

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

STUDY 270: Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern
California during Fiscal Year 2018–2019

Robert Budd July 2018

#### 1.0 INTRODUCTION

Urban runoff is an important source of pesticide loading into surrounding waterways, justifying monitoring efforts to characterize pesticide composition in surface waters receiving urban inputs. In California, the Department of Pesticide Regulation (CDPR) receives pesticide use reports for urban applications by licensed applicators. Reported use is categorized into agricultural and non-agricultural use. Agricultural use includes both production and non-production agricultural (i.e., golf courses, rights-of way, parks) applications. Non-agricultural use includes applications for residential, industrial, institutional, structural, or vector control purposes (CDPR, 2014). However, urban pesticide use by individual homeowners is not reported, so total use is greater than reported use. It has been estimated that urban pesticide use accounts for over 70% of the total pesticide use in California (UP3 Project, 2006). Approximately 3,256,145 pounds of pesticides were applied in 2016 for landscape maintenance and structural pest control in Los Angeles, Orange and San Diego counties (CDPR, 2018).

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

breakdown products) insecticides, as well as synthetic auxin herbicides have been detected at high frequency at CDPR monitoring locations in southern California (Ensminger et al., 2013a).

Study 270 is a continuation of monitoring efforts of CDPR Studies 249 and 265. Data from this study will be used to evaluate urban pesticide water quality trends and efficacy of implemented best management practices (BMPs). For example, surface water regulations were implemented in California in July 2012, with the intent of reducing pyrethroid concentrations in California surface waters (CDPR, 2013). Also, new California use restrictions have been placed on products registered for outdoor use containing fipronil. Long-term monitoring will help determine the effectiveness of the regulations and label changes on the presence of pyrethroids and fipronil, respectively, in urban waterways. This project will continue to monitor storm drain outfalls and urban waterways at selected monitoring sites from CDPR's 2008 study as well as at monitoring stations established by the University of California (Oki and Haver, 2009). This long-term monitoring may be used to track the performance of local mitigation measures or public outreach programs. Modifications from the FY 17–18 sampling plan are presented in section 4.9.

# 2.0 OBJECTIVE

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

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

#### 3.0 PERSONNEL

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

Project Leader: Robert Budd, Ph.D. Field Coordinator: KayLynn Newhart

Reviewing Scientist: Michael Ensminger, Ph.D.

Statistician: Dan Wang, Ph.D. Laboratory Liaison: Sue Peoples

Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture

(CDFA)

Collaborator: Darren Haver, Ph.D., University of California at Davis, Center Director/Water Resources and Water Quality Advisor, South Coast Research and Extension Center, 7601 Irvine Blvd., Irvine, CA, 92618, Phone: (949) 653-1814, email: <a href="mailto:dlhaver@ucdavis.edu">dlhaver@ucdavis.edu</a>.

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## 4.0 STUDY PLAN

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

Ambient water quality monitoring will be conducted at six sampling locations within Salt Creek (SC, Figure 1), three locations within Wood Creek Canyon (WC, Figure 2) and Bolsa Chica Channel (BCC, Figure 3) in Orange County. In Los Angeles County, samples will be collected within Ballona (BAL), Bouquet (BOQ), Los Angeles River (LAR), San Gabriel River (SGR), and Dominguez Channel (DC) watersheds (Figure 4). Two stations within the San Diego River watershed as well as one within Chollas Creek will be monitored in San Diego County (Figure 5). Details of site descriptions are provided below (Table 1, Appendix 2).

Sampling stations within Salt Creek 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 several urban inputs and will serve to evaluate pesticide concentrations in the watershed as well as downstream transport of pesticides. Sampling locations within the five watersheds in Los Angeles County and two in San Diego County are located near the base of their respective watersheds. A storm drain outfall location has been added within the San Diego

River watershed to serve as a source identification site. Ballona Creek, Los Angeles River, Dominguez Channel, and San Gabriel River are large watersheds with mixed residential and commercial land use. A sampling location has been added on the Bolsa Chica Channel in Orange County. This watershed is located within the highest priority HUC8 in southern California based on estimated urban pesticide use within the delineated HUC.

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

CDPR has been engaged in a collaborative effort with the 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. The SPOT program 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, including BAL, BOQ, LAR1, SGR, and SC5.

