Department of Pesticide Regulation
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 Water Year 2024-2025

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1. Introduction

Southern California urban areas have considerable pest pressures, which result in high urban pesticide use. According to the Pesticide Use Report (PUR) over 17,250,000 pounds of pesticide of active ingredient were applied for non-agricultural use in 2018 (CDPR, 2021). 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 pesticide use is higher. Los Angeles, Orange, and San Diego counties, accounted for 19.9% of the statewide reported non-agricultural use in 2018. Specifically, 2,295,342 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, which monitors for pesticides in urban areas of Northern California (Ensminger, 2019, Smith, 2020). Study 329 is a continuation of Study 299, DPR's urban monitoring study in Northern California (Ensminger, 2019). 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). SWPP is particularly interested in cases where pesticide concentrations repeatedly reach or exceed USEPA Aquatic Life Benchmarks, which are a type of toxicity threshold 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, Budd, et al., 2020). 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 aquatic life benchmarks 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 (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 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 aquatic life benchmarks. These monitoring activities assist DPR in evaluating the effectiveness of regulations and label changes.

A recent evaluation was conducted of SWPP's urban pyrethroid monitoring data in relation to the implementation of the surface water regulations (Budd, et al., 2020). This study showed decreasing trends in bifenthrin and cypermethrin concentrations in Northern California, complemented by an increase in deltamethrin concentrations. However, there were few observed trends in pyrethroid concentrations in the Southern California region (Budd, et al., 2020). Pyrethroids were still detected at levels that exceeded aquatic life benchmarks in both regions. Continuing monitoring efforts are essential to evaluate the effectiveness of both the surface water regulations and California use restriction labels of fipronil containing products.

This protocol details proposed sampling at DPR monitoring locations receiving urban runoff in southern California for Water Year 2024-2025.

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 waterways 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,* the midge *Chironomus,* and branchiopod water flea *Ceriodaphnia dubia*;
5) Monitor deposition of sediment-bound pyrethroids within selected watersheds;
6) Evaluate sources of pesticide loading through land use comparisons;
7) Evaluate effectiveness of carbon-filled socks to reduce pesticides in urban runoff under field - conditions; and
8) 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 Protection Manager I. Key personnel are listed below:

Project Leader: Robert Budd, Ph.D.
Scientific Advisor: Xin Deng, Ph.D.
Field Coordinator: Rio Lininger
Laboratory Liaison: Josh Alvarado
Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)
Toxicity Tests: University of California at Davis, Aquatic Health Program

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 Robert Budd, Research Scientist III, at (916) 415-2505 or robert.budd@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 9/6/2024). 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) (Monitoring Prioritization, version 4, Report ran on 9/6/2024). Of these, SWPP currently has monitoring sites within eight 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, and budgetary constraints direct site selection in the remaining HUCs. Sampling locations in receiving water 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, Santa Ana River). For WY2024-2025 there are a total of 21 monitoring sites, with approximately half located within receiving waters (Table 1). Detailed sampling site information is provided in Appendix 2.

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 large watersheds with mixed residential and commercial land-uses. BAL is in the Santa Monica Bay HUC8 and drains mostly residential land-uses with single- and multi-family homes. 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. BOQ is not located at the base of the watersheds, but below the confluence of Bouquet Canyon Creek and Dry Canyon, a tributary of BOQ. LAR1, in the Los Angeles River HUC8, drains 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. SGR consists primarily of wastewater effluent during low flow conditions.

4.1.2 Orange County

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

Sampling stations 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-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. 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 will continue during the dry season.

Monitoring locations within WC are located in the Aliso-San Onofre HUC8 and 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 (~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. Sediment sampling will continue at WC1. 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.

PCC within the Newport Bay HUC, just upstream of the confluence of PCC 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. This site was added during the WY 2023-2024 monitoring cycle.

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 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.

