



Ventura Countywide Stormwater Quality Management Program

PYRETHROID INSECTICIDES STUDY

2012 - 2021 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

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CITY OF VENTURA

December 15, 2021

EXECUTIVE SUMMARY

Monitoring of sediment for pyrethroids, total organic carbon (TOC), and toxicity to the amphipod, *Hyalella azteca*, was conducted at two sites in the Calleguas Creek (CC), Ventura River (VR), and Santa Clara River (SCR) watersheds in 2012, 2015, 2018, and 2021, as 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 2020/21 water year was exceptionally dry, and Ventura County received only 20-30% of normal rainfall, with most of the rain falling in December, January, and March. Sampling was conducted on March 23 and 24, 2021, one to two weeks after the March storm. Two of the usual sites were dry with no evidence of seasonal flow: CC Up and SCR Down. A replacement site with similar land use approximately 5.5 miles upstream was sampled for SCR Down (SCR Down-a), but an appropriate replacement site was not found for CC Up. Pyrethroids were not detected in the 2021 round of the Study, however the laboratory's reporting levels for 2021 were higher than previous years, which could have obscured detection of some pyrethroids at previously detected levels. All 2021 samples displayed significant toxicity and a toxicity identification evaluation (TIE) was conducted, which determined that the toxicity was likely caused by the naturally occurring chironomids in the sample preying on the *H. azteca* organisms used for the test. The removal of the chironomids eliminated the toxicity in the samples.

There was no toxicity or detections of pyrethroids in 2018. In 2012 and 2015, the most detected pyrethroids were bifenthrin and permethrin. The hypothetical contribution to toxicity (TU_H) was calculated for each detection based on the sample's pyrethroid concentration, TOC amount, and a pyrethroid reference concentration known to cause significant toxicity to *H. azteca* in sediment samples. The hypothetical and observed toxicity agreed that the pyrethroid concentrations should not result in significant toxicity for all samples, although WOOD 2012, a predominately agricultural site, showed bifenthrin near the TU_H threshold for toxicity. In two samples, SCR Up 2015 and VR Down 2015, significant toxicity was observed but TU_H was low, indicating that the cause of the toxicity was a pollutant not part of this study. These two sites are associated with multiple land uses, including urban and agriculture.

Bifenthrin and permethrin are both used in significant quantities for regulated applications for structural and agricultural pest control in Ventura County but are also known to have unregulated applications for residential and industrial uses, which are not tracked. The lack of correlation between pyrethroid TU_H and corresponding observed toxicity for samples collected over four study terms, except at the agricultural-dominated WOOD site in 2012, suggests that the current approach to mitigate urban contributions of pyrethroids by targeting pesticide use in the Ventura Countywide Stormwater Management Program's (Program) education and outreach campaigns is effective and should be continued. The agricultural contributions are not under the jurisdiction of the Program and would need to be addressed through other avenues.

No trends in pyrethroid detections were apparent over the Permit term, however the lack of correlation between observed toxicity and detections of pyrethroids indicates that pyrethroid insecticide concentrations are not at or approaching levels known to be toxic to sediment-dwelling aquatic organisms.

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 (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 Study was conducted in April 2012 by the District at two locations in both the Ventura River and Santa Clara River watersheds. Data from the Calleguas Creek Watershed Toxicity Total Maximum Daily Load (TMDL) monitoring program was used to meet the requirements for that watershed, as allowed by the Permit. However, 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 were included in the 2015 report. Two sites in the Calleguas Creek Watershed were added to the District monitoring in 2015 to increase comparability and avoid issues with different detection levels, sampling strategies, and reporting cycles between the TMDL and this Study. Therefore, only TMDL data from 2012 is included in these reports. The second, third, and fourth rounds of the Study were conducted in April 2015, May 2018, and March 2021, respectively, by the District at two sites each in the Ventura River, Santa Clara River, and Calleguas Creek¹ watersheds.

The samples were analyzed for total organic carbon (TOC) and eight specific pyrethroid pesticides required by the Permit (bifenthrin, cyfluthrin, cypermethrin, deltamethrin (co-elutes with tralomethrin, which is listed in the Permit if the laboratory is capable of analyzing for it), esfenvalerate (co-elutes with the non-required fenvalerate), lambda-cyhalothrin, and permethrin, as well as several pyrethroid and non-pyrethroid pesticides that are not required by the permit but are standard outputs of the analytical method. All sediment samples were tested for toxicity through a 10-day survival bioassay using 7–10-day old *Hyalella azteca*.

Hypothetical toxicity units (TU_H) were calculated to compare the expected relative toxicity of different samples and pyrethroids. TU_H are calculated by normalizing the sediment pyrethroid concentrations to TOC concentration (to account for hydrophobicity) and then dividing by the *H. azteca* 10-day median lethal concentration (LC50²) for each detected pyrethroid, if available. TU_H cannot be calculated for detected analytes without LC50s in the reference documents (e.g. non-pyrethroids such as pendimethalin and dichloran) or for analytes that may be present at levels below the method detection limit (i.e. non-

¹ Only one site in Calleguas Creek Watershed in 2021 due to a very dry year (20-30% normal rainfall).

² LC50 is the lethal concentration required to kill 50% of the population.

detects), so their hypothetical contributions to toxicity are unknown. Pollutants other than those analyzed may also be contributing to toxicity, however this study was focused on pyrethroid pollutants.

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). All TU_H 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, except for 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.

In 2015, two of the eight Permit-required pyrethroid pesticides 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. All TU_H were less than one except for bifenthrin in the CC Down duplicate, however there was not significant toxicity in the measured sample. Some toxicity was observed in 2015 at SCR Up and VR Down. 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.

In 2018, the third round of the study was conducted and pyrethroids were not detected in any of the Study samples. One non-pyrethroid pesticide (Dichloran) was detected at one site. Significant toxicity was not observed in any of the 2018 samples.

In 2021, the fourth round of the study was conducted following a very dry wet season (20-30% of normal rainfall) and no pyrethroids were detected, however laboratory reporting limits were higher than in previous years which could obscure the presence of pyrethroids. Two non-pyrethroids (dichloran and pendimethalin) were detected at one site. Significant toxicity was initially observed in all samples, but the toxicity identification evaluation (TIE) determined that the likely cause was chironomids (midges) present naturally in the samples, which preyed upon the *H. azteca* during the test.

METHOD

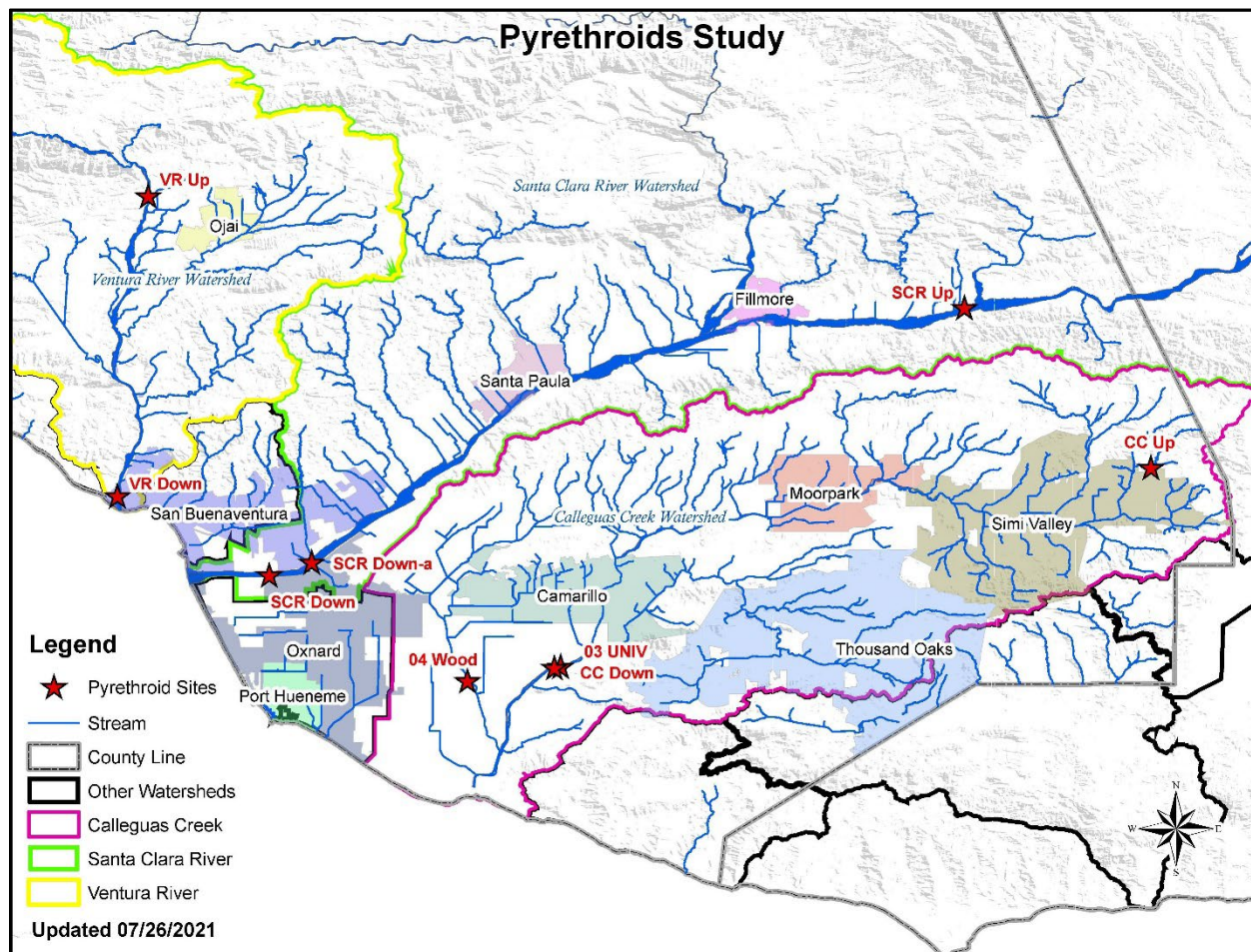
The Permit specifies that monitoring is to be conducted every three years for the duration of the Permit (i.e. 2012, 2015, 2018, 2021), after sediment has settled within the water body and safe access can be assured. In-stream sediment samples for chemical analysis and toxicity testing were collected 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 (when possible) to obtain a sample representative of the site.

Two sites, an upstream site and a downstream site, were selected on the main stem 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 in all cases to exclude upstream sources of agriculture and/or urban runoff, including some sources outside of Ventura County. For the Ventura River watershed, the upstream site (VR Up) is on the Ventura River above the Casitas Municipal Water District's diversion structure near the north end of Rice Road in Meiners Oaks. The downstream site (VR Down) is on the Ventura River near the Main Street Bridge in Ventura. For the Santa Clara River watershed, the upstream site (SCR Up) is on the Santa Clara River east of Torrey Road near the Los Angeles/Ventura County Line and the downstream site (SCR Down) is on the Santa Clara River near the Victoria Avenue Bridge in Ventura. For 2021, SCR Down was completely dry with no evidence of recent flow, so the site was moved upstream near Los Angeles Avenue (SCR Down-a). For the Calleguas Creek watershed, the upstream site (CC Up) is in Las Lajas Canyon above Las Lajas Dam, north of Simi Valley, and the downstream site (CC Down) 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.

For the first round of the Study (2012), two sites from the Calleguas Creek Watershed Toxicity Total Maximum Daily Load (TMDL) monitoring program were used to meet the requirements for that watershed, as allowed by the Permit. The TMDL sites were 03_UNIV (UNIV) – co-located with CC Down, and 04_WOOD (WOOD) – Revolon Slough at Wood Road. To increase comparability between samples, watersheds, and years, and eliminate differences between the Study and the TMDL (e.g. detection levels, sampling strategies, collection methods, reporting cycles, etc.), the TMDL sites in the study were replaced with CC Up and CC Down beginning in 2015.

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

Figure 1. Pyrethroid Sampling Locations



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 one to 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 for pickup by the chemistry lab courier the following day. The remaining sediment (~ 3 liters) was double-bagged and kept on ice until delivered to the toxicity laboratory.

