Department of Pesticide Regulation
Environmental Monitoring Branch
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STUDY 265. URBAN PESTICIDE MONITORING IN SOUTHERN CALIFORNIA

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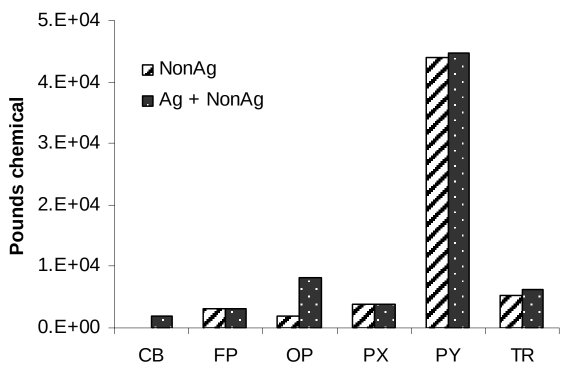
January 26, 2010

I. INTRODUCTION

Urban pesticide uses include structural pest control, landscape maintenance, rights-of-way applications, public health protection, and residential applications. In California, the Department of Pesticide Regulation (CDPR) receives pesticide use reports for urban applications by licensed applicators. Yearly, applicators generally report over 12 million pounds active ingredient (a.i.) of urban pesticide use in California (CDPR, 2009a). However, urban pesticide use by individual homeowners is not reported, so that total use is greater than reported use. Based on pesticide sales records, the total use of all urban pesticide products likely exceeds 500 million pounds (UP3 Project, 2008). It should be noted that much of the estimated usage includes pesticides such as bleach and other disinfectants used by non-residential entities such as industry and municipalities. It has been estimated that urban pesticide use accounts for over 70% of the total pesticide use in California (UP3 Project, 2007). Figure 1 below shows the reported agricultural and non-agricultural usage of pesticide active ingredients within Orange County, CA, for the year 2008 (CDPR 2010). There were a total of 57,860 pounds of selected active ingredients (a.i.) used for non-agricultural use in 2008, with pyrethroids making up 76% of total usage.



	Non-Ag
Carbamates	19
Fipronil + Metabolites	3053
Organophosphates	1816
Phenoxy herbicides	3764
Pyrethroids	43949
Triazine herbicides	5259

Figure 1. 2008 pesticide usage (lb a.i.) by chemical class in Orange County, CA

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 2006 Federal Clean Water Act Section 303(d) list due to the historical presence of organophosphorus (OP) pesticides (Cal/EPA, 2009), 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, OP, and fipronil insecticides. Many of the detected pesticides are at concentrations that exceed the acute toxicity to sensitive aquatic organisms (Oki and Haver, 2009; 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, 2009b). In addition to the above mentioned pesticides, CDPR also detected degradates of fipronil, carbaryl, diuron, simazine, prometon, pendimethalin, oryzalin, prodiamine, triclopyr, dicamba, 2,4-D, and MCPA (He *et al.*, 2009).

Due to the numerous detections in CDPR's 2008 study, additional urban monitoring is warranted to assess urban pesticide water quality trends. With new surface water regulations being proposed in California, long term monitoring at selected urban sites will help determine the effectiveness of any new regulations (CDRP, 2009c). 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 potentially be used to track the performance of mitigation measures or public outreach programs.

II. OBJECTIVE

The overall goal of this project is to assess urban pesticide use and water quality in drainages and receiving waters within two typical southern California urbanized areas during stormwater runoff and baseflow conditions. Specific objectives include:

1) Determine presence and concentrations of selected pesticides in urban runoff under baseflow and stormwater conditions;
2) Evaluate any long term (~5 years) trends in residential pesticide use within watersheds of interest;
3) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity benchmarks;
4) Observe the mitigation effects of a small constructed wetland on pesticide concentrations in receiving waters.

III. PERSONNEL

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Sheryl Gill, Senior Environmental Scientist. Key personnel are listed below:

- Project Leader: Robert Budd, Ph.D.
- Field Coordinator: Xin Deng, Ph.D.