**4.2 Monitoring Candidates**. The SWMP Model was utilized to assist in pesticide selection for ambient monitoring (Budd et al., 2013; Luo et al., 2013). The model is based on current use (2014–2016) patterns and aquatic toxicity benchmark data. The product of the use and toxicity scores produces a final score that represents a relative prioritization of pesticides. In addition, the output also generates a recommendation to monitor or not based on physiochemical properties such as half-life and solubility. The output provides guidance to SWPP staff on pesticides to consider for monitoring. However, the decision to monitor for a pesticide is influenced by additional factors such as previous monitoring data, budgetary constraints, and analytical capabilities. Pesticides that receive a final score of nine or higher are given priority for monitoring. Pesticides with lower scores have either low use in urban environments and/or low associated toxicity. Thirty-three pesticides received a final score equal to or greater than nine using use data for Los Angeles, San Diego, and Orange counties, California and acute and chronic aquatic benchmarks (Appendix 3). Twenty-four of these will be monitored under the current sampling plan (Appendix 4). Analytical method development is needed for DDVP, PCNB, prallethrin, dithiopyr, tebuconazole, chlorsulfuron, thiamethoxam, imazapyr, and sulfometuron-methyl. All suites cannot be analyzed at every monitoring location due to budgetary constraints. Four sampling locations (SC3, SC7, BOQ and LAR) will serve as representative watersheds for analytical methods containing pesticides with lower detection frequencies (CF, DN) or benchmark exceedances (PX) (Appendix 4).

**4.3 Water sampling.** Whole water samples will be collected for both ambient and mitigation monitoring during two dry season and two storm sampling events. Dry season sampling will occur between August–September, 2018 and May–June, 2019. CDPR will attempt to collect storm samples during the first major storm (rain) event of fiscal year 2018–2019 and during a second major storm in the winter or early spring of 2019 (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 secondary stainless steel container will be used to initially collect the water samples. Water samples collected during storm events at SC1, SC2, SC3, SC4, WC1, and WC2 may be collected as composite samples utilizing automated sampling equipment set up by UC Cooperative Extension (CDPR, 2011; Sisneroz et al., 2012). Flow-weighted storm runoff will be collected at BAL and LAR1 by the Los Angeles County Public Works Department. Storm runoff 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 or field blanks will be collected during each sampling event for quality assurance.

- **4.4 Sediment sampling.** Sediment samples will be collected at a subset of locations and sampling events (Table 2). Where applicable, sediment samples will be collected in 1-quart glass Mason Jars using passive sediment-collection samplers (Budd, 2009) and analyzed for pyrethroids. Otherwise, enough sediment will be collected using stainless steel scoops from the top of the bed layer, biasing for fine sediments where possible. All sediments will be passed through a 2-mm sieve to remove plant debris and then homogenized.
- **4.5 Toxicity sampling.** Water samples will be collected at a subset of sampling sites for toxicity analysis (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* in water (96-hr).
- **4.6 Field Measurements.** Physico-chemical properties of water column will be determined using a YSI-EXO 1 multi-parameter Sonde (<a href="https://www.ysi.com/productsdetail.php?EXO1-Water-Quality-Sonde-89">https://www.ysi.com/productsdetail.php?EXO1-Water-Quality-Sonde-89</a>) according to the methods describe by Doo and He (2008). At each site, water parameters measured *in situ* will include pH, temperature, conductivity, salinity, total dissolved solids, and dissolved oxygen. Stormdrain discharge or stream flow rates will be measured to characterize the flow regime and to estimate the total loading of target pesticides. Discrete time flow estimations will be determined using either a Global portable velocity flow probe (Goehring, 2008), utilizing a float, or fill-bucket method. Continuous flow rates will be obtained at SC2, SC3, and WC2 using an installed Hach Sigma 950 flow meter (Sisneroz et al., 2012; Oki and Haver, 2009).
- **4.7 Sample transport.** CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample.