Water quality field measurements were taken with hand-held probes. All sediment samples were analyzed for total organic carbon (TOC) by EPA 9060, pyrethroids by GC/MS NCI-SIM, and toxicity to 7–10-day old *Hyalella azteca*, as described in *Aquatic Toxicity Due to Residential use of Pyrethroid Insecticides*³. A toxicity identification evaluation (TIE) procedure was conducted in 2021 to remove the native *Chironomus* population as a suspected cause of observed toxicity of the samples. The procedure is adapted from US EPA/600/R-07/080 and is a widely accepted means of organism removal treatment in TIE analysis. Two liters of control water were added to half of the remaining sediment and stirred with a stainless-steel paddle. *Chironomus* that were dislodged from the sediment were scooped off using stainless sieves and stored for an additional QC test. The added water was poured off and used as the

³ *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.

overlying/control water for the treatment setup and renewals. The samples were then run side by side with the untreated samples. A known non-toxic sample was also run in the batch with the saved chironomids from one site (VR Up) added to it, as well as on its own without the chironomids. All samples used 100 ml of sediment with 175 ml of control water, of which ~50 ml of control water was poured off and new control water added each day during the 10-day test.

The stainless-steel trowels used for the Study were cleaned prior to sample collection with Alconox⁴ laboratory detergent and tap water, rinsed with distilled water, and air dried. They were then sealed 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 it 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.

RESULTS

Three pyrethroids were detected in environmental samples during the Study: bifenthrin and permethrin, which were required analytes in the Permit, and fenpropathrin (danitol) which was not required by the Permit but was included in the analytical method. Two non-pyrethroid pesticides, dichloran and pendimethalin, were also detected but were not required by the Permit. These non-pyrethroid analytes were not part of the TMDL analytical method so data is not available for the 2012 TMDL sites.

Study Equipment Blanks

No pyrethroids (or non-pyrethroid constituents) were detected by the pyrethroid analytical method for the 2021 equipment blank (trowel). A small amount of TOC was detected below the reporting limit (Table 1). The 2021 TOC analysis was subbed out to another lab due to broken equipment at the primary laboratory, so the detection limit is higher for 2021. The equipment blank detections are similar to those seen in equipment blank samples in previous years of the Study. The detection of TOC was insignificant in relation to expected environmental concentrations, so no follow up testing was required in 2021. Additional testing following detections of parameters of interest was done in previous studies, i.e., 2012 and 2015, due to detections above the reporting limit in the initial blanks. The follow up testing showed reduced detections, as explained in the 2012 and 2015 reports.

⁴ Alconox laboratory detergent in 2018 and 2021, Citranox laboratory detergent in 2012 and 2015.

Table 1. Equipment Blank Results 2012 - 2021

Analyte	2012 Initial Trowel Blank ($\mu\text{g/L}$, MDL varies)	2012 2 nd Trowel Blank (same trowel, 2nd rinse) ($\mu\text{g/L}$, MDL varies)	2015 Initial Trowel Blank ($\mu\text{g/L}$, MDL varies)	2015 2 nd Trowel Blank (2 nd trowel) ($\mu\text{g/L}$, MDL varies)	2018 Trowel Blank ($\mu\text{g/L}$, MDL varies)	2021 Trowel Blank ($\mu\text{g/L}$, MDL varies)
Allethrin	ND (<0.00085)	ND (<0.00085)	ND (<0.00085)	ND (<0.00085)	ND (<0.00085)	ND (<0.00085)
Bifenthrin	<u>0.0041</u>	ND (<0.00079)	<u>0.0026</u>	<u>0.00091 (DNQ)</u>	<u>0.00085 (DNQ)</u>	ND (<0.00079)
Cyfluthrin	ND (<0.00083)	ND (<0.00083)	ND (<0.00083)	ND (<0.00083)	ND (<0.00083)	ND (<0.00083)
Cypermethrin	<u>0.0026</u>	ND (<0.00066)	ND (<0.00066)	ND (<0.00066)	<u>0.00087 (DNQ)</u>	ND (<0.00066)
Deltamethrin/Tralomethrin	ND (<0.0019)	ND (<0.0019)	ND (<0.0019)	ND (<0.0019)	ND (<0.0019)	ND (<0.0019)
Dichloran	ND (<0.00080)	ND (<0.00080)	ND (<0.00080)	ND (<0.00080)	ND (<0.00080)	ND (<0.00080)
Esfenvalerate	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)
Fenpropathrin			ND (<0.0020)	ND (<0.0020)	ND (<0.0020)	ND (<0.0020)
Fenvalerate	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)	ND (<0.00098)
L-Cyhalothrin	ND (<0.0012)	ND (<0.0012)	ND (<0.0012)	ND (<0.0012)	ND (<0.0012)	ND (<0.0012)
Pendimethalin	<u>0.0025</u>	ND (<0.00050)	ND (<0.00050)	ND (<0.00050)	ND (<0.00050)	ND (<0.00050)
Permethrin	ND (<0.0050)	ND (<0.0050)	ND (<0.0050)	ND (<0.0050)	ND (<0.0050)	ND (<0.0050)
Prallethrin	ND (<0.00092)	ND (<0.00092)	ND (<0.00092)	ND (<0.00092)	ND (<0.00092)	ND (<0.00092)
Sumithrin	ND (<0.0024)	ND (<0.0024)	ND (<0.0024)	ND (<0.0024)	ND (<0.0024)	ND (<0.0024)
Tefluthrin	ND (<0.00093)	ND (<0.00093)	ND (<0.00093)	ND (<0.00093)	ND (<0.00093)	ND (<0.00093)
TOC	<u>0.17 mg/L (DNQ)</u>	N/A	<u>0.18 mg/L (DNQ)</u>	<u>0.23 mg (DNQ)</u>	<u>0.23 mg/L</u>	<u>0.49 mg/L (DNQ)</u>

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

2021 Study

The 2020/21 water year was exceptionally dry, and Ventura County received only 20-30% of normal rainfall, with most of the rain falling in December, January, and March. Sampling was conducted on March 23 and 24, 2021, one to two weeks after the March storm. VR Up (Figure 2), VR Down (Figure 3), SCR Up (Figure 4), and CC Down (Figure 7) were flowing, however CC Up (Figure 6) and SCR Down (Figure 8) were completely dry with no evidence of recent flow. An alternate wet SCR Down site was identified approximately 5.5 miles upstream at the Los Angeles Avenue Bridge and access permission obtained, so sampling was conducted at this alternate site, SCR Down-a (Figure 5). There was not a suitable backup site for CC Up so samples above the urban influence in the Calleguas Creek watershed were not collected for this event.

Figure 2. VR Up



Figure 3. VR Down



Figure 4. SCR Up



Figure 5. SCR Down-a



Figure 6. CC Up (Dry)



Figure 7. CC Down



Figure 8. SCR Down (Dry)



The chemistry laboratory was instructed to perform the pyrethroid analyses with reporting limits (RLs) below or as close to 1 ng/g as possible, per the permit and as done for the previous three rounds of the study, however the laboratory did not achieve these limits for 2021. No pyrethroids were detected in the 2021 sediment samples, including the eight pyrethroids specified by the Permit for analysis (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, I-cyhalothrin, permethrin, and tralomethrin), however the RLs were high enough that they would have obscured detections at levels seen in previous events. Dichloran and pendimethalin, two non-pyrethroid pesticides, were detected above the RL (49 and 16 ng/g, respectively) at one site (SCR Down-a). TOC amounts ranged from 5.19 g/kg at CC Down to 43.1 g/kg at VR Up and this range is similar to previous years, although it varies between sites.

All samples were subjected to a 10-day survival and growth sediment bioassay using *Hyalella azteca*. The laboratory observed *Chironomus* and *Ostracoda* present in all samples during setup. Substantial survival and growth toxicity occurred in all⁵ samples. Laboratory staff observed the chironomids attacking and attaching to the *H. azteca* and so suspected that the measured toxicity was due to the *Chironomus* preying on the *H. azteca* during the test. A toxicity identification evaluation (TIE) was initiated with a treatment to

⁵ VR Down did not exhibit toxicity for growth. Growth was higher for VR Down than for its field duplicate (VR Down (Dup)*) and the control. Survival was similar with significant toxicity in VR Down and VR Down (Dup). *Field duplicate named VR Down 2 in laboratory reports.

remove the *Chironomus* from the sample. 10-day survival bioassays of the treated samples were run side by side with untreated samples. The treated samples did not display significant toxicity, but the untreated samples displayed toxicity levels similar to the original tests. Similarly, the chironomids that were removed from the VR Up sample were added to a known non-toxic sample and this treated sample was run side by side with an untreated sample from the same site. The formerly non-toxic sample was still non-toxic without the chironomids (100% survival) but was toxic with the added chironomids (0% survival).

The field duplicate (VR Down (Dup)) results were within allowed limits for relative percent difference for pyrethroids, TOC, and toxicity survival, however there was a difference in growth toxicity, as VR Down outperformed the control unlike all other Study samples, including its field duplicate.

Table 2. Laboratory Results 2021

Analyte	CC Down	SCR Up	SCR Down-a	VR Up	VR Down	VR Down (Dup)	Non-Toxic Tox QA	Units
<u>Chemistry</u>								
Allethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Bifenthrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Cyfluthrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Cypermethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Deltamethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Dichloran	<4.2	<4.0	49	<1.7	<4.3	<7.4	NA	ng/g
Esfenvalerate	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Fenpropathrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Fenvalerate	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
L-Cyhalothrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Pendimethalin	<4.2	<4.0	16	<1.7	<4.3	<7.4	NA	ng/g
Permethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Prallethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Sumithrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Tefluthrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
Tralomethrin	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	NA	ng/g
TOC	5.19	7.04	15.3	43.1	10.7	16.2	NA	g/kg
<u>Toxicity to <i>H. azteca</i>: Initial</u>								
Survival	12.50 SG	62.50 SG	35.00 SG	7.50 SG	75.00 SG	67.50 SG	NA	% Survival
Growth	57.69 SG	38.46 SG	65.38 SG	73.08 SG	-50.00	61.54 SG	NA	% Effect
<u>Toxicity to <i>H. azteca</i>: TIE</u>								
Survival, with chironomids	17.50 SG	72.50 SG	45.00 SG	0.00 SG	NA	52.50 SG	0.00 SG	% Survival
Survival, without chironomids	100.00	97.50	100.00	97.50	NA	100.00	100.00	% Survival

Analyte listed in Permit

< Not detected at method detection limit
NA = Not Applicable
SG = Significant effect compared to control

Detected (chemistry) or Significant effect (toxicity)

Dup = field duplicate
- Sample performed better than the control

2012, 2015 and 2018 Combined Results⁶

Data from the Calleguas Creek Watershed Toxicity Total Maximum Daily Load (TMDL) monitoring program was used to meet the requirements for that watershed in 2012, as allowed by the Permit. However, TMDL site 04_WOOD (WOOD) is not co-located with CC Up, and although TMDL site 03_UNIV (UNIV) is co-located with CC Down, the sample collection methods and protocols for the TMDL are different to this Study. To increase comparability between samples and watersheds, two sites in the Calleguas Creek Watershed were added in 2015 to avoid issues with different detection levels, sampling strategies, and reporting cycles. TMDL data (except for 2012) is not included in this report. The 2012-2018 laboratory results are grouped by watershed in Table 3, Table 4, and Table 5.

⁶ Since 2021 reporting limits were higher than those of previous study years, the 2021 results have not been added to the 2012-2018 results tables.

