

Department of Pesticide Regulation Environmental Monitoring Branch Surface Water Protection Program 1001 I Street Sacramento, CA 95812

STUDY 270 (2017-18): Ambient and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2017–2018

Robert Budd, PhD August 2017

1.0 INTRODUCTION

Urban runoff is an important source of pesticide loading into surrounding waterways, justifying monitoring efforts to characterize pesticide composition in surface waters receiving urban inputs. In California, the Department of Pesticide Regulation (CDPR) receives pesticide use reports for urban applications by licensed applicators. Reported use is categorized into agricultural and non-agricultural use. Agricultural use includes both production and non-production agricultural (i.e. golf courses, rights-of way, parks) applications. Non-agricultural use includes applications for residential, industrial, institutional, structural, or vector control purposes (CDPR, 2014). However, urban pesticide use by individual homeowners is not reported, so that total use is greater than reported use. It has been estimated that urban pesticide use accounts for over 70% of the total pesticide use in California (UP3 Project, 2006). Approximately 4,744,000 pounds of pesticides were applied in 2014 for landscape maintenance and structural pest control in Los Angeles, Orange and San Diego Counties (CDPR, 2016).

With this high volume of urban pesticide use there is a potential for pesticide runoff into urban creeks and rivers via storm drains. Numerous urban creeks are listed on the 2010 Federal Clean Water Act Section 303(d) list, due to the presence of pyrethroid and organophosphate (OP) pesticides (Cal/EPA, 2014). While urban uses of OPs have been sharply curtailed due to Federal regulatory actions, recent monitoring has continued to identify the presence of OPs in some samples (Oki and Haver, 2009). Additionally, recent monitoring has shown that urban waterways are frequently contaminated with pyrethroids, fipronil, and imidacloprid. Many of the detected pesticides are at concentrations that exceed the acute toxicity to sensitive aquatic organisms (Gan et al., 2012; Oki and Haver, 2009; Weston et al., 2014; Weston et al., 2005; Weston et al., 2009). In 2008 CDPR initiated a statewide urban monitoring project to more fully characterize the presence of pesticides in urban waterways (He, 2008). Preliminary monitoring data has been previously summarized. Several pyrethroids, imidacloprid, and fipronil (and breakdown products) insecticides, as well as synthetic auxin herbicides have been detected at high frequency at CDPR monitoring locations in southern California (Ensminger et al., 2013a).

Study 270 is a continuation of monitoring efforts of CDPR Studies 249 and 265. Data from this study will be used to evaluate urban pesticide water quality trends and efficacy of implemented best management practices (BMPs). For example, surface water regulations were implemented in California in July 2012, with the intent of reducing pyrethroid concentrations in California surface waters (CDPR, 2013). Long-term monitoring will help determine the effectiveness of these regulations on the presence of pyrethroids in urban waterways. This project will continue to monitor storm drain outfalls and urban waterways at selected monitoring sites from CDPR's 2008 study as well as at monitoring may be used to track the performance of local mitigation measures or public outreach programs. Modifications from the FY 16-17 sampling plan is presented in section 4.9.

2.0 OBJECTIVE

The overall goal of this project is to assess pesticide concentrations found in runoff at drainages and receiving waters within typical southern California urbanized areas during rain events and dry season conditions. Specific objectives include:

- 1) Determine presence and concentrations of selected pesticides in urban runoff under dry and storm conditions;
- 2) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity thresholds;
- 3) Evaluate the effectiveness of surface water regulations through long-term (multiple year) monitoring at selected sampling locations;
- 4) Determine the toxicity of water samples using toxicity tests conducted with the amphipod *Hyalella azteca* or the midge *Chironomus*;
- 5) Observe effects of a small constructed wetland to mitigate pesticide concentrations in urban runoff to surrounding receiving waters; and
- 6) Monitor deposition of sediment-bound pyrethroids within the watershed.