- Senior Scientist: Frank Spurlock, 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, Environmental Scientist, at (916) 445-2505 or rbudd@cdpr.ca.gov.

IV. STUDY PLAN

4.1 Monitoring Sites

Water quality monitoring will be conducted at 10 sites within Orange County, California (Table 1). Four of these sites were previously monitored under CDPR Study 249. These location IDs have been changed for this study. Details of site descriptions are provided in Appendix 1. There are seven sampling locations within the Salt Creek watershed (Figure 2) and three within the Wood Creek watershed (Figure 3).

Automated sampling 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.

Surrounding drainage areas at both watersheds consist of single family dwellings, multiple family dwellings, light commercial buildings, parks, and schools.

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

Area	Stormdrain Outfall	Receiving Water	Total Sites
Salt Creek	4	3	7
Wood Creek	2	1	3
Total	6	4	10

4.2 Sampling

Water sampling. Samples will be collected during two baseflow and two storm sampling events. Baseflow sampling will occur in August, 2009 and May, 2010. We will conduct storm sampling with the first major storm (rain) event of the 2009-2010 season (average highest precipitation is December – March) and with a major storm in the winter or early spring of 2010 (Table 2).

CDPR staff will collect water samples for chemical analysis and for determining total suspended solids (TSS) and total organic carbon (TOC). Grab samples will be collected from the center channel of the creek using an extendable pole directly into 1-L amber glass bottles. When collecting water samples from storm drains, samples will be collected by hand directly into 1-L bottles. Composite storm samples may also be collected by automated samplers where set up by the University of California (Oki and Haver, 2009). All bottles will be sealed with Teflon® lined lids following CDPR SOP FSWA002.00 (Bennett, 1997). Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed.

Sediment sampling. Sediment samples will be collected once at two sampling locations within each watershed during the second baseflow event. Sediment samples will be collected following CDPR SOP FSWA016.00 (Mamola, 2005) and analyzed for pyrethroids, chorpyrifos, and for TOC.

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.

Table 2. Sampling schedule for urban pesticide monitoring in Southern California.

Sample Type	August 2009	May 2010	December 2009	Jan-Mar 2010	Total
Event	Baseflow	Baseflow	Stormwater	Stormwater	
Water Samples					
Number of sites	6[1]	10	9[3]	10	35
Number of samples	70[2]	100	85	100	355
Sediment Samples					
Number of samples		4			4

[1]Samples include those sampled under Study 249
[2]Includes TSS and TOC samples
[3]SC5 dropped from this sampling event.

4.3 Field Measurements

Physiochemical properties of water will be determined using a YSI 6920 V2-2 multiparmeter 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, and dissolved oxygen. Salinity and total dissolved solids will be estimated from conductivity.

Stormdrain discharge or stream flow rates will be measured to characterize the flow regime and to estimate the total loading of target pesticides. Flow will be calculated using a Global portable velocity flow probe (Goehring, 2008) or estimated utilizing a float or fill-bucket method.

4.4 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995). Ten percent of the total number of samples will be submitted as field blanks, blind spikes, or field duplicates. In addition, QA/QC procedures developed by US EPA (2002) and for the Surface Water Ambient Monitoring Program (SWAMP) by California's State Water Resources Control Board (SWRCB; 2008) will be consulted where applicable.

V. LABORATORY ANALYSIS

The Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) will conduct the pesticide analysis for the study. They will analyze six different analyte groups which will include up 57 chemical compounds for analysis (Table 3). Based on previous monitoring data, short screens for OPs and triazine herbicides will be used beginning in 2010, reducing the total number to 40 chemical compounds (Appendix 2).

CDPR will analyze TSS in the water samples and will analyze TOC in both water samples and sediment samples. TSS samples will be analyzed following US EPA method 160.2 (US EPA, 1971) and as described in Kelley and Starner in CDPR Study Memo 219 (2004). TOC will be analyzed with a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan).

Table 3. Chemical analysis of pesticides in the Southern California urban monitoring study.

