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STUDY 270 (2015-16): Ambient and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2015 – 2016

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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, 2010). However, urban pesticide use by individual homeowners is not reported, so that total use is greater than reported use. It has been estimated that urban pesticide use accounts for over 70% of the total pesticide use in California (UP3 Project, 2007). In 2012, over 790,000 pounds of pesticides were used for landscape maintenance and structural pesticide control in Los Angeles, Orange and San Diego Counties (CDPR, 2014a).

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 historical presence of organophosphate (OP) pesticides (Cal/EPA, 2014), partially attributable to their presence in urban runoff. 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, OPs, and fipronil. 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 (CDPR, 2008). Preliminary monitoring data has been previously summarized. Several pyrethroids, imidacloprid, and fipronil (and breakdown products) insecticides, as well as synthetic auxin herbicides have been detected at high frequency at CDPR monitoring locations in southern California (Ensminger et al., 2013).

Study 270 is a continuation of monitoring efforts of 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, 2012). Long term monitoring will help determine the effectiveness of these regulations on the presence of pyrethroids in urban waterways. This project will continue to monitor storm drains 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 14-15 sampling plan is presented in section 4.1.

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 storm water and dry weather runoff under dry and storm conditions;
2) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity thresholds;
3) Evaluate the effectiveness of CDPR's surface water regulations Section 6970 through long term (multiple year) monitoring at selected sampling locations;
4) Observe effects of a small constructed wetland to mitigate pesticide concentrations in urban runoff to surrounding receiving waters;
5) Observe the mitigation effects of a small water treatment facility receiving dry weather runoff flow;
6) Monitor deposition of sediment-bound pyrethroids within the watershed;
7) Determine the toxicity of water samples using toxicity tests conducted with *Hyalella azteca*.

3.0 PERSONNEL

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

Project Leader: Robert Budd, Ph.D.
Field Coordinator: KayLynn Newhart.
Reviewing Scientist: Michael Ensminger, Ph.D.
Statistician: Dan Wang, Ph.D.
Laboratory Liaison: Sue Peoples
Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)
Collaborator: Darren Haver, Ph.D., University of California at Davis, Center Director/Water Resources and Water Quality Advisor, South Coast Research and Extension Center, 7601 Irvine Blvd., Irvine, CA, 92618, Phone: (949) 653-1814, email: dlhaver@ucdavis.edu

Please direct questions regarding this study to Robert Budd, Senior Environmental Scientist, at (916) 445-2505 or rbudd@cdpr.ca.gov.

4.0 STUDY PLAN

4.1 Monitoring Sites

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

Sampling stations within Salt Creek have been monitored consistently since 2009 as part of CDPRs urban monitoring program. The surrounding drainage areas within the Salt Creek watershed consist of single family dwellings, multiple family dwellings, light commercial buildings, parks, schools, and two golf courses. SC5 and SC7are 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. SC7A is located adjacent to SC7. During the dry season water is pumped from an intake at SC7 through a small ozone water treatment facility and returning through an outlet at SC7A. Samples are collected at SC7A during the dry season to determine the effect of the ozone treatment system on pesticide removal from the water column. Sampling locations within the four watersheds in Los Angeles County and two in San Diego County are located near the base of their respective watersheds. Ballona Creek, Los Angeles River and San Gabriel River are large watersheds with mixed residential and commercial land use. Samples collected at all ambient sampling sites will be monitored for fipronil (and breakdown products), imidacloprid, pyrethroid insecticides, and synthetic auxin herbicides. Chlorfenapyr, carbaryl, organophosphate insecticides, dinitroaniline, and photosynthetic inhibitor herbicides will be monitored in a subset of sites (Table 2). Sediment samples will also be collected at a subset of sites for pyrethroid analysis dependent on available sediment deposition.

Monitoring locations within Wood Creek have also been monitored since 2009 as part of SWPPs 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 pesticide concentrations between outlet and inlet. Water samples will be collected during four events, with sediment collected during two dry season events.

