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Environmental Monitoring Branch
Surface Water Protection Program
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STUDY 320: Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019–2020

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1. Introduction

Southern California urban areas have considerable pest pressures, which results in high urban pesticide use. According to the Pesticide Use Report (PUR) over 15,700,000 pounds of pesticides were applied in urban areas in 2017 (CDPR, 2019). Non-agricultural use includes applications for residential, industrial, institutional, structural, or vector control purposes (CDPR, 2014). PUR data do not account for non-professional applications by residents and homeowners, so actual use is higher. Los Angeles, Orange, and San Diego counties, all counties in Southern California, accounted for 22.5% of the total reported non-agricultural use. Urban areas in Southern California are highly developed, with a high percentage of impervious surfaces. Impervious surfaces enhance surface water runoff, which increases the potential for pesticides to enter urban creeks and rivers via storm drains.

The California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program (SWPP) has been monitoring pesticides in urban waterways since 2008. Study 320 is a continuation of CDPR Study 270 (Budd, 2018). The work described herein complements Study 299, which monitors for pesticides in urban areas of Northern California (Ensminger, 2017). All of these studies have shown that urban-use pesticides (e.g., pyrethroids, fipronil, imidacloprid, and synthetic auxin herbicides) are commonly detected in urban waterways (Ensminger et al., 2013a). SWPP is particularly interested in cases where pesticide concentrations repeatedly reach or exceed USEPA Aquatic Life Benchmarks, which are a type of toxicity thresholds used to gauge potential risks to sensitive aquatic organisms (Gan et al., 2012; Oki and Haver, 2009; Weston et al., 2014; Weston et al., 2005; Weston et al., 2009). Numerous urban waterways are listed on the 2016 Federal Clean Water Act Section 303(d) list due to the confirmed presence of pyrethroid and organophosphate pesticides (Cal EPA, 2018). High use, high potential for pesticide runoff to enter urban waterways, and historical exceedances of aquatic life benchmarks justify the need to continue monitoring California's urban waterways.

This study is also designed to evaluate water quality trends that could show changes in pesticide concentrations over time particularly at long-term monitoring sites. CDPR has taken significant mitigation actions to address water quality exceedances for pyrethroids and fipronil in recent years. Surface water regulations (Chapter 3, Sections 6970 and 6972 in the California Code of Regulations) went in effect in July 2012 to address pyrethroid concentrations in California surface waters (CDPR, 2013); and in 2018, new California specific labels were adopted for fipronil-containing products registered for outdoor use. These mitigation actions were designed to reduce loading of pyrethroids and fipronil to surface waters. Long-term monitoring could provide data that allow CDPR to assess improvements in water quality, such as downward trends in pesticide concentrations and/or decreased exceedances of toxicity thresholds.

Exploratory sites will be added to the current monitoring protocol to measure pesticide loading from commercial sites. Previous monitoring efforts have focused on pesticide loading into receiving waters from residential areas; however, there is little known about the relative contribution of pesticides from other land-uses, such as commercial and industrial sites. Specific modifications from the Study 270 Fiscal Year (FY) 18–19 sampling plan are presented in Section 4.9.

2. Objectives

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

- 1) Determine presence and concentrations of selected priority pesticides in runoff and receiving waters of Southern California urban watersheds under dry and storm conditions;
- 2) Compare measured concentrations of pesticides to aquatic toxicity thresholds;
- 3) Evaluate pesticide concentration trends through long-term monitoring;
- 4) Determine the acute toxicity of water samples using laboratory tests conducted with the amphipod *Hyalella azteca* and the midge *Chironomus* species;
- 5) Evaluate the effectiveness of a small constructed wetland to remove pesticides from runoff;
- 6) Monitor deposition of sediment-bound pyrethroids within selected watersheds; and
- 7) Evaluate commercial land-use as potential source of pesticides to urban waterways.

3. Personnel

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Nan Singhasemanon, Environmental Program Manager I. Key personnel are listed below:

Project Leader: Aniela Burant, Ph.D.

Field Coordinator: Annette Narzynski
Reviewing Scientist: Robert Budd, Ph.D.
Statistician: Dan Wang, Ph.D.
Laboratory Liaison: Sue Peoples
Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)

Collaborators: University of California - Cooperative Extension Orange County – South Coast Research and Extension Center, Los Angeles Public Works, Los Angeles Sanitation District, City of San Diego, County of San Diego, and Orange County Public Works.

Please direct questions regarding this study to Aniela Burant, Senior Environmental Scientist (Specialist), at (916) 445-2799 or Aniela.Burant@cdpr.ca.gov

4. Study Plan

4.1 Site Selection

All of the sites described in this protocol, with the exception of the exploratory sites, have been previously sampled by CDPR (Budd, 2018). These sites were selected using the watershed prioritization component of the Surface Water Monitoring Prioritization (SWMP) Model. The SWMP model, which is extensively described in Luo, et al. (2017), identifies priority hydrologic-unit codes (HUC) based on reported pesticide use and toxicity data. Using the SWMP Model and its aggregation tool (Luo, et al., 2017), the top ten priority HUC8s are identified for Southern California (Appendix 1). Of these, SWPP currently has monitoring sites within six of the top HUC8s. These watersheds, located throughout heavily urbanized areas 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). Other factors such as site accessibility, perennial flow, other monitoring agency representation, and budgetary constraints direct site selection in the remaining HUCs.

4.1.1. Los Angeles County

Ballona Creek (BAL), Bouquet Canyon Creek (BOQ), Los Angeles River (LAR), San Gabriel River (SGR), and Dominguez Channel (DC) are the watersheds of interest in Los Angeles County (Figure 1). All sites are located on concrete-lined channels. All of these sites are large watersheds with mixed residential and commercial land-use. BAL is located in the Santa Monica Bay HUC8 and drains mostly residential land-uses with single- and multi- family homes. BOQ consists of predominantly affluent single-family homes with a small amount of commercial land-use. Although not in a HUC8 identified by the SWMP Model, BOQ has historically high pesticide detections. LAR, in the Los Angeles HUC8, drains residential land-uses, but has a higher percentage of commercial and industrial land-uses than BAL or BOQ. DC has

the highest percentage of commercial and industrial land-uses of the any of the receiving waters in this study. SGR consists primarily of wastewater effluent during low flows. Both DC and SGR are in the San Gabriel HUC8.