Analyte Group	Analytical Method	Method Detection Limit ($\mu g\ L^{-1}$)	Reporting Limit ($\mu g\ L^{-1}$)
Carbamate Insecticides	HPLC	0.01 – 0.02	0.05
Fipronil & Degradates	GC-MSD (SIM)	0.003 – 0.005	0.05
Organophosphorus Insecticides	GC-FPD	0.008 – 0.0142	0.05
	GC-MS	0.0012 – 0.0079	0.01
Phenoxy Herbicides	GC-MS	0.064	0.1
Pyrethroid Insecticides	GC-ECD	1.09 – 7.68 (ng L^{-1})	5 – 15 (ng L^{-1})
Triazine Herbicides	LC-MS/MS	0.01 – 0.031	0.05

VI. 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. All data will be shared between CDPR and Darren Haver, University of California. 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.

VII. LABORATORY BUDGET

The total cost for the CDFA chemical analyses is $139,490. This cost includes QC sample analysis (Table 4).

Table 4. Analytical cost estimates for urban samples collected in Southern California.

	Sampling Sites		Sampling Event			Chemical Analyses										
								Organophosphorus					Triazine Herbicides			
Sample Type	Salt Creek	Wood Creek	Baseflow	Storm event	Number of Sample Sets*	Carbamates	Fipronil	long screen	short screen	Chlorpyrifos	Pyrethroids	Phenoxy Herbicides	long screen	short screen	Price per sample	Cost
Water	3	3	1	0	7	$800	$500	$650			$800	$575	$720	--	$4045	$28,315
Water**	7	3	1	2	29*	$800	$500	--	$500		$800	$575	--	$450	$3625	$106,775
Sediment			1	0	4	--	--	--		$300	$800				$1100	$4,400
Total	10	6	3	2	40											$139,490

* Sample number has a modified number of screens (ie carbamates not taken during each event)

**includes short screens in place of long screens.

VIII. LITERATURE CITED

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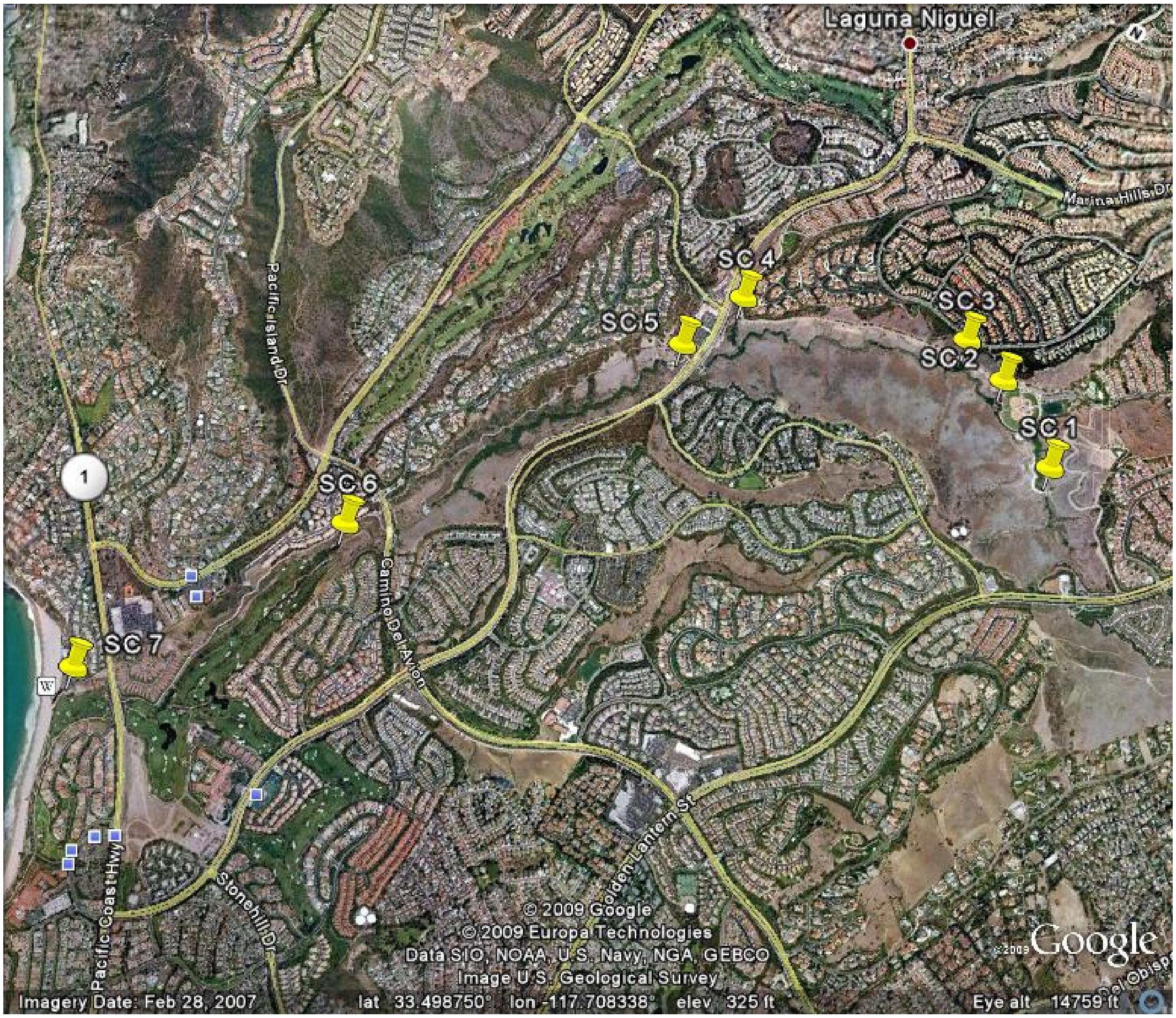

