Department of Pesticide Regulation
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STUDY 320: Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Water Year 2023-2024

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1. Introduction

Southern California urban areas have considerable pest pressure, which results in high urban pesticide use. According to the Pesticide Use Report (PUR) over 17,250,000 pounds of pesticide active ingredient were applied for non-agricultural use in 2018 (DPR, 2021). Non-agricultural use includes applications for residential, industrial, institutional, structural, or vector control purposes (DPR, 2014). However, as PUR data do not account for non-professional applications by residents and homeowners, actual use may be higher. Los Angeles, Orange, and San Diego counties, accounted for 20% of the statewide reported non-agricultural use in 2018. Specifically, about 2.3 million pounds of pesticides were applied for professional structural pest control or landscape maintenance in Los Angeles, Orange, and San Diego counties in 2018. 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 (Gan et al., 2012).

The California Department of Pesticide Regulation's (DPR) Surface Water Protection Program (SWPP) has been monitoring pesticides in urban waterways since 2008. Study 320 is a continuation of DPR's urban monitoring in Southern California (Budd, 2022, Burant 2019, Burant, 2020). The work described herein complements Study 329 (a continuation of Study 299), which monitors for pesticides in urban areas of Northern California (Ensminger, 2019, Smith, 2020). These studies have shown that urban-use pesticides (e.g., pyrethroids, fipronil, imidacloprid, and synthetic auxin herbicides) are commonly detected in urban waterways (Burant, 2021, Ensminger, 2021). The SWPP is particularly interested in cases where pesticide concentrations repeatedly reach or exceed USEPA Aquatic Life Benchmarks (ALBs), which are a type of toxicity threshold used to gauge potential risks to sensitive aquatic organisms (Budd, et al., 2020; Gan et al., 2012;

Oki and Haver, 2009; Weston et al., 2014; Weston et al., 2009; Weston et al., 2005). Numerous urban waterways are listed on the 2018 Federal Clean Water Act Section 303(d) list due to the confirmed presence of pyrethroid and organophosphate pesticides (Cal EPA, 2021). High use, high potential for pesticide runoff to enter urban waterways, and historical exceedances of ALBs justify the need to continue monitoring California's urban waterways.

This study is designed to evaluate water quality trends that could show changes in pesticide concentrations over time, particularly at long-term monitoring sites. In recent years, DPR has taken significant mitigation actions to address water quality exceedances for pyrethroids and fipronil. Surface water regulations (Chapter 3, Sections 6970 and 6972 in the California Code of Regulations) went into effect in July 2012 to address pyrethroid concentrations in California surface waters (DPR, 2013). A recent evaluation was conducted of the SWPP's urban pyrethroid monitoring data in relation to the implementation of the surface water regulations. There were very few observed significant trends in concentrations, highlighting the need for continued monitoring of these high priority pesticides (Budd, et al., 2020). In 2018, new California-specific labels were adopted for fipronil-containing products registered for outdoor use. These mitigation actions were designed to reduce the loading of pyrethroids and fipronil to surface waters. Long-term monitoring data allows DPR to assess water quality improvements, such as downward trends in pesticide concentrations or fewer exceedances of ALBs. These monitoring activities assist DPR in evaluating the effectiveness of regulations and label changes.

This protocol details proposed sampling at DPR monitoring sites receiving urban runoff in Southern California for Water Year (WY) 2023-2024.

2. Objectives

The goal of this project is to assess pesticide concentrations within Southern California urbanized areas during WY 2023-2024 rain events and dry season conditions. Specific objectives include:

1) Determine presence and concentrations of selected priority pesticides in Southern California urban storm drainages and waterways;
2) Compare measured concentrations of pesticides to aquatic toxicity thresholds, specifically USEPA aquatic life benchmarks;

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 branchiopod water flea *Ceriodaphnia dubia*;

5) Monitor deposition of sediment-bound pyrethroids within selected watersheds;

6) Evaluate effectiveness of carbon-filled socks to reduce pesticides in urban runoff under field -conditions; and

7) Evaluate effect of filtering samples on pyrethroid concentrations and *Hyalella azteca* toxicity.

3. Personnel

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

- Project Leader: Harihar Nepal
- Scientific Advisor: Robert Budd, Ph.D.
- Field Coordinator: Rio Lininger
- Statistician: Xuyang Zhang, Ph.D.
- Laboratory Liaison: Josh Alvarado
- 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 Harihar Nepal, Senior Environmental Scientist (Specialist), at (916) 324-4111 or harihar.nepal@cdpr.ca.gov.

4. Study Plan

4.1 Site Selection

Most sites described in this protocol have been previously sampled by DPR (Budd, 2022). These sites were selected using the watershed prioritization component of the Surface Water Monitoring Prioritization (SWMP) model (Monitoring Prioritization, version 4, Report ran on

9.5.2023; Appendix 1: Table 1 and Figure 6). 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, Table 1). Of these, SWPP currently has monitoring sites within seven 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, contributing land use, perennial flow, other monitoring agency representation, historical monitoring results, and budgetary constraints direct site selection in the remaining HUCs. Sampling sites in waterway sites are located near the base of their respective watersheds (i.e., the downstream portion of the watersheds), with a few notable exceptions (e.g., Bouquet Canyon Creek).

4.1.1 Los Angeles County

Ballona Creek (BAL), Bouquet Canyon Creek (BOQ), Los Angeles River (LAR1, LAR3, and LAR4), and San Gabriel River (SGR), are the watersheds of interest in Los Angeles County (Figure 1). All sites are located within concrete-lined sections of the waterway. These sites are located at large watersheds with mixed residential and commercial land-use. Site BAL is in the Santa Monica Bay HUC8 and drains mostly from residential land-uses with single- and multi-family homes. Site BOQ consists of predominantly single-family homes with a small amount of commercial land-use. Although not in a HUC8 prioritized by the SWMP Model, BOQ has historically high pesticide detections.

The BOQ site is not located at the base of the watersheds, but below the confluence of Bouquet Canyon Creek and Dry Canyon, a tributary of BOQ. In the Los Angeles River HUC8, LAR1 drains from residential land-uses, but has a higher percentage of commercial and industrial land-uses than BAL or BOQ. Two storm drain sites along the LA River (LAR3 and LAR4) are included to determine relative contributions from commercial-dominated land-use sites. These sites drain from downtown Los Angeles. In contrast, SGR consists primarily of wastewater effluent during low flows.

4.1.2 Orange County

Ambient water quality monitoring will be conducted at six sampling sites within Salt Creek (SC, Figure 2), three site within Wood Creek Canyon (WC, Figure 3), one site in the Anaheim-Barber City Channel (ABCC), one site along Peters Canyon Channel (PCC, Figure 4) and one site in the Santa Ana River (SAR) in Orange County.