4.1.4 Collaborative Monitoring

DPR has been engaged in a collaborative effort with the State Water Resources Control Board through its SPoT (Stream Pollution Trends) 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 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 locations 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 (Monitoring Prioritization, version 4, Report ran on 9/6/2024). 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 current pesticide reported professional use patterns 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 product of use score × toxicity score yields a final score that represents a relative prioritization of pesticides. 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 (Appendix 3). Pesticides with lower scores have either low use in urban environments or low associated aquatic toxicity. At each aqueous sampling site, collected samples will be analyzed for all pesticides in the liquid chromatography (LC) multi-analyte screen and the pyrethroid (PY) screen. Samples collected at select sites will also be analyzed for pesticides in the neonicotinoid (NN), glyphosate (GL), dinitroaniline (DN), and phenoxy screens (PX; 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). All suites cannot be analyzed at every monitoring location due to budgetary and space constraints. The SWMP model also identified six analytes in need of method development: dithiopyr, dichlorvos (DDVP), novaluron, prallethrin, imazapyr, and sulfoteruron-methyl (Appendix 3).

4.3 Water Sampling

Whole water samples will be collected during two dry-season and two storm sampling events using methods described by Deng and Ensminger, 2021. Dry-season sampling will occur in June and August 2025. DPR will attempt to collect storm samples during the first major storm (rain) event of WY 24–25 and during a second major storm in the winter or early spring of 2025 (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 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). 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 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 locations (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 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,* the midge *Chironomus,* or the water flea *Ceriodaphnia dubia* in water over 96-hours. 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 an Aqua TROLL® 400 Multiparameter Probe according to the methods described by 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 and SC3 using an installed Keller AccuLevel pressure transducer and Hach Sigma 950 flow meter, respectively (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 Vario TOC Cube TOC/TNb Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Water samples will also be analyzed for suspended sediment (Ensminger, 2013b). 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 WY 23-24

This sampling plan is continuous of Study 320 WY 2023-2024. This sampling and analysis schedule is similar to that of Study 320 WY 2023-2024 except the following:

1. Toxicity testing will alternate using the midge *Chironomus* and the water flea *Ceriodaphnia dubia* between events.
2. Field matrix spikes will be collected during each sampling event for pyrethroid analysis.
3. Added a study objective to compare observed concentrations against land use data for source identification purposes.

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 six analytical suites (Appendix 4). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, surrogate spikes, and blind spikes (Segawa, 1995). Laboratory blanks and matrix spikes will be included in each extraction set. In addition, one field matrix spike and one field matrix spike duplicate will be collected during each sampling event for pyrethroid analysis.

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) of past monitoring data indicated that the 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 4).

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 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 over 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 spatial-temporal factors.

7. Timeline

Field Sampling: Oct 2024 – Sept 2025

Chemical Analysis: Oct 2024 – Dec 2025

Report to Management: Jan 2026 – Mar 2026

Data Entry into SURF: May 2026 – Jun 2026

8. Literature Cited

Budd, R., O'Geen, A., Goh, K.S., Bondarenko, S., Gan, J. 2009. Efficacy of Constructed Wetlands in Pesticide Removal from Tailwaters in the Central Valley, California. *Environmental Science and Technology,* 43(8): 2925-2930.

Budd, R., Ensminger, M., Kanawi, W., Goh, K. 2012. A Tale of Two Wetlands: Using Constructed Wetlands to Mitigate Pesticides in Urban Runoff. Department of Pesticide Regulation. Poster presented at SETAC North America Meeting.

Budd, R., Deng, X., Ensminger, M., Starner, K., Luo, Y. 2013. Method for prioritizing urban pesticides for monitoring California's urban surface waters. Department of Pesticide Regulation. Analysis memo.

Budd, R. 2022. https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study_320_sampling_plan_2022.pdf . Department of Pesticide Regulation. Study Report.

Budd, R., Wang, D., Ensminger, M., Phillips B. 2020. An evaluation of temporal and spatial trends of pyrethroid concentrations in California surface waters. *Science of the Total Environment*, 718, 137402.

Burant, A. 2019. Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019-2020. Department of Pesticide Regulation, Protocol.

Burant, A. 2020. Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2020-2021. Department of Pesticide Regulation, Protocol.

Burant, A. 2021. Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019-2020. Department of Pesticide Regulation, Study Report.