- **4.8 Organic carbon and suspended sediment analysis.** CDPR staff will analyze water and sediment samples for total organic carbon (TOC) and dissolved organic carbon (DOC) using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger, 2013b). Water samples will also be analyzed for suspended sediment (Ensminger, 2013c). Lab blanks and calibration standards will be run before every sample set to ensure the quality of the data.
- **4.9 Modifications from FY 17–18.** The current sampling plan is an extension of sampling conducted during fiscal years 2010–2018. Details of the previous year's sampling protocol are described in the document titled Study 270: Urban pesticide monitoring in southern California, available at: <a href="https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study\_270\_2017-2018.pdf">https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study\_270\_2017-2018.pdf</a>. The sampling and analysis schedule is similar to that for FY 17–18, with a few notable modifications (Table 4).

## 5.0 CHEMICAL ANALYSIS

Water and sediment samples will be sent to the Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) for pesticide analysis. CDFA will analyze five different analyte groups, which will include up to 41 chemical compounds for analysis (Appendix 4). Sediment samples will be analyzed for pyrethroid pesticides (Appendix 4). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995). Laboratory blanks and matrix spikes will be included in each extraction set.

# 6.0 DATA ANALYSIS

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

Our preliminary analysis (Ensminger and Budd, 2014) indicated that the sample data are heavily 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). In order to appropriately address the characteristics of the sample data, a more generic and distribution-free approach, such as non-parametric statistics, will be used in this study. Helsel (2012) illustrated the application of non-parametric procedures to skewed and censored environmental data. We will primarily reference Helsel (2012) as a general guideline for data analysis of this study. The data will be analyzed by using the R statistical program (R Core Team, 2014), specifically the Nondetects 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 (i.e., Appendix 4) at multiple locations (i.e., Salt Creek, Wood Creek) with different site types (i.e., stormdrain outfalls and receiving water), and between different seasons (i.e., dry and wet seasons)(Tables 1 and 2). Plots, such as boxplots, histograms, probability plots, and empirical distribution functions, will be produced to explore any potential patterns implied by the data.
- 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 season, 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 RL.
- 3) Trend analysis will be included to depict the change in concentration over time. We are specifically interested in determining the effectiveness of CDPR regulations (i.e., CCR 6970) which went into effect July 19, 2012 to mitigate pyrethroid contamination in urban waters. Ambient surface water monitoring data from Salt Creek monitoring locations, as well as WC1 in Wood Creek will be used. For the trend analysis, we will use Akritas-Thenil-Sen non-parametric regression, which regresses the censored concentration on time, or the Kaplan-Meier method, which tests the effects of year, month and location by developing a mixed linear model between the censored concentration and the spatial-temporal factors.

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

#### 7.0 TIMELINE

Field Sampling: Jul 2018 – Jun 2019 Chemical Analysis: Jul 2018 – Oct 2019 Report to Management: Jan 2020 – Mar 2020 Data Entry into SURF: Mar 2020 – Jun 2020

# **8.0 LABORATORY BUDGET**

The estimated total cost for chemical analyses for water and sediment samples is \$168,590. (Table 2).

# 9.0 LITERATURE CITED

Bennett, K. 1997. California Department of Pesticide Regulation SOP FSWA002.00: Conducting surface water monitoring for pesticides. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa002.pdf">http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa002.pdf</a>.

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

http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis\_memos/budd\_et\_al\_2013.pdf.

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.

Cal/EPA. 2015. Central Valley Regional Water Quality Control Board. The Integrated Report – 303(d) list of water quality limited segments and 305(b) surface water quality assessment. Available at:

http://www.waterboards.ca.gov/water\_issues/programs/tmdl/integrated2012.shtml

CDPR. 2011. Department of Pesticide Regulation Standard Agreement No. 10-C0101. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts/ucdavis\_10-C0101.pdf">http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts/ucdavis\_10-C0101.pdf</a>.

CDPR. 2013. California Code of Regulations (Title3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Available at: <a href="http://cdpr.ca.gov/docs/legbills/calcode/040501.htm#a690">http://cdpr.ca.gov/docs/legbills/calcode/040501.htm#a690</a>.

CDPR. 2014. Department of Pesticide Regulation's Agricultural and Non-Agricultural Pest Control Use. Bulletin number ENF-003. Available at: http://www.cdpr.ca.gov/docs/enforce/bulletins/ag nonag.pdf.

CDPR. 2018. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed on August 7, 2018. Available at: <a href="http://www.cdpr.ca.gov/docs/pur/purmain.htm">http://www.cdpr.ca.gov/docs/pur/purmain.htm</a>

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. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/sops/eqwa010.pdf.

