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STUDY 269 (FY2013-2014). Urban Monitoring in Roseville and Folsom, California

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I. INTRODUCTION

Pesticides are routinely found in urban waterways. Their presence has been attributed to both high urban pesticide use and a lack of consumer awareness (Holmes et al. 2008, Weston et al. 2009, Wittmer et al. 2011, Gan et al. 2012, Ensminger et al. 2013). Correspondingly, numerous California urban creeks have been listed as impaired water bodies in the Clean Water Act Section 303(d) list due to the presence of organophosphorus (OP) and pyrethroid insecticides (Cal/EPA 2013). Although chlorpyrifos and diazinon (both OPs) urban use has decreased, recent monitoring has shown that urban waterways are frequently contaminated with pyrethroids, fipronil, OPs, and herbicides. Frequently, these detections have exceeded US EPA aquatic benchmarks or there has been an association between pesticide detections and toxicity to sensitive aquatic organisms in laboratory bioassays (Holmes et al. 2008, Weston et al. 2009, Gan et al. 2012; Ensminger et al. 2013). High use and frequent detections warrant additional monitoring to better understand spatial and temporal trends and to indentify effective mitigation measures. The California Department of Pesticide Regulation (CDPR) Surface Water Program has been monitoring urban pesticide runoff since 2008 (He 2008). Specifically in the Sacramento area of northern California, CDPR has detected 24 different pesticides (or pesticide degradates). Bifenthrin, 2,4-D, dicamba, fipronil, imidaclopriod, and triclopyr are most frequently detected; bifenthrin and fipronil are often detected at concentrations exceeding the US EPA aquatic benchmarks (Ensminger et al. 2013). CDPR's recent monitoring work in Folsom has also examined constructed water quality treatment ponds (CWQTPs) to mitigate pesticide runoff and toxicity to aquatic organisms. Preliminary results indicate that CWQTPs can partially mitigate these problems (Budd et al. 2013a).

Study 269 is a continuation of CDPR's urban monitoring in northern California, with some changes to monitoring frequency, site locations, and pesticides of interest for analysis. The main study objective is to determine the detection frequency of specific pesticides and their concentrations in urban runoff from long-term monitoring sites in Roseville (sites established since 2008). Monitoring at these sites will help determine the effectiveness of new regulations placed into effect July 19, 2012 in an attempt to reduce pyrethroids in urban waterbodies (CDPR 2010). A second objective is to assess the effectiveness of CWQTPs in Folsom to reduce pesticide concentrations, frequency, and load from urban runoff and to reduce toxicity to *Hyalella azteca*.

II. OBJECTIVES

For FY 2013–2014, the objectives of this Study 269 are:

1) Determine the presence and concentrations of selected pesticides in urban runoff at stormdrain outfalls (both during the dry season and during storm runoff) in Roseville and Folsom;
2) Determine the presence and concentrations of selected pesticides from one downstream receiving site in Pleasant Grove Creek, in Roseville;
3) Evaluate the effectiveness of CWQTPs to reduce pesticides from urban runoff;
4) Evaluate the effectiveness of CWQTPs to reduce toxicity to *H. azteca*;
5) Assess whether detected pesticides are at concentrations that could be potentially toxic to aquatic organisms by comparing the data to US EPA aquatic life benchmarks (US EPA 2012) or to water quality criteria (Fojut 2012a, 2012b).

III. PERSONNEL

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

- Project Leader: Michael Ensminger, Ph.D.
- Field Coordinator: Kevin Kelley
- Senior Scientist: Frank Spurlock, Ph.D.
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry, water: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)
- Analytical Chemistry, sediment: California Department of Fish and Wildlife
- Collaborator: Lorence Oki, Ph.D., University of California at Davis, CE Assistant Specialist, Landscape Horticulture, Department of Environmental Horticulture, Phone: (530) 754-4135, Email: lroki@ucdavis.edu

Please direct questions regarding this study to Michael Ensminger, Staff Environmental Scientist, at (916) 324-4186 or mensminger@cdpr.ca.gov.

IV. STUDY PLAN

Monitoring sites. Sampling will occur in Folsom and Roseville, CA, located in the greater Sacramento area. In Roseville, samples will be collected from three different stormdrain outfalls from three separate neighborhoods and from an established downstream sampling site (Table 1; Figure 1). The Roseville sites have been sampled since 2008 (2009 for pyrethroids), providing a baseline for tracking future changes in pesticide concentrations.