Table 3. Laboratory Results 2012-2018 – Calleguas Creek Watershed

Analyte	<u>WOOD</u>	CC Up		<u>UNIV (co-located with CC Down)</u>		CC Down			Units
	2012	2015	2018	2012	2012 Dup	2015	2015 Dup	2018	
Allethrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Bifenthrin	<u>2.7</u>	<0.93	<0.85	<u>1^</u>	<u>0.9^</u>	<u>3.3</u>	<u>5.9</u>	<0.93	ng/g
Cyfluthrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Cypermethrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Deltamethrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Dichloran	NS	<0.93	<0.85	NS	NS	<0.93	<0.92	<0.93	ng/g
Esfenvalerate	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Fenpropathrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Fenvalerate	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
L-Cyhalothrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Pendimethalin	NS	<0.93	<0.85	NS	NS	<u>3.8</u>	<u>2.5</u>	<0.93	ng/g
Permethrin	<5	<0.93	<0.85	<5	<5	<u>3.3</u>	<u>5.4</u>	<0.93	ng/g
Prallethrin	<0.5	<0.93	<0.85	<0.5	<0.5	<0.93	<0.92	<0.93	ng/g
Sumithrin	NS	<0.93	<0.85	NS	NS	<0.93	<0.92	<0.93	ng/g
Tefluthrin	NS	<0.93	<0.85	NS	NS	<0.93	<0.92	<0.93	ng/g
Tralomethrin	NS	<0.93	<0.85	NS	NS	<0.93	<0.92	<0.93	ng/g
TOC	<u>5.6</u>	<u>12.2</u>	<u>1.43</u>	<u>4.4</u>	<u>3.3</u>	<u>12.3</u>	<u>8.27</u>	<u>7.01</u>	g/kg
Toxicity to <i>H. azteca</i>, Survival	<u>66.3</u> <u>SG</u>	95.0	100 100*	<u>75.0</u> <u>SG</u>	NS	82.5	87.5	95 100*	% Survival
Toxicity to <i>H. azteca</i>, Mortality	<u>33.7</u> <u>SG</u>	5.0	0 0*	<u>25.0</u> <u>SG</u>	NS	17.5	12.5	5.0 0*	% Mortality
Toxicity to <i>H. azteca</i> , Growth	<u>69.4</u> <u>SG</u>	-565	-304	-7.71	NS	-216	-161	-189	% Effect

TMDL = Samples collected at TMDL sites using TMDL methods. Only applicable to 2012 results.

Analyte listed in Permit

- < Not detected at method detection limit
- ^ Detected not quantified
- * Samples re-run to include growth
- Sample performed better than control

Detected (chemistry) or Significant (toxicity)

- Dup = Duplicate
- NS = Not sampled
- SG = Significant effect compared to control

Table 4. Laboratory Results 2012-2018 – Santa Clara River Watershed

Analyte	SCR Up			SCR Down			Units
	2012	2015	2018	2012	2015	2018	
Allethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Bifenthrin	<u>0.78</u>	<0.92	<0.88	<u>0.74</u>	<u>2.6</u>	<0.93	ng/g
Cyfluthrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Cypermethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Deltamethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Dichloran	<0.5	<0.92	<0.88	<u>0.54</u>	<u>1.1</u>	<u>2.1</u>	ng/g
Esfenvalerate	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Fenpropathrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Fenvalerate	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
L-Cyhalothrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Pendimethalin	<u>0.69</u>	<u>1.4</u>	<0.88	<u>5.4</u>	<u>8.8</u>	<0.93	ng/g
Permethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Prallethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Sumithrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Tefluthrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
Tralomethrin	<0.5	<0.92	<0.88	<0.5	<0.94	<0.93	ng/g
TOC	<u>5.4</u>	<u>17</u>	<u>13.3</u>	<u>11</u>	<u>11.4</u>	<u>14.6</u>	g/kg
Toxicity to H. azteca, Survival	98.75	<u>55.0 SG</u>	95.0 100*	96.25	90.0	100 97.5*	% Survival
Toxicity to H. azteca, Mortality	1.25	<u>45.0 SG</u>	5.0 0*	3.75	10.0	0 2.50*	% Mortality
Toxicity to <i>H. azteca</i> , Growth	NS	58.06	-226.35	NS	-387.10	-292.00	% Effect

Analyte listed in Permit

- < Not detected at method detection limit
- * Samples re-run to include growth
- Sample performed better than control

Detected (chemistry) or Significant (toxicity)

- NS = Not sampled
- SG = Significant effect compared to control

Table 5. Laboratory Results 2012-2018 – Ventura River Watershed

Analyte	VR Up			VR Down				Units
	2012	2015	2018	2012	2015	2018	2018 Dup	
Allethrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Bifenthrin	<0.5	<0.83	<0.90	<u>1.2</u>	<u>2.8</u>	<0.99	<0.93	ng/g
Cyfluthrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Cypermethrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Deltamethrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Dichloran	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Esfenvalerate	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Fenpropathrin	<0.5	<0.83	<0.90	<0.5	<u>1.4</u>	<0.99	<0.93	ng/g
Fenvalerate	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
L-Cyhalothrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Pendimethalin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Permethrin	<u>5.3</u>	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Prallethrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Sumithrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Tefluthrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
Tralomethrin	<0.5	<0.83	<0.90	<0.5	<0.82	<0.99	<0.93	ng/g
TOC	<u>22</u>	<u>33.8</u>	<u>13</u>	<u>26</u>	<u>18.8</u>	<u>27.1</u>	<u>31.4</u>	g/kg
Toxicity to H. azteca, Survival	83.75	95.0	100 100*	88.75	<u>20.0 SG</u>	97.5 97.5*	NS	% Survival
Toxicity to H. azteca, Mortality	16.25	5.0	0 0*	11.25	<u>80.0 SG</u>	2.5 2.5*	NS	% Mortality
Toxicity to H. azteca, Growth	NS	5.00	-147.58	NS	54.84	-162.08	NS	% Effect

Analyte listed in Permit

- < Not detected at method detection limit
- * Samples re-run to include growth
- Sample performed better than control

Detected (chemistry) or Significant (toxicity)

- Dup = Duplicate
- NS = Not sampled
- SG = Significant effect compared to control

2012 - 2021 Charts

The three pyrethroids (bifenthrin, fenpropathrin, and permethrin) and two non-pyrethroid pesticides (dichloran and pendimethalin) that were detected during the Study (2012 - 2021) are graphed by watershed in Figure 9, Figure 10, and Figure 11. The MDLs are included to show the limitations of the laboratory to detect the pyrethroids each year.

Figure 9. 2012-2021 Detected Pyrethroids/Non-Pyrethroids and MDLs - Calleguas Creek Watershed

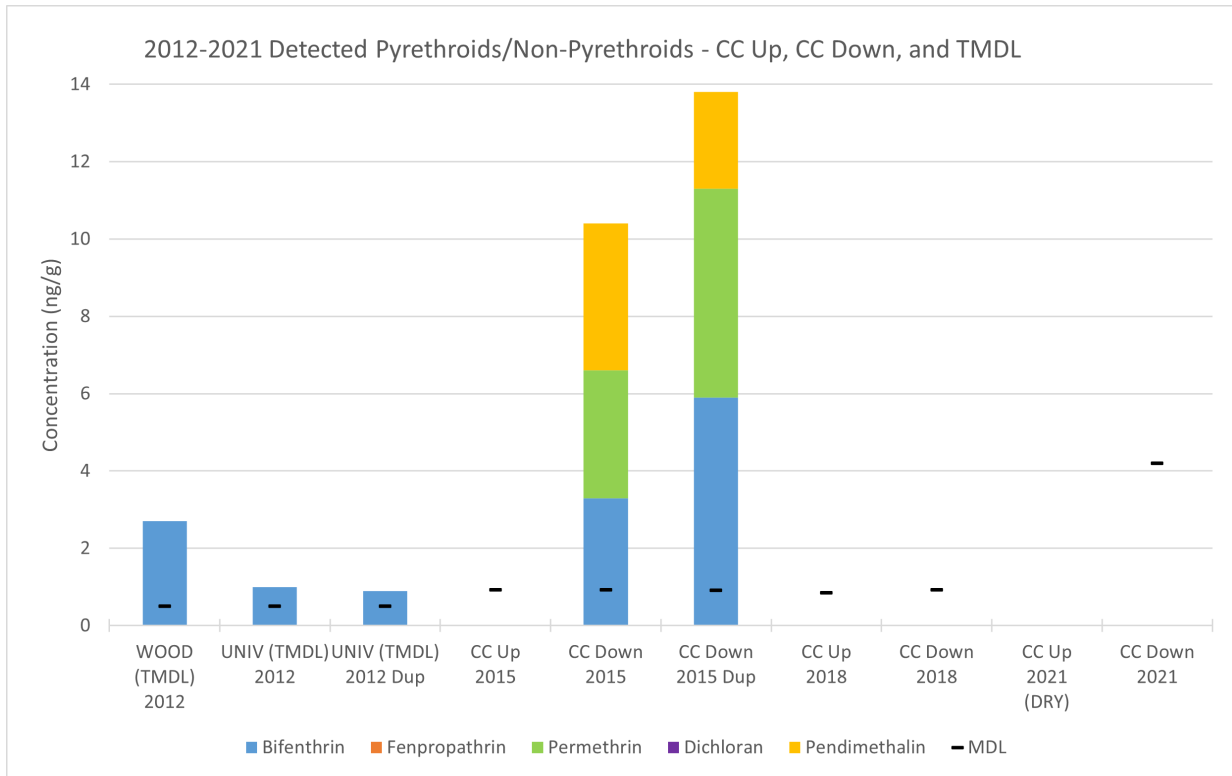


Figure 10. 2012-2021 Detected Pyrethroids/Non-Pyrethroids and MDLs - Ventura River Watershed