Cal EPA, 2021. State Water Resources Control Board. The Integrated Report – 303(d) list of water quality limited segments and 305(b) surface water quality assessment - Appendix A.

CDPR. 2011. Department of Pesticide Regulation Standard Agreement No. 10-C0101.

CDPR. 2013. California Code of Regulations. (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations.

CDPR. 2014. Department of Pesticide Regulation's Agricultural and Non-Agricultural Pest Control Use. Bulletin number ENF-003.

CDPR. 2021. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed on July 12, 2021.

Deng, X. and Ensminger, M. 2021. California Department of Pesticide Regulation SOP FSWA017.00: Procedures for Collecting Water and Sediment Samples for Pesticide Analysis. California Department of Pesticide Regulation.

Doo, S. and L-M. He. 2008. California Department of Pesticide Regulation SOP EQWA010.00: Calibration, field measurement, cleaning, and storage of the YSI 6920 V2-2 multiparameter sonde.

Ensminger, M., Budd, R., Kelley, K., and K. Goh. 2013a. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008 – 2011. *Environmental Monitoring and Assessment*, 185 (5): 3697-3710.

Ensminger, M. 2013b. Water TOC analysis using the Shimadzu TOC-VCSN and ASI-V Autosampler.

Ensminger, M. 2021. Pesticide monitoring in urban areas of Northern California (FY2019/2020). Department of Pesticide Regulation. Study Report.

Ensminger. 2020. Study 299: Pesticide Monitoring in Urban Areas of Northern California (FY 2019/2020). Department of Pesticide Regulation, Protocol.

Gan, J., Bondarenko, S., Oki, L., Haver, D. and Li, J.X. 2012. Occurrence of Fipronil and Its Biologically Active Derivatives in Urban Residential Runoff. *Environmental Science and Technology,* 46: 1489-1495.

Goehring, M. 2008. California Department of Pesticide Regulation SOP FSWA014.00: Instructions for the use of the Global FP101 and FP201 flow probe for estimating velocity in wadable streams.

He, Li-Ming. 2008. Study 249 Statewide Urban Pesticide Use and Water Quality Monitoring.

Helsel, D.R., 2012. Statistics for Censored Environmental Data Using Minitab and R (2nd Ed.). John Wiley and Sons. New Jersey.

In-Situ Inc. 2019. Aqua TROLL® 400 Instrument Operator's Manual. https://in-situ.com/pub/media/support/documents/Aqua_TROLL_400_Manual.pdf

Oki, L. and D. Haver. 2009. Monitoring pesticides in runoff in northern and southern California neighborhoods.

Jones, D. 1999. California Department of Pesticide Regulation SOP QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory.

Luo, Y., Deng, X., Budd, R., Starner, K., and M. Ensminger. 2013. Methodology for prioritizing pesticides for surface water monitoring in agricultural and urban areas: Analysis memo.

Luo, Y, M. Ensminger, R. Budd, D. Wang, X. Deng. 2017. Methodology for prioritizing areas of interest for surface water monitoring in urban receiving waters of California.

R Core Team, 2014. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry Laboratory Quality Control.

Sisneroz, J., Q. Xiao, L.R. Oki, B.J. Pitton, D.L. Haver, T. J. Majcherek, R.L. Mazalewski, and M. Ensminger. 2012**.** Automated sampling of storm runoff from residential areas.

SWAMP. 2017. SPoT: Stream Pollution Trends Monitoring Program. Trends in chemical contamination, toxicity and land use in California watersheds.

Weston, D.P., R.L. Holmes, J. You, and M.J. Lydy. 2005. Aquatic toxicity due to residential use of Pyrethroid Insecticides. *Environmental Science and Technology*, 39:9778-9784.

Weston, D.P., R.L. Holmes, and M.J. Lydy. 2009. Residential runoff as a source of Pyrethroid pesticides to urban creeks. *Environmental Pollution*, 157:287-294.

Weston, D.P and M. J. Lydy. 2014. Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environmental Science and Technology* 48:1290-1297.