3.0 PERSONNEL

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Kean S. Goh, Ph.D., Environmental Program Manager. Key personnel are listed below:

Project Leader: Robert Budd, Ph.D. Field Coordinator: KayLynn Newhart Reviewing Scientist: Michael Ensminger, Ph.D. Statistician: Dan Wang, Ph.D. Laboratory Liaison: Sue Peoples Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)

Collaborator: Darren Haver, Ph.D., University of California at Davis, Center Director/Water Resources and Water Quality Advisor, South Coast Research and Extension Center, 7601 Irvine Blvd., Irvine, CA, 92618, Phone: (949) 653-1814, email: dlhaver@ucdavis.edu Please direct questions regarding this study to Robert Budd, Senior Environmental Scientist, at (916) 445-2505 or <u>rbudd@cdpr.ca.gov</u>.

4.0 STUDY PLAN

4.1 Site Selection. Monitoring sites are chosen based on the need to collect the necessary data to address the study objectives. Several monitoring locations are established sites that have longterm temporal data sets (SC1, SC2, SC3, SC4, SC7, WC1, WC2) that enable trend analysis and mitigation effectiveness evaluation. CDPRs Surface Water Prioritization Model (SWPM) was utilized to identify additional priority watersheds to monitor. These watersheds located throughout the urban centers of southern California provide data to evaluate the spatial distribution of priority pesticides in southern California surface waters (Budd et al., 2013; Luo et al., 2013). The watershed prioritization component of the SWPM identifies priority hydrologic unit codes (HUC) based on reported use and toxicity data. For the purposes of monitoring, SWPP has defined southern California of consisting of two HUC4s (1807 and 1810). The SWPM is based on the HUC12 scale, the highest resolution of watersheds. Luo et al. (2017) developed a method for aggregating the HUC12s into a larger HUC8 scale. Eleven of the top twenty identified statewide priority HUC8s are located in southern California (Appendix 1). Of these, SWPP currently has monitoring sites within five of the top HUC8s. Other factors such as site accessibility, perennial waters, other monitoring agency representation, and budgetary constraints limit site selection in the remaining HUCs.

Ambient water quality monitoring will be conducted at six sampling locations within Salt Creek (SC) in Orange County (Figure 1), one each within Ballona (BAL), Bouquet (BOQ), Los Angeles River (LAR), San Gabriel River (SGR), and Dominguez Channel (DC) watersheds in Los Angeles County (Figure 2), and two within San Diego River (SDR) watersheds in San Diego County (Figure 3) (Table 1). Tecolote Canyon (TCC) will serve as an alternate site in San Diego if samples are unattainable at SDR4. Mitigation monitoring will be conducted at the inlet and outlet of a small constructed wetland located within Wood Creek watershed (Figure 4). Details of site descriptions are provided in Appendix 2.

Sampling stations within Salt Creek have been monitored consistently since 2009 as part of CDPRs urban monitoring program. The surrounding drainage areas within the Salt Creek watershed consist of single family dwellings, multiple family dwellings, light commercial buildings, parks, schools, and two golf courses. SC1-SC4 are located directly below storm drains that receive runoff from residential neighborhoods. SC5 and SC7 are located at the receiving waters of several urban inputs and will serve to evaluate pesticide concentrations in the watershed as well as downstream transport of pesticides. Sampling locations within the five watersheds in Los Angeles County and two in San Diego County are located near the base of their respective watersheds. A storm drain outfall location has been added within the San Diego River watershed to serve as a source identification site. Ballona Creek, Los Angeles River, Dominguez Channel, and San Gabriel River are large watersheds with mixed residential and commercial land use.

Monitoring locations within Wood Creek have also been monitored since 2009 as part of Surface Water Protection Program's mitigation evaluation monitoring. The monitoring sites are situated at the inlet (WC1) and outlet (WC2) of a small (~0.18 acres) constructed wetland designed to mitigate pollutants in the urban runoff. The wetland receives urban runoff from a drainage area consisting of entirely single and multiple family residential units. The primary objective of monitoring at these stations is to observe the efficacy of pesticide removal within the wetland system. Efficacy will be evaluated through comparisons in average pesticide concentrations between outlet and inlet. A second storm drain (WC3) located within the Wood Creek watershed that was previously monitored will be added for pyrethroid analysis. This data will serve as background information for future field trial evaluations.