Inclusion of two exploratory sites to determine relative contributions from commercial-dominated land-use sites are currently under consideration. The two sampling sites under consideration will likely be storm drains; access to sampling of the potential storm drains along the Los Angeles River is currently the primary consideration.

4.1.2 Orange County

Ambient water quality monitoring will be conducted at six sampling locations within Salt Creek (SC, Figure 2), three locations within Wood Creek Canyon (WC, Figure 3), and one site in the Anaheim-Barber City Channel (ABCC, Figure 4) in Orange County. ABCC was misidentified as Bolsa Chica Channel (BCC) in FY 18-19; these are the same sampling sites.

Sampling stations within Salt Creek (SC1, SC2, SC3, SC4, SC5, and SC7) have been monitored consistently since 2009 as part of CDPR's 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 urban inputs and will allow evaluation of pesticide concentrations in the watershed as well as downstream transport of pesticides. All SC sites are located in the Aliso-San Onofre HUC8.

Monitoring locations within Wood Creek, all located in the Aliso-San Onofre HUC8, have been monitored since 2009 as part of SWPP's mitigation evaluation monitoring in urban settings. The monitoring sites are situated at the inlet (WC1) and outlet (WC2) of a small (~0.18 acres) constructed wetland designed to reduce pollutants in urban runoff (Budd, et al., 2012). The wetland receives urban runoff from a drainage area consisting entirely of 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 the inlet and outlet. A second storm drain (WC3), located within the Wood Creek Watershed, will be monitored for pyrethroids only.

Sampling will continue at a location that was added in FY 18–19 on the Anaheim-Barber City Channel, which is concrete-lined. This watershed is a mixed residential, commercial, and industrial area. This watershed is located within the Seal Beach HUC8, the highest priority HUC8 in Southern California based on estimated urban pesticide use within the delineated HUC.

4.1.3 San Diego County

Two stations within the San Diego River Watershed, as well as one within the Chollas Creek Watershed, will be monitored in San Diego County (Figure 5, Table 1, and Appendix 2). The sites in San Diego County drain a relatively high percentage of residential land-use in comparison to the Los Angeles or Orange County sites. San Diego River and Chollas Creek are not channelized or concrete-lined, which may account for historically lower pesticide concentrations (Budd, 2018). Each of these sites are located within high priority HUC8s in Southern California (Appendix 1). Sampling locations within San Diego County are located near the base of their respective watersheds (i.e., the downstream portion of the watersheds).

4.1.4 Collaborative Monitoring

CDPR has been engaged in a collaborative effort with the State Water Resources Control Board through its Stream Pollution Trends (SPoT) Monitoring Program to increase the data available for trend analysis of current-use pesticides (SWAMP, 2017). The synergistic partnership allows each agency to maximize information gained with limited resources. In coordination with CDPR, the SPoT Program also collects sediments throughout California for pyrethroid and fipronil analyses, which greatly adds to the spatial representation of pesticide monitoring data. Several sites described in this protocol also serve as SPoT monitoring locations for sediments, including BAL, BOQ, LAR1, SGR, and SC5. CDPR collects and analyzes the aqueous samples, while SPoT monitors for pyrethroids and fipronil in sediment. Both sets of data are considered in long-term trend analysis.

4.2 Selection of Pesticides for Monitoring

The SWMP Model was utilized for pesticide selection for ambient monitoring (Budd et al., 2013; Luo et al., 2013). Luo, et al. (2013) describes the SWMP Model in detail, but briefly, the model is based on current pesticide use (PUR, 2015–2017) patterns and aquatic toxicity threshold values. Use data from Los Angeles, Orange, and San Diego counties and U.S. EPA aquatic life benchmarks were considered. The product of the use and toxicity scores yields a final score that represents a relative prioritization of pesticides. In addition, the output generates a monitoring recommendation based on physical-chemical properties such as half-life and solubility. 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 aquatic toxicity. However, the decision to monitor a pesticide is also influenced by additional factors such as previous monitoring data, budgetary constraints, and analytical capabilities. Forty-one pesticides received a final score equal to or greater than nine (Appendix 3). These pesticides will be analyzed using five analytical screens: a pyrethroid screen, liquid chromatography (LC) multi-analyte screen, dinitroaniline screen, phenoxy herbicide screen, and chlorfenapyr screen. All suites cannot be

analyzed at every monitoring location due to budgetary constraints. Priority is given to the pyrethroid and pesticides included in the liquid chromatography (LC) multi-analyte screen. Four sampling locations (SC3, SC7, BAL and LAR) will serve as representative watersheds to determine the extent of pesticide concentrations, where all five analytical method screens will be run (Table 2). At these sites, screens that contain pesticides with lower detection frequencies in previous monitoring, such as the chlorfenapyr screen and dinitroaniline screen, or pesticides that have not previously exceeded benchmarks (e.g., phenoxy herbicides), will be analyzed (Appendix 4).

4.3 Water Sampling

Whole water samples will be collected during two dry-season and two storm sampling events. Dry-season sampling will occur in August 2019 and June 2020. CDPR will attempt to collect storm samples during the first major storm (rain) event of FY 19–20 and during a second major storm in the winter or early spring of 2020 (Table 2).

Dry-season 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 stainless-steel container will be used to initially collect the water samples. Water samples collected during storm events at up to five locations within Salt Creek or Wood Creek watersheds may be collected as time-weighted 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. Storm runoff composite samples collected at SDR4 and CHO1 will be collected by the County and City of San Diego, respectively. Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed. Field duplicates and/or field blanks will be collected during each sampling event for quality assurance.