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

County	Watershed	Storm drain Outfall	Receiving Water/ 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
ABCC	BU, TSS, LC, PY	BU, TSS, LC, PY, NN, TOX		BU, TSS, LC, PY, NN, TOX
BAL	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, DN, NN, GL, TOX		BU, TSS, LC, PY, DN, NN, GL, TOX
BOQ	BU, TSS, LC, PY, PX, NN, GL TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, NN, TOX
CHO*		BU, TSS, LC, PY		
LAR1	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY	BU, TSS, LC, PY, TOX	
LAR3			BU, TSS, LC, PY, TOX	
LAR4			BU, TSS, LC, PY	
PCC	BU, TSS, LC, PY		BU, TSS, LC, PY, TOX	
SAR	BU, TSS, LC, PY, PX, NN, GL, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, DN, NN, GL, TOX
SC1		BU, TSS, LC, PY	BU, TSS, LC, PY	
SC2	BU, TSS, LC, PY	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY
SC3	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY, DN, NN, GL, TOX	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY, TOX, PY-SED
SC4	BU, TSS, LC, PY, PX, GL	BU, TSS, LC, PY	BU, TSS, LC, PY, PX, NN, GL	BU, TSS, LC, PY, TOX
SC5				BU, TSS, LC, PY
SC7	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY, TOX
SDR1				BU, TSS, LC, PY, NN, TOX
SDR4*		BU, TSS, LC, PY		BU, TSS, LC, PY
SGR	BU, TSS, LC, PY, NN, TOX	BU, TSS, LC, PY, DN, NN, GL, TOX	BU, TSS, LC, PY, TOX	BU, TSS, LC, PY, DN, NN, GL TOX
WC1	BU, TSS, LC, PY	BU, TSS, LC, PY, DN, NN, GL, TOX	BU, TSS, LC, PY	BU, TSS, LC, PY, PY-SED
WC2	BU, TSS, LC, PY		BU, TSS, LC, PY	
WC3	BU, TSS, LC, PY, PX, NN, GL, TOX	BU, TSS, LC, PY	BU, TSS, LC, PY, PX, NN, GL, TOX	BU, TSS, LC, PY, TOX
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-, DN- Dinitroaniline, NN- Neonicotinoids, GL- Glyphosate, PX – Phenoxy, 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, SC2, SC3, SC4, SC7, ABCC, SDR1, BAL, SGR, LAR3, WC1, WC2	*Hyalella azteca*	11	11	12	12
LAR1, BOQ, SC3, WC3, SDR1, BAL	*Ceriodaphnia dubia/ Chironomus*	0	0	4	4

Table 4. 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 *Peto Peto 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