Automated sampling and flow measurement equipment has been installed at two sites within Salt Creek and two within Wood Creek by the University of California (Oki and Haver, 2009); we will evaluate these sites for potential long-term monitoring in collaboration with the University of California.

Modifications from FY 14-15. The current sampling plan is an extension of sampling conducted during fiscal years 2010-2015. Details of the previous sampling are described in the document titled Study 270: Urban pesticide monitoring in southern California, available at: http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study270protocol2014_15.pdf. The sampling and analysis schedule is similar to that for FY 14-15, with a few notable modifications (Table 3).

To increase both the spatial representation of southern California waterways and the diversity of land use types within watersheds, monitoring locations were added within Los Angeles and San Gabriel Rivers (Los Angeles County), and Tecolote Canyon Creek (San Diego County) watersheds. These watersheds are generally larger than Salt and Wood Creek watersheds, and have additional inputs from commercial and light industrial areas. Agricultural inputs are limited to non-existent within all watersheds.

Modifications to the chemical analysis list were based on previous monitoring data and a SWPP model designed to assist in prioritizing pesticides for monitoring surface waters in California (Budd et al., 2013; Luo et al., 2013). The model is based on current use patterns and aquatic toxicity benchmark data. The product is a relative prioritization score. Appendix 2 is an abbreviated (top 50) list of pesticides from the most current prioritization of urban pesticides in Los Angeles, San Diego, and Orange counties, California for the years 2010 – 2012. The list provides guidance to EM staff on pesticides to focus attention; however, the decision to monitor for a pesticide is influenced by additional factors. The model generates a recommendation for monitoring based on physiochemical properties. For example, although chlorothalonil has a relatively high final score (25) based on toxicity and use data, it is not recommended for monitoring due to its quick dissipation under field conditions. Pesticides recommended for monitoring not included in this protocol are awaiting method development.

4.2 Sampling

Water sampling. Samples will be collected for both ambient and mitigation monitoring during two dry season and two storm sampling events. Dry season sampling will occur between August - September, 2015 and May-June, 2016. We will conduct storm sampling with the first major storm (rain) event of the 2015-2016 season and with a major storm in the winter or early spring of 2016 (Table 4).

Most water samples will be collected as grab samples directly into 1-L amber bottles (Bennett, 1997). Where the stream is too shallow to collect water directly into these bottles, a secondary stainless steel container will be used to initially collect the water samples. Water samples collected at SC1, SC2, SC3, SC4, WC1, and WC2 during storm events may be collected as composite samples utilizing automated sampling equipment set up by UC Cooperative Extension (CDPR, 2014b; Sisneroz et al., 2012). Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed.

CDPR staff will collect and analyze water and sediment samples for total organic carbon (TOC) using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger, 2013a). Water samples will also be analyzed for suspended sediment (Ensminger, 2013b).

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

Toxicity sampling. Water samples will be collected at a subset of sampling sites for toxicity analysis during four events of FY 15-16. 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* in water (96-hr).

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.

4.3 Field Measurements

Physiochemical properties of water column will be determined using a YSI-EXO 1 multiparameter Sonde according to the methods describe by Doo and He (2008). At each site, water parameters measured *in situ* will include pH, temperature, conductivity, turbidity, 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. At SC2, SC3, and WC2 continuous flow rates will be determined by using an installed Hach Sigma 950 flow meter (Sisneroz et al., 2012).

5.0 CHEMICAL ANALYSIS

Water samples will be sent to the Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) for pesticide analysis. They will analyze nine different analyte groups which will include up to 33 chemical compounds for analysis (Table 5, Appendix 3). Sediment samples will be sent to the California Department of Fish and Wildlife, Sacramento, CA (CDFW). Sediment samples will be analyzed for pyrethroids pesticides (Table 5). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995). Laboratory blanks and matrix spikes will be included in each extraction set.