4.4 Sediment Sampling

Sediment samples will be collected at three locations (Table 2). Sediment samples will be collected in 1-quart glass Mason Jars using passive sediment-collection samplers (Budd, 2009). If passive samplers are not deployed at these sites, one quart of sediment will be collected using stainless-steel scoops from the top of the bed layer, biasing for fine sediments where possible (Mamola, 2005). All sediments will be passed through a 2-mm sieve to remove plant debris and then homogenized (Mamola, 2005). Samples will be analyzed for pyrethroids.

4.5 Toxicity Sampling

Water samples will be collected at a subset of sampling sites for toxicity analysis (Table 3). 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 sp.* in water over 96-hours (Table 3). Several sites described in this protocol also serve as SPoT monitoring locations for sediment toxicity, including BAL, BOQ, LAR1, SGR, and SC5. Data will be shared between monitoring programs.

4.6 Field Measurements

Physical-chemical properties of water column will be determined using a YSI-EXO 1 multi-parameter Sonde according to the methods describe by Doo and He (2008). At each site, water chemistry parameters measured *in situ* will include pH, temperature, salinity, total dissolved solids, and dissolved oxygen. Storm drain 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 Analyses

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 Study 270 FY 18-19

The current sampling plan is an extension of Study 270 conducted during fiscal years 2010–2019. Details of the previous year’s sampling protocol are described in the document titled “Study 270: Urban Pesticide Monitoring in Southern California” (Budd, 2018). The sampling and analysis schedule is similar to that for FY 18–19, with a few notable modifications (Table 4), including the addition of two exploratory sites to determine pesticide loading from commercial land-use.

5. Chemical Analysis

Pesticide analysis will be conducted by the Center for Analytical Chemistry at the California Department of Food and Agriculture, Sacramento, CA (CDFA). CDFA will analyze five analytical suites (Appendix 4). Sediment samples will be analyzed for pyrethroids (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. Data Analysis

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 non-parametric statistical methods to analyze the data. The data collected from this project may be used to develop or calibrate urban pesticide runoff models.

Preliminary analysis (Ensminger and Budd, 2014) indicated that the sample data are skewed and contain 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). The application of non-parametric procedures to skewed and censored environmental data is most appropriate for this study (Helsel, 2012). The data will be analyzed by using the R statistical program (R Core Team, 2014), specifically the Non-detects And Data Analysis for environmental data (NADA) package for R (<http://cran.r-project.org/web/packages/NADA/NADA.pdf>), and Minitab (<http://www.minitab.com/en-us/>).

Based on the study objectives, preliminary analysis, and data availability, we propose the following statistical procedures for data analysis (Table 5).

- 1) Explanatory data analysis will be performed to summarize the characteristics of the sample data. Urban monitoring data have been collected since 2008 for a variety of analytes (Appendix 4) at multiple locations (e.g., Salt Creek, Wood Creek) with different site types (i.e., storm drain outfalls and receiving waters), and between different seasons (i.e., dry and wet seasons) (Tables 1 and 2). Boxplots, histograms, probability plots, and empirical distribution functions will be produced to explore any potential patterns demonstrated by the data.
- 2) 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 seasons, or between the different locations. Non-parametric procedures will be used to compute the statistics for hypothesis testing. Data with multiple reporting limits will be censored at the highest limit before proceeding if the test procedure allows only one reporting limit.
- 3) Trend analysis will be included to demonstrate changes in concentration over time (if any). 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 statistical models to assess the factors potentially affecting pesticide concentrations in surface water. We intend to develop a logistic regression model to estimate and predict

the likelihood of detection or exceedance of reporting limits or toxicity thresholds. A series of explanatory variables will be examined, including but not limited to: rainfall, field measurements (e.g., flow rate, pH, water TOC, sediment TOC, and TSS), number of households contributing to the storm drain outfall/creek, residential density, percent of impervious areas, season (or month), year, and regulation. Further literature review will be conducted to identify possible explanatory variables in favor of the model.

7. Timeline

Field Sampling: Aug 2019 – Jun 2020
Chemical Analysis: Jul 2019 – Oct 2020
Report to Management: Jan 2021 – Mar 2021
Data Entry into SURF: Mar 2021 – Jun 2021

8. Laboratory Budget

The estimated total cost for chemical analyses water and sediment samples is \$171,960. (Table 2).

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

County	Watershed	Stormdrain Outfall	Receiving Water/ Mitigation Outfall	Total Sites
Los Angeles	Ballona Creek	-	1	1
Los Angeles	Bouquet Creek	-	1	1
Los Angeles	Los Angeles River	-	1	1
Los Angeles	San Gabriel River	-	1	1
Los Angeles	Dominguez Channel	-	1	1
Los Angeles	Los Angeles River (Downtown)	1		1
Los Angeles	Compton Creek	1		1
Orange	Anaheim-Barber City Channel	-	1	1
Orange	Salt Creek	4	2	6
Orange	Wood Creek	2	1	3
San Diego	San Diego River	1	1	2
San Diego	Chollas Creek	-	1	1
	Total	9	11	20

Table 2. Ambient surface water and mitigation sampling schedule.