Sampling sites within Salt Creek (SC1, SC2, SC3, SC4, SC5, and SC7) have been monitored consistently since 2009 as part of DPR's urban monitoring program. The surrounding drainage areas within the Salt Creek watershed consist of single-or multiple-family residential units, light commercial buildings, parks, schools, and two golf courses. Sites SC1–SC4 are located directly below storm drains that receive runoff from residential neighborhoods. Sampling sites SC5 and SC7 are located at the waterways of urban inputs and will allow evaluation of pesticide concentrations in the watershed as well as downstream transport of pesticides. Geographically, SC5 is located upstream of SC7, which is located at the base of the Salt Creek watershed. All SC sites are located in the Aliso-San Onofre HUC8. Sediment pyrethroid sampling at SC3 and SC5 will continue during the dry season.

Monitoring sites 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. Two sites are situated at the inlet (WC1) and outlet (WC2) of a small constructed wetland (~0.18 acres) 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. Sediment sampling will continue at WC1. Site WC3 receives runoff from a small residential neighborhood to the north of the wetland. A carbon sock will be deployed at the outfall of WC3 during dry season conditions. Effectiveness of this treatment technology will be measured by comparing pre- and post- carbon sock pesticide concentrations.

Sampling along the ABCC is a concrete-lined watershed draining mixed residential, commercial, and industrial areas. The watersheds are located within the Seal Beach HUC8, the highest priority HUC8 in Southern California based on estimated urban pesticide use within the delineated HUC.

Peters Canyon Channel within the Newport Bay HUC, just upstream of the confluence of Peters Canyon Channel and San Diego Creek, explores the relative contributions from commercial-dominated land-use sites. This site is situated upstream of a site monitored by the State Water Resources Control Board's Stream Pollution Trends (SPoT) Monitoring Program (San Diego Creek at Alton Parkway) and has historic detections of pyrethroids in sediment (SWAMP, 2017).

The SAR site is a concrete-lined river draining mixed residential, and commercial area. The site is located within high priority HUC8 in Southern California (Appendix 1). This is an exploratory site with no previous DPR monitoring data.

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 3). San Diego River is not channelized or concrete-lined, which may account for historically lower pesticide concentrations (Budd, 2018). Both sites are located within high priority HUC8s in Southern California (Appendix 1).

4.1.4 Collaborative Monitoring

DPR has been engaged in a collaborative effort with the State Water Resources Control Board through its SPoT 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 DPR, 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 sites for sediments, including BAL, BOQ, LAR1, and SGR. DPR 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 is utilized to prioritize pesticides for monitoring. From the generated list, pesticides needing analytical method development can be identified. Luo, et al. (2013) describes the SWMP Model in detail, but briefly, the model is based on the mass of pesticide use reported by professional applicators and aquatic toxicity threshold values. Use data from Los Angeles, Orange, and San Diego counties and aquatic life benchmarks set by the U.S. EPA are considered. The AI of use score × toxicity score yields a final score that represents a relative prioritization of pesticides (Appendix 6). Additionally, 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 method development. Pesticides with lower scores have either low use in urban environments or low associated aquatic toxicity. All pesticides in the liquid chromatography (LC) multi-analyte screen and the pyrethroid (PY) screen will be analyzed for at each sampling site. The dinitroaniline screen (DN) and phenoxy screen (PX) will be analyzed for at selected sampling sites (Appendix 4, Table 2). These screens represent pesticides that historically have had lower detection frequencies in previous monitoring efforts (e.g., the dinitroanilines) or pesticides that have not previously exceeded benchmarks (e.g., synthetic auxin herbicides). In addition, the neonicotinoid (NN) and glyphosate (GL) screens will be added this WY for analysis at selected sampling sites (Appendix 4, Table 2). All chemical suites cannot be analyzed at every monitoring site due to budgetary and space constraints. In addition to the analytes included in the present analytical suites, the SWMP model identified seven analytes in need of method development: dichlorvos (DDVP), dithiopyr, imazapyr, pentachloronitrobenzene (PCNB), prallethrin, and sulfometuron-methyl.

4.3 Water Sampling

Whole water samples will be collected during two dry-season and two storm events (Deng and Ensminger, 2021). Dry-season sampling will occur in June and August 2024. DPR will attempt to collect storm samples during the first major storm (rain) event of WY 23–24 and during a second major storm in the winter or early spring of 2024 (Appendix 1, Table 2).

Dry-season water samples will be collected as grab samples directly into 1-L amber bottles (Deng and Ensminger, 2021). 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 sites within Salt Creek or Wood Creek watersheds may be collected. 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 SDR1, 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. Duplicate samples will be collected at two sites during the first storm and both dry season events. These duplicate samples will be filtered through a glass fiber prior to submission for pyrethroid analysis and toxicity testing on *H. azteca*. Field matrix spike and field matrix spike duplicates will be collected during each sampling event for quality assurance.

4.4 Sediment Sampling

Sediment samples will be collected at three sites (Appendix 1, Table 2). Enough sediment will be collected to fill ½ pint (237 mL) Mason jars using stainless-steel scoops from the top of the bed layer, biasing for fine sediments where possible (Deng and Ensminger, 2021). All sediments will be passed through a 2-mm sieve to remove plant debris and then homogenized (Deng and Ensminger, 2021). Samples will be analyzed for pyrethroids.

4.5 Toxicity Testing

Water samples will be collected at a subset of sampling sites for toxicity analysis (Appendix 1, 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 water flea *Ceriodaphnia dubia* in water over 96-hours (Appendix 1, Table 3). Several sites described in this protocol also serve as SPoT monitoring sites for sediment toxicity testing, including BAL, BOQ, LAR1, SGR, and SC5. Other sites, such as LAR3, LAR4, SC3, SDR1, DC, and ABCC will be considered for toxicity sampling. Data will be shared between monitoring programs.

4.6 Field Measurements

Physical-chemical properties of the water column will be determined using a YSI-EXO 1 Multi-parameter Sonde or Aqua TROLL® 400 Multiparameter Probe according to the methods describe by Doo and He (2008) and In-Situ (2019). 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 the float method, or fill-bucket method. Continuous flow rates will be obtained at SC2, SC3, and WC3 using an installed Hach Sigma 950 flow meter (Sisneroz et al., 2012; Oki and Haver, 2009).

4.7 Sample Transport

DPR staff will transport samples following the procedures outlined in DPR 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

DPR 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) (Goh, 2011; Ensminger, 2013a). The system will be upgraded to a Vario TOC Cube TOC/TNb Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany), where TOC and DOC analyses will continue once operational, based on previously outlined methods (Goh, 2011; Ensminger, 2013a). 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 320 FY 22-23

This sampling plan is a continuation of Study 320 FY 2022-2023. This sampling and analysis schedule is similar to that of Study 320 WY 2022-2023 with modifications (Table 4).

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). The CDFA laboratory will analyze six analytical suites (Appendix 4, Table 1). Laboratory QA/QC will follow DPR 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 (Budd et al., 2020) indicated that the monitoring 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 (NADA Package for R).