6.0 DATA ANALYSIS

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

Our preliminary analysis (Ensminger and Budd, 2014) indicated that the sample data is heavily skewed and contains a number of non-detects with multiple reporting limits, which may violate the normality and equal variance assumptions of the parametric procedures (e.g., ANOVA and *t*-tests). In order to appropriately address the characteristics of the sample data, a more generic and distribution-free approach, the non-parametric statistics, will be used in this study. Helsel (2012) illustrated the application of non-parametric procedures to skewed and censored environmental data. We will primarily reference Helsel as a general guideline for data analysis of this study. The data will be analyzed by using R statistical program (R Core Team, 2014), the Nondetects And Data Analysis for environmental data (NADA) package for R (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 6).

1) Explanatory data analysis will be performed to summarize the characteristics of the sample data. Urban monitoring data has been collected since 2008 for a variety of analytes (i.e., Tables 5, Appendix 3) at multiple locations (i.e., Salt Creek, Wood Creek; Table 2) with different site types (i.e., stormdrain outfalls and receiving water), and between different seasons (i.e., dry and wet seasons). 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 or not there is significant difference in concentration between the dry and wet season, or between the difference locations. Non-parametric procedures will be used to compute the statistics for hypothesis test. For data with multiple reporting limits, it will be censored at the highest limit before proceeding if the test procedure allows only one RL.
3) Trend analysis will be included to depict the change in concentration over time. We are specifically interested in determining the effectiveness of CDPR regulation 6970 which went into effect July 19, 2012 to mitigate pyrethroid contamination in urban waters. Ambient monitoring data from Salt Creek monitoring locations, as well as WC1 in Wood Creek will be used. For the trend analysis, we will use Akritas-Thenil-Sen non-parametric regression, which regresses the censored concentration on time, or the Kaplan-Meier method, which tests the effects of year, month and location by developing a mixed linear model between the censored concentration and the spatial-temporal factors.

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

7.0 TIMELINE

Field Sampling: Jul 2015 – Jun 2016
Chemical Analysis: Jul 2015 – Oct 2016
Report to Management: Jan 2017 – Mar 2017
Data Entry into SURF: Mar 2017 – Jun 2017

8.0 LABORATORY BUDGET

The estimated total cost for chemical analyses is $154, 170 (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: http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa002.pdf.

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. 2014. 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.swrcb.ca.gov/centralvalley/water_issues/tmdl/impaired_waters_list/index.shtml

CDPR. 2014a. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Available at: http://www.cdpr.ca.gov/docs/pur/purmain.htm on June 30, 2014.

CDPR. 2014b. Department of Pesticide Regulation Standard Agreement No. 10-C0101. Available at: http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts/ucdavis_10-C0101.pdf

CDPR. 2012. California Code of Regulations (Title3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Available at: http://cdpr.ca.gov/docs/legbills/calcode/040501.htm#a690.

CDPR. 2010. 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. 2008. Department of Pesticide Regulation Environmental Monitoring Study 249 Protocol. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/protocol/study249protocol.pdf.

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., Budd, R., Kelley, K., and K. Goh. 2013. 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. 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_pyrethroid_trends.pdf.

Ensminger, M. 2013a. Analysis of whole sample suspended sediments in water. Available at: http://cdpr.ca.gov/docs/emon/pubs/sops/meth01000.pdf.

Ensminger, M. 2013b. Water TOC analysis using the Shimadzu TOC-VCSN and ASI-V autosampler.Available at: http://cdpr.ca.gov/docs/emon/pubs/sops/meth01100.pdf.

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.

Helsel, D.R., 2012. *Statistics for Censored Environmental Data Using Minitab and R* (2nd 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: http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/oki_2009.pdf.

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: http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc0401.pdf.

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: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report.pdf

R Core Team, 2014. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. URL http://www.R-project.org/.

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

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**.**

UP3 Project. 2007. Pesticide Sales and Use Information. Pesticides in urban surface water: Urban pesticide use trends report 2007. Available at: http://www.up3project.org/up3_use.shtml

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.