Ensminger, M. and R. Budd. 2014. *Pyrethroid detections in urban surface waters post regulations*. Available at:

http://cdpr.ca.gov/docs/emon/surfwtr/presentations/ensminger\_2014\_jan\_13\_pyrethro id trends.pdf.

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. Analysis of whole sample suspended sediments in water. Available at: http://cdpr.ca.gov/docs/emon/pubs/sops/meth010.01.pdf.

Ensminger, M. 2013c. Water TOC analysis using the Shimadzu TOC-VCSN and ASI-V autosampler. Available at: <a href="http://cdpr.ca.gov/docs/emon/pubs/sops/meth01100.pdf">http://cdpr.ca.gov/docs/emon/pubs/sops/meth01100.pdf</a>.

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. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa01401.pdf.

He, Li-Ming. 2008. Department of Pesticide Regulation Environmental Monitoring Protocol. Study 249 Statewide Urban Pesticide Use and Water Quality Monitoring. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/protocol/study249protocol.pdf">http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/protocol/study249protocol.pdf</a>

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

Oki, L. and D. Haver. 2009. Monitoring pesticides in runoff in northern and southern California neighborhoods. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/oki\_2009.pdf">http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/oki\_2009.pdf</a>.

Jones, D. 1999. California Department of Pesticide Regulation SOP QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc0401.pdf">http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc0401.pdf</a>.

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 May 28, 2013. Analysis memo, available at: <a href="http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis\_memos/prioritization\_rep">http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis\_memos/prioritization\_rep</a> ort.pdf.

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. Available at: <a href="http://www.R-project.org/">http://www.R-project.org/</a>.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry Laboratory Quality Control. Available at: <a href="http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf">http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf</a>.

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. http://cdpr.ca.gov/docs/emon/surfwtr/swposters/auto\_sampling\_residential\_areas.pdf.

SWAMP. 2017. SPoT: Stream Pollution Trends Monitoring Program. Trends in chemical contamination, toxicity and land use in Californial watersheds. Available at: <a href="http://www.waterboards.ca.gov/water\_issues/programs/swamp/spot/">http://www.waterboards.ca.gov/water\_issues/programs/swamp/spot/</a>.

UP3 Project. 2006. Pesticide Sales and Use Information. Pesticides in urban surface water: Urban pesticide use trends report 2007. Available at: http://www.tdcenvironmental.com/UP3%20Use%20Report%202006.pdf.

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           | Stormdrain<br>Outfall | Receiving Water/<br>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           |
| Orange      | Bolsa Chica Channel | -                     | 1                                      | 1           |
| Orange      | Salt Creek          | 4                     | 2                                      | 6           |
| Orange      | Wood Creek          | 2                     | 1                                      | 2           |
| San Diego   | San Diego River     | 1                     | 1                                      | 1           |
| San Diego   | Chollas Creek       | -                     | 1                                      | 1           |
|             | Total               | 7                     | 10                                     | 17          |