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 sites (e.g., Salt Creek, Wood Creek) with different site types (i.e., storm drain outfalls and waterways), and between different seasons (i.e., dry and wet seasons) (Appendix 1, 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 sites. 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 over time, or the Kaplan-Meier method, which tests the effects of year, month, and site by developing a mixed linear model between the censored concentration and spatial-temporal factors.

7. Timeline

Field Sampling: Oct 2023 – Sept 2024

Chemical Analysis: Oct 2023 – Dec 2024

Report to Management: Jan 2025 – Mar 2025

Data Entry into SURF: Mar 2025 – Jun 2025

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Tables:

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

County	Watershed	Storm drain Outfall	Waterways/ Mitigation Outfall	Total Sites
Los Angeles	Ballona Creek	-	1	1
Los Angeles	Bouquet Creek	-	1	1
Los Angeles	Los Angeles River	2	1	3
Los Angeles	San Gabriel River	-	1	1
Orange	Anaheim-Barber City Channel	-	1	1
Orange	Salt Creek	4	2	6
Orange	Wood Creek	2	1	3
Orange	Peters Canyon Channel	1	-	1
Orange	Santa Ana River	-	1	1
San Diego	San Diego River	1	1	2
San Diego	Chollas Creek	-	1	1
	Total	10	11	21

Table 2. Ambient surface water and mitigation sampling schedule. Subject to change. Samples with asterisks (*) are collected by our sampling partners.

Site	First Storm	Second Storm	First Dry	Second Dry
BOQ	BU, TSS, LC, PY, PX, DN, NN, GL TOX	BU, TSS, LC, PY, PX, DN, NN, GL, TOX	BU, TSS, LC, PY, PX, GL, TOX	BU, TSS, LC, PY, PX, DN, NN, GL TOX
LAR1	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY	BU, TSS, LC, PY	BU, TSS, LC, PY, TOX
LAR3			BU, TSS, LC, PY	BU, TSS, LC, PY
LAR4			BU, TSS, LC, PY	BU, TSS, LC, PY
BAL	BU, TSS, LC, PY	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY
SGR	BU, TSS, LC, PY, PX, DN, NN, GL TOX	BU, TSS, LC, PY, PX, DN, NN, GL TOX	BU, TSS, LC, PY, PX, GL, TOX	BU, TSS, LC, PY, PX, DN, NN, GL TOX
ABCC	BU, TSS, LC, PY			BU, TSS, LC, PY
PCC		BU, TSS, LC, PY	BU, TSS, LC, PY	
SC1	BU, TSS, LC, PY	BU, TSS, LC, PY		
SC2	BU, TSS, LC, PY	BU, TSS, LC, PY	BU, TSS, LC, PY	BU, TSS, LC, PY
SC3	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX, PY-SED
SC4	BU, TSS, LC, PY, PX, DN, NN, GL	BU, TSS, LC, PY, PX, DN, NN, GL	BU, TSS, LC, PY, PX, GL	BU, TSS, LC, PY, PX, DN, NN, GL
SC5	BU, TSS, LC, PY	BU, TSS, LC, PY, TOX		
SC7	BU, TSS, LC, PY, TOX		BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX, PY-SED
SAR		BU, TSS, LC, PY		BU, TSS, LC, PY
WC1	BU, TSS, LC, PY	BU, TSS, LC, PY, PX, DN, NN, GL	BU, TSS, LC, PY	BU, TSS, LC, PY, PY-SED
WC2	BU, TSS, LC, PY			BU, TSS, LC, PY
WC3	BU, TSS, LC, PY TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY	BU, TSS, LC, PY
SDR1			BU, TSS, LC, PY	
SDR4*	BU, TSS, LC, PY		BU, TSS, LC, PY	
CHO*	BU, TSS, LC, PY			
SC3_BMP			BU, TSS, LC, PY	BU, TSS, LC, PY
WC3_BMP			BU, TSS, LC, PY	BU, TSS, LC, PY
Filt #1	BU, PY, TOX	BU, PY, TOX	BU, PY, TOX	BU, PY, TOX
Filt #2	BU, PY, TOX	BU, PY, TOX		

FMS	PY	PY	PY	PY
FMSD	PY	PY	PY	PY

BU – Backup, PY- Pyrethroid, LC- Liquid Chromatography, TSS-Total Suspended Solids, PX-Phenoxy auxin, DN- Dinitroaniline, NN- Neonicotinoids, GL- Glyphosate, SED-Sediment, TOX-Toxicity, Filt-Filtered, FMS-Field Metrix Spike, FMSD-Field Matrix Spike Duplicate.

Table 3. Toxicity sampling schedule: sites will be rotated.

Site	Test Species	First Storm	Second Storm	First Dry	Second Dry
LAR1, BOQ, SC3, SC7, ABCC, SDR1, BAL, SGR, LAR4, CHO1	*Hyalella azteca*	8	8	6	6
LAR1, BOQ, SC3, SDR1, BAL, SGR, LAR4	*Ceriodaphnia dubia*	3	3	3	0

Table 4. Modifications from sampling plan for fiscal year 2022-2023

Change from FY 20-21	Justification
Change in sampling schedule from fiscal to water year	Alignment of sampling schedule with annual precipitation patterns
Toxicity testing will be conducted with the water flea.	Toxicity testing will be conducted with the water flea *Ceriodaphnia dubia* instead of the midge Chironomus.
Addition of glyphosate and neonicotinoid analysis	Provides supporting information on presence of high interest pesticide in surface waters. NN and GL screen provides quantifiable concentrations of several insecticides that are not currently available within the LC screen.
Addition of SAR site	SAR site is being added to this sampling plan as an exploratory site with no previous DPR monitoring data. The site is located within Orange County and drains mixed residential and industrial land use areas, identified within a high priority watershed in the SWMP Model.

Table 5. Non-parametric procedures frequently used for comparing paired data, two 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 reporting limit *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 reporting limit *Score tests* for censored data with multiple reporting limits (the *Gehan test* and generalized *Wilcoxon test*)
Three or more samples in one-way layout	*Kruskal-Wallis test* (for unordered alternative) or *Jonckheere-Terpstra test* (for ordered alternative) for censored data with one reporting limits *Generalized Wilcoxon score test* for censored data with multiple reporting limits *Multiple comparison* to detect which group is different
Three or more samples in two-way layout	*Friedman's test* (for unordered alternative) or *Page's test* (for ordered alternative) for censored data with one reporting limits Multiple comparison to detect which group is different

Figures:

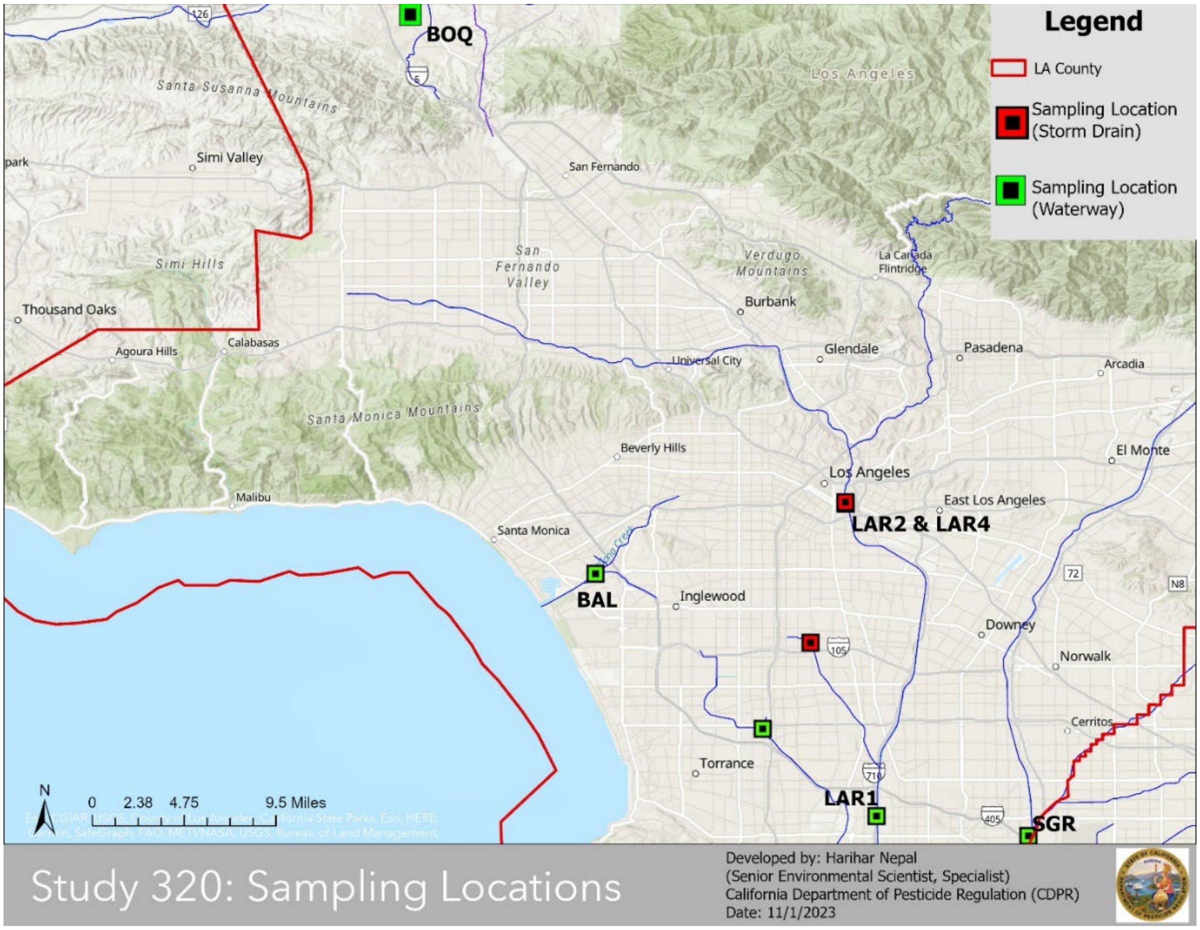

Figure 1. Sampling sites within Los Angeles County, CA.