		Number Samples						
Site	Screen	August Dry	First Storm	Second Storm	June Dry	Total Samples	Cost/Sample	Budget
<i>Ambient Monitoring</i>								
LAR, SC7	CF	2	2	2	2	8	\$540	\$4,320
	DN	2	2	2	2	8	\$720	\$5,760
	PX	2	2	2	2	8	\$690	\$5,520
	LC Long		2			2	\$2,500	\$5,000
	LC	2		2	2	6	\$1,700	\$10,200
	PY6	2	2	2	2	8	\$600	\$4,800
SC3, BAL	CF	2	2			4	\$540	\$2,160
	DN	2	2			4	\$720	\$2,880
	PX	2	2	2	2	8	\$690	\$5,520
	LC	2	2	2	2	8	\$1,700	\$13,600
	PY6	2	2	2	2	8	\$600	\$4,800
SC1, SC2, SC4, SC5, WC1	LC	5	5	5	5	20	\$1,700	\$34,000
	PY6	5	5	5	5	20	\$600	\$12,000
BOQ, SDR1, WC2	LC	3	3		3	9	\$1,700	\$15,300
	PY6	3	3		3	9	\$600	\$5,400
DC, SGR	LC	2			2	4	\$1,700	\$6,800
	PY6	2			2	4	\$600	\$2,400
CHO, SDR4	LC		2		2	4	\$1,700	\$6,800
	PY6		2		2	4	\$600	\$2,400
ABCC	LC	1		1		2	\$1,700	\$3,400
	PY6	1		1		2	\$600	\$1,200
WC3	PY6	1	1	1	1	4	\$600	\$2,400
LAR3, CC1^	LC Long	2	1			3	\$2,500	\$5,000
	PY6	2	1			3	\$600	\$2,400
SC3, SC5, WC1	PY6-Sed	3			3	10	\$600	\$6,000
QC	PY	1	1	1	1	4	\$600	\$2,400
Ambient Monitoring Sub-total								\$171,960

*Pesticides includes in screens detailed in Appendix 4. CF=chlorfenapyr, DN=dinitroanline, LC = Liquid chromatography, PX=phenoxy, PY=pyrethroid.

**QC=quality control. Screens will rotate by event.

^Exploratory Sites

Table 3. Toxicity sampling schedule.

Site	Test Species	August Dry	June Dry	First Storm	Second Storm
LAR, BOQ, SC3, SC7*, SDR, BAL*	<i>Hyalella azteca</i>	5	—	5	5
LAR, BOQ, SC3, SC7*, SDR, BAL*	<i>Chironomus sp.</i>	5	—	5	5

*SC7 and BAL will be rotated each event.

Table 4. Modifications from sampling plan for fiscal year 2018–2019.

Change from FY 18-19	Justification
Adding LC Long Screen	Validation of model with addition of low priority pesticides
Adding additional toxicity tests	Collaborative monitoring efforts with SPoT program
Remove CF and DN from Second Storm and First Dry	Low detections for these compounds, additional budget needed for LC Long Screen
Adding EXP1 and EXP2	Adding drainage locations that receive runoff from either commercial or industrial land-use to evaluate their potential contribution to pesticide loading

Table 5. Non-parametric procedures frequently used for comparing paired data, two samples and three or more samples.

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

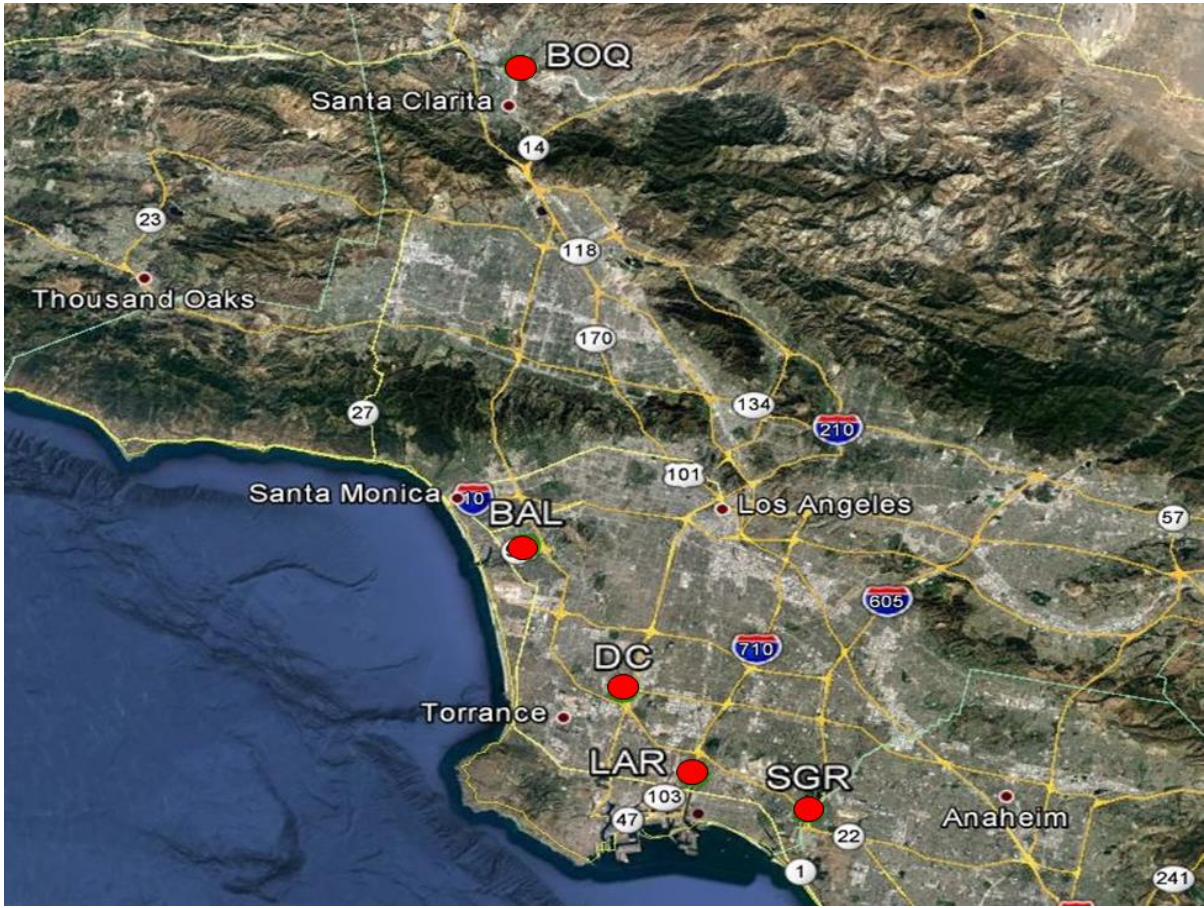


Figure 1. Sampling locations within Los Angeles County, CA.