Watershed	Stormdrain Outfall	Receiving Water/ Mitigation Outfall	Total Sites
Ambient Monitoring			
Salt Creek	4	3	7
Ballona Creek	-	1	1
Bouquet Creek	-	1	1
Los Angeles River	-	1	1
San Gabriel River	-	1	1
San Diego River	-	1	1
Tecolote Canyon Creek	-	1	1
Mitigation Monitoring			
Wood Creek	1	1	2
Total	**5**	**10**	**15**

Table 2. Analysis schedule and budget by site

Site	Analytical Suite	# Sites	Storm Samples	Dry Season Samples	Cost/ Sample	Cost
Ambient Monitoring						
SC3, SC7	Carbaryl	2	1	2	480	2880
	Chlorfenapyr	2	1	2	540	3240
	Fipronil + OP (short)	2	2	2	840	6720
	Imidacloprid	2	2	2	600	4800
	Dinitroanalines	2	1	2	840	5040
	Synthetic auxin herbicides	2	2	2	690	5520
	Pyrethroids-6	2	2	2	600	4800
	Photosynthetic inhibitor herbicides	2	1	2	540	3240
SC1, SC2, SC4, SC5	Fipronil + Met	4	2	2	600	9600
	Imidacloprid	4	2	2	600	9600
	Synthetic auxin herbicides	4	2	2	690	11040
	Pyrethroids-6	4	2	2	600	9600
BOQ, LAR1	Carbaryl	2	1	2	480	2880
	Chlorfenapyr	2	1	2	540	3240
	Fipronil + OP (short)	2	1	2	840	5040
	Imidacloprid	2	1	2	600	3600
	Dinitroanalines	2	1	2	840	5040
	Synthetic auxin herbicides	2	1	2	690	4140
	Pyrethroids-6	2	1	2	600	3600
	Photosynthetic inhibitor herbicides	2	1	2	540	3240
BAL	Fipronil + Met	1	1	2	600	1800
	Imidacloprid	1	1	2	600	1800
	Synthetic auxin herbicides	1	1	2	690	2070
	Pyrethroids-6	1	1	2	600	1800
SC7a, SGR SDR, TCC	Fipronil + Met	4	-	2	600	4800
	Imidacloprid	4	-	2	600	4800
	Synthetic auxin Herbicides	4	-	2	690	5520
	Pyrethroids-6	5	-	2	600	4800
		Ambient Monitoring Sub-total				134,250
WC1, WC2	Fipronil + Met	2	2	2	600	4800
	Imidacloprid	2	2	2	600	4800
	Synthetic auxin Herbicides	2	2	2	690	5520
	Pyrethroids-6	2	2	2	600	4800
		Mitigation Monitoring Sub-total				19,920
				Total		**$154,170**

OP = organophosphate, Met.=Metabolites

Table 3. Modifications from sampling plan for fiscal year 2014-2015

Change from FY 13-14	Justification
Removed Chollas Creek from sampling	Sites were ponded or dry during previous sampling events
Removed SC6	Minimal spatial information gained from site
Added Los Angeles river (LAR1) San Gabriel river (SGR), and Tecolote Canyon creek (TCC)	Highly urbanized watersheds, increases size of represented watersheds and spatial distribution in region
Removed chlorothalonil screen	Model does not recommend monitoring based on physiochemical properties, very low detection rate (1.5%)
Replacing norflurazon and prometon with atrazine and diflubenzuron in TR screen*	Higher prioritization score**
Replacing diazinon with dichlorvos in OP* screen	Higher prioritization score, diazinon very low rate of detection (6.1%)
Added carbaryl screen	High prioritization score

*TR=photosynthetic inhibitor herbicides, OP = organophosphate

** Luo et al., 2013

Table 4. Sampling schedule for urban pesticide monitoring in Southern California.