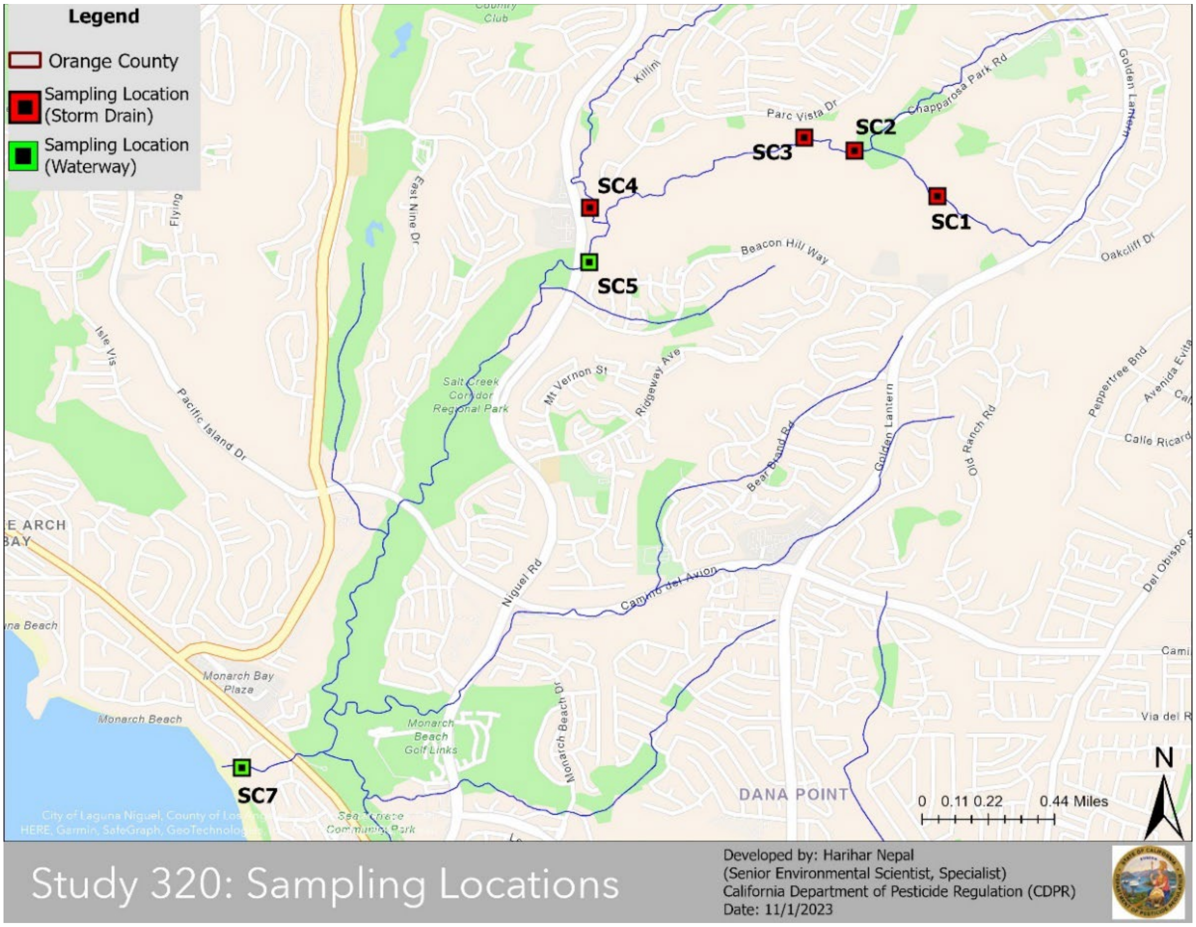

Figure 2. Sampling sites within Salt Creek Watershed, Orange County

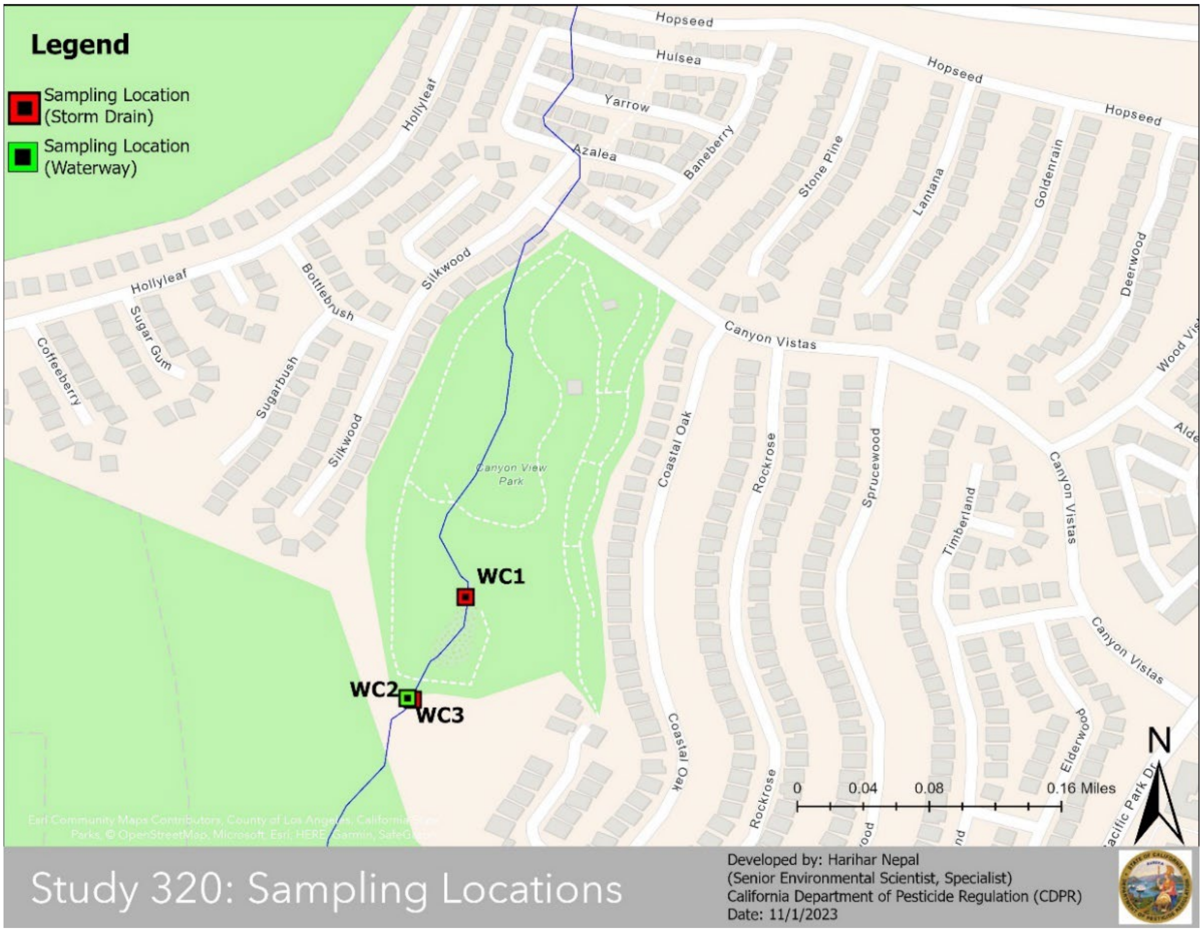

Figure 3. Sampling sites within Wood Creek Watershed, Orange County, CA.

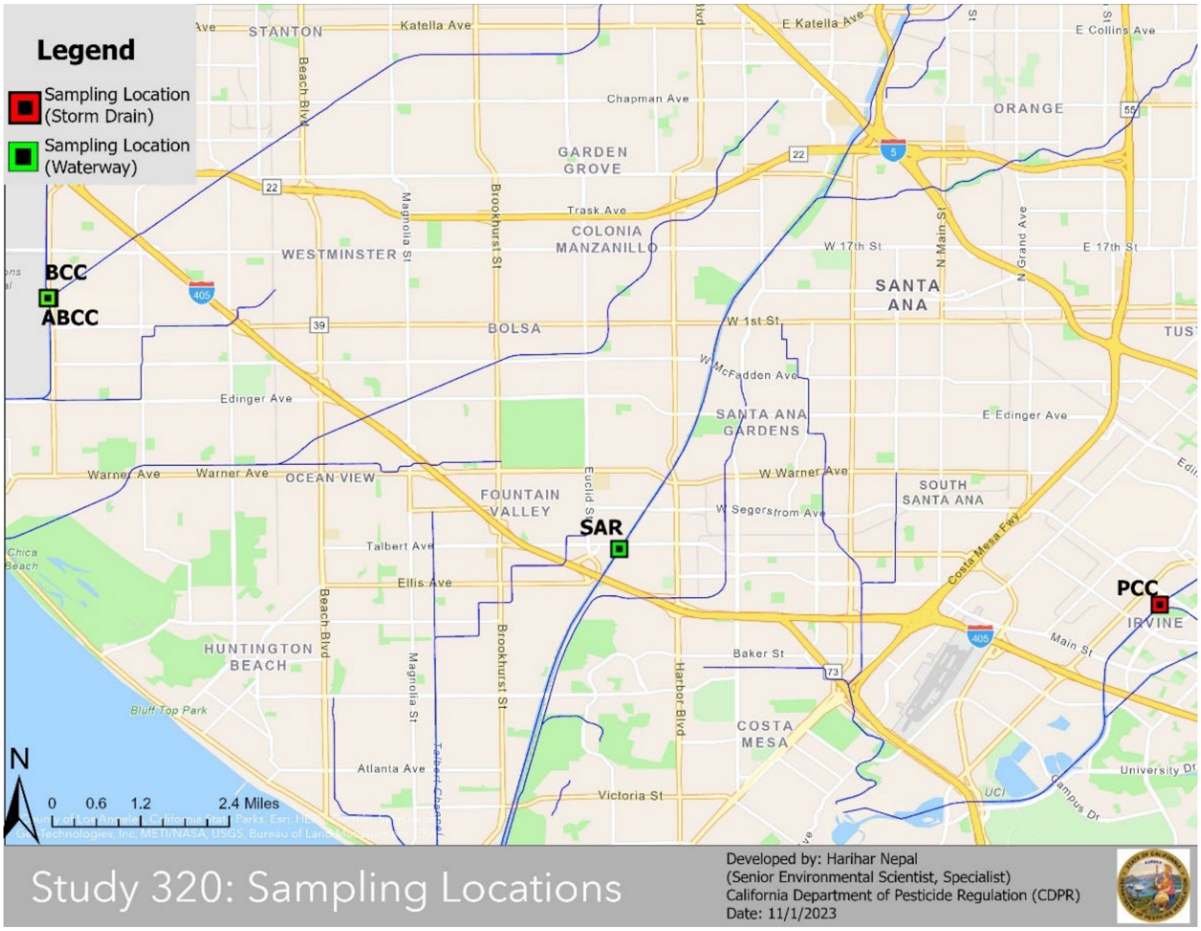

Figure 4. Sampling sites with Anaheim-Barber City Channel, Bolsa-Chica Channel, and Peters Canyon Channel in Orange County, CA.