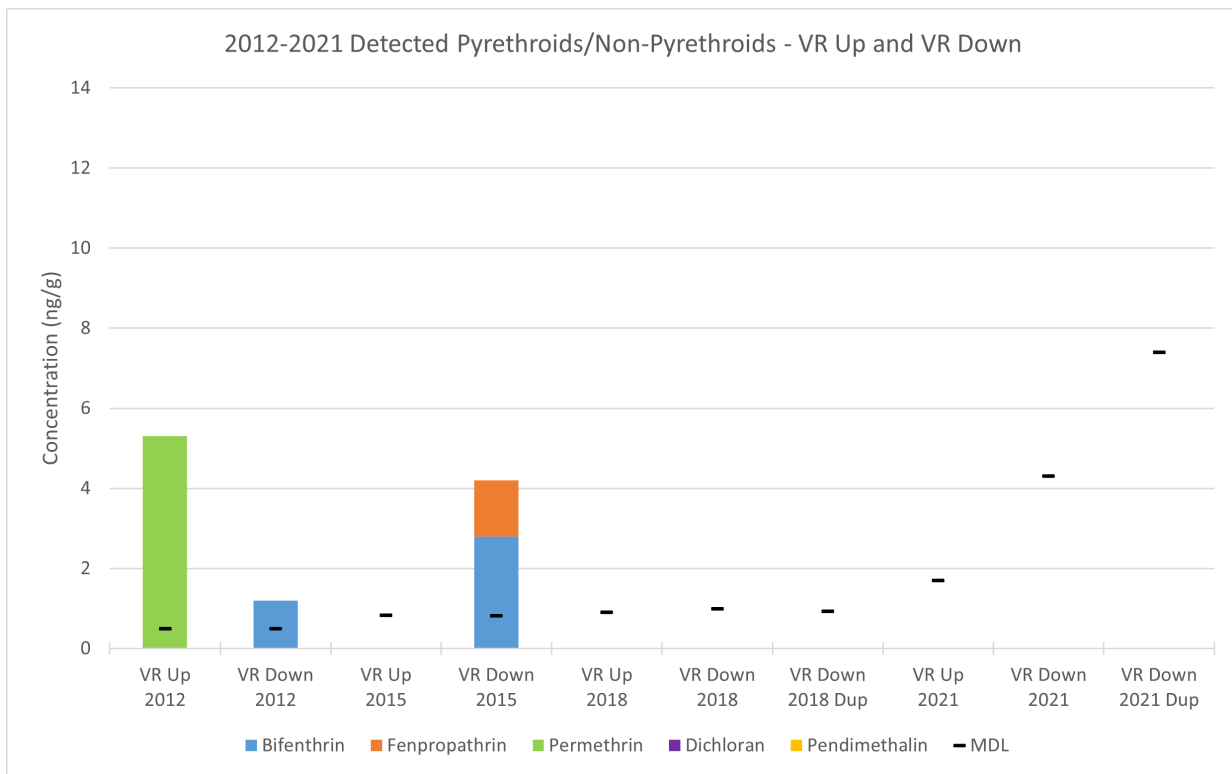
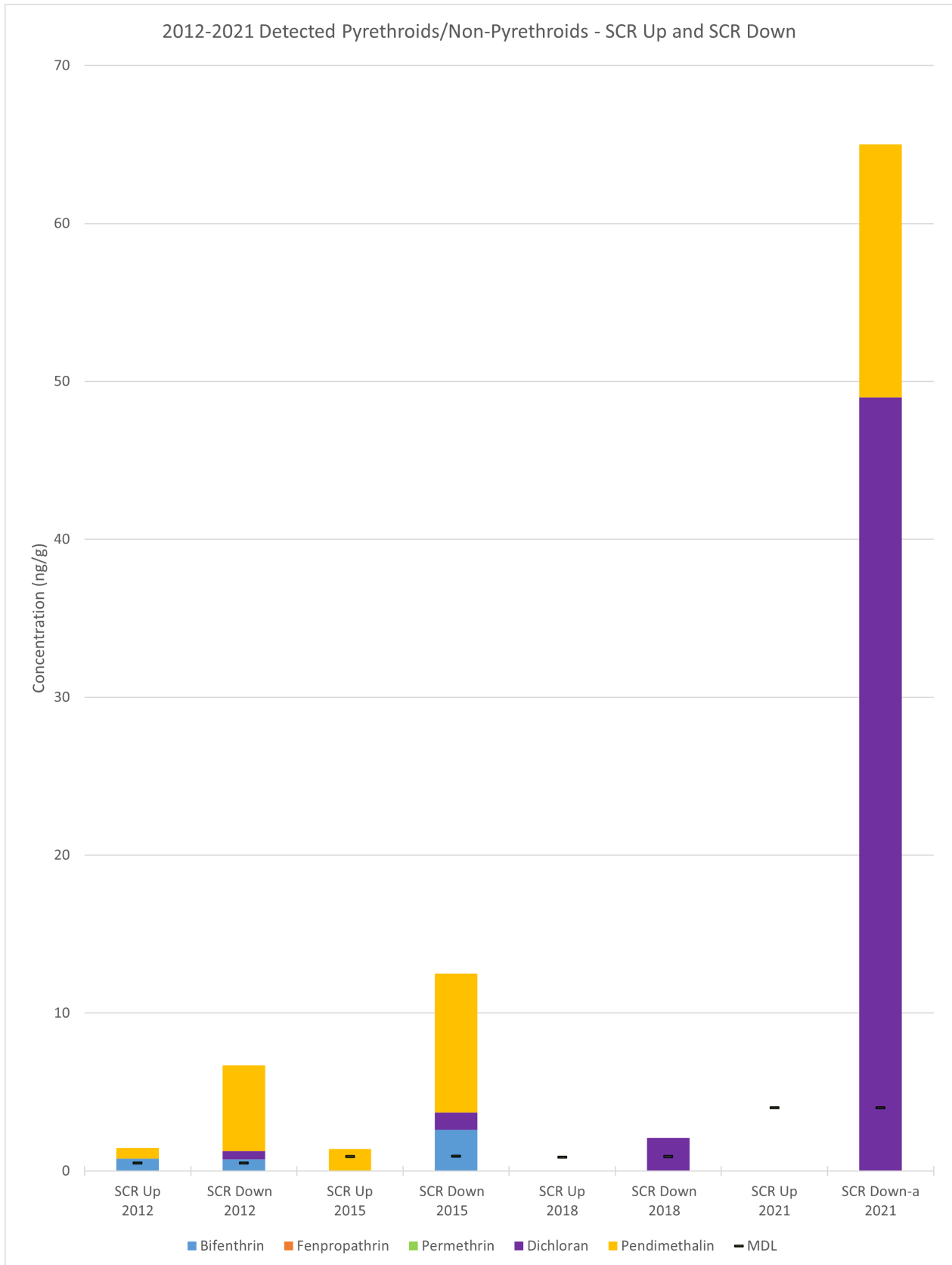


Figure 11. 2012-2021 Detected Pyrethroids/Non-Pyrethroids and MDLs – Santa Clara River Watershed



DISCUSSION OF RESULTS

The 2020/21 wet season was very dry, and only 20-30% of normal seasonal rainfall (approximately two to six inches) fell between October 2020 and March 2021. Sampling was conducted on March 23 and 24, 2021, approximately one to two weeks after the last storm. VR Up, VR Down, SCR Up, and CC Down were flowing, however SCR Down and CC Up were completely dry with no evidence of recent flow. SCR Down was moved to an alternate site approximately 5.5 miles upstream where water was still present in the Santa Clara River, SCR Down-a, however there was not a suitable backup site for CC Up so an alternate location was not sampled.

Equipment Blank

No pyrethroids (or non-pyrethroid constituents) were detected by the pyrethroid analytical method for the 2021 equipment blank (trowel) but a small amount of TOC was detected below the reporting limit (RL). The amount of TOC is similar to the equipment blank samples in previous years of the Study and is insignificant in relation to expected environmental concentrations.

The pyrethroid method has detected bifenthrin, cypermethrin, and pendimethalin in the equipment blank in previous years of the study, including in 2012 when the trowel was new, however the source of the contamination is unknown. The trowels do not appear to have contaminated the environmental samples as the detected levels of contamination were several orders of magnitude below the amounts measured in the samples. Pendimethalin has not been detected in the equipment blank since 2012. 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, so a replicate is not feasible. The laboratory QC was within limits for all pyrethroid method equipment blank batches 2012-2021, i.e. constituents were not detected above the RL of 0.0020 µg/L in the laboratory method blank, and the laboratory control samples and duplicates were all within acceptance limits.

A detectable amount of TOC was measured in all equipment (trowel) blanks for the study (2012-2021), including (DNQ) 0.49 mg/L in 2021, which was below the RL of 1.0 mg/L⁷. TOC was not detected in the 2021 laboratory method blank. Small (DNQ) amounts of TOC were seen in the laboratory method blanks in 2012-2018, but these amounts (≤ 0.0898 mg/L) were significantly less than seen in the equipment blanks (≤ 0.23 mg/L) which in turn are significantly less than the amounts seen in the environmental samples (≥ 1.43 g/kg, equal to 1430 mg/kg), so are not considered to be enough to significantly impact the sediment TOC results (i.e. TOC measured in the equipment blank was at least three orders of magnitude below the environmental samples).

Potential sources of the contamination in previous years could be from air drying, during rinsate collection and/or during analysis at the laboratory. The trowels were washed before and after they were used (with Citranox for 2012 and 2015 and with Alconox for 2018 and 2021). Alconox appears to have worked as

⁷ The 2021 equipment blank TOC sample was subbed to another laboratory due to broken equipment at the primary laboratory and the sub laboratory had a higher RL. The TOC RL for the previous study years was 0.30 mg/L.

well or better than Citranox for bifenthrin removal, and similarly or better than Citranox for cypermethrin removal.

Pyrethroids and Toxicity

The initial toxicity observed in the 2021 samples appears to be due to predation of the *H. azteca* by chironomids that were naturally present in the samples. Removing the chironomids from the samples coincided with the removal of toxicity. Transferring the removed chironomids from a study sample to a previously non-toxic non-study sample resulted in 100% mortality of the formerly non-toxic sample. While the higher pyrethroid RLs for the 2021 samples could obscure levels of pyrethroids previously measured in the study, the high survival rates in the TIE samples in which the chironomids were removed, support the supposition that the 2021 samples did not contain toxic levels of pyrethroids.

Table 6. 2021 Toxicity Results including TIE

Analyte	CC Down	SCR Up	SCR Down-a	VR Up	VR Down	VR Down (Dup)	Non-Toxic Tox QA	Units
<u>Toxicity to <i>H. azteca</i>: Initial</u>								
Survival	12.50 SG	62.50 SG	35.00 SG	7.50 SG	75.00 SG	67.50 SG	NA	% Survival
Growth	57.69 SG	38.46 SG	65.38 SG	73.08 SG	-50.00	61.54 SG	NA	% Effect
<u>Toxicity to <i>H. azteca</i>: TIE</u>								
Survival, with chironomids	17.50 SG	72.50 SG	45.00 SG	0.00 SG	NA	52.50 SG	0.00 SG	% Survival
Survival, without chironomids	100.0 NSG	97.5 NSG	100.0 NSG	97.5 NSG	NA	100.0 NSG	100.0 NSG	% Survival

Dup = field duplicate

- Sample performed better than the control

SG = Significant effect compared to control

NSG = Non-significant effect compared to control

Toxicity levels vary between pyrethroids. Hypothetical toxicity units (TU_H) can be calculated to compare the expected relative toxicity of different samples and pyrethroids. This is done by normalizing the sediment pyrethroid concentrations to TOC concentration to account for hydrophobicity and then dividing by the *H. azteca* ten-day median lethal concentration (LC50⁸) for each detected pyrethroid, if available. 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 sample can be calculated by summing all

⁸ LC50 is the lethal concentration required to kill 50% of the population.

the pyrethroid TU_H for that sample. TU_H greater than one indicates significant hypothetical toxicity. The non-pyrethroids were not included in these analyses as they are not pyrethroids and do not have LC50s in the Permit-referenced study.

Since the 2021 MDLs were higher than previous years and there were no detections of pyrethroids, the MDL and the measured TOC were used to calculate a worst-case scenario TU_H for the pyrethroids previously detected in the study (Table 7). This would be the hypothetical toxicity if the pyrethroid concentration was just below the detection limit for bifenthrin, fenpropathrin, and permethrin. The MDL concentration TU_H for fenpropathrin and permethrin were below 1 for all samples, supporting the evidence from the toxicity TIE (Table 6) that they were not contributing to toxicity in the samples. The MDL TU_H for bifenthrin at CC Down and SCR Up was above 1, which indicates that toxicity could be expected if bifenthrin was present in the samples at/above the MDL, however, the lack of corresponding toxicity seen in the TIE samples supports the likelihood that the level of bifenthrin in the samples was well below the MDL.

Table 7. 2021 Hypothetical Toxicity Calculated at the MDL

Analyte	CC Down	SCR Up	SCR Down-a	VR Up	VR Down	VR Down (Dup)	Units
<u>2021 Chemistry Results</u>							
Pyrethroids MDL	<4.2	<4.0	<4.0	<1.7	<4.3	<7.4	ng/g
TOC	5.19	7.04	15.3	43.1	10.7	16.2	g/kg
<u>2021 MDL Normalized to TOC (= [Pyrethroid MDL] / TOC Result)</u>							
Pyrethroid MDL normalized to TOC	<0.81	<0.57	<0.26	<0.04	<0.40	<0.46	ng/g
<u>Maximum Hypothetical Toxicity Units (TU_H) = (Pyrethroid MDL / TOC Result) / [LC50 (ug/g TOC)]</u>							
Bifenthrin [LC50=0.52 (ug/g TOC)]	<1.56	<1.09	<0.50	<0.08	<0.77	<0.88	TU _H
Fenpropathrin [LC50=1.1 (ug/g TOC)]	<0.74	<0.52	<0.24	<0.04	<0.37	<0.42	TU _H
Permethrin [LC50=10.83 (ug/g TOC)]	<0.08	<0.05	<0.02	<0.004	<0.04	<0.04	TU _H
Total TU_H	<2.37	<1.67	<0.77	<0.115	<1.18	<1.34	TU_H

< Not detected at method detection limit Dup = field duplicate

Conversely, since the TIE samples without chironomids were non-toxic, a hypothetical maximum concentration of each pyrethroid could be back-calculated using a TU_H=1, which would give the hypothetical pyrethroid concentration equivalent to the LC50 concentration for the measured TOC concentration at each site (Table 8). These calculated concentrations were above the MDL at all sites for fenpropathrin and permethrin, and at all sites except SCR Up and CC Down for bifenthrin, which indicates that the 2021 MDLs were sufficiently low to detect these pyrethroids at toxic levels in most cases. The two exceptions are bifenthrin at the two sites with the lowest TOC concentrations, SCR Up and CC Down which have calculated maximum bifenthrin concentrations of 3.7 and 2.7 and ng/g, respectively, which

could be considered upper limits of concentration for bifenthrin and would have been obscured by the MDLs of 4.0 and 4.2 ng/g, respectively. However, since survival rates were very high in the toxicity samples once the chironomids were removed, these calculated upper limits are likely higher than the actual pyrethroid concentrations in the samples.