**Table 2.** Ambient surface water and mitigation sampling schedule.

| First Second First Second Total Cost/ |                          |     |     |       |       |         |           |          |
|---------------------------------------|--------------------------|-----|-----|-------|-------|---------|-----------|----------|
| Site                                  | Screen                   | Dry | Dry | Storm | Storm | Samples | Sample    | Budget   |
| Water Samples                         |                          |     |     |       |       |         |           |          |
|                                       | CF                       | 4   | 4   | 4     | 4     | 16      | \$540     | \$8,640  |
| CC2 CC7 DAI                           | DN                       | 4   | 4   | 4     | 4     | 16      | \$720     | \$11,520 |
| SC3, SC7, BAL,<br>LAR                 | PX                       | 4   | 4   | 4     | 4     | 16      | \$690     | \$11,040 |
| LAIX                                  | LC                       | 4   | 4   | 4     | 4     | 16      | \$1,700   | \$27,200 |
|                                       | PY6                      | 4   | 4   | 4     | 4     | 16      | \$600     | \$9,600  |
| SC1, SC2, SC4,                        | LC                       | 5   | 5   | 5     | 5     | 20      | \$1,700   | \$34,000 |
| SC5, WC1                              | PY6                      | 5   | 5   | 5     | 5     | 20      | \$600     | \$12,000 |
| BOQ, SDR1,                            | LC                       | 3   | 3   | 3     |       | 9       | \$1,700   | \$15,300 |
| WC2                                   | PY6                      | 3   | 3   | 3     |       | 9       | \$600     | \$5,400  |
| DC, SGR                               | LC                       | 2   | 2   |       |       | 4       | \$1,700   | \$6,800  |
| DC, SGR                               | PY6                      | 2   | 2   |       |       | 4       | \$600     | \$2,400  |
| CHO* CDD4*                            | LC                       |     | 2   | 2     |       | 4       | \$1,700   | \$6,800  |
| CHO*, SDR4*                           | PY6                      |     | 2   | 2     |       | 4       | \$600     | \$2,400  |
| BCC                                   | LC                       | 1   |     |       | 1     |         | \$1,700   | \$3,400  |
| ВСС                                   | PY6                      | 1   |     |       | 1     |         | \$600     | \$1,200  |
| WC3                                   | PY6                      | 1   | 1   | 1     | 1     | 4       | \$600     | \$2,490  |
| QC**                                  | PY                       | 1   | 1   | 1     | 1     | 4       | \$600     | \$2,400  |
| Sediment Samples                      |                          |     |     |       |       |         |           |          |
| SC3, SC5, WC1                         | PY6                      | 3   | 3   | 2     | 2     | 10      | \$600     | \$6,000  |
|                                       | Ambient Monitoring Total |     |     |       |       |         | \$168,590 |          |

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

**Table 3.** Toxicity sampling schedule.

| 2 and ev 10 merty sumpring semeative. |                 |           |            |             |              |  |  |
|---------------------------------------|-----------------|-----------|------------|-------------|--------------|--|--|
| Site                                  | Test Species    | First Dry | Second Dry | First Storm | Second Storm |  |  |
| LAR, BOQ, SC3, SC7, SDR               | Hyalella azteca | 5         | 5          | 5           | -            |  |  |
| LAR, BOQ, SC3                         | Chironomus sp.  | 3         | 3          | 3           | -            |  |  |

<sup>\*</sup>Depending on access and flows may substitute storm event for dry event.
\*\*QA=quality assurance. Screens will rotate by event.

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

| Change from FY 17-18   | Justification   |
|------------------------|---|
| Remove carbaryl screen | Included in LC screen   |
| Adding CHO1            | Highest priority HUC12 identified based on priority Als reported use and toxicity |
| Adding BCC             | Highest priority HUC8 aggregated watershed  |

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

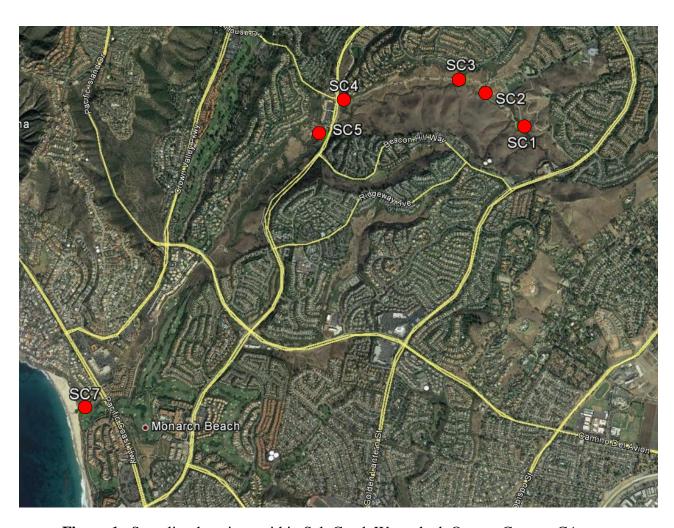


Figure 1. Sampling locations within Salt Creek Watershed, Orange County, CA.