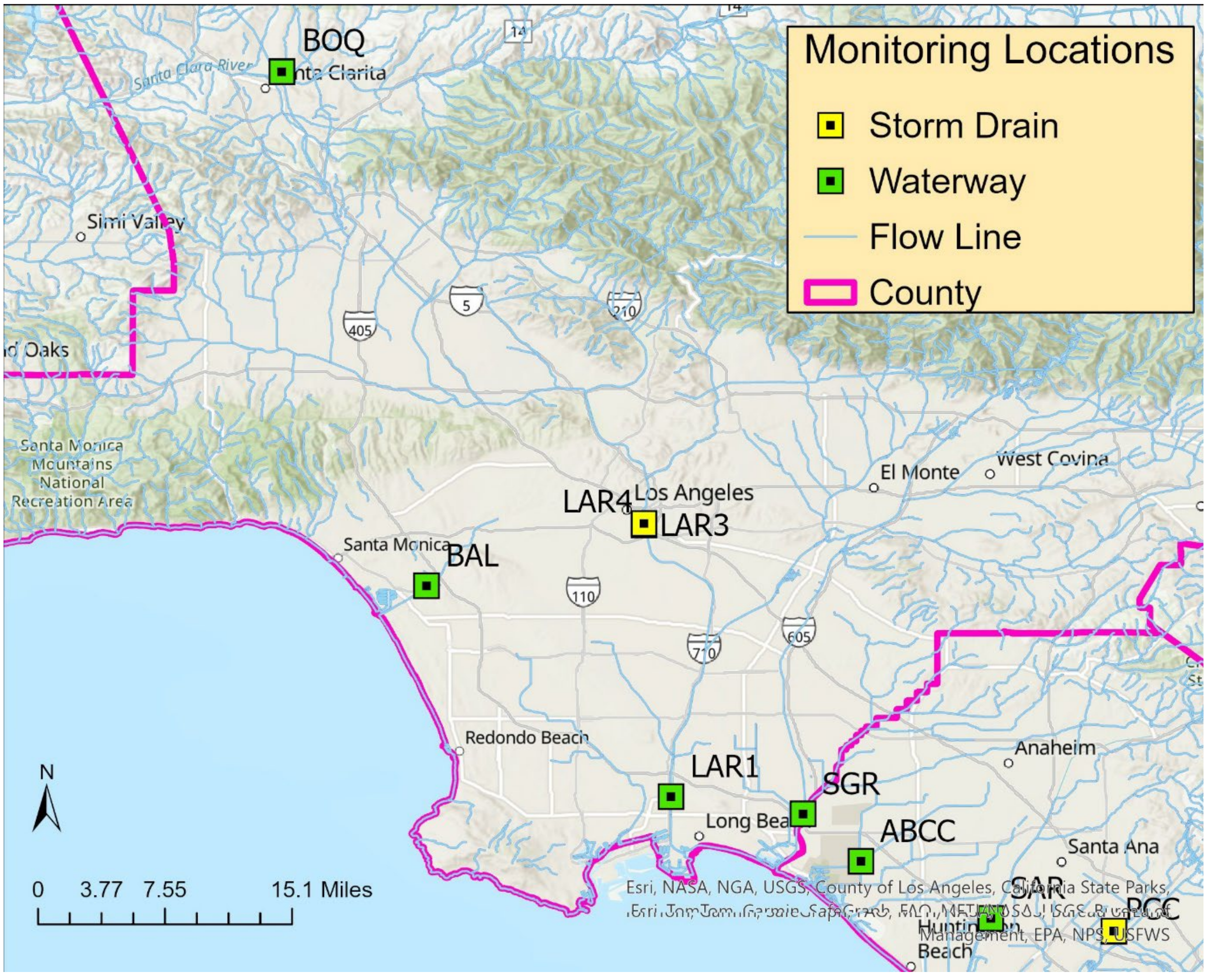

Figure 1. Sampling locations within Los Angeles County, CA.