Event Type	Date	IM	PX	PY-6	FP + Met	FP+OP	CB	CF	DN	TR	PY-Sed	Tox	Total
Dry 1	Aug-Sep, 2015	15	15	15	11	4	4	4	4	4	4	5	85
Rain 1	Oct-Nov, 2015	11	11	11	7	4	4	4	4	4	-	3	63
Rain 2	Feb-Mar, 2016	8	8	8	6	2	0	0	0	0	-	-	32
Dry 2	May-Jun 2016	15	15	15	11	4	4	4	4	4	4	5	85
	Total	49	49	49	35	14		12	12	12	8	13	240

CF=chlorfenapyr, FP+Met=fipronil+metabolites, OP=organophosphates, IM=imidacloprid, DN=dinitroanaline herbicides, PX=synthetic auxin herbicides, PY=pyrethroid, TR=photosynthetic inhibitor herbicides, Sed=sediment, Tox=toxicity

Table 5. Chemical analysis of pesticides in the Southern California urban monitoring study.

Analyte Group	Media	Analytical Method	Method Detection Limit ($\mu g\ L^{-1}$)	Reporting Limit ($\mu g\ L^{-1}$)
Carbaryl	Water[a]	HPLC	0.011	0.05
Chlorfenapyr	Water	GC-MS/MS	0.0624	0.1
Dinitroanaline herbicides	Water	LC-MS/MS	0.01 – 0.015	0.05
Fipronil & degradates	Water	GC-MSD (SIM)	0.003 – 0.005	0.05
Imidacloprid	Water	GC-MS	0.01	0.05
Organophosphate insecticides	Water	GC-FPD	0.008 – 0.0142	0.05
	Water	GC-MS	0.0012 – 0.0079	0.01
Synthetic auxin herbicides	Water	GC-MS	0.064	0.1
Pyrethroid insecticides	Water	GC-ECD	1.09 – 7.68 (ng L^{-1})	5 – 15 (ng L^{-1})
	Sediment	GC-ECD	-	0.02 – 0.2 (ng g^{-1})
Photosynthetic inhibitor herbicides	Water	LC-MS/MS	0.0063 – 0.043	0.05

[a] Water samples analyzed by California Department of Food and Agriculture, sediment samples analyzed by the California Department of Fish and Wildlife.

Table 6: 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 in one-way layout	*Kruskal-Wallis test* (for unordered alternative) or *Jonckheere-Terpstra 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 in two-way layout	*Friedman's test* (for unordered alternative) or *Page's test* (for ordered alternative) for censored data with one RL Multiple comparison to detect which group is different