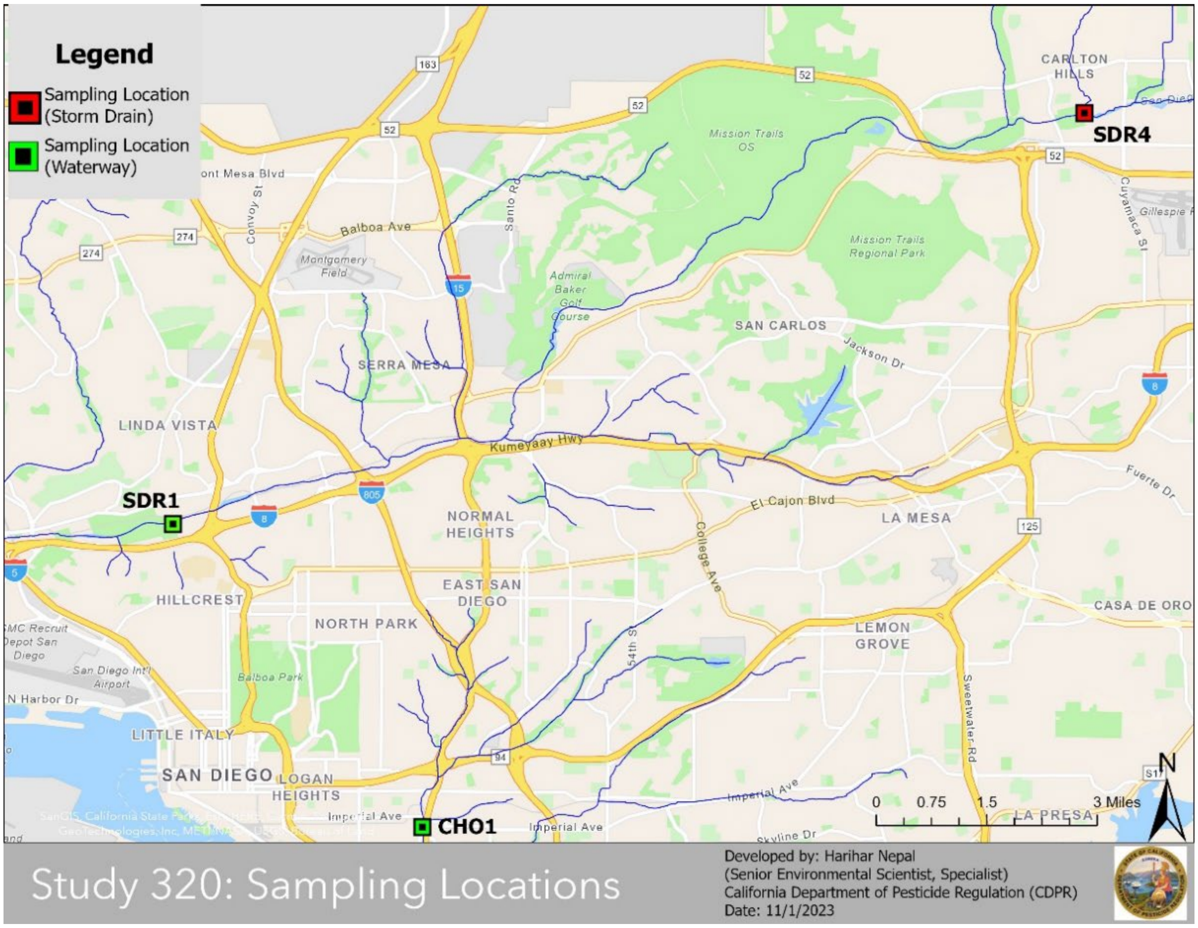

Figure 5. Sampling sites within San Diego County, CA.