DPR has engaged in a collaborative effort with the Stream Pollution Trends (SPOT) Monitoring Program to increase the data available for trend analysis of current used pesticides (SWAMP, 2017). The synergistic partnership allows each agency to maximize information gained with limited resources. The SPOT program collects sediments throughout California for pyrethroid and fipronil analysis, which greatly adds to the spatial representation of pesticide monitoring data. Several sites described in this protocol also serve as SPOT monitoring locations, including BAL, BOQ, LAR1, SGR, and SC5.

4.2 Monitoring Candidates. The SWPM was utilized to assist in pesticide selection for ambient monitoring (Budd et al., 2013; Luo et al., 2013). The model is based on current use (2013-2015) patterns and aquatic toxicity benchmark data. The product of the use and toxicity scores produces a final score that represents a relative prioritization of pesticides. In addition, the output also generates a recommendation to monitor or not based on physiochemical properties such as half-life and solubility. The output provides guidance to EM staff on pesticides to consider for monitoring. However, the decision to monitor for a pesticide is influenced by additional factors such as previous monitoring data, budgetary constraints, and analytical capabilities. Pesticides that receive a final score of nine or higher are given priority for monitoring. Pesticides with lower scores have either low use in urban environments and/or low associated toxicity. Thirty pesticides received a final score equal to or greater than nine using use data for Los Angeles, San Diego, and Orange counties, California and acute and chronic aquatic benchmarks benchmarks (Appendix 3). Twenty-four of these will be monitored under the current sampling plan (Appendix 4). Analytical methods are currently being developed for DDVP, PCNB, prallethrin, dithiopyr, tebuconazole, and sulfometuron-methyl. All suites cannot be analyzed at every monitoring location due to budgetary constraints. Four sampling locations (SC3, SC7, BOQ and LAR) will serve as representative watersheds for analytical methods containing pesticides with lower detection frequencies (CB, CF, DN, TR) or benchmark exceedances (PX) (Appendix 4).

4.3 Water sampling. Samples will be collected for both ambient and mitigation monitoring during two dry season and two storm sampling events. Dry season sampling will occur between August - September, 2017 and May-June, 2018. DPR will attempt to collect storm samples during the first major storm (rain) event of fiscal year 2017-2018 and during a second major storm in the winter or early spring of 2018 (Table 2).

Most water samples will be collected as grab samples directly into 1-L amber bottles (Bennett, 1997). Where the stream is too shallow to collect water directly into these bottles, a secondary stainless steel container will be used to initially collect the water samples. Water samples collected during storm events at SC1, SC2, SC3, SC4, WC1, and WC2 may be collected as composite samples utilizing automated sampling equipment set up by UC Cooperative Extension (CDPR, 2011; Sisneroz et al., 2012). Flow-weighted storm runoff will be collected at BAL and LAR1 by the Los Angeles County Public Works Department. Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed. Field duplicates or field blanks will be collected during each sampling event for quality assurance.

4.4 Sediment sampling. Sediment samples will be collected at a subset of locations and sampling events (Table 2). Where applicable, sediment samples will be collected in 1 quart glass Mason Jars using passive sediment collection samplers (Budd, 2009) and analyzed for pyrethroids. Otherwise, enough sediment will be collected using stainless steel scoops from the top of the bed layer, biasing for fine sediments where possible. All sediments will be sieved through a 2-mm sieve to remove plant debris and then homogenized.

4.5 Toxicity sampling. Water samples will be collected at a subset of sampling sites for toxicity analysis during at least one dry and one storm event. Grab samples will be collected in 1-L amber I-Chem certified 200 bottles (or equivalent) and transported to the Aquatic Health Program at the University of California, Davis. Toxicity testing will measure percent survival of the amphipod *Hyalella azteca* or the midge *Chironomus* in water (96-hr).