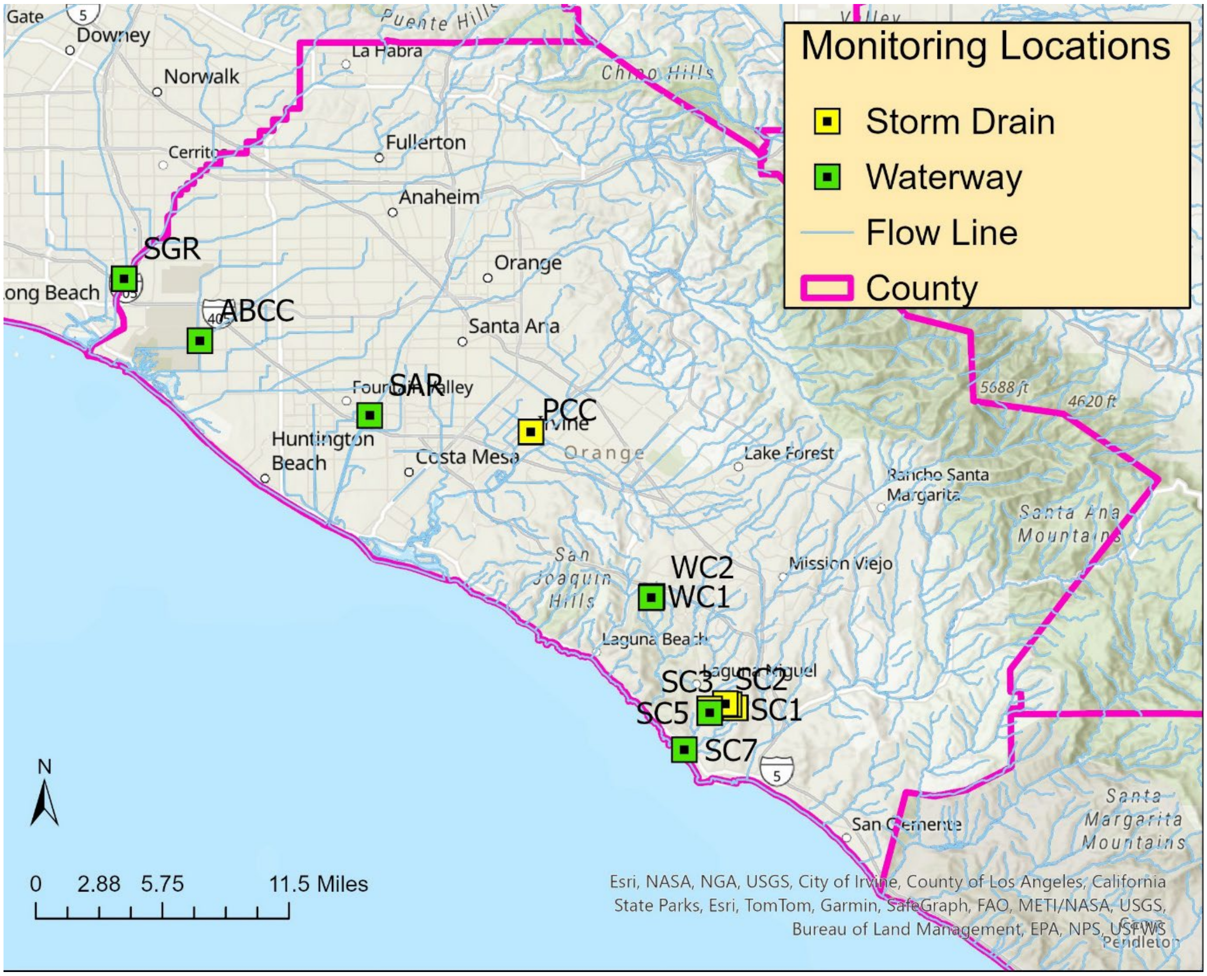

Figure 2. Sampling locations within Salt Creek Watershed, Orange County, CA.