Table 8. Maximum Calculated Pyrethroid Concentrations for $TU_H = 1$

Maximum Calculated Concentration (if $TU_H = 1$) = $TU_H \times TOC \text{ Result} \times [LC50 \text{ (ug/g TOC)}]$							
Analyte	CC Down	SCR Up	SCR Down-a	VR Up	VR Down	VR Down (Dup)	Units
Pyrethroids MDL	4.2	4.0	4.0	1.7	4.3	7.4	ng/g
Bifenthrin [LC50=0.52 (ug/g TOC)]	2.7	3.7	8.0	22.4	5.6	8.4	TU_H
Fenpropathrin [LC50=1.1 (ug/g TOC)]	5.7	7.7	16.8	47.4	11.8	17.8	TU_H
Permethrin [LC50=10.83 (ug/g TOC)]	56.2	76.2	165.7	466.8	115.9	175.4	TU_H

Dup = field duplicate

No pyrethroids were detected in the 2018 Study samples, so all TU_H for 2018 are equal to zero and toxicity due to pyrethroids is not expected. This was supported by the lack of toxicity observed in the sediment samples for both survival and growth. The 2012-2018 results are summarized by watershed below, showing their measured toxicity (% mortality) as compared to their hypothetical pyrethroid toxicity units. In some cases, e.g. UNIV (2012), SCR Up (2015), and VR Down (2015), significant toxicity was observed but the TU_H were low, in which case a different contaminant is likely the cause of the observed toxicity. At WOOD (2012), pyrethroids may have contributed to or been the cause of the toxicity observed in the sample, since the pyrethroid TU_H is close to 1. For CC Down Dup (2015), the TU_H were high but the observed toxicity was not, which may be due to other factors such as antagonistic effects with other components in the sample or subsample differences (e.g. differences in concentrations of TOC and pyrethroids). Subsample differences seem a likely cause since CC Down (2015) had a similar observed toxicity but a lower TU_H mostly due to higher TOC and lower bifenthrin concentrations.

Except for the CC Down Dup (2015), the TU_H for the Study samples were all less than one (Table 9) and so pyrethroid toxicity is not expected to be an issue for these samples according to this evaluation method. For the 2015 CC Down Duplicate, even though the 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 TU_H of less than one for these analytes. The TU_H were not correlated with the observed toxicity, possibly due to the presence of unanalyzed constituents in the samples.

Table 9. 2012-2018 Hypothetical Toxicity Units Vs. Observed Toxicity – By Watershed

Calleguas Creek Watershed										
Analyte	LC50 (ug/g TOC)	Units	WOOD	CC Up			UNIV	CC Down		
			2012	2015	2018	2012	2015	2015 Dup	2018	
Bifenthrin	0.52	TU _H	0.927				0.437 [^]	0.516	1.372	
Fenpropathrin	1.1	TU _H								
Permethrin	10.83	TU _H						0.025	0.060	
Summed Hypothetical TU _H		TU _H	0.927				0.437 [^]	0.541	1.432	
Significant Observed Toxicity			Yes	No	No		Yes	No	No	No

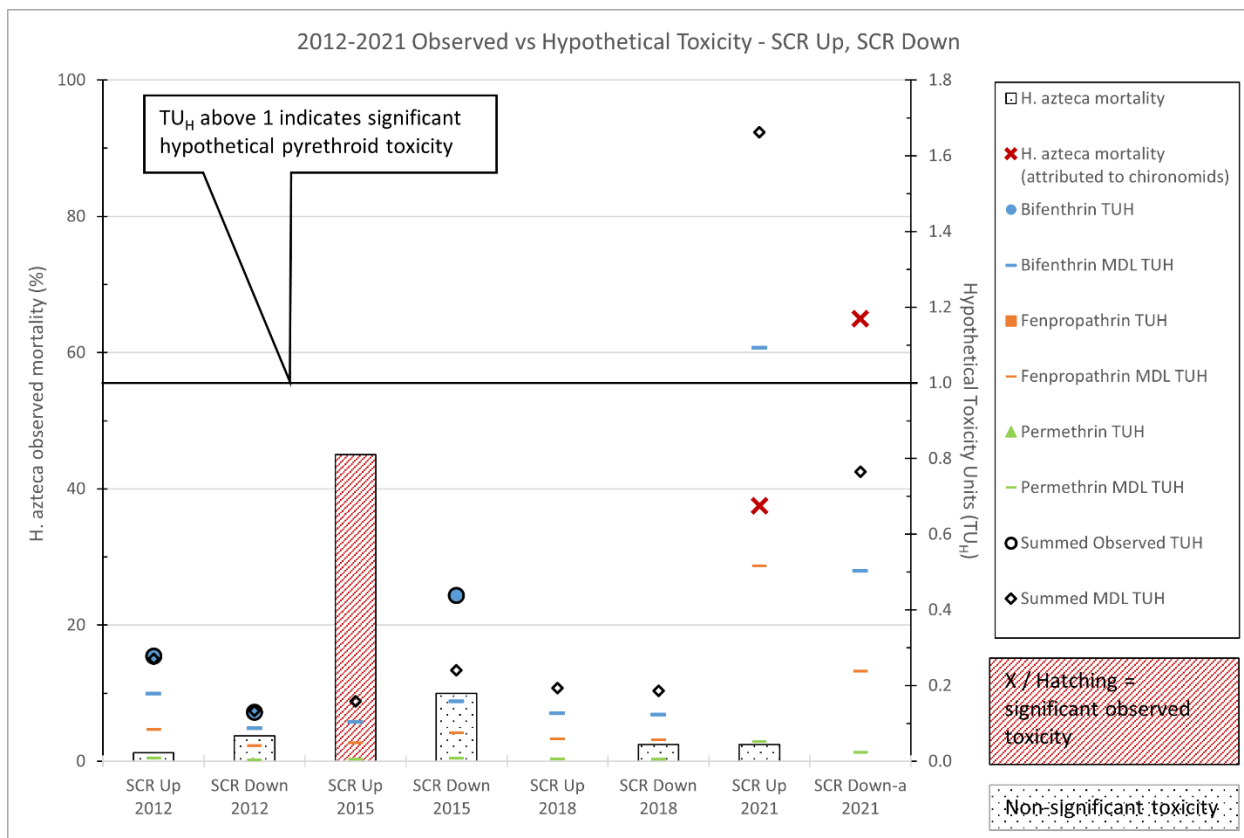
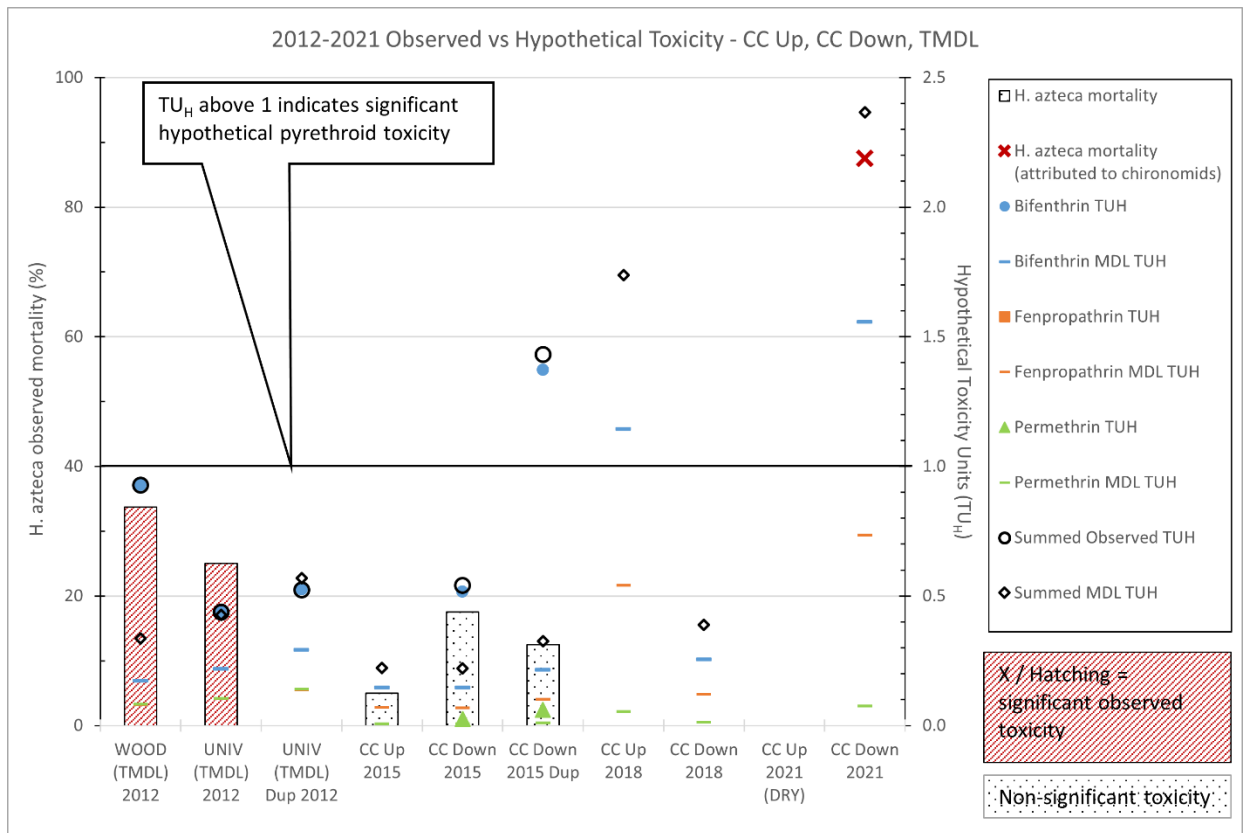
[^] DNQ

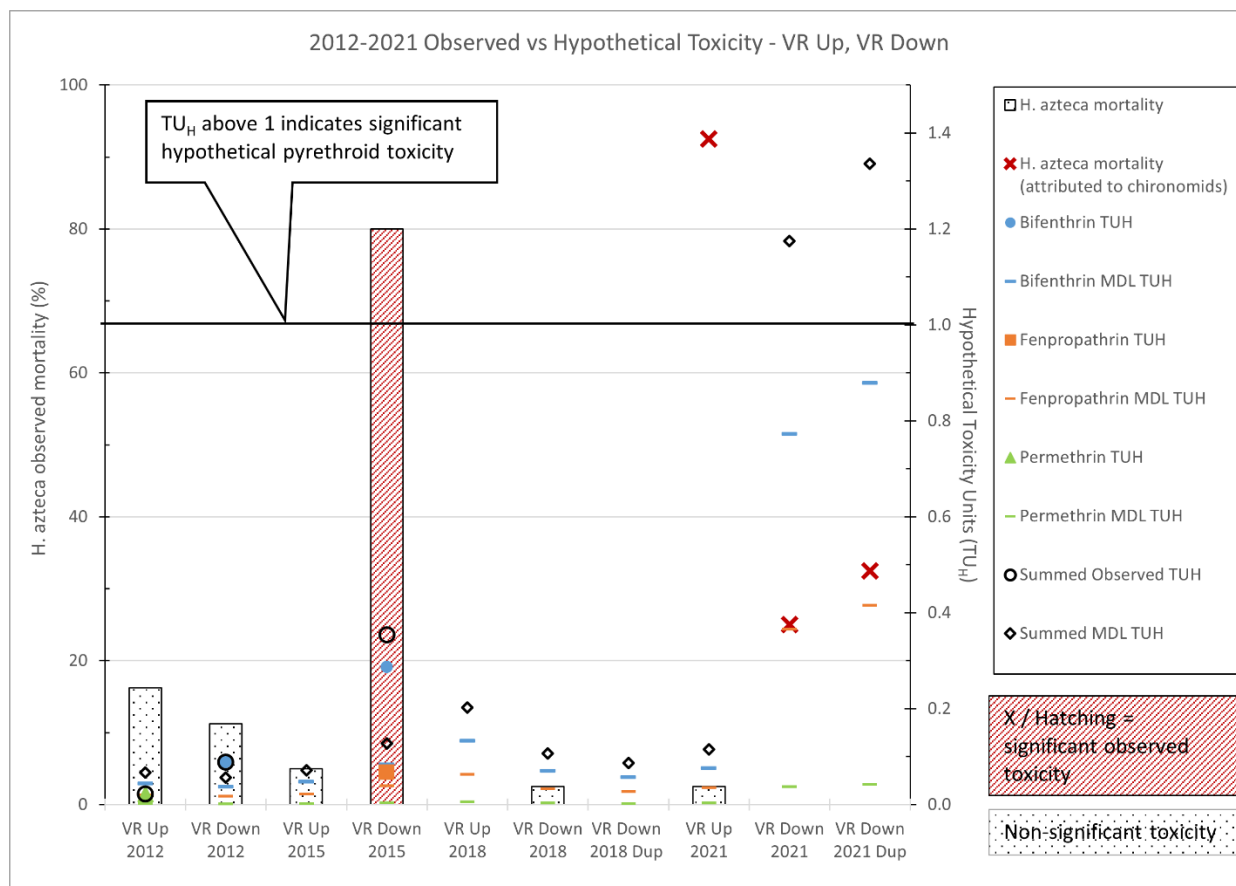
Santa Clara River Watershed								
Analyte	LC50 (ug/g TOC)	Units	SCR Up			SCR Down		
			2012	2015	2018	2012	2015	2018
Bifenthrin	0.52	TU _H	0.278			0.129	0.439	
Fenpropathrin	1.1	TU _H						
Permethrin	10.83	TU _H						
Summed Hypothetical TU _H		TU _H	0.278			0.129	0.439	
Significant Observed Toxicity			No	Yes	No	No	No	No

Ventura River Watershed								
Analyte	LC50 (ug/g TOC)	Units	VR Up			VR Down		
			2012	2015	2018	2012	2015	2018
Bifenthrin	0.52	TU _H				0.089	0.286	
Fenpropathrin	1.1	TU _H					0.068	
Permethrin	10.83	TU _H	0.022					
Summed Hypothetical TU _H		TU _H	0.022			0.089	0.354	
Significant Observed Toxicity			No	No	No	No	Yes	No

Figure 12 shows toxicity results (left vertical axis) and TU_H (right vertical access, calculated from pyrethroid detections and from MDLs for samples that were all ND for pyrethroids) from 2012-2021 by watershed (including the 2021 TIE results in which survival was so high that toxicity does not register on the graph scale).