4.6 Field Measurements. Physiochemical properties of water column will be determined using a YSI-EXO 1 multiparameter Sonde (https://www.ysi.com/productsdetail.php?EXO1-Water-Quality-Sonde-89) according to the methods describe by Doo and He (2008). At each site, water parameters measured *in situ* will include pH, temperature, conductivity, salinity, total dissolved solids, and dissolved oxygen. Stormdrain discharge or stream flow rates will be measured to characterize the flow regime and to estimate the total loading of target pesticides. Discrete time flow estimations will be determined using either a Global portable velocity flow probe (Goehring, 2008), utilizing a float, or fill-bucket method. Continuous flow rates will be obtained at SC2, SC3, and WC2 using an installed Hach Sigma 950 flow meter (Sisneroz et al., 2012; Oki and Haver, 2009).

4.7 Sample transport. CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample.

4.8 Organic **carbon and suspended sediment analysis.** CDPR staff will analyze water and sediment samples for total organic carbon (TOC) and dissolved organic carbon (DOC) using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger, 2013b). Water samples will also be analyzed for suspended sediment (Ensminger, 2013c). Lab blanks and calibration standards will be run before every sample set to ensure the quality of the data.

4.9 Modifications from FY 16-17. The current sampling plan is an extension of sampling conducted during fiscal years 2010-2017. Details of the previous sampling are described in the

document titled Study 270: Urban pesticide monitoring in southern California, available at: <u>http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study_270_2016-2017.pdf</u>. The sampling and analysis schedule is similar to that for FY 16-17, with a few notable modifications (Table 3).

5.0 CHEMICAL ANALYSIS

Water and sediment samples will be sent to the Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) for pesticide analysis. They will analyze six different analyte groups which will include up to 42 chemical compounds for analysis (Appendix 4). Sediment samples will be analyzed for pyrethroid pesticides (Appendix 4). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995). Laboratory blanks and matrix spikes will be included in each extraction set.

6.0 DATA ANALYSIS

All data generated by this project will be entered into a central database that holds all data including field information, field measurements, and laboratory analytical data. We will use various nonparametric and parametric statistical methods to analyze the data. The data collected from this project may be used to develop or calibrate an urban pesticide runoff model.

Our preliminary analysis (Ensminger and Budd, 2014) indicated that the sample data is heavily skewed and contains a number of non-detects with multiple reporting limits, which may violate the normality and equal variance assumptions of the parametric procedures (e.g., ANOVA and *t*-tests). In order to appropriately address the characteristics of the sample data, a more generic and distribution-free approach, the non-parametric statistics, will be used in this study. Helsel (2012) illustrated the application of non-parametric procedures to skewed and censored environmental data. We will primarily reference Helsel as a general guideline for data analysis of this study. The data will be analyzed by using R statistical program (R Core Team, 2014), the Nondetects And Data Analysis for environmental data (NADA) package for R (<u>http://cran.r-project.org/web/packages/NADA/NADA.pdf</u>), and Minitab (<u>http://www.minitab.com/en-us/</u>).

Based on the study objectives, preliminary analysis, and data availability, we propose the following statistical procedures for data analysis (Table 4).

- Explanatory data analysis will be performed to summarize the characteristics of the sample data. Urban monitoring data has been collected since 2008 for a variety of analytes (i.e., Appendix 4) at multiple locations (i.e., Salt Creek, Wood Creek) with different site types (i.e., stormdrain outfalls and receiving water), and between different seasons (i.e., dry and wet seasons)(Tables 1 and 2). Plots, such as boxplots, histograms, probability plots, and empirical distribution functions, will be produced to explore any potential patterns implied by the data.
- Hypothesis tests will be conducted to compare the concentration between groups of interest. For example, we will test whether there is significant difference in concentration between the dry and wet season, or between the difference locations. Non-parametric procedures will be used to compute the statistics for hypothesis test. For data with multiple reporting limits, it

will be censored at the highest limit before proceeding if the test procedure allows only one RL.