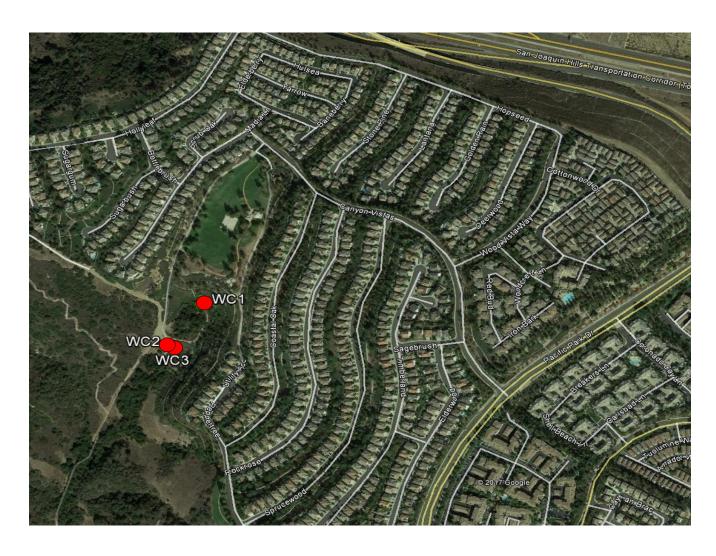


Figure 2. Sampling locations within Wood Creek Watershed, Orange County, CA.

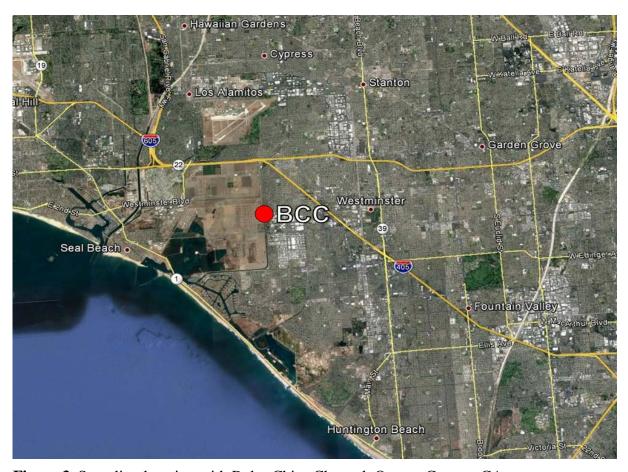


Figure 3. Sampling location with Bolsa Chica Channel, Orange County, CA.

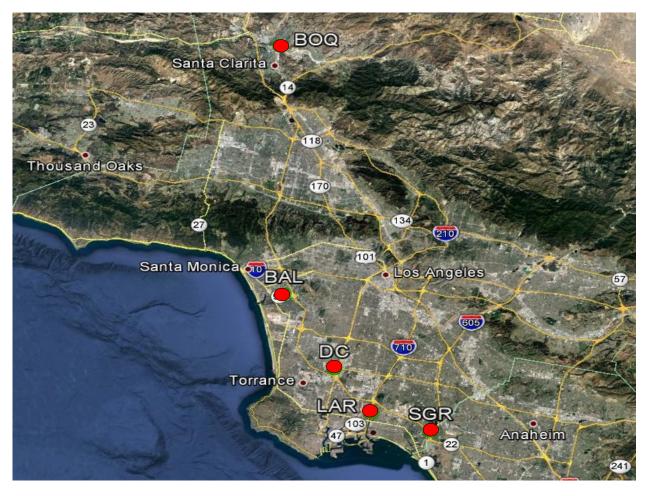


Figure 4. Sampling locations within Los Angeles County, CA.



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

Appendix 1. Top ten HUC8's identified for urban monitoring in southern California, order

by the ranking process.

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

<sup>\*</sup>Non-CDPR monitoring locations evaluated using California Environmental Data Exchange Network (CEDEN) available at: 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 |
| Bolsa Chica Channel | BCC     | 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>9) based on acute and chronic aquatic benchmarks and 2014–2016 urban pesticide usage in Los Angeles, Orange, and San Diego counties, California. All pesticides recommended to monitor based on physiochemical properties. All pesticides are either within current analytical screens or are undergoing method development.