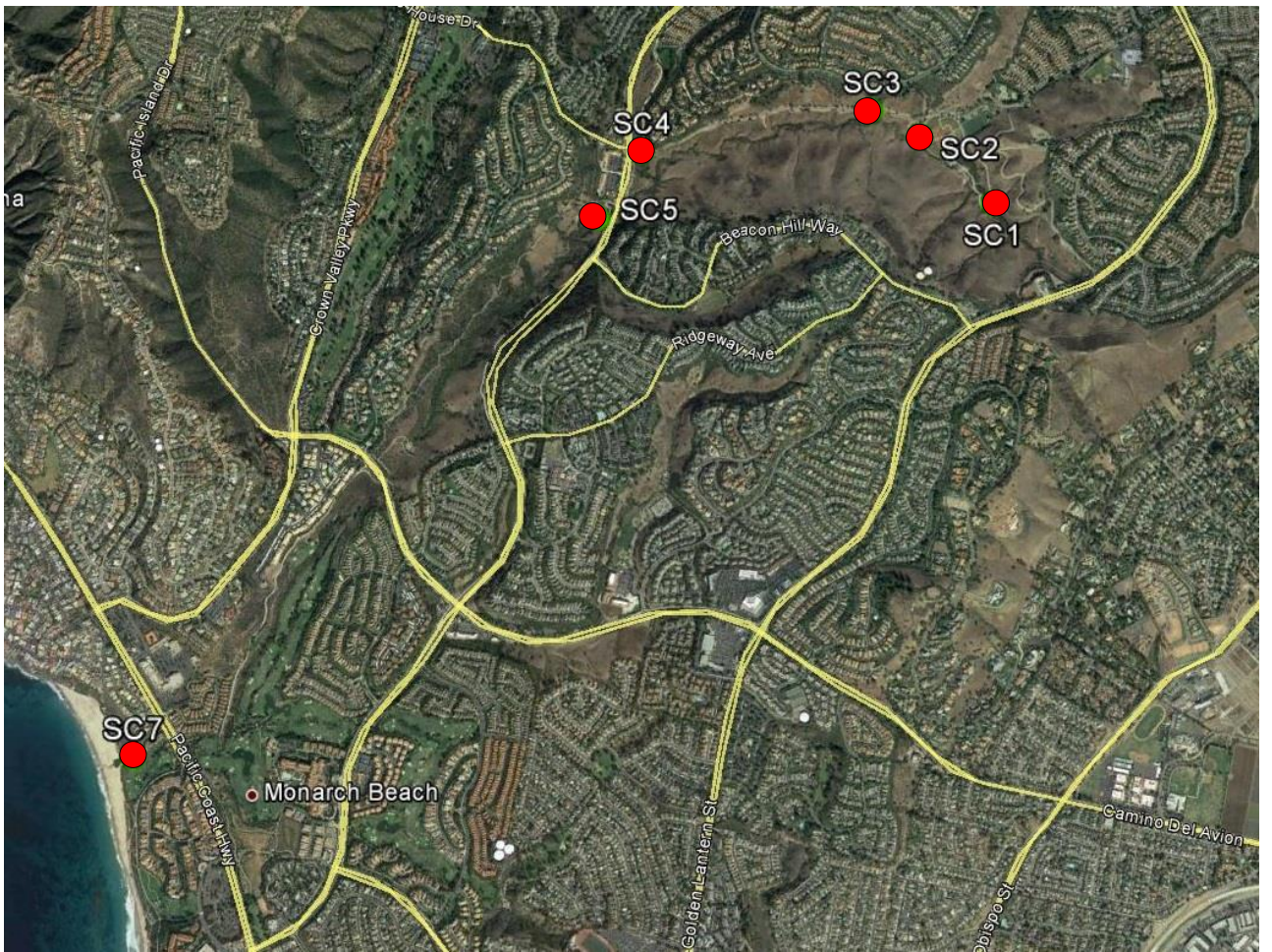


Figure 2. Sampling locations within Salt Creek Watershed, Orange County, CA.