3) Trend analysis will be included to depict the change in concentration over time. We are specifically interested in determining the effectiveness of CDPR regulation 6970 which went into effect July 19, 2012 to mitigate pyrethroid contamination in urban waters. Ambient monitoring data from Salt Creek monitoring locations, as well as WC1 in Wood Creek will be used. For the trend analysis, we will use Akritas-Thenil-Sen non-parametric regression, which regresses the censored concentration on time, or the Kaplan-Meier method, which tests the effects of year, month and location by developing a mixed linear model between the censored concentration and the spatial-temporal factors.

Finally, we will attempt to develop complicated statistical models to assess the factors potentially impacting pesticide concentration in surface water. One possible attempt is to develop a logistic regression model to estimate and predict the likelihood of detection or exceedance. The response variable will be the probability of the concentration being greater than or equal to the RLs or the toxicity benchmark. A series of explanatory variables will be examined, including: rainfall, field measurements (e.g., flow rate, pH, water TOC, sediment TOC, and TSS), number of household drains water into the storm drain outfall/creek, residential density (percent of impervious areas), season (or month), year, regulation, and so on. Further literature review will be conducted to identify possible explanatory variables in favor of the model.

7.0 TIMELINE

Field Sampling: Jul 2017 – Jun 2018 Chemical Analysis: Jul 2017 – Oct 2018 Report to Management: Jan 2019 – Mar 2019 Data Entry into SURF: Mar 2019 – Jun 2019

8.0 LABORATORY BUDGET

The estimated total cost for chemical analyses for water samples is \$163,370. The estimated cost for chemical analysis of sediment samples is \$4,800 (Table 2).

9.0 LITERATURE CITED

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Watershed	Stormdrain Outfall	Receiving Water/ Mitigation Outfall	Total Sites
Ambient Monitoring			
Salt Creek	4	2	6
Ballona Creek	-	1	1
Bouquet Creek	-	1	1
Los Angeles River	-	1	1
San Gabriel River	-	1	1
Dominguez Channel	-	1	1
San Diego River	1	1	1
Tecolote Canyon Creek	-	1	1
Mitigation Monitoring			
Wood Creek	2	1	2
Total	7	10	17

Table 1. Summary of urban pesticide monitoring locations in southern California.

		Final	Number	Samples	s/Event			
	•	First	Second	First	Second		Cost/	
Site	Screen*	Dry	Dry	Storm	Storm	Total	Sample	Budget
Amplent Monitor	ing							
			Water	Samples				
	CB	4	4	4	4	16	\$480	\$7,680
	CF	4	4	4	4	16	\$540	\$8,640
SC3, SC7,	DN	4	4	4	4	16	\$720	\$11,520
LAR1, BAL	LC	4	4	4	4	16	\$1,700	\$27,200
	PX	4	4	4	4	16	\$690	\$11,040
	PY6	4	4	4	4	16	\$600	\$9,600
SC1, SC2,	LC	4	4	4	4	16	\$1,700	\$27,200
SC4, SC5	PY6	4	4	4	4	16	\$600	\$9,600
BOQ, SDR1,	LC	3	3	3		9	\$1,700	\$15,300
SDR4/TCC**	PY6	3	3	3		9	\$600	\$5,400
	LC	2	2			4	\$1,700	\$6,800
DC, 36K	PY6	2	2			4	\$600	\$2,400
WC3	PY6	1	1	1	1	4	\$600	\$2,400
QA Samples***		1	1	1	1	4		\$2,490
			Sedimen	t Sample	es			
SC3, SC5, WC1, WC2	PY6	4	4			8	\$600	\$4,800
					Ambient Mo	onitoring	Sub-total	\$149,580
Mitigation Monito	oring							
			Water	Samples				
WC1	LC	1	1	1	1	4	\$1,700	\$6,800
	PY6	1	1	1	1	4	\$600	\$2,400
WC2	LC	1	1	1		3	\$1,700	\$5,100
VV 02	PY6	1	1	1		3	\$600	\$1,800
				N	litigation Mo	onitoring	Sub-total	\$16,100

Table 2. Ambient and mitigation sampling schedule.