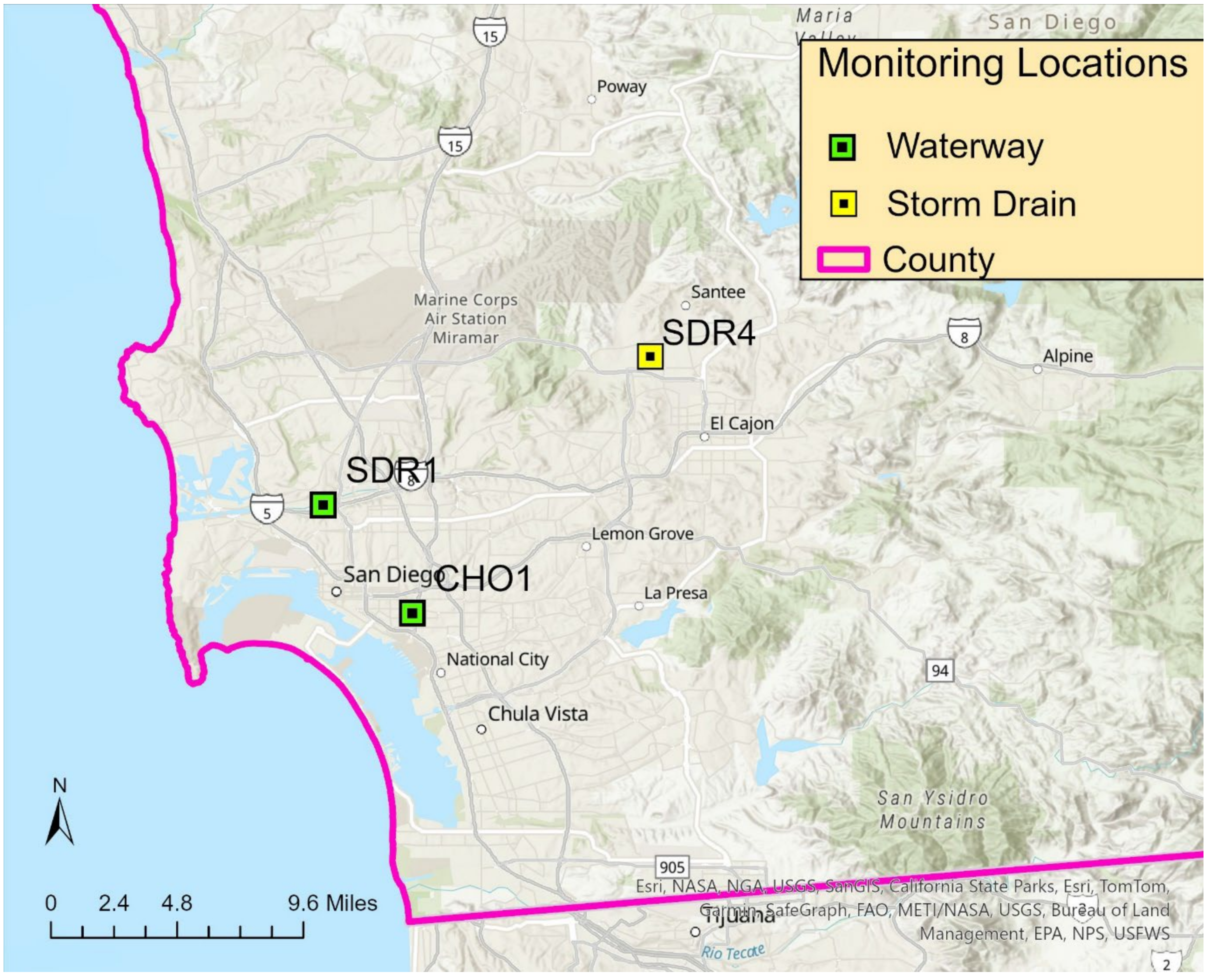

Figure 3. Sampling locations within San Diego County, CA.

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

HUC8 Code	HUC8 Name	CDPR Monitoring Location	Comments
18070201	Seal Beach (Anaheim Bay)	ABCC	
18070105	Los Angeles	LAR1, LAR3, LAR4	
18070204	Newport Bay	PCC	
18070104	Santa Monica Bay	BAL	
18070106	San Gabriel	SGR	
18070203	Santa Ana	SAR	
18070202	San Jacinto		SWAMP monitoring location along Santa Margarita River*
18070304	San Diego	SDR1, SDR4, CHO1	
18070301	Aliso-San Onofre	SC1, SC2, SC3, SC4, SC5, SC7, WC1, WC2, WC3	
18070303	San Luis Rey-Escondido		

*Non-DPR 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	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	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
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	Receiving water
Anaheim-Barber City Channel	ABCC	33.750297	-118.042183	Receiving water
Peters Canyon Channel	PCC	33.690339	-117.824827	Storm drain
Santa Ana River	SAR	33.701233°	-117.930629°	Receiving Water
San Diego River	SDR4	32.8450.37	-116.9912 06	Storm drain
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	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: Monitoring Prioritization, PREM 4.0 Report Summary

(Shorted by final score, shown only final score more than 8, Model ran on 9/27/2024)