The Folsom sites do not have historical monitoring data but rather have been established to determine the mitigation effects of two CWQTPs (Figure 2). One CWQTP, located near Marsh Hawk Drive, consists of two stormdrain outfalls from two neighborhoods (FOL2 and FOL3) and one outfall of the CWQTP (FOL5). Currently there is automated sampling equipment at FOL2 and FOL3 whereby samples can be collected by autosamplers; flow data and other water quality data can also be obtained from this equipment (Sisneroz et al. 2012). The second CWQTP, located on Natoma Station Drive, consists of one stormdrain outfall (TRP1) and one outfall of the CWQTP (TRP2). Determining the pesticide and toxicity differences between the input and output of these CWQTPs can determine their ability to mitigate pesticide runoff (Budd et al. 2013a).

Water sampling. Roseville sites will be sampled four times during the year (two dry season events and two rainstorm events). The dry season events will take place in August 2013 and in June 2014. The rainstorm events will occur in October – November 2013 (first flush rainstorm) and in the winter of 2014. A full suite of chemicals will be analyzed at these long term monitoring sites (Table 2). CDPR has determined that many of these pesticides are top priority urban pesticides for monitoring (Tables 3 and 4; Appendix; Budd et al. 2013b).

The Folsom sites at the CWQTP near Marsh Hawk Drive will be sampled six times (Table 2). These sites will be sampled at the same time as the Roseville sites. In addition we will monitor these sites in July 2013 and April-May 2014; both will be non-rainstorm events. To determine the efficacy of the CWQTP to reduce pesticide runoff, we will only look at analytes that have greater than 30% detection frequency. This will include analyte screens for pyrethroids, fipronil, imidacloprid, and synthetic auxin herbicides (Table 2).

At the Natoma Station Drive CWQTP, we will only look for pyrethroids and synthetic auxin herbicides. These analyte screens contain bifenthrin and 2,4-D, respectively, the two most commonly detected pesticides in our monitoring program. These sites will only be monitored during the July, August, and April-May sampling times (Table 2).

All 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. During rainstorm events, water will be collected as a composite sample at sites FOL2 and FOL3, where automated sampling equipment exists. Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed. At least 10% of the field samples will be field blanks or field duplicates.

Water samples will be analyzed for total organic carbon (TOC) using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan). Water samples will also be analyzed for whole sample suspended sediment concentration (SSC) (Guo 2006).

Sediment sampling. Sediments will be collected up to four times a year at up to eight sampling sites during the study and analyzed for pyrethroids (Table 5). Sediments will be collected as a composite sample with stainless steel trowels and divided into analytical samples, backup samples, and a sample for TOC analysis (Mamola 2005). At some sites sediment will be collected using passive sediment collection samplers (Budd 2009). At least 10% of the field samples will be field duplicates.

Toxicity sampling. During dry season monitoring, water will be collected from a subset of the sampling sites and sent to the University of Davis, Aquatic Health Program, to be tested for toxicity to *Hyalella azteca*. The CWQTP at Marsh Hawk Dr. will be the main focus of toxicity testing (sites FOL2, FOL3, and FOL5).

Field measurements. Water physiochemical properties (dissolved oxygen, electrical conductivity, pH, turbidity, and temperature) will be measured *in situ* during all sampling events with a calibrated YSI 6920 V2 meter (YSI Incorporated, Yellow Springs, OH, USA) (Doo and Lee 2008). Flow rates will be estimated with a Global portable velocity flow probe (Goehring 2008) or by the bucket method (Appropedia 2012). At FOL 2 and FOL3, flow rates will also be determined by using an installed Hach Sigma 950 flow meter (Sisernoz et al. 2012).

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.

Modifications for FY13 -14. The current sampling plan is an extension of urban monitoring in Northern California conducted during fiscal years 2010-2013 (for details of previous sampling protocols, see http://www.cdpr.ca.gov/docs/emon/pubs/protocol.htm for Study 269). The sampling and analysis schedule is similar to that for FY 12-13, with a few notable modifications (Table 6). Modifications were based on previous monitoring data and from the results of a newly developed model to assist in prioritizing pesticides for monitoring in surface water (Luo et al. 2013). Briefly, the model uses US EPA aquatic benchmarks (or equivalents) and CDPR pesticide use data to determine a priority score. Top ranking pesticides warrant consideration for monitoring although other factors need to be considered (percentage of previous detections, physiochemical properties, bioavailable or toxic forms, background levels, etc.). See the Appendix for a list of the top priority pesticides for monitoring in the Sacramento area of Northern California.