Total \$168,170

*Pesticides included in screens detailed in Appendix 4. CB=carbaryl, CF=chlorfenapyr, DN=dinitroaniline, LC=liquid chromatography, PX=phenoxy, PY=pyrethroid.

**SDR4 is primary monitoring location. TCC will serve as replacement site when SDR4 is without measurable runoff.

^{*}QA=quality assurance. Screens will rotate by event.

Change from FY 15-16	Justification
Abamectin replaces trifloxystobin in LC screen.	Abamectin has a higher prioritization score.
Adding previously monitored storm drain WC3.	Pyrethroid data will be used to evaluate future field trials.
Replacing TCC with SDR4.	TCC has few detections. There are currently no source identification stations in San Diego county.
Reducing number of PX screen samples.	High detection frequency for several pesticides, however no corresponding concentrations above toxicity thresholds. Reducing number of samples frees up funds to increase spatial representation of sites.

Table 3. Modifications from sampling plan for fiscal year 2017-2018.

Table 4: Non-parametric procedures frequently used for comparing paired data, samples and three or more samples.

Data	Non-Parametric Procedure
Paired data	Wilcoxon signed-rank test for uncensored data
	Sign test (modified for ties) for censored data with one RL
	Score tests for censored data with multiple RLs (the PPW test and the
	Akritas test)
Two samples	Wilcoxon rank-sum (or Mann-Whitney) test or Kolmogorov-Smirnov
	test for censored data with one RL
	Score tests for censored data with multiple RLs (the Gehan test and
	generalized Wilcoxon test)
Three or more samples	Kruskal-Wallis test (for unordered alternative) or Jonckheere-Terpstra
in one-way layout	test (for ordered alternative) for censored data with one RL
	Generalized Wilcoxon score test for censored data with multiple RLs
	Multiple comparison to detect which group is different
Three or more samples	Friedman's test (for unordered alternative) or Page's test (for ordered
in two-way layout	alternative) for censored data with one RL
	Multiple comparison to detect which group is different



Figure 1. Sampling locations within Salt Creek watershed, Orange County, CA.



Figure 2. Sampling locations within Los Angeles County, CA.



Figure 3. Sampling locations within San Diego County, CA.



Figure 4. Sampling locations within Wood Creek watershed, Orange County, CA.

Appendix 1. Top twenty HUC8's identified for urban monitoring in southern California, order by the ranking process.

		DPR Monitoring	
HUC8 Code	HUC8 Name	Location	Comments
19070201	Soal Boach		CDPR Evaluating potential
10070201	Seal Beach		access point
18070105	Los Angeles	LAR1	
			Southern California Bight
18070203	Santa Ana		Project monitoring site at base
			of Santa Ana River*
			SWAMP location, NPDES
19070204	Nowport Boy		permit monitoring at several
10070204	Newport Bay		locations along San Diego
			Creek*
18070106	San Gabriel	SGR, DC	
18070104	Santa Monica Bay	BAL	
19070202	San Jacinto		SWAMP monitoring location
10070202	San Jacinto		along Santa Margarita River*
18070304	San Diego	SDR1, SDR4, TCC	
		SC1, SC2, SC3,	
18070301	Aliso-San Onofre	SC4, SC5, SC7,	
		WC1, WC2, WC3	
18070302	Santa Margarita		Mixed use watershed
19100201	Whitewater Diver		Agricultural inputs in lower part
10100201			of watershed

*Non-CDPR monitoring locations evaluated using California Environmental Data Exchange Network (CEDEN) available at: www.ceden.org