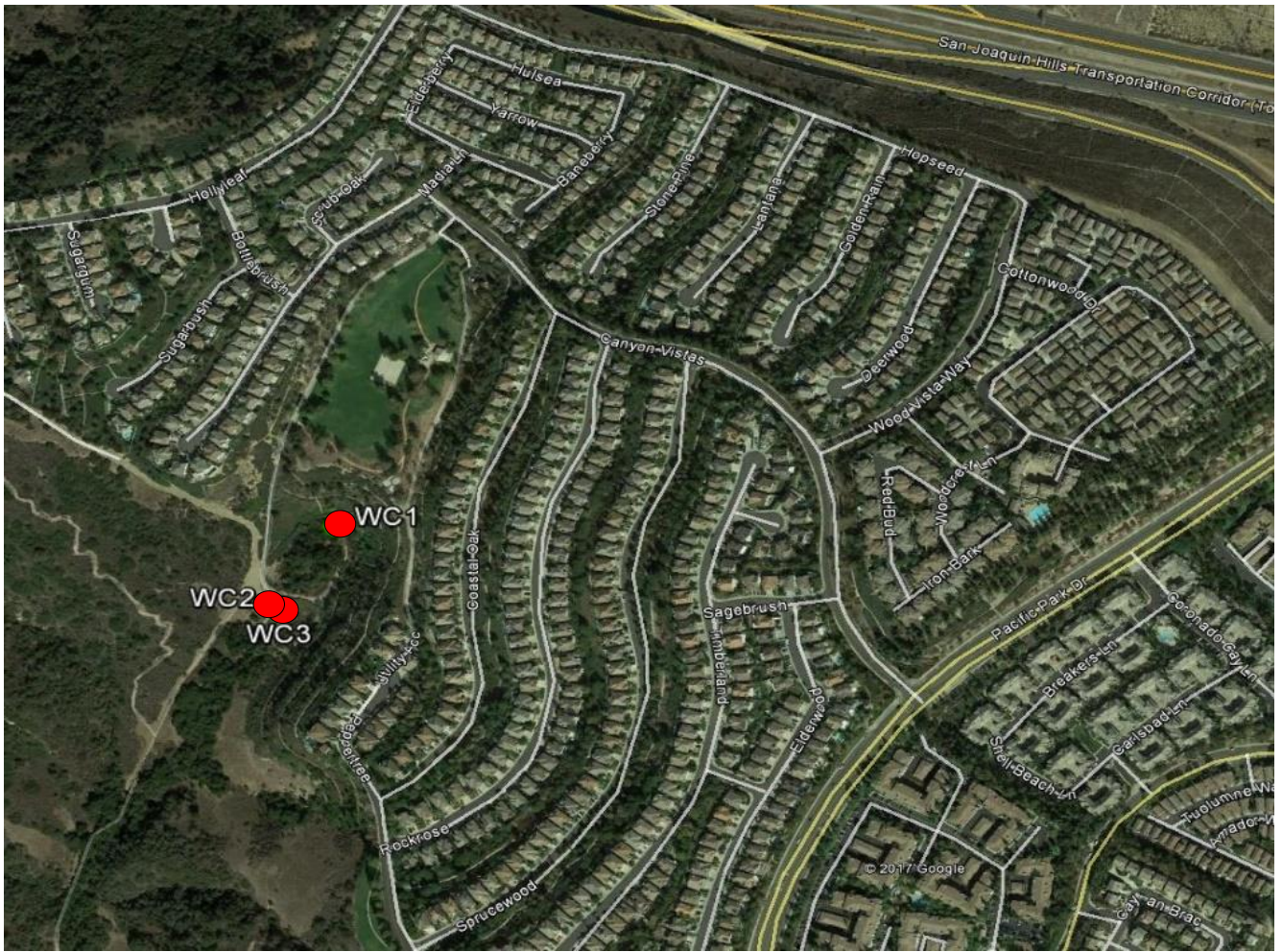


Figure 3. Sampling locations within Wood Creek Watershed, Orange County, CA.

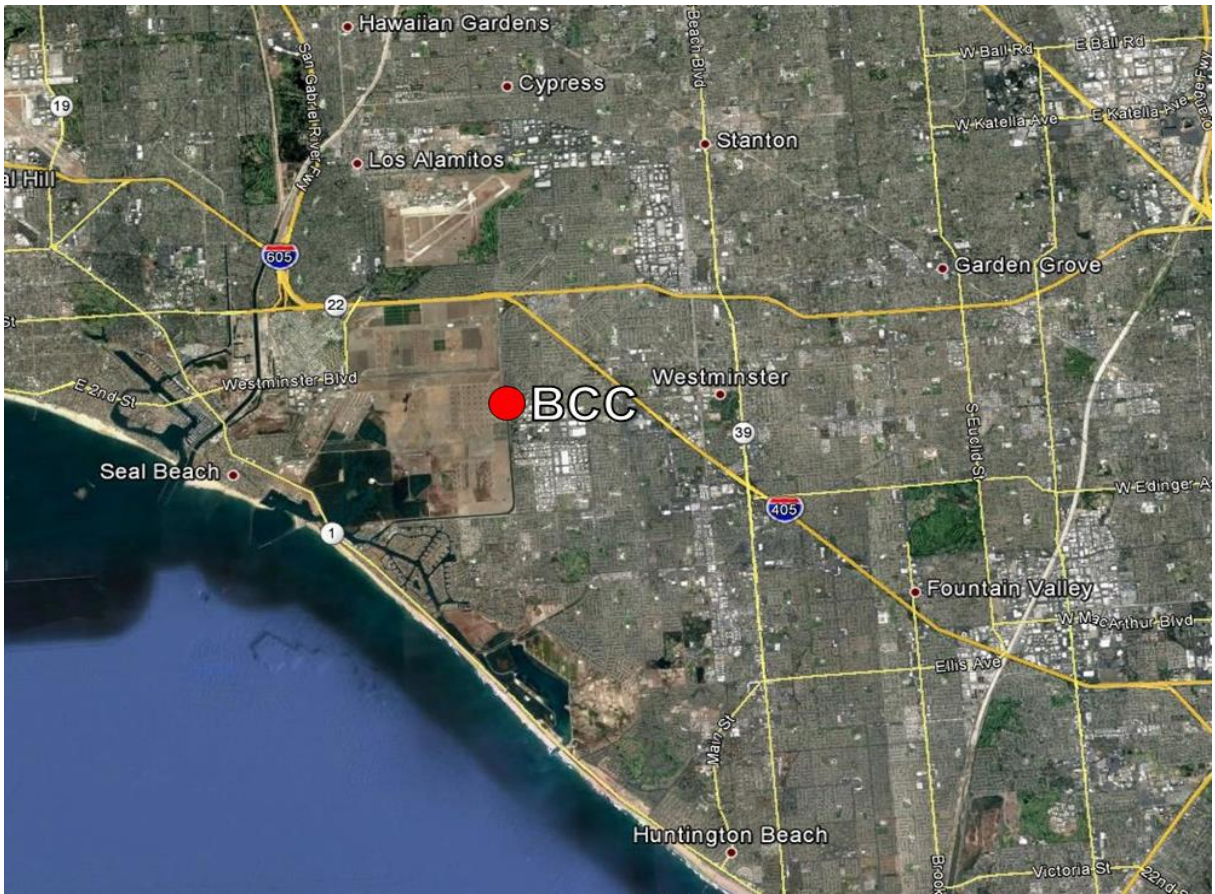


Figure 4. Sampling location with Anaheim-Barber City Channel, Orange County, CA.