Figure 2. Sampling locations within Salt Creek Watershed, Orange County, CA

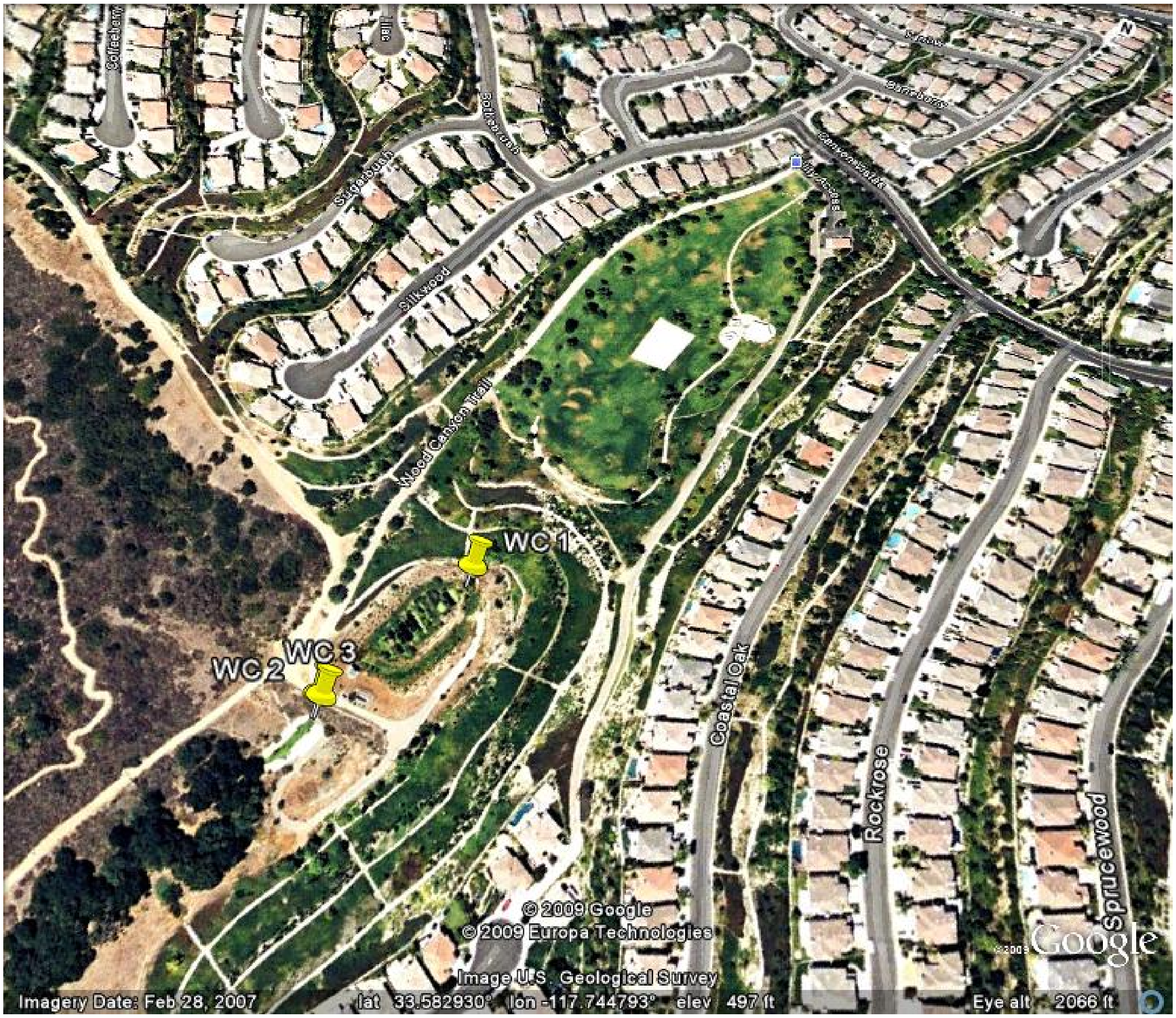

Figure 3. Sampling locations within Wood Creek Watershed, Orange County, CA

Appendix 1. Detailed Sampling Site Information

Watershed	Site ID	Previous ID	Northing	Easting	Site type
Salt Creek	SC-1	LN-9	33 30 32.92	117 41 26.53	Stormdrain
Salt Creek	SC-2		33 30 40.57	117 41 40.67	Stormdrain
Salt Creek	SC-3	LN-8	33 30 43.02	117 41 49.55	Stormdrain
Salt Creek	SC-4		33 30 31.00	117 42 26.34	Stormdrain
Salt Creek	SC-5	LN-0	33 30 20.23	117 42 30.87	Receiving Water
Salt Creek	SC-6		33 29 31.91	117 43 02.68	Receiving Water
Salt Creek	SC-7		33 28 54.18	117 43 27.77	Receiving Water
Wood Creek	WC-1	AV-4	33 34.56.56	117 44 43.02	Stormdrain
Wood Creek	WC-2	AV-5	33 34 53.70	117 44 44.65	Receiving Water
Wood Creek	WC-3	AV-4a	33 34 53.69	117 44 44.60	Stormdrain

Appendix 2. Active ingredient chemical analysis list

Carbamates	**Fipronil + Metabolites**	**Organophosphates**
3-OH Carbofuran	Desulfinyl fipronil	Chlorpyrifos
Aldicarb	Desulfinyl fipronil amide	Diazinon
Aldicarb Sulfone	Fipronil	Dimethoate
Aldicarb Sulfoxide	Fipronil amide	Malathion
Carbaryl	Fipronil sulfide	Methidathion
Carbofuran	Fipronil sulfone	
Methiocarb		
Methomyl		
Oxymyl		
Pyrethroids	**Phenoxy Herbicides**	**Triazine Herbicides**
Bifenthrin	2,4-D	Bromacil
Cyfluthrin	Dicamba	DACT
Cypermethrin	MCPA	Diuron
Deltamethrin	Triclopyr	Hexazinone
Fenopropathrin		Simazine
Fenvalerate/esfenvalerate		
Lambda-cyhalothrin		
Lambda-cyhalothrin epimer		
Permethrin cis		
Permethrin trans		
Resmethrin		