Watershed	Site ID	Northing	Easting	Site type
Salt Creek	SC1	33.3032.92	-117.4126.53	Stormdrain
Salt Creek	SC2	33.3040.57	-117.4140.67	Stormdrain
Salt Creek	SC3	33.3043.02	-117.4149.55	Stormdrain
Salt Creek	SC4	33.3031.00	-117.4226.34	Stormdrain
Salt Creek	SC5	33.3020.23	-117.4230.87	Receiving water
Salt Creek	SC7	33.2853.97	-117.4326.55	Receiving water
Ballona Creek	BAL	33.5912.92	-118.2455.90	Receiving water
Bouquet Creek	BOQ	34.2542.05	-118.3223.45	Receiving water
Los Angeles River	LAR1	33.8058.09	-118.2054.53	Receiving water
San Gabriel River	SGR	33.7751.08	-118.0974.18	Receiving water
Dominguez Channel	DC	33.8710.5	-118.2905 69	Receiving water
San Diego River	SDR4	32.8450.37	-116.9912 06	Stormdrain
San Diego River	SDR1	32.4551.79	-117.1012.24	Receiving water
Tecolote Canyon Creek	тсс	32.7754.93	-117.2004.84	Receiving water
Wood Creek	WC1	33.3456.56	-117.4443.02	Stormdrain
Wood Creek	WC2	33.5815.83	-117.7457.72	Wetland outfall
Wood Creek	WC3	33.5815.7	-117.7457.27	Stormdrain

Appendix 2. Detailed sampling site information.

Appendix 3. Priority model pesticides (Final Score≥9) based on acute and chronic aquatic benchmarks and 2013-2015 urban pesticide usage in Los Angeles, Orange, and San Diego counties, California. All pesticides recommended to monitor based on physiochemical properties. All pesticides are either within current analytical screens or are undergoing method development.

	Use (3-yr	Use	Benchmark	Тох	Final
Pesticide	ave. Ibs a.i.)	Score	(ug/L)	Score	Score
Permethrin	62,754	5	0.0014	7	35
Cyfluthrin	29,731	5	0.0074	7	35
Fipronil	30,926	5	0.011	6	30
Bifenthrin	26,874	4	0.0013	7	28
Cypermethrin	6,082	4	0.069	6	24
Deltamethrin	4,150	3	0.0041	7	21
Lambda-cyhalothrin	3,393	3	0.002	7	21
Imidacloprid	40,690	5	1.05	4	20
Pyriproxyfen	2,836	3	0.015	6	18
Esfenvalerate	1,571	3	0.017	6	18
Prodiamine	17,679	4	1.5	4	16
Chlorfenapyr	15,803	4	2.915	4	16
Oxadiazon	1,077	3	0.88	5	15
Triclopyr, butoxyethyl ester	5,513	4	19	3	12
2,4-D	5,482	4	13.1	3	12
Oryzalin	4,482	4	15.4	3	12
Diuron	2,792	3	2.4	4	12
Pendimethalin	2,474	3	5.2	4	12
Bromacil	2,254	3	6.8	4	12
Malathion	944	2	0.035	6	12
Chlorpyrifos	273	2	0.04	6	12
Carbaryl	276	2	0.5	5	10
Propiconazole	3,309	3	21	3	9
Indoxacarb	2,737	3	75	3	9
Pesticides under analytical me	ethod developm	ent			
Sulfometuron-methyl	1,829	3	0.45	5	15
DDVP	685	2	0.0058	7	14
PCNB	5,029	4	13	3	12
Prallethrin	141	2	0.65	5	10
Dithiopyr	1,495	3	20	3	9
Tebuconazole	1,165	3	12	3	9