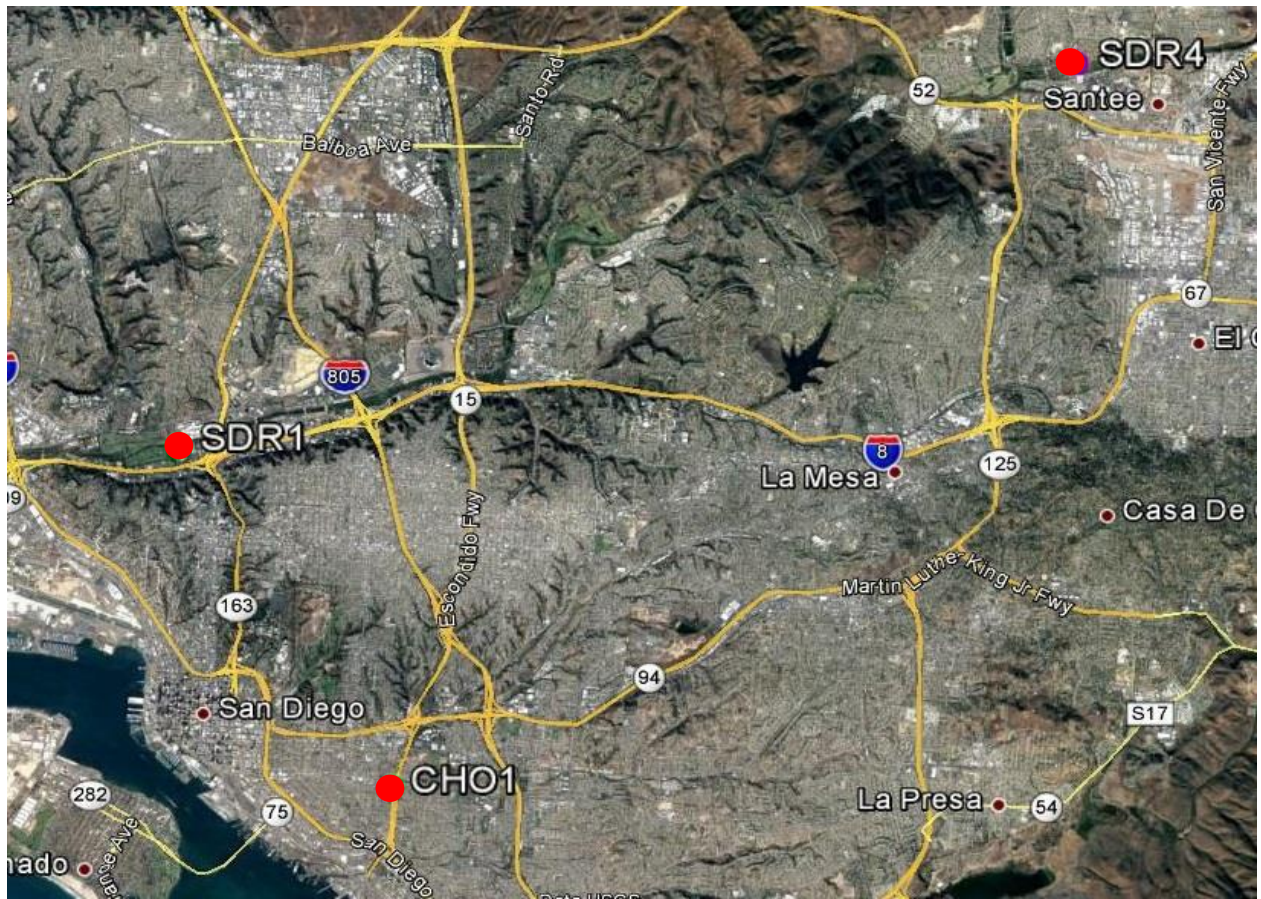


Figure 5. Sampling locations within San Diego County, CA.

Appendix 1. Top ten HUC8's identified for urban monitoring in Southern California, ordered by the ranking process.

HUC8 Code	HUC8 Name	CDPR Monitoring	Comments
18070201	Seal Beach (Anaheim Bay)	ABCC	
18070105	Los Angeles	LAR1	
18070204	Newport Bay		SWAMP location, NPDES permit monitoring at several locations along San Diego Creek*
18070104	Santa Monica Bay	BAL	
18070106	San Gabriel	SGR, DC	
18070203	Santa Ana		Southern California Bight Project monitoring site at base of Santa Ana River*
18070304	San Diego	SDR1, SDR4, CHO1	
18070202	San Jacinto		SWAMP monitoring location along Santa Margarita River*
18070301	Aliso-San Onofre	SC1, SC2, SC3, SC4, SC5, SC7, WC1, WC2, WC3	
18080303	San Luis Rey-Esccondido		SWAMP monitoring location along San Luis River*

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

Appendix 2. Detailed sampling site information.

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
Anaheim-Barber City Channel	ABCC	33.750297	-118.042183	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
Chollas Creek	CHO1	32.704850	-117.121143	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 3. Priority model pesticides (Final Score \geq 9) based on acute and chronic aquatic benchmarks and 2015–2017 urban pesticide usage in Los Angeles, Orange, and San Diego counties, California. All pesticides recommended to monitor based on physical-chemical properties. All pesticides are either within current analytical screens or are undergoing method development.