V. CHEMICAL ANALYSIS

The Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) will conduct the pesticide analysis for water samples. CDFA will analyze seven different analyte groups which will include 34 pesticides and degradates (Table 3). The California Department of Fish and Wildlife (CDFW) will conduct pesticide analyses for eight pyrethroids in sediment (Table 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.

VI. DATA ANALYSIS

All data generated by this project will be entered to an access database that holds weather and field information, field measurements, and laboratory analytical data. All analytical data will also be uploaded into the CDPR Surface Water Database. We will use various nonparametric and parametric statistical methods to analyze the data, and the data will be compared to aquatic life benchmarks or water quality criteria (US EPA 2013, Fojut 2012a; 2012b). The data collected from this project may be used to develop or calibrate an urban pesticide runoff model.

VII. TIMETABLE

Field Sampling:	July 2013 – June 2014
Chemical Analysis:	July 2013 – October 2014
Summary Report:	April 2015

VIII. LABORATORY BUDGET

The total cost for the CDFA chemical analyses will be $140,310 (water samples; Table 2) and for CDFW chemical analysis will be $16,436 (sediment samples; Table 5). This cost includes field QC sample analysis (field blanks and field duplicates).

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Table 1. Sampling sites in Folsom and Roseville CA.

Site	Type/Describe	No. Homes[§]	Area[§] (Acres)	GPS Coordinates (NAD83)	
				Latitude	Longitude
Folsom, California					
FOL002	Stormdrain outfall; input into CWQTP* at Brock Circle	252	65	38.6503	-121.14494
FOL003	Stormdrain outfall; input into CWQTP at Marsh Hawk Dr.	91	27	38.64938	-121.14494
FOL005	CWQTP outfall near Marsh Hawk Dr. (CWQTP area: 0.7 acres)			38.64969	-121.14459
TRP1	Stormdrain outfall; input into CWQTP at Turn Pike and Natoma Station Dr.	385	110	38.64979	-121.18014
TRP2	CWQTP outfall near Turn Pike Dr. (CWQTP area: 1.2 acres)			38.65062	-121.18098
Roseville, California					
PGC010	Stormdrain outfall at Diamond Woods Circle, Roseville	250	56	38.80477	-121.32733
PGC021	Single storm drain outfall at Opal Drive, Roseville	130	44	38.802707	-121.338524
PGC022	Dual stormdrain outfall at Opal Drive, Roseville	375	112	38.802599	-121.338787
PGC040	Receiving water, downstream Pleasant Grove Creek			38.649253	-121.144276

[§]Approximate number of homes and area (Goggle Earth Pro, Mountain View, CA)
*Constructed water quality treatment pond as defined by the city of Folsom, CA

Table 2. Analytical cost estimates for urban water samples collected in Study 269, FY 2013-2014, and analyzed by CDFA.

Site	Analyte Group*	No. of Sites	Dry Season Monitoring Events[§]				Rainstorm Monitoring Events[§]		Total Number Samples	QC Field samples	Cost/ Sample	Total Cost
			Jy 13	Ag 13	A-M 14	Ju 14	O-N 13	W 14				
PGC010 PGC021 PGC022 PGC040	CY	4		X		X	X	X	16	2	$480	$8,640
	FP/OP			X		X	X	X	16	2	$840	$15,120
	IMD			X		X	X	X	16	4	$600	$12,000
	DN			X		X	X	X	16	2	$800	$14,400
	PX			X		X	X	X	16	4	$690	$13,800
	PY-6			X		X	X	X	16	4	$600	$12,000
	TR			X		X	X	X	16	2	$450	$8,100
FOL2 FOL3 FOL5	FP	3	X	X	X	X	X	X	18	3	$600	$12,600
	IMD		X	X	X	X	X	X	18	1	$600	$11,400
	PX		X	X	X	X	X	X	18	1	$690	$13,110
	PY-6		X	X	X	X	X	X	18	1	$600	$11,400
TRP1 TRP2	PX	2	X	X	X				6	0	$690	$4,140
	PY-6		X	X	X				6	0	$600	$3,600
Totals	--	--	--				--		196	26	--	$140,310

*CY = carbaryl; FP = fipronil + degradates; OP = organophosphates (chlorpyrifos, diazinon, and malathion); IMD = imidacloprid; DN = dinitroaniline herbicides + oxyfluorfen; PX = synthetic auxin herbicides; PY-6 = pyrethroid (six analyte screen); TR = photosynthetic inhibitor herbicides + norflurazon (short screen).