	W	ater Sample Analysis		
0	EMON Method	Destiside	Method Detection Limit	Reporting Limit
Screen	Number^	Pesticide	(µg/L)	(µg/L)
	-	AZOXYSTRODIN	0.0012	0.02
	-	Corbory	0.000977	0.02
	-	Calbalyi	0.011	0.05
	-	Chlorovrifos	0.00182	0.02
			0.00123	0.02
	-	Desulfinyl fipropil amide	0.00244	0.01
	-	Diflubenzuron	0.00244	0.01
	-	Diuron	0.00116	0.02
	-	Etofenorox	0.00184	0.02
	-	Fipronil	0.000864	0.01
	-	Fipronil amide	0.00157	0.01
LC	EMON-SM-05-037	Fipronil sulfide	0.00111	0.01
		Fipronil sulfone	0.000732	0.01
		Imidacloprid	0.00135	0.02
		Indoxacarb	0.00066	0.02
		Isoxaben	0.0014	0.02
		Malathion	0.00103	0.02
		Oryzalin	0.0035	0.02
		Oxadiazinon	0.00071	0.02
		Propiconazole	0.00142	0.02
		Pyraclostrobin	0.000535	0.02
		Pyriproxyfen	0.00114	0.02
		Simazine	0.000916	0.02
СВ	EMON-SM-11.3	Carbaryl	0.011	0.05
CF	EMON-SM-05-033	Chlorfenapyr	0.0624	0.1
DN	EMON-SM-05-006	Oxyfluorfen	0.01	0.05
	-	Pendimethalin	0.012	0.05
		Prodiamine	0.012	0.05
		Trifluralin	0.014	0.05
		2,4-D	0.015	0.05
PX	EMON-SM-05-012	Dicamba	0.017	0.05
	EMON-SM-05-012	MCPA	0.022	0.05
		Triclopyr	0.02	0.05

Appendix 4. Analytical method reporting levels for pesticides analyzed withi
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	v	Vater Sample Analysis		
0	EMON Method	Protisida	Method Detection Limit	Reporting Limit
Screen	Number^	Pesticide	(µg/L)	(µg/L)
		Bifenthrin	0.00091	0.002
		Cyfluthrin	0.00146	0.005
		Cypermethrin	0.00154	0.005
PV	EMON-SM-05-022	Deltamethrin/Tralomethrin	0.00177	0.005
		Fenvalerate/Esfenvalerate	0.00166	0.005
		Lambda-cyhalothrin	0.00174	0.005
		Permethrin cis	0.00105	0.005
		Permethrin trans	0.00105	0.005
	Sa	diment Comple Analysis		
	580	diment Sample Analysis		-
	500		Method	
	EMON Mothod		Method Detection	Reporting
Screen	EMON Method Number	Pesticide	Method Detection Limit (ug/kg)	Reporting Limit (ug/kg)
Screen	EMON Method Number	Pesticide Bifenthrin	Method Detection Limit (µg/kg) 0.108	Reporting Limit (µg/kg) 1
Screen	EMON Method Number	Pesticide Bifenthrin Cyfluthrin	Method Detection Limit (µg/kg) 0.108 0.183	Reporting Limit (µg/kg) 1
Screen	EMON Method Number	Pesticide Bifenthrin Cyfluthrin Cypermethrin	Method Detection Limit (μg/kg) 0.108 0.183 0.107	Reporting Limit (µg/kg) 1 1 1
Screen	EMON Method Number	Pesticide Bifenthrin Cyfluthrin Cypermethrin Deltamethrin/Tralomethrin	Method Detection Limit (µg/kg) 0.108 0.183 0.107 0.0661	Reporting Limit (µg/kg) 1 1 1 1
Screen PY	EMON Method Number EMON-SM-52-9	Pesticide Bifenthrin Cyfluthrin Cypermethrin Deltamethrin/Tralomethrin Fenvalerate/Esfenvalerate	Method Detection Limit (μg/kg) 0.108 0.183 0.107 0.0661 0.0661	Reporting Limit (µg/kg) 1 1 1 1 1 1
Screen PY	EMON Method Number EMON-SM-52-9	Pesticide Bifenthrin Cyfluthrin Cypermethrin Deltamethrin/Tralomethrin Fenvalerate/Esfenvalerate Lambda-cyhalothrin	Method Detection Limit (µg/kg) 0.108 0.183 0.107 0.0661 0.0661 0.115	Reporting Limit (μg/kg) 1 1 1 1 1 1 1
Screen PY	EMON Method Number EMON-SM-52-9	Pesticide Bifenthrin Cyfluthrin Cypermethrin Deltamethrin/Tralomethrin Fenvalerate/Esfenvalerate Lambda-cyhalothrin Permethrin cis	Method Detection Limit (μg/kg) 0.108 0.183 0.107 0.0661 0.0661 0.115 0.116	Reporting Limit (μg/kg) 1

*Full analytical methods are available at: http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm?filter=surfwater