summer months, there is no need to water every day. Routinely fix leaks and damaged sprinkler heads to minimize runoff that carries pollutants into the storm drain system.

**Fertilizers & Pesticides**  
 Overuse of any pesticide or fertilizer is a key contributor to stormwater pollution. Apply only as needed and as directed on the label, and always store under cover, out of the rain. Never use fertilizers or pesticides around water, drains, bare ground or if rain is predicted within 24 hours. Avoid using copper sulfate root-killing products. Pesticides that contain diazinon or chlorpyrifos have been banned and should be disposed of at your local Household Hazardous Waste\* collection center or event.

**Integrated Pest Management (IPM)**  
 IPM is an eco-friendly approach to effective pest management. Its goal is to use less-toxic methods to reduce the use of pesticides, creating a system that is safe for your family and the environment. To learn more, go to the UC Davis IPM resource site at [ipm.ucdavis.edu](http://ipm.ucdavis.edu).

**Maintenance**  
 Clear, remove and recycle yard debris such as leaves and grass cuttings by placing them in your yard waste bin or by composting. Even organic waste, when flushed or blown into storm drains, can create flooding and pollute the watershed. Rotting plant material can also reduce the oxygen available for aquatic wildlife and increase the presence of harmful bacteria.

\*Go to [watershed.org](http://watershed.org) for locations and hours of Household Hazardous Waste collection centers and events throughout Ventura County.

## **RECOMMENDATIONS**

Urban use of pesticides remains one of the priority pollutants for the Program. Through maintaining a strong public outreach effort to educate the public on the use and handling of pesticides coupled with household hazardous waste collections providing proper disposal of unwanted products, the Program expects to reduce the pesticide contamination in stormwater discharge. The results of this study, and the previous one three years ago, do not directly show a link between pyrethroids and significant toxicity in the samples, meaning the toxicity could be from other pesticides or other pollutants. The Program is committed to reducing all pollutants in MS4 runoff and through the continued implementation of the Program, these other potential causes to toxicity will be addressed.

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