|                               | ı             |              | E E 1           |              |                |
|-------------------------------|---------------|--------------|-----------------|--------------|----------------|
| Pesticide                     | Use (lbs)     | Use<br>Score | Benchmark (ppb) | Tox<br>Score | Final<br>Score |
| Bifenthrin                    | 35,389.4      | 5            | 1.30E-03        | 7            | 35             |
| Imidacloprid                  | 42,683.8      | 5            | 0.01            | 7            | 35             |
| Permethrin                    | 53,806.9      | 5            | 1.40E-03        | 7            | 35             |
| Fipronil                      | 35,675.6      | 5            | 0.01            | 6            | 30             |
| Cyfluthrin                    | 28,305.4      | 4            | 7.40E-03        | 7            | 28             |
| Lambda-cyhalothrin            | 8,664.0       | 4            | 2.00E-03        | 7            | 28             |
| Cypermethrin                  | 4,980.7       | 4            | 0.06            | 6            | 24             |
| Esfenvalerate                 | 10,165.7      | 4            | 0.01            | 6            | 24             |
| Deltamethrin                  | 3,887.7       | 3            | 4.10E-03        | 7            | 21             |
| Malathion                     | 932.9         | 3            | 0.05            | 6            | 18             |
| Pyriproxyfen                  | 3,910.6       | 3            | 0.02            | 6            | 18             |
| Chlorfenapyr                  | 15,961.7      | 4            | 2.91            | 4            | 16             |
| Prodiamine                    | 16,360.6      | 4            | 1.5             | 4            | 16             |
| Bromacil                      | 1,414.7       | 3            | 6.8             | 4            | 12             |
| Chlorpyrifos                  | 224.7         | 2            | 0.04            | 6            | 12             |
| Diuron                        | 1,684.6       | 3            | 2.4             | 4            | 12             |
| Oryzalin                      | 4,655.3       | 4            | 13              | 3            | 12             |
| Oxadiazon                     | 1,227.6       | 3            | 5.2             | 4            | 12             |
| Pendimethalin                 | 1,994.7       | 3            | 5.2             | 4            | 12             |
| Triclopyr, butoxyethyl ester  | 4,862.9       | 4            | 26              | 3            | 12             |
| Carbaryl                      | 354.4         | 2            | 0.5             | 5            | 10             |
| Azoxystrobin                  | 929.3         | 3            | 44              | 3            | 9              |
| Indoxacarb                    | 3,051.2       | 3            | 75              | 3            | 9              |
| Propiconazole                 | 3,752.2       | 3            | 21              | 3            | 9              |
| Pesticides needing analytical | method develo | pment        | 1               |              |                |
| Prallethrin                   | 2,287.1       | 3            | 0.65            | 5            | 15             |
| Sulfometuron-methyl           | 1,277.6       | 3            | 0.45            | 5            | 15             |
| DDVP                          | 660.0         | 2            | 5.80E-03        | 7            | 14             |
| Chlorsulfuron                 | 181.8         | 2            | 0.35            | 5            | 10             |
| Dithiopyr                     | 1,561.8       | 3            | 20              | 3            | 9              |
| Imazapyr, isopropylamine salt | 1,299.1       | 3            | 18              | 3            | 9              |
| PCNB                          | 3,661.7       | 3            | 13              | 3            | 9              |
| Tebuconazole                  | 1,594.1       | 3            | 11              | 3            | 9              |
| Thiamethoxam                  | 907.5         | 3            | 17.5            | 3            | 9              |