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

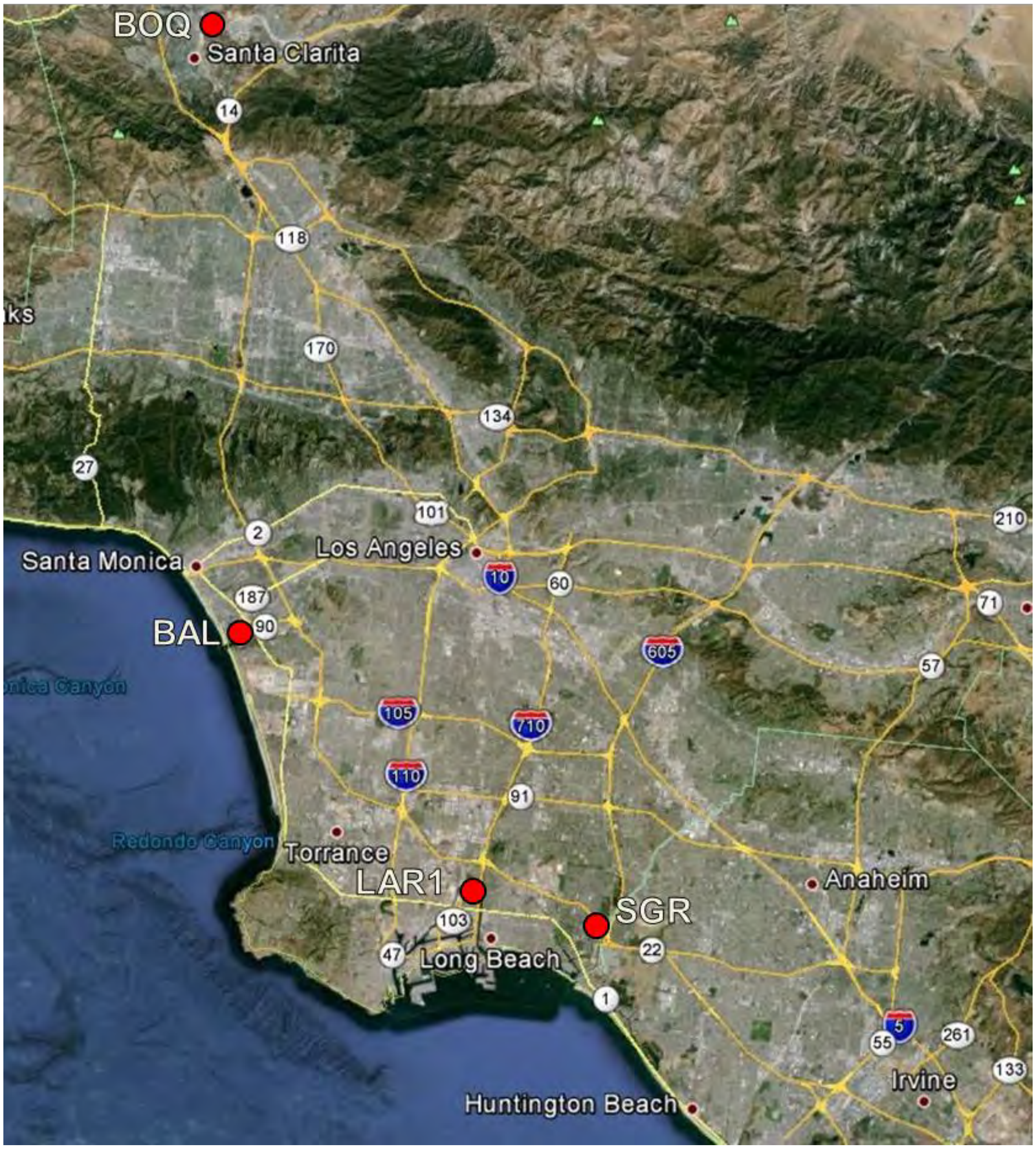

Figure 2. Sampling locations within Los Angeles County, CA

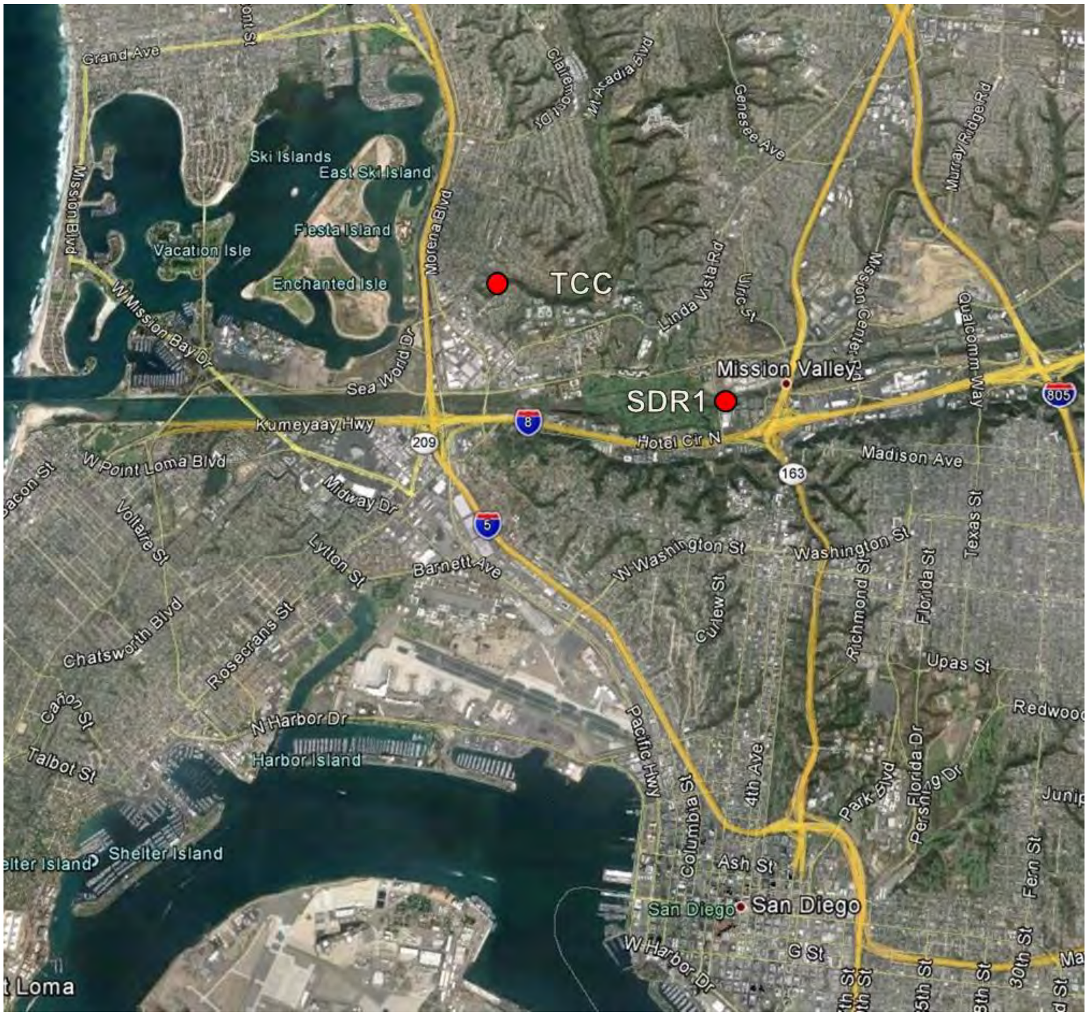

Figure 3. Sampling locations within San Diego County, CA

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

Appendix 1. Detailed sampling site information

Watershed	Site ID	Northing	Easting	Site type
Salt Creek	SC1	33 30 32.92	117 41 26.53	Stormdrain
Salt Creek	SC2	33 30 40.57	117 41 40.67	Stormdrain
Salt Creek	SC3	33 30 43.02	117 41 49.55	Stormdrain
Salt Creek	SC4	33 30 31.00	117 42 26.34	Stormdrain
Salt Creek	SC5	33 30 20.23	117 42 30.87	Receiving water
Salt Creek	SC7	33 28 53.97	117 43 26.55	Receiving water
Salt Creek	SC7A	33 28 54.12	117 43 27.37	Receiving water
Ballona Creek	BAL	33 59 12.92	118 24 55.90	Receiving water
Bouquet Creek	BOQ	34 25 42.05	118 32 23.45	Receiving water
Los Angeles River	LAR-1	33 80 58.09	118 20 54.53	Receiving water
San Gabriel River	SGR	33 77 51.08	118 09 74.18	Receiving water
San Diego River	SDR	32 45 51.79	117 10 12.24	Receiving water
Tecolote Canyon Creek	TCC	32 77 54.93	117 20 04.84	Receiving water
Wood Creek	WC1	33 34.56.56	117 44 43.02	Stormdrain
Wood Creek	WC2	33 34 53.70	117 44 44.65	Wetland outfall

Appendix 2. Priority model pesticides (top 50) based on urban usage in Los Angeles, Orange, and San Diego counties, California (2010-2012).