Figure 12. Hypothetical Toxicity Units Vs. Observed Toxicity – By Watershed





Pyrethroid pesticides were more prevalent in the downstream samples for most analytes/watersheds. The high pyrethroid RLs in 2021 at all sites precludes drawing conclusions regarding trends in pyrethroid concentrations over the term of the study, however the lack of toxicity in these samples (after accounting for chironomid predation) supports the data collected in previous years which showed that pyrethroids are not likely causing or contributing to toxicity at the study sites.

POTENTIAL PESTICIDE SOURCES

The application of pesticides for residential, industrial, and commercial use is not tracked, except for 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 California Department of Pesticide Regulation (CDPR) Certified Pesticide Applicators.

The pounds of pesticides applied annually for agriculture and structural pest control is tracked by the CDPR. The *Annual Pesticide Use Report Indexed by Chemical (PUR)* for Ventura County summarizes the annual reported pesticide use for regulated applications, including agriculture (e.g. food and ornamental), structural pest control, and other purposes (e.g. animal premise, golf course turf, landscape maintenance, public health, regulatory pest control, rights of way, vertebrate control). These reports typically become

available two years after the year referenced, so 2019-2021 reports were unavailable for this Study report, although data for 2019 was obtained by special request. The pounds used for regulated uses of the detected pesticides in this Study are summarized in Table 10.

Five pesticides (three pyrethroids and two non-pyrethroids) were detected by the laboratory's pyrethroid analytical method during the Study. Bifenthrin and permethrin are pyrethroid insecticides that have general and restricted applications for agricultural and urban use. Bifenthrin and permethrin are both used in significant quantities for regulated applications for structural and agricultural pest control in Ventura County but are also known to have unregulated applications for residential and industrial uses, which are not tracked. The pyrethroid insecticide fenpropathrin and the non-pyrethroid fungicide dichloran are agricultural pesticides without urban uses. The non-pyrethroid herbicide pendimethalin is used for agricultural and urban uses. Fenpropathrin, dichloran, and pendimethalin are not used for structural pest control in Ventura County.

Bifenthrin is used as a restricted use pesticide in orchards, nurseries, and buildings (e.g. structural pest control). Some products with lower concentrations are available for unrestricted residential use for indoor and outdoor insect control. Bifenthrin was detected at all Study sites except CC Up and VR Up at least once from 2012-2021. All the sites at which bifenthrin was detected (TMDL sites in 2012, CC Down in 2015, VR Down in 2012 and 2015, SCR Up in 2012, and SCR Down in 2012 and 2015) have both urban and agricultural influences but are in predominantly agricultural areas. In contrast, CC Up doesn't have urban or agricultural influences and VR Up has a small amount of agriculture and low-density housing. WOOD 2012 is a predominantly agricultural site and given its location within the Oxnard Plain, an area notable for its large crops of strawberries, peppers, and leafy green vegetables, the source of the bifenthrin is likely agricultural, however there are upstream discharges from urban areas.

Table 10. Ventura County Pesticide Use (Pounds) Reported to California Department of Pesticide Regulation (DPR)

Pesticide	2011					2012				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
Bifenthrin	2771.79	1732.74	1005.79	33.26	Strawberry 1499	2911.63	1673.06	1211.49	27.08	Strawberry 1364
Permethrin	4742.67	3635.45	1059.45	47.77	Celery 2162	4625.02	2060.4	2515.73	48.89	Celery 873
Fenpropathrin (Danitol)**	969.21	969.21	0	0	Strawberry 849	788.71	788.08	0	0.63	Strawberry 595
Dichloran*,**	22733.97	22733.97	0	0	Celery 21916	15545.81	15545.81	0	0	Celery 14854
Pendimethalin*,**	2788.84	2627.32	0	161.52	Strawberry 2515	5983.35	5739.14	0	244.21	Strawberry 5140

Pesticide	2013					2014				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
Bifenthrin	3350.01	1635.33	1684.09	30.59	Strawberry 1253	4699.88	2453.05	2133.09	113.74	Strawberry 1413
Permethrin	4678.32	2408.77	2201.2	68.35	Celery 1142	3807.76	2755.71	933.95	118.1	Celery 945
Fenpropathrin (Danitol)**	1668.9	1668.9	0	0	Strawberry 1307	1820.92	1820.92	0	0	Strawberry 1215
Dichloran*,**	19557.51	19557.51	0	0	Celery 18984	19983.11	19983.11	0	0	Celery 19347
Pendimethalin*,**	11899.69	11862.37	0	37.32	Strawberry 10855	12617.4	12557.56	0	59.84	Strawberry 11255

Pesticide	2015					2016				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
Bifenthrin	6048.4	2657.4	3362.52	28.48	Strawberry 1615	3239.03	2003.42	1123.58	112.03	Strawberry 1068
Permethrin	3222.6	2503.93	660.79	57.88	Container plants 906, Celery 657	2865.9	2193.48	612.48	59.94	Celery 721
Fenpropathrin (Danitol)**	2131.63	2130.85	0	0.78	Strawberry 1852	1831.09	1831.09	0	0	Strawberry 1250
Dichloran*,**	18702.35	18702.35	0	0	Celery 18146	17521.95	17521.95	0	0	Celery 17400
Pendimethalin*,**	11350.8	11296.26	0	54.54	Strawberry 8854	12068.51	11978.68	0	89.83	Strawberry 10089

Pesticide	2017					2018				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
Bifenthrin	3192.05	2118.75	1047.19	26.11	Strawberry 1205	2735.61	1637.93	1074.84	22.84	Strawberry 919
Permethrin	2517.57	1988.14	495.51	33.92	Celery 1016	2289.62	1531.88	720.47	37.27	Celery 791
Fenpropathrin (Danitol)**	2976.84	2975.47	0	1.37	Lemon 1537, Strawberry 934	3162.96	3162.96	0	0	Lemon 1693, Strawberry 918
Dichloran*,**	15560.57	15560.57	0	0	Celery 15547	10631.66	10631.66	0	0	Celery 10619
Pendimethalin*,**	9697.88	9695.22	0	2.66	Strawberry 7328	10352.18	10264.51	0	87.67	Strawberry 8514

Pesticide	2019				
	Total Pounds	Agriculture	Structural	Other	Major crop - pounds
Bifenthrin	2780.6	1616.33	1145.93	18.35	Strawberry 983
Permethrin	2360.13	1656.2	681.22	22.71	Celery 909
Fenpropathrin (Danitol)**	3505.56	3505.56	0	0	Lemon 2009, Strawberry 907
Dichloran*,**	7329.65	7329.65	0	0	Celery 7297
Pendimethalin*,**	5015.211	4923.74	0	91.47	Strawberry 3651

* Not analyzed by TMDL ** Analytes not required by Permit

Other - Includes animal premise, golf course turf, landscape maintenance, public health, regulatory pest control, rights of way, vertebrate control, unknown
Data from Pesticide Use Annual Summary Reports at <https://www.cdpr.ca.gov/docs/pur/purmain.htm>, indexed by Chemical and restricted to Ventura County
E.g "Department of Pesticide Regulation 2015 Annual Pesticide Use Report Indexed by Chemical - Ventura County"

There is approximately a two-year delay for the California Department of Pesticide Regulation Annual Pesticide Use Reports (PUR) to become available online. This means that 2011 and 2012 PUR were unavailable for the 2012 Study report, 2014 and 2015 PUR were unavailable for the 2015 Study report, 2017 and 2018 PUR were unavailable for the 2018 Study Report, and 2019-2021 PUR were unavailable for the 2021 Report (2019 PUR data was made available on request).

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. According to the United States Environmental Protection Agency's "Reregistration Eligibility Decision (RED) for Permethrin (Revised May 2009)", 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. Permethrin was only detected at VR Up in 2012, which is downstream of a small amount of agriculture and low-density housing, and at CC Down in 2015, which has both urban and agricultural influences. The TMDL permethrin detection limit of 5 ng/g was 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. The CDPR reports show that the regulated use of permethrin in Ventura County is predominantly for row crops and structural pest control, however according to the Environmental Health Tracking Program (www.cehtp.org/pesticidetool), which uses CDPR data, there were no applications near VR Up, so the source may be from unregistered residential users but the data is inconclusive at this time.

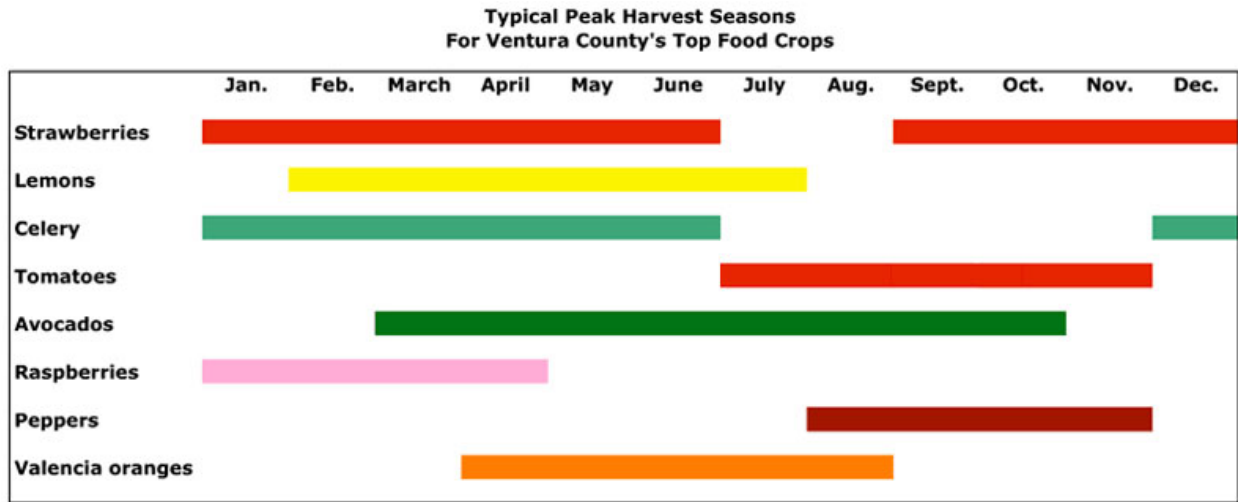
Fenpropathrin is a pyrethroid insecticide that is registered for multiple crops, but its restricted use designation makes it unlikely to have an urban source, however it can be used to treat Asian citrus psyllid infestations (as can cyfluthrin, which was not detected), which have become a problem in Ventura County. It was only detected once during the Study, at VR Down in 2015.