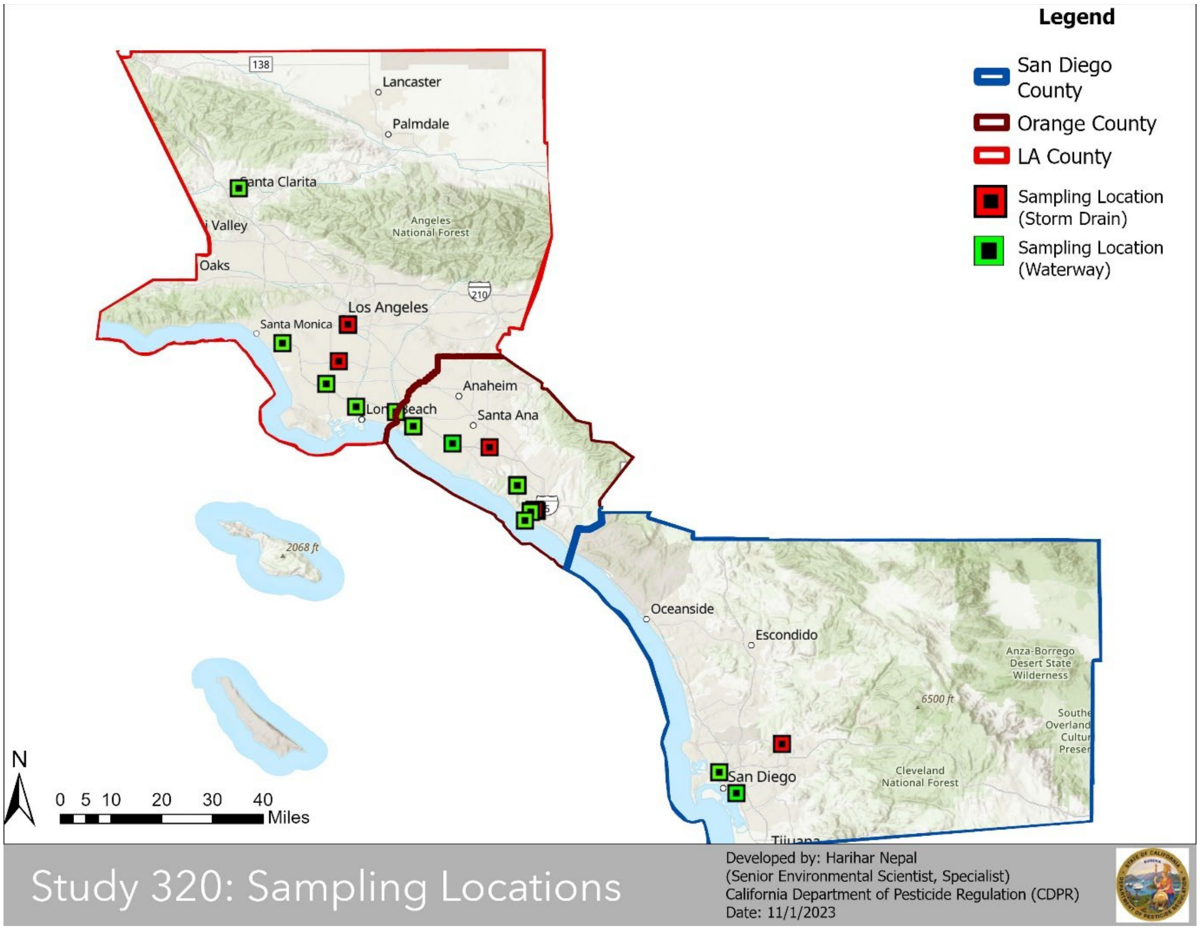

Figure 6. All sampling sites for Study 320 within Los Angeles, Orange, and San Diego Counties.

Appendix 1:

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

HUC8 Code	HUC8 Name	DPR Monitoring Site	Comments
18070201	Seal Beach (Anaheim Bay)	ABCC	
18070105	Los Angeles	LAR1, LAR3, LAR4	
18070204	Newport Bay	PCC	SWAMP location, NPDES permit monitoring at several locations along San Diego Creek*
18070104	Santa Monica Bay	BAL	
18070106	San Gabriel	SGR	
18070203	Santa Ana	SAR	
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	
18070303	San Luis Rey-Escondido		

*Non-DPR monitoring sites evaluated using California Environmental Data Exchange Network (CEDEN) available at: http://www.ceden.org/

Appendix 2:

Table 1. Detailed sampling site information

Watershed	Site ID	Northing	Easting	Site type
Salt Creek	SC1	33.3032.92	-117.4126.53	Storm Drain
Salt Creek	SC2	33.3040.57	-117.4140.67	Storm Drain
Salt Creek	SC3	33.3043.02	-117.4149.55	Storm Drain
Salt Creek	SC4	33.3031.00	-117.4226.34	Storm Drain
Salt Creek	SC5	33.3020.23	-117.4230.87	Waterway
Salt Creek	SC7	33.2853.97	-117.4326.55	Waterway
Ballona Creek	BAL	33.5912.92	-118.2455.90	Waterway
Bouquet Creek	BOQ	34.2542.05	-118.3223.45	Waterway
Los Angeles River	LAR1	33.8058.09	-118.2054.53	Waterway
Los Angeles River	LAR3	34.0385676	118.228332	Storm Drain
Los Angeles River	LAR4	34.0385676	118.228332	Storm Drain
San Gabriel River	SGR	33.7751.08	-118.0974.18	Waterway
Anaheim-Barber City Channel	ABC C	33.750297	-118.042183	Waterway
Peters Canyon Channel	PCC	33.690339	-117.824827	Storm Drain
Santa Ana River	SAR	33.701233°	-117.930629°	Waterway
San Diego River	SDR4	32.8450.37	-116.9912 06	Storm Drain
San Diego River	SDR1	32.4551.79	-117.1012.24	Waterway
Chollas Creek	CHO1	32.704850	-117.121143	Waterway
Wood Creek	WC1	33.3456.56	-117.4443.02	Storm Drain
Wood Creek	WC2	33.5815.83	-117.7457.72	Wetland outfall
Wood Creek	WC3	33.5815.7	-117.7457.27	Storm Drain

Appendix 3*:
Table 1: LC Analytical Suites EMON-SM-05-037

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Abamectin	Botanical, Macrocyclic Lactone	0.004	0.02
Acetamiprid	Neonicotinoid	0.004	0.02
Atrazine	Triazine	0.004	0.02
Azoxystrobin	Strobin	0.004	0.02
Bensulide	Organophosphorus	0.004	0.02
Boscalid	Carboxamide	0.004	0.02
Bromacil	Uracil	0.004	0.02
Carbaryl	Carbamate	0.004	0.02
Chlorantraniliprole	Anthranilic diamide	0.004	0.02
Chlorpyrifos	Organophosphorus	0.004	0.02
Clothianidin	Neonicotinoid	0.004	0.02
Cyprodinil	Anilinopyrimidine	0.004	0.02
Desulfinyl Fipronil	Fiprole	0.004	0.01
Desulfinyl Fipronil Amide	Fiprole	0.004	0.01
Diazinon	Organophosphorus	0.004	0.02
Diflubenzuron	Benzoylurea	0.004	0.02
Dimethoate	Organophosphorus	0.004	0.02
Diuron	Urea	0.004	0.02
Ethoprop	Organophosphorus	0.004	0.02
Etofenprox	Pyrethroid Ether	0.004	0.02
Fenamidone	Imidazole	0.004	0.02
Fenhexamid	Hydroxyanilide	0.005	0.02
Fipronil	Fiprole	0.004	0.01
Fipronil Amide	Fiprole	0.004	0.01
Fipronil Sulfide	Fiprole	0.004	0.01
Fipronil Sulfone	Fiprole	0.004	0.01

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Fludioxonil	Unclassified	0.004	0.02
Hexazinone	Triazinone	0.004	0.02
Imidacloprid	Neonicotinoid	0.004	0.01
Indoxacarb	Oxadiazine	0.004	0.02
Isoxaben	Amide	0.004	0.02
Kresoxim-methyl	Strobin	0.004	0.02
Malathion	Organophosphorus	0.004	0.02
Mefenoxam	Xylylalanine	0.004	0.02
Methidathion	Organophosphorus	0.004	0.02
Methomyl	Carbamate	0.004	0.02
Methoxyfenozide	Diacylhydrazine	0.004	0.02
Metribuzin	Triazinone	0.004	0.02
Norflurazon	Pyridazinone	0.004	0.02
Oryzalin	2,6-Dinitroaniline	0.004	0.02
Oxadiazon	Unclassified	0.004	0.02
Prometon	Triazine	0.004	0.02
Prometryn	Triazine	0.004	0.02
Propanil	Anilide	0.004	0.02
Propargite	Unclassified	0.004	0.02
Propiconazole	Azole	0.004	0.02
Pyraclostrobin	Strobin	0.004	0.02
Pyriproxyfen	Juvenile hormone mimic	0.004	0.015
Quinoxyfen	Quinoline	0.004	0.02
Simazine	Triazine	0.004	0.02
S-Metolachlor	Chloroacetanilide	0.004	0.02
Tebuconazole	Azole	0.004	0.02
Tebufenozide	Diacylhydrazine	0.004	0.02
Tebuthiuron	Urea	0.004	0.02
Thiabendazole	Benzimidazole	0.004	0.02
Thiacloprid	Neonicotinoid	0.004	0.02