Pesticide	Use (lbs)	Use Score	Benchmark (ug/L)	Tox Score	Final Score	Recom.
Bifenthrin	32173	5	0.0013	7	35	TRUE
Permethrin	79227	5	0.0014	7	35	TRUE
Fipronil	32101	5	0.011	6	30	TRUE
Cyfluthrin	18773	4	0.0074	7	28	TRUE
Cypermethrin	10178	4	0.069	6	24	TRUE
Lambda-cyhalothrin	4642	3	0.002	7	21	TRUE
Deltamethrin	2481	3	0.0041	7	21	TRUE
Imidacloprid	18832	5	1.05	4	20	TRUE
Malathion	1519	3	0.035	6	18	TRUE
Diuron	14226	4	2.4	4	16	TRUE
Chlorfenapyr	7241	4	2.915	4	16	TRUE
Pendimethalin	4917	4	5.2	4	16	TRUE
Oxadiazon	2011	3	0.88	5	15	TRUE
Dichlorvos	661	2	0.0058	7	14	TRUE
Pyriproxyfen	171	2	0.015	6	12	TRUE
Esfenvalerate	250	2	0.017	6	12	TRUE
Chlorpyrifos	308	2	0.04	6	12	TRUE
Prodiamine	4337	3	1.5	4	12	TRUE
Bromacil	4046	3	6.8	4	12	TRUE
2,4-D	5253	4	13.1	3	12	TRUE
Triclopyr, butoxyethyl ester	7304	4	19	3	12	TRUE
Sulfometuron-methyl	539	2	0.45	5	10	TRUE
Carbaryl	443	2	0.5	5	10	TRUE
PCNB	2498	3	13	3	9	TRUE
Oryzalin	4822	3	15.4	3	9	TRUE
Dithiopyr	1930	3	20	3	9	TRUE
Propiconazole	3119	3	21	3	9	TRUE
Azoxystrobin	884	3	44	3	9	TRUE
Diflubenzuron	10	1	0.00025	8	8	TRUE
Atrazine	3	1	0.001	8	8	TRUE
Trifluralin	289	2	1.14	4	8	TRUE
Pyraclostrobin	453	2	1.5	4	8	TRUE
Simazine	257	2	2.24	4	8	TRUE
Propoxur	206	2	5.5	4	8	TRUE
Fenoxycarb	1	1	0.0016	7	7	TRUE
Tralomethrin	1	1	0.0044	7	7	TRUE
Trichlorfon	33	1	0.0057	7	7	TRUE
Endosulfan	12	1	0.01	7	7	TRUE
Disulfoton	6	1	0.01	7	7	TRUE
Chlorothalonil	44531	5	0.6	5	25	FALSE
Mancozeb	18144	4	1.1	4	16	FALSE
Thiophanate-methyl	9198	4	2	4	16	FALSE
Diquat dibromide	2505	3	0.75	5	15	FALSE
2,2-dibromo-3-nitrilopropionamide	965	3	10	4	12	FALSE
Flumioxazin	274	2	0.49	5	10	FALSE
Hydroprene	3198	3	25	3	9	FALSE
Maneb	257	2	1.15	4	8	FALSE
Halosulfuron-methyl	167	2	5.3	4	8	FALSE
Iprodione	7068	4	120	2	8	FALSE
Fosetyl-al	5591	4	1000	2	8	FALSE

Yellow = in current monitoring plan. Recom. = Monitoring recommendation: True, Model supports monitoring; False, Model does not support monitoring

Appendix 3. Active ingredients within analytical chemical suites

CB	**CF**	**IM**
Carbaryl	Chlorfenapyr	Imidacloprid
DN	**OP**	**PY**
Oryzalin	Chlorpyrifos	Bifenthrin
Pendimethalin	Dichlorvos	Cyfluthrin
Prodiamine	Malathion	Cypermethrin
Trifluralin		Deltamethrin/Tralomethrin
		Fenvalerate/Esfenvalerate
		λ-Cyhalothrin/epimer
		cis-Permethrin
		trans-Permethrin
FP +Met	**PX**	**TR**
Desulfinyl fipronil	2,4-D	Bromacil
Desulfinyl fipronil amide	Dicamba	Diuron
Fipronil	MCPA	Atrazine
Fipronil amide	Triclopyr	Diflubenzuron
Fipronil sulfide		Simazine
Fipronil sulfone		