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 not from an urban source. Dichloran was only detected at the downstream SCR sites (SCR Down and SCR Down-a) and was detected during all four study years (2015, 2015, 2018, and 2021).

Pendimethalin is a (non-pyrethroid) general use selective herbicide used to control broadleaf weeds and grassy seed species in agricultural and non-agricultural settings. Pendimethalin was predominantly detected in the Santa Clara River Watershed at SCR Up (2012, 2015) and SCR Down in (2012, 2015, 2021) but it was also detected at CC Down in 2015. It is unknown if the detection of this non-pyrethroid is related to an urban source, but its concentrations tended to be higher at the downstream sites, where agriculture is a more direct influence.

The PUR are summarized by calendar year, however samples for this Study were collected in March-May so the previous year's applications are also relevant. Strawberry and celery are among the top 10 crops grown in Ventura County, and are also the major crops on which the five detected pesticides (3 pyrethroids and 2 non-pyrethroids) are applied. Additionally, as seen in Figure 13, the strawberry and celery growing seasons lead into the sampling period. This suggests that the pesticides could have an agricultural source, however it does not exclude an urban source for those pesticides which have urban uses.

Figure 13. Peak Harvest Seasons



(Chart obtained from <http://www.farmbureauvc.com/new/images/typical-peak.jpg>)

PESTICIDE USE TRENDS

According to the most recently available CDPR Pesticide Use Report (2018) (<https://www.cdpr.ca.gov/docs/pur/pur18rep/18sum.htm>), “Since 1990, the reported pounds of pesticides applied and acres treated have fluctuated from year to year. These fluctuations can be attributed to a variety of factors, including changes in planted acreage, crop plantings, pest pressures, and weather conditions. An increase or decrease in use from one year to the next or in the span of a few years may not necessarily indicate a general trend in use, but rather variations related to changes in weather, pricing, supply of raw ingredients, or regulations. Regression analyses on use over the last twenty years do not indicate a significant trend of either increase or decrease in total pesticide use.” These factors combined with differences in rainfall and runoff intensities and amounts could all contribute to the variations in concentrations seen in the Study.

The 2019-2021 PUR reports were not released by CDPR in time for this report, however the 2019 data was available by special request, so the comparison of analytical data to pesticide application amounts to look for trends are limited to the 2011-2019 period. The multiple factors that can affect fluctuations and the lack of PUR data for 2020-2021, combine to prevent drawing conclusions from any apparent trends. However, some possible trends from the current available data are visible in Figure 14, Figure 15, Figure 16, Figure 17, and Figure 18, and are described below.

Figure 14. 2011-2019 Bifenthrin Use in Ventura County (CDPR)

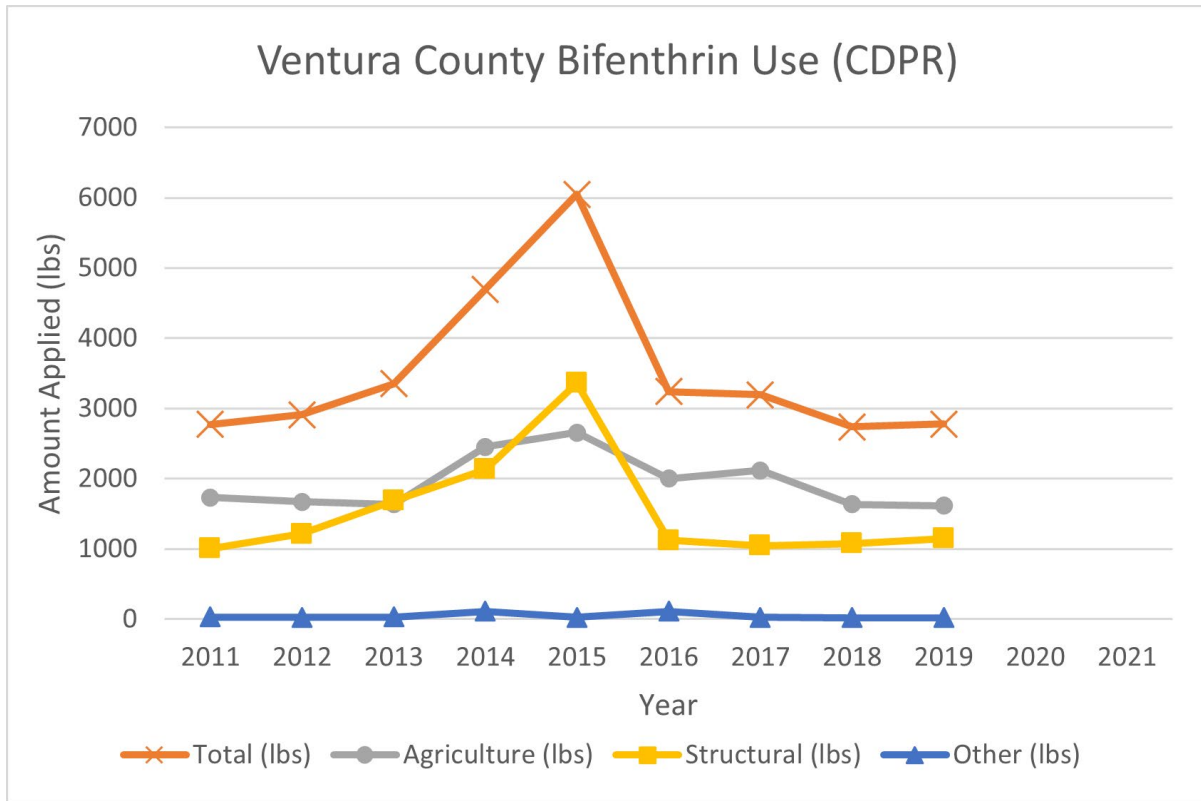


Figure 15. 2011-2019 Permethrin Use in Ventura County (CDPR)

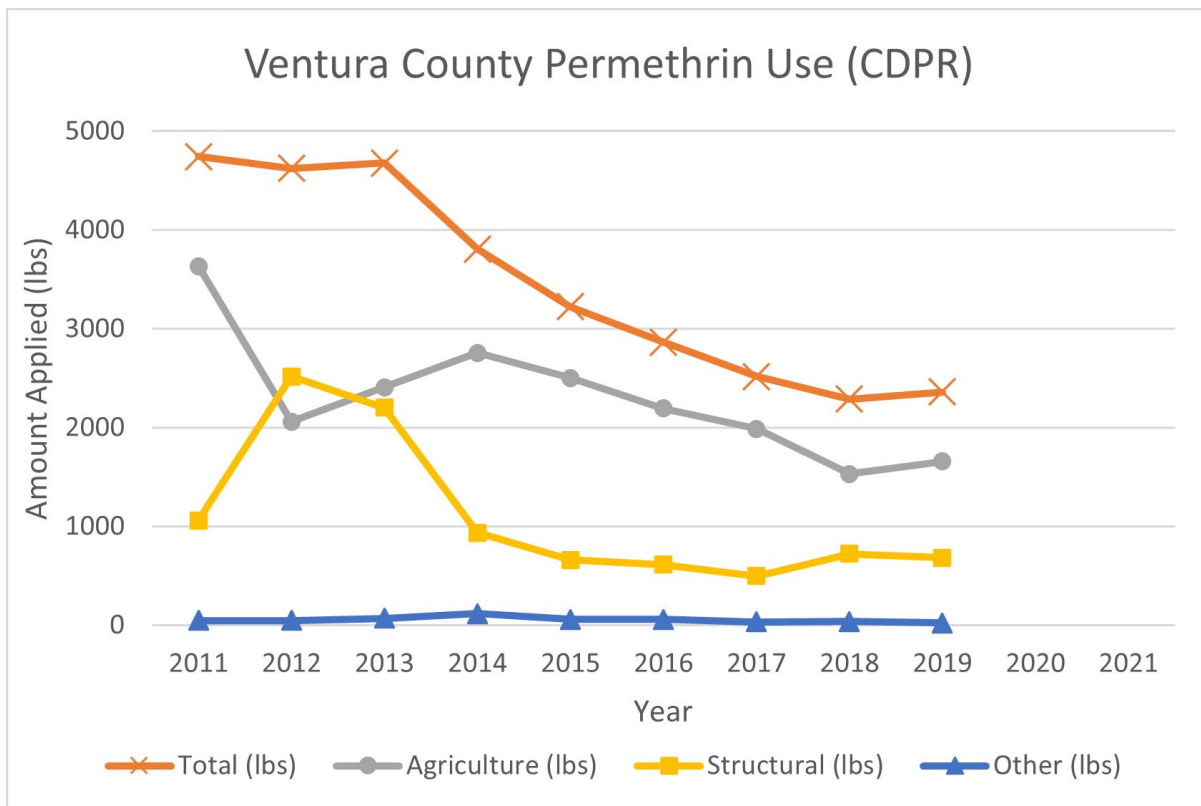


Figure 16. 2011-2019 Fenpropathrin Use in Ventura County (CDPR)

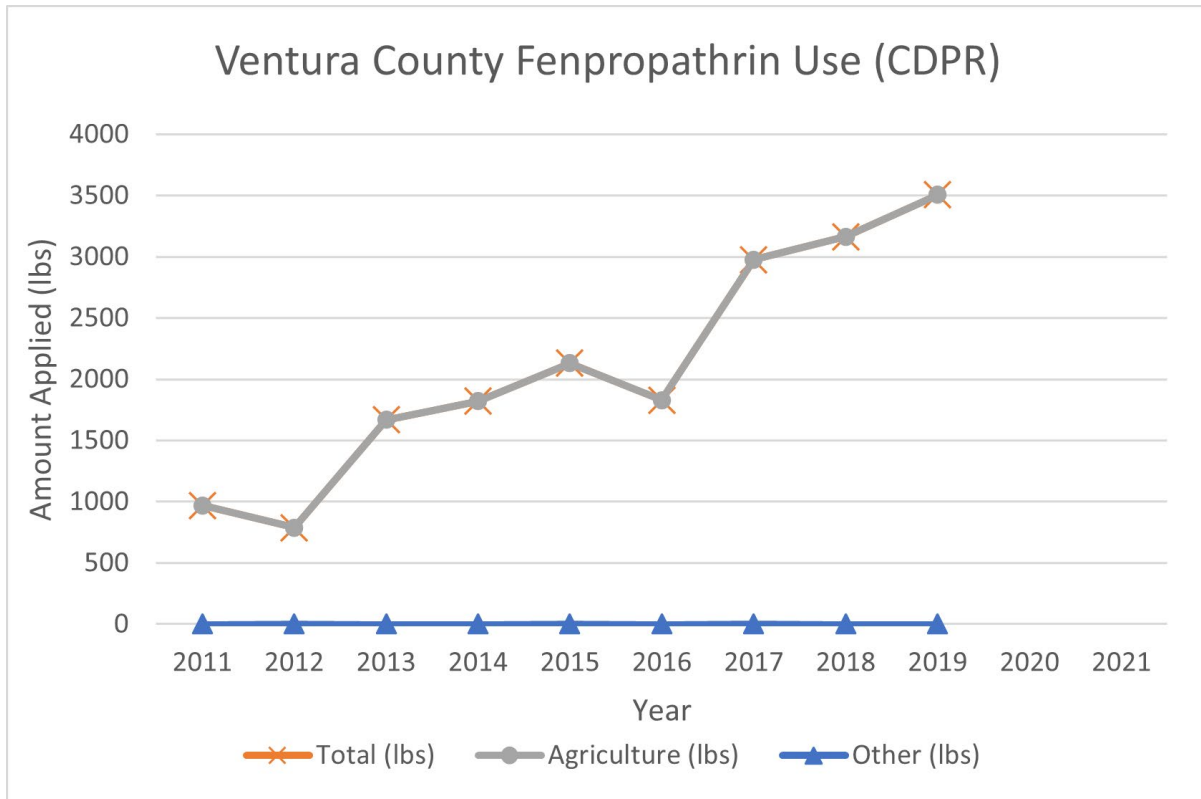


Figure 17. 2011-2019 Dichloran Use in Ventura County (CDPR)