Pesticide	Pesticide Class	Use (lbs)	Use Score	Benchmark (ppb)	Tox Score	Final Score
Permethrin	Pyrethroid	31664	5	1.40E-03	7	35
Bifenthrin	Pyrethroid	22446	5	1.30E-03	7	35
Imidacloprid	Neonicotinoid	20588	5	0.01	7	35
Cyfluthrin	Pyrethroid	13797	4	7.40E-03	7	28
Fipronil	Phenylpyrazole	19707	4	0.01	6	24
Lambda-Cyhalothrin	Pyrethroid	4567	3	2.00E-03	7	21
Deltamethrin	Pyrethroid	3424	3	4.10E-03	7	21
Pyriproxyfen	Pyridine	3866	3	0.02	6	18
Cypermethrin	Pyrethroid	3833	3	0.06	6	18
Esfenvalerate	Pyrethroid	1746	3	0.01	6	18
Chlorfenapyr	Pyrrole	12928	4	2.91	4	16
Isoxaben	Benzamide	5367	4	10	4	16
Oryzalin	Dinitroaniline	22227	5	13	3	15
Triclopyr, butoxyethyl ester	Pyridine	6766	4	26	3	12
Prodiamine	Dinitroaniline	4299	3	1.5	4	12
Pendimethalin	Dinitroaniline	3140	3	5.2	4	12
Diuron	Substituted urea	2359	3	2.4	4	12
Chlorpyrifos	Organophosphate	925	2	0.04	6	12
Malathion	Organophosphate	569	2	0.05	6	12
Thiamethoxam	Neonicotinoid	938	2	0.74	5	10
Carbaryl	Carbamate	505	2	0.5	5	10
Oxyfluorfen	Diphenyl-ether	362	2	0.29	5	10
Propiconazole	Triazole	3547	3	21	3	9
Indoxacarb	Oxadiazine	2355	3	75	3	9
Tebucabazole	Triazole	2176	3	11	3	9
<i>Pesticides needing analytical method development</i>						
Dichlobenil	Nitrile	77788	5	30	3	15
Sulfometuron-methyl	Urea	2637	3	0.45	5	15
DDVP	Organophosphate	695	2	5.80E-03	7	14
Dithiopyr	Pyridine	5336	4	20	3	12
Chlorsulfuron	Sulfonylurea	980	2	0.35	5	10
Prallethrin	Pyrethroid	319	2	0.65	5	10
PCNB	Chlorophenyl	2919	3	13	3	9
Imazapyr, isopropylamine salt	Imidazolinone	2131	3	18	3	9
Tebuthiuron	Urea	2092	3	50	3	9

Appendix 4. Analytical method reporting levels for pesticides analyzed within screens.

Water Sample Analysis					
Screen	EMON Method Number*	Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
LC	EMON-SM-05-037	Azoxystrobin	Methoxy-acrylate	0.0012	0.02
		Bromacil	Uracil	0.000977	0.02
		Carbaryl	Carbamate	0.011	0.02
		Chlorantraniliprole	Anthranilic diamide	0.00182	0.02
		Chlorpyrifos	Organophosphate	0.00123	0.02
		Desulfinyl fipronil	Phenylpyrazole	0.0011	0.01
		Desulfinyl fipronil amide	Phenylpyrazole	0.00244	0.01
		Diuron	Substituted urea	0.00116	0.02
		Fipronil	Phenylpyrazole	0.000864	0.01
		Fipronil amide	Phenylpyrazole	0.00157	0.01
		Fipronil sulfide	Phenylpyrazole	0.00111	0.01
		Fipronil sulfone	Phenylpyrazole	0.000732	0.01
		Imidacloprid	Phenylpyrazole	0.00135	0.01
		Indoxacarb	Oxadiazine	0.00066	0.02
		Isoxaben	Benzamide	0.0014	0.02
		Malathion	Organophosphate	0.00103	0.02
		Oryzalin	Dinitroaniline	0.0035	0.02
		Oxadiazinon	Oxadiazole	0.00071	0.02
		Propiconazole	Triazole	0.00142	0.02
		Pyraclostrobin	Methoxy-carbamate	0.000535	0.02
		Pyriproxyfen	Pyridine	0.00114	0.015
		Tebucabazole	Triazole	0.003	0.02
Thiamethoxam	Neonicotinoid	0.001	0.02		
Acetamiprid	Neonicotinoid	0.002	0.02		
CF	EMON-SM-05-033	Chlorfenapyr	Pyrrole	0.0624	0.1
DN	EMON-SM-05-006	Oxyfluorfen	Dinitroaniline	0.01	0.05
		Pendimethalin	Dinitroaniline	0.012	0.05
		Prodiamine	Dinitroaniline	0.012	0.05
		Trifluralin	Dinitroaniline	0.014	0.05
PX	EMON-SM-05-012	2,4-D	Phenoxy	0.015	0.05
		Dicamba	Benzoic acid	0.017	0.05
		MCPA	Phenoxy	0.022	0.05
		Triclopyr	Pyridine	0.02	0.05

Appendix 4. Analytical method reporting levels for pesticides analyzed within screens.

Water Sample Analysis					
Screen	EMON Method Number*	Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
PY	EMON-SM-05-022	Bifenthrin	Pyrethroid	0.00091	0.001
		Cyfluthrin	Pyrethroid	0.00146	0.002
		Cypermethrin	Pyrethroid	0.00154	0.005
		Deltamethrin/Tralome thrin	Pyrethroid	0.00177	0.005
		Fenvalerate/Esfenvale rate	Pyrethroid	0.00166	0.005
		Lambda-cyhalothrin	Pyrethroid	0.00174	0.002
		Permethrin cis	Pyrethroid Pyrethroid	0.00105	0.002
		Permethrin trans		0.00105	0.005
Sediment Sample Analysis					
Screen	EMON Method Number	Pesticide	Pesticide Class	Method Detection Limit (µg/kg)	Reporting Limit (µg/kg)
PY	EMON-SM-52-9	Bifenthrin	Pyrethroid	0.108	1
		Cyfluthrin	Pyrethroid	0.183	1
		Cypermethrin	Pyrethroid	0.107	1
		Deltamethrin/Tralome thrin	Pyrethroid	0.0661	1
		Fenvalerate/Esfenvale rate	Pyrethroid	0.0661	1
		Lambda-cyhalothrin	Pyrethroid	0.115	1
		Permethrin cis	Pyrethroid	0.116	1
		Permethrin trans	Pyrethroid	0.135	1

*Full analytical methods are available at:

http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm?filter=surfwater