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Thiamethoxam	Neonicotinoid	0.004	0.02
Thiobencarb	Thiocarbamate	0.004	0.02
Trifloxystrobin	Strobin	0.004	0.02

Table 2. Dinitroaniline Screen: EMON-SM-05-006

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Oxyfluorfen	Dinitroaniline	0.01	0.05
Pendimethalin	Dinitroaniline	0.012	0.05
Prodiamine	Dinitroaniline	0.012	0.05
Trifluralin	Dinitroaniline	0.014	0.05
Chlorfenapyr	Pyrrole	0.0333	0.10

Table 3. Phenoxy Screen: EMON-SM-05-012

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
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

Table 4. Pyrethroid Screen: EMON-SM-05-022

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Bifenthrin	Pyrethroid	0.00091	0.001
Cyfluthrin	Pyrethroid	0.00146	0.002
Cypermethrin	Pyrethroid	0.00154	0.005
Deltamethrin/Tralomethrin	Pyrethroid	0.00177	0.005
Fenvalerate/Esfenvalerate	Pyrethroid	0.00166	0.005
Lambda-cyhalothrin	Pyrethroid	0.00174	0.002
Permethrin cis	Pyrethroid	0.00105	0.002

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Permethrin trans	Pyrethroid	0.00105	0.005

Table 5. Sediment Pyrethroid Screen: EMON-SM-52-9

Pesticide	Pesticide Class	Method Detection Limit (µg/kg)	Reporting Limit (µg/kg)
Bifenthrin	Pyrethroid	0.108	1
Cyfluthrin	Pyrethroid	0.183	1
Cypermethrin	Pyrethroid	0.107	1
Deltamethrin/Tralomethrin	Pyrethroid	0.0661	1
Fenvalerate/Esfenvalerate	Pyrethroid	0.0661	1
Lambda-cyhalothrin	Pyrethroid	0.115	1
Permethrin cis	Pyrethroid	0.116	1
Permethrin trans	Pyrethroid	0.135	1

Table 6. Neonicotinoids Screen: EMON-SM-05-052

Pesticide	Pesticide Class	Method Detection Limit (µg/kg)	Reporting Limit (µg/kg)
Acetamiprid	Neonicotinoid	0.00213	0.02
Clothianidin	Neonicotinoid	0.00071	0.02
Dinotefuran	Neonicotinoid	0.00074	0.02
Imidacloprid	Neonicotinoid	0.00184	0.01
Sulfoxaflor	Neonicotinoid	0.00137	0.02
Thiacloprid	Neonicotinoid	0.00159	0.02
Thiamethoxam	Neonicotinoid	0.00198	0.02

Table 6. Glyphosate Screen: EM-SM-05-046

Pesticide	Pesticide Class	Method Detection Limit (µg/kg)	Reporting Limit (µg/kg)
Glufosinate-ammonium	Glyphosate	0.01154	0.07
Aminomethyl Phosphonic Acid (AMPA)	Glyphosate	0.02786	0.2
Glyphosate	Glyphosate	0.00495	0.07

*Full analytical methods are available at: [Analytical Method Page on DPR Website]

Appendix 4: Monitoring Prioritization, PREM 4.0 Report Summary**
(Shorted by final score, shown only final score more than 8, Model ran on 9/5/2023; model was run for San Diego, Orange, and Los Angeles County only)

chem_code	CHEMNAME	Use	Use score	Tox score	Final score	recommendation
2300	BIFENTHRIN	15523.5	5	8	40	TRUE
3849	IMIDACLOPRID	17182.8	5	7	35	TRUE
2223	CYFLUTHRIN	7417.3	4	8	32	TRUE
3010	DELTAMETHRIN	5641.9	4	8	32	TRUE
2297	LAMBDA-CYHALOTHRIN	7177.7	4	8	32	TRUE
2008	PERMETHRIN	9433.7	4	7	28	TRUE
677	CHLOROTHALONIL	35413.3	5	5	25	FALSE
2171	CYPERMETHRIN	1936.4	3	8	24	TRUE
2321	ESFENVALERATE	2232.1	3	8	24	TRUE
3995	FIPRONIL	7679.6	4	6	24	TRUE
229	DIQUAT DIBROMIDE	4329.8	4	5	20	FALSE
4019	PYRIPROXYFEN	1155.4	3	6	18	TRUE
211	MANCOZEB	9448.6	4	4	16	FALSE
3938	CHLORFENAPYR	7369.3	4	4	16	TRUE
5964	CHLORANTRANILIPROLE	6887.4	4	4	16	FALSE
1696	THIOPHANATE-METHYL	12352.4	5	3	15	FALSE
105	CARBARYL	1915.4	3	5	15	TRUE
2017	OXADIAZON	1202.8	3	5	15	TRUE
5598	THIAMETHOXAM	1511.9	3	5	15	TRUE
253	CHLORPYRIFOS	121.6	2	7	14	TRUE
187	DDVP	509.4	2	7	14	TRUE
5792	CLOTHIANIDIN	302	2	6	12	TRUE
2308	DITHIOPYR	3299.3	3	4	12	TRUE
3946	GLUFOSINATE-AMMONIUM	10795.9	4	3	12	TRUE
367	MALATHION	502.8	2	6	12	TRUE
1929	PENDIMETHALIN	1152.2	3	4	12	TRUE
2236	PRODIAMINE	4025.5	3	4	12	TRUE
597	TRIFLURALIN	966.2	3	4	12	TRUE
3919	HALOSULFURON-METHYL	137.6	2	6	12	FALSE
5754	NOVALURON	115.7	2	6	12	FALSE
231	DIURON	272.2	2	5	10	TRUE
3898	FLUAZINAM	477.3	2	5	10	FALSE
3985	PRALLETHRIN	487.7	2	5	10	TRUE
5802	FLUMIOXAZIN	295.1	2	5	10	FALSE
2149	SULFOMETURON-METHYL	333.6	2	5	10	TRUE

2093	PHENOTHRIN	149.5	2	5	10	FALSE
5024	DIFENOCONAZOLE	140.2	2	5	10	FALSE
4037	AZOXYSTROBIN	1089.4	3	3	9	TRUE
2257	IMAZAPYR, ISOPROPYLAMINE SALT	2015.8	3	3	9	TRUE
1868	ORYZALIN	3678	3	3	9	TRUE
464	PCNB	943.3	3	3	9	TRUE
2276	PROPICONAZOLE	3131.7	3	3	9	TRUE
3850	TEBUCONAZOLE	3509.1	3	3	9	TRUE
2170	TRICLOPYR, BUTOXYETHYL ESTER	3382.4	3	3	9	TRUE

****: Some AI flagged as "False" recommendations are analyzed as the part of existing analysis suites.**