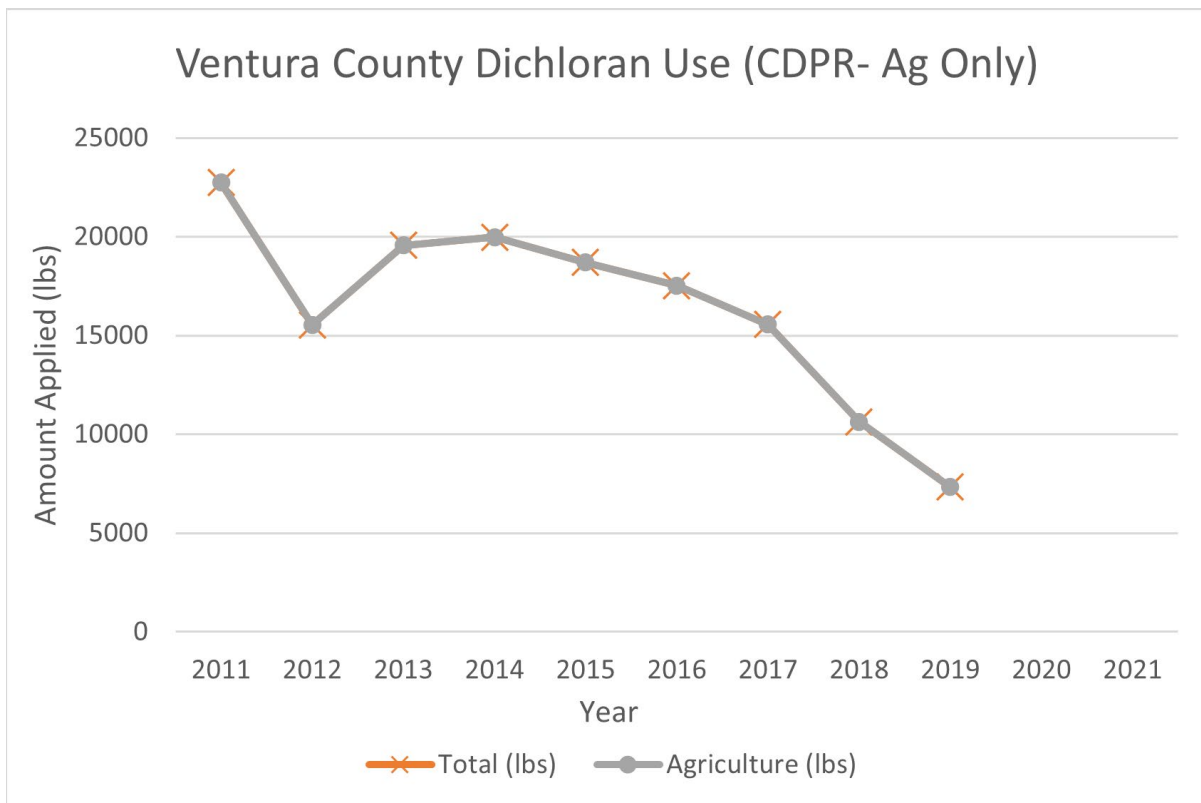
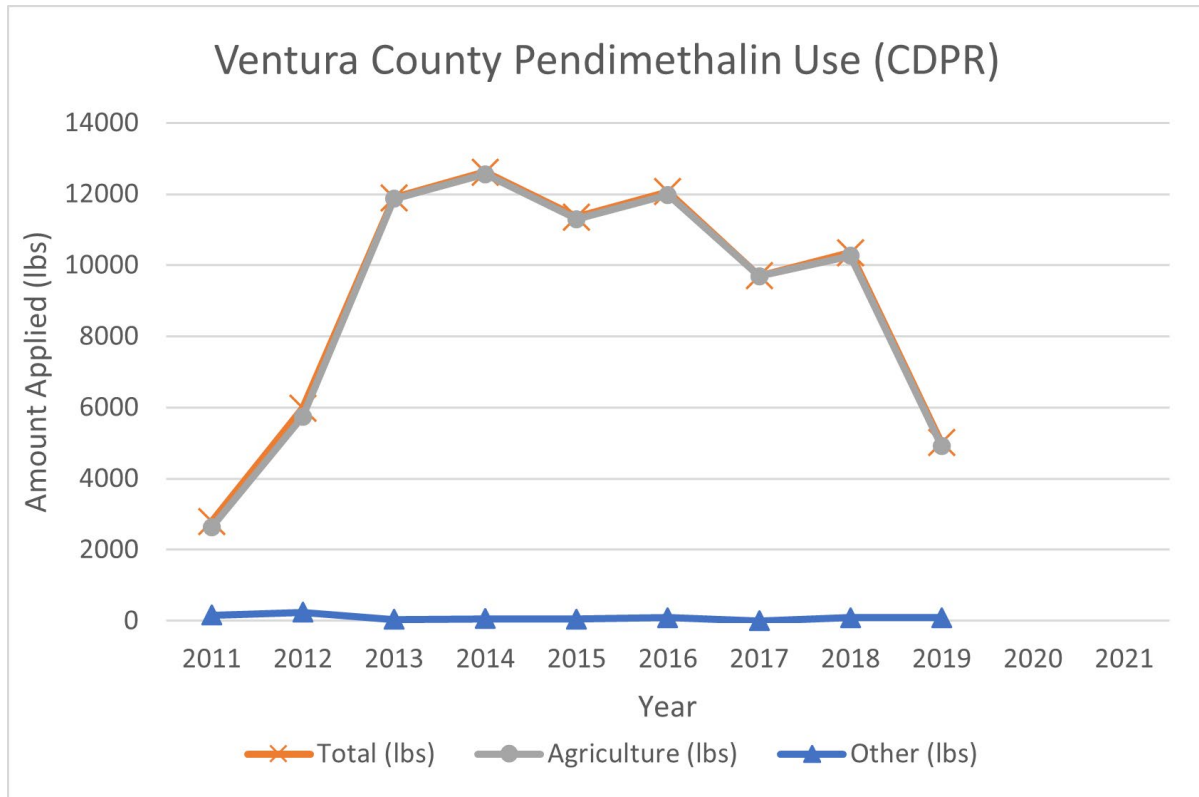


Figure 18. 2011-2019 Pendimethalin Use in Ventura County (CDPR)



The 2011-2019 PUR data show dichloran and pendimethalin (non-pyrethroids) are used in larger quantities (pounds) for regulated applications (primarily agriculture) in the County than the pyrethroids bifenthrin, permethrin, and fenpropathrin, however their use trended down between 2014-2019. Overall, bifenthrin and permethrin use has been trending down due to lower agricultural and structural use. While initially the bifenthrin and permethrin use drop was largely due to decreasing structural use, use amounts have remained relatively steady in recent years. In contrast, fenpropathrin use has trended upward since 2011 due to increasing agricultural use. These five pesticides are all applied to strawberry or celery as their major crop (fenpropathrin major crop is lemon, followed by strawberry), and these are among the top ten crops in Ventura County and are mainly grown in the lower regions of each watershed.

Bifenthrin use (according to CDPR) was highest in 2015, which correlates with the concentrations measured at downstream sites, however, use amounts for the other pesticides do not correlate with detection amounts for the Study years. The 2020 and 2021 CDPR data are unavailable to see if the trends continue.

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 induced); 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.
- The 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

Ventura County’s Community for a Clean Watershed (CCW) is the Program’s public outreach effort, and it regularly targets pesticide use in its campaigns. CCW has developed creative materials to promote the safe and correct use of outdoor pesticides. The outreach campaigns are run in the spring to coincide with the spring planting season.

In 2018-2020, CCW developed new radio, video, and print materials in English and Spanish for their “yard chemical” public outreach campaigns. The new English and Spanish radio spots were developed and run in annual campaigns beginning in 2018, and the video and print materials were added to the annual campaigns in 2019 (English) and 2020 (Spanish). The materials encourage the use of eco-friendly options and the importance of following product application instructions. Campaigns include a variety of outreach methods, such as radio ads, digital display ads, print media, and paid social media.



2019/20 Pesticide Outreach Examples

In 2018, radio ads in English and Spanish were run for four weeks. In 2019, radio ads were run for five weeks on five English-language and two Spanish-language stations, and digital ads were run for eight weeks. In addition, print ads were placed in a monthly magazine targeting homeowners.

The 2020 campaign expanded to include print ads in several local newspapers and ran for longer with each media type utilized for 6-9 weeks. The campaign in 2021 followed a similar outline to 2020, with most outreach types targeted for 4-8 weeks.

Spring CCW campaigns prior to 2018 also included radio, video, and print materials in English and Spanish to encourage the responsible use of pesticide and herbicide products. Outreach materials for the previous campaigns included the animated “More, Better” television commercial, which graphically demonstrated how using too much pesticide results in runoff into the storm drains, eventually making it into the Watershed where it adversely affects plants and animals.

PESTICIDES:
 "ARGGHHHH! SNAILS & ANTS...."

"MORE POISON, MORE, MORE MORE!
 MORE MUST BE BETTER!"

REMEMBER:
 WHEN USING PESTICIDES, A LITTLE GOES A LONG WAY. AND IF YOU OVERUSE THEM, THEY END UP IN THE WATERSHED.

"AND THAT'S VERY BAD!"

COMMUNITY FOR A CLEAN WATERSHED

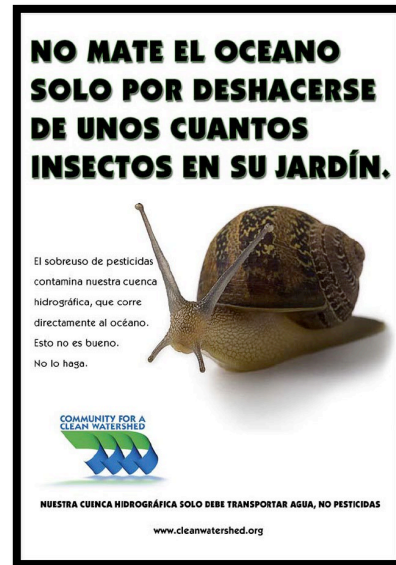
The watershed should only shed water.
 CLEANWATERSHED.ORG

Newspaper Advertisement

The television ad was also adapted into a radio spot 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.”

In 2010, CCW ran a five-week campaign on television and radio, as well as animated web banners and transit shelter posters. A similar campaign was run in 2016 for four weeks, utilizing the thirty second radio spot, digital web banner, and six transit shelters showing the snail poster. The radio spot was also run for four weeks on Pandora in January – February 2017.

In February 2016, April 2016, and twice in January 2017, CCW sent out e-blasts targeting 100,000 homeowners in Ventura County each time. The e-blast promoted the Program’s rain barrel and compost bin truckload sale and included links to the Program’s “Yard Care Watershed Protection Tips” brochure and “Pesticides, Herbicides, & Fertilizer Application Best Practices” BMP sheet.



Spanish Language Pesticide Outreach

Retail Partnership Brochures: Nurseries and Gardeners

“Watershed Protection Tips for Gardeners” pamphlets were created in 2010 to encourage residents to follow best practices in their homes and yards when gardening and dealing with pests. These brochures were distributed to targeted retail stores and numerous outreach events across the county to reach the population that is likely involved in the activities. The colorful pamphlet defines the Watershed, explains the storm drain system, how and why polluted water is damaging, and gives both overall and topic-specific tips for how to keep the Watershed clean. The pamphlet covers plant selection, irrigation, fertilizer and pesticide practices, integrated pest management, and proper yard maintenance. The pamphlet was updated in 2016 to include pictures of drought tolerant plants and an updated link to Integrated Pest Management resources.

The Program also created a best management practices fact sheet covering commercial pesticide, herbicide, & fertilizer application and a poster covering best management practices for nurseries. These were distributed during stormwater business inspections. All the materials are also posted on the CCW website www.cleanwatershed.org.



Watershed Protection Tips for Gardeners

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 Ventura County 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.

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 College Creeks and the streams and estuaries that flow into the Pacific Ocean.

cleanwatershed.org

Printed on recycled paper.

2010 Gardening Retail Partnership Brochure



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 beawaterwise.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.

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 wasteinfo.org for locations and hours of Household Hazardous Waste collection centers and events throughout Ventura County.



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cleanwatershed.org

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 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.

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*Contact your local city government to request a ban on the use of household hazardous waste collection events in your area.

2016 Gardening Retail Partnership Brochure

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 studies in 2012, 2015 and 2018, do not directly show a link between pyrethroids and significant toxicity in the samples, therefore the instances of measured 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 of toxicity will be addressed.

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