Chem Code	CHEMNAME	Use	Use Score	Benchmark	Tox Score	Final Score	Recom
2300	BIFENTHRIN	16158.1	5	5.00E-05	8	40	TRUE
3849	IMIDACLOPRID	18593.1	5	0.01	7	35	TRUE
2008	PERMETHRIN	13386.6	5	3.30E-03	7	35	TRUE
2297	LAMBDA-CYHALOTHRIN	9641.1	4	4.00E-05	8	32	TRUE
3010	DELTAMETHRIN	8401.9	4	2.60E-05	8	32	TRUE
2223	CYFLUTHRIN	6832.6	4	1.20E-04	8	32	TRUE
677	CHLOROTHALONIL	34806.4	5	0.6	5	25	FALSE
3995	FIPRONIL	8455.2	4	0.01	6	24	TRUE
2321	ESFENVALERATE	2445	3	3.09E-05	8	24	TRUE
2171	CYPERMETHRIN	1817.3	3	5.00E-05	8	24	TRUE
229	DIQUAT DIBROMIDE	9756.6	4	0.75	5	20	FALSE
4019	PYRIPROXYFEN	1728	3	0.01	6	18	TRUE
3938	CHLORFENAPYR	9656.4	4	2.91	4	16	TRUE
211	MANCOZEB	8967.5	4	1.35	4	16	FALSE
5964	CHLORANTRANILIPROLE	7776.4	4	3.02	4	16	FALSE
2236	PRODIAMINE	4117.2	4	1.5	4	16	TRUE
3946	GLUFOSINATE-AMMONIUM	13194.8	5	72	3	15	TRUE
105	CARBARYL	1954.6	3	0.5	5	15	TRUE
5598	THIAMETHOXAM	1678.4	3	0.74	5	15	TRUE
2017	OXADIAZON	831.3	3	0.88	5	15	TRUE
187	DDVP	500.3	2	5.80E-03	7	14	TRUE
1696	THIOPHANATE-METHYL	12424.1	4	90	3	12	FALSE
2308	DITHIOPYR	3592.2	3	6.11	4	12	TRUE
1929	PENDIMETHALIN	1191.7	3	5.2	4	12	TRUE
597	TRIFLURALIN	875.9	3	1.9	4	12	TRUE
367	MALATHION	584.4	2	0.04	6	12	TRUE
5792	CLOTHIANIDIN	325.7	2	0.05	6	12	TRUE
5754	NOVALURON	150.4	2	0.03	6	12	TRUE
3919	HALOSULFURON-METHYL	146.3	2	0.04	6	12	FALSE
3898	FLUAZINAM	601.1	2	0.69	5	10	FALSE
3985	PRALLETHRIN	493.8	2	0.65	5	10	TRUE
2149	SULFOMETURON-METHYL	415.3	2	0.45	5	10	TRUE
5802	FLUMIOXAZIN	390.1	2	0.49	5	10	FALSE
231	DIURON	261.8	2	0.13	5	10	TRUE
5024	DIFENOCONAZOLE	175.9	2	0.86	5	10	FALSE
3850	TEBUCONAZOLE	3936.2	3	11	3	9	TRUE
2170	TRICLOPYR, BUTOXYETHYL ESTER	3534.8	3	26	3	9	TRUE
2276	PROPICONAZOLE	3132.6	3	15	3	9	TRUE
1868	ORYZALIN	2326.5	3	13	3	9	TRUE

Chem Code	CHEMNAME	Use	Use Score	Benchmark	Tox Score	Final Score	Recom
2257	IMAZAPYR, ISOPROPYLAMINE SALT	1747.3	3	18	3	9	TRUE
4037	AZOXYSTROBIN	1171.8	3	44	3	9	TRUE
2244	HYDROPRENE	917.1	3	25	3	9	FALSE

Note: Yellow highlighted cells indicate pesticide included in current analytical screen.

Appendix 4: Analytical Methods

Appendix 4.1 Multianalyte Screen 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
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

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

Appendix 4.2 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

Appendix 4.3 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

Appendix 4.4 Pyrethroid Screen: EMON-SM-05-022

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Bifenthrin	Pyrethroid	0.00091	0.001

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

Appendix 4.5 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

Appendix 4.6 Neonicotinoids Screen: EMON-SM-05-052

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Clothianidin	Neonicotinoid	0.00071	0.02
Dinotefuran	Neonicotinoid	0.00074	0.02
Sulfoxaflor	Neonicotinoid	0.00137	0.02

Appendix 4.7 Glyphosate Screen: EMON-SM--050046

Pesticide	Pesticide Class	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
AMPA	Organophosphate	0.02786	0.2
Glufosinate	Organophosphate	0.01154	0.07
Glyphosate	Organophosphate	0.00495	0.07

*Full analytical methods are available at: **Analytical Method Page on CDPR Website**