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

| Water Sample Analysis  Method Detection Report |                        |                           |                 |                 |  |  |
|--|------------------------|---------------------------|-----------------|-----------------|--|--|
| Screen   | EMON Method<br>Number* | Pesticide                 | Limit<br>(µg/L) | Limit<br>(µg/L) |  |  |
|  |                        | Azoxystrobin              | 0.0012          | 0.02            |  |  |
|  |                        | Bromacil                  | 0.000977        | 0.02            |  |  |
|  |                        | Carbaryl                  | 0.011           | 0.02            |  |  |
|  |                        | Chlorantraniliprole       | 0.00182         | 0.02            |  |  |
|  |                        | Chlorpyrifos              | 0.00123         | 0.02            |  |  |
|  |                        | Desulfinyl fipronil       | 0.0011          | 0.01            |  |  |
|  |                        | Desulfinyl fipronil amide | 0.00244         | 0.01            |  |  |
|  |                        | Diflubenzuron             | 0.000603        | 0.02            |  |  |
|  |                        | Diuron                    | 0.00116         | 0.02            |  |  |
|  |                        | Etofenprox                | 0.00184         | 0.02            |  |  |
|  |                        | Fipronil                  | 0.000864        | 0.01            |  |  |
| 1.0  | EMON-SM-05-037         | Fipronil amide            | 0.00157         | 0.01            |  |  |
| LC   |                        | Fipronil sulfide          | 0.00111         | 0.01            |  |  |
|  |                        | Fipronil sulfone          | 0.000732        | 0.01            |  |  |
|  |                        | Imidacloprid              | 0.00135         | 0.01            |  |  |
|  |                        | Indoxacarb                | 0.00066         | 0.02            |  |  |
|  |                        | Isoxaben                  | 0.0014          | 0.02            |  |  |
|  |                        | Malathion                 | 0.00103         | 0.02            |  |  |
|  |                        | Oryzalin                  | 0.0035          | 0.02            |  |  |
|  |                        | Oxadiazinon               | 0.00071         | 0.02            |  |  |
|  |                        | Propiconazole             | 0.00142         | 0.02            |  |  |
|  |                        | Pyraclostrobin            | 0.000535        | 0.02            |  |  |
|  |                        | Pyriproxyfen              | 0.00114         | 0.015           |  |  |
|  |                        | Simazine                  | 0.000916        | 0.02            |  |  |
| CF   | EMON-SM-05-033         | Chlorfenapyr              | 0.0624          | 0.1             |  |  |
| DN   | EMON-SM-05-006         | Oxyfluorfen               | 0.01            | 0.05            |  |  |
|  |                        | Pendimethalin             | 0.012           | 0.05            |  |  |
|  |                        | Prodiamine                | 0.012           | 0.05            |  |  |
|  |                        | Trifluralin               | 0.014           | 0.05            |  |  |
|  |                        | 2,4-D                     | 0.015           | 0.05            |  |  |
| DV   | EMONI ON OF 040        | Dicamba                   | 0.017           | 0.05            |  |  |
| PX   | EMON-SM-05-012         | MCPA                      | 0.022           | 0.05            |  |  |
|  |                        | Triclopyr                 | 0.02            | 0.05            |  |  |

| Water Sample Analysis |                        |                                  |   |                               |  |  |
|-----------------------|------------------------|----------------------------------|---|-------------------------------|--|--|
| Screen                | EMON Method<br>Number* | Pesticide                        | Method<br>Detection<br>Limit<br>(μg/L)  | Reporting<br>Limit<br>(µg/L)  |  |  |
|                       |                        | Bifenthrin                       | 0.00091                                 | 0.001                         |  |  |
|                       |                        | Cyfluthrin                       | 0.00146                                 | 0.002                         |  |  |
|                       |                        | Cypermethrin                     | 0.00154                                 | 0.005                         |  |  |
| PY                    | EMON-SM-05-022         | Deltamethrin/Tralomethrin        | 0.00177                                 | 0.005                         |  |  |
| FI                    | EIVIOIN-3IVI-03-022    | Fenvalerate/Esfenvalerate        | 0.00166                                 | 0.005                         |  |  |
|                       |                        | Lambda-cyhalothrin               | 0.00174                                 | 0.002                         |  |  |
|                       |                        | Permethrin cis                   | 0.00105                                 | 0.002                         |  |  |
|                       |                        | Permethrin trans                 | 0.00105                                 | 0.005                         |  |  |
|                       | Sec                    | diment Sample Analysis           |   |                               |  |  |
| Screen                | EMON Method<br>Number  | Pesticide                        | Method<br>Detection<br>Limit<br>(µg/kg) | Reporting<br>Limit<br>(µg/kg) |  |  |
|                       |                        | Bifenthrin                       | 0.108                                   | 1                             |  |  |
|                       |                        | Cyfluthrin                       | 0.183                                   | 1                             |  |  |
| PY                    |                        | Cypermethrin                     | 0.107                                   | 1                             |  |  |
|                       | EMON-SM-52-9           | Deltamethrin/Tralomethrin 0.0661 |   | 1                             |  |  |
|                       |                        | Fenvalerate/Esfenvalerate 0.0661 |   | 1                             |  |  |
|                       |                        | Lambda-cyhalothrin 0.115         |   | 1                             |  |  |
|                       |                        | Permethrin cis 0.116             |   | 1                             |  |  |
|                       |                        | Permethrin trans                 | 0.135                                   | 1                             |  |  |

\*Full analytical methods are available at:

http://www.cdpr.ca.gov/docs/emon/pubs/em\_methd\_main.htm?filter=surfwater