[§]Jy 13, July 2013; Ag 13, August 2013; A-M 14, April or May 2014; Ju 14, June 2014; O-N 13, October or November 2013; W 14, Winter 2014.

Table 3. Chemical analysis of pesticides in the northern California urban monitoring Study 269. All samples collected in water and the California Department of Food and Agriculture (CDFA) will conduct the analyses. Specific methods can be found at http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm.

Pesticide	Analyte Screen (Method ID)	Method Detection Limit (µg L^{-1})	Reporting Limit (µg L^{-1})
Carbaryl	Carbaryl (CY) (EMON-SM11.3)	0.0111	0.05
Fipronil*	Fipronil (FP) + Organophosphate (OP) (EMON-SM 05-013)	0.004	0.05
Fipronil sulfide		0.003	0.05
Fipronil sulfone		0.005	0.05
Fipronil desulfinyl		0.003	0.05
Fipronil desulfinyl amide		0.005	0.05
Fipronil amide		0.005	0.05
Diazinon		0.0012	0.01
Chlorpyrifos		0.0079	0.01
Malathion*		0.0117	0.04
Imidacloprid*	Imidacloprid (IMD)	0.0101	0.05
Bifenthrin*	Pyrethroid (PY-6) (EMON-SM 05-022)	0.00176	0.005
Cyfluthrin*		0.00173	0.015
Cypermethrin*		0.00175	0.015
Deltamethrin/Tralomethrin*		0.00177	0.005
Lambda-cyhalothrin*		0.00115	0.015
Permethrin cis*		0.00352	0.015
Permethrin trans*		0.00768	0.015
Benfluralin	Dinitroaniline (DN) (EMON-SM-05-006)	0.012	0.05
Ethalfluralin		0.015	0.05
Oryzalin*		0.021	0.05
Oxyfluorfen*		0.0101	0.05
Pendimethalin*		0.012	0.05
Prodiamine*		0.0124	0.05
Trifluralin		0.0144	0.05
Bromacil*	Photosynthetic Inhibitor Herbicides and Norflorazon (TR) (EMON-SM-62.9)	0.031	0.05
Diuron*		0.022	0.05
Hexazionone		0.04	0.05
Norflorazon		0.019	0.05
Prometon		0.016	0.05
Simazine		0.013	0.05
2,4-D*	Synthetic Auxin Herbicides (PX) EMON-SM-05-012)	0.015	0.05
Dicamba		0.017	0.05
MCPA		0.022	0.05
Triclopyr*		0.020	0.05

*These pesticides are in CDPR's list of the top 25 pesticides with highest priority for urban monitoring (Budd et al. 2013b).

Table 4. Chemical analysis of pesticides in the northern California urban monitoring Study 269. All samples collected in sediments and the Department of Fish and Wildlife (DFW) will conduct the analyses.

Pesticide	**Method Detection Limit (ng g^{-1} dry wt)**	**Reporting Limit (ng g^{-1} dry wt)**
Bifenthrin*	0.063	0.25
Cyfluthrin*	0.129	1.25
Cypermethrin*	0.131	1.25
Deltamethrin/Tralomethrin*	0.222	1.0
Esfenvalerate/Fenvalerate	0.131	0.5
Fenpropathrin	0.044	0.25
Lambda cyhalothrin*	0.053	0.5
Permethrin, cis*	0.484	1.25
Permethrin, trans*	0.8	2.5

*These pesticides are in CDPR's list of the top 25 pesticides with highest priority for urban monitoring (Budd et al. 2013b).

Table 5. Analytical cost estimates for sediment samples collected in Study 269, FY 2013-2014, and analyzed by CDFW.

Sampling Date (season)	Sites	No. of Samples	Cost per Sample	Cost[§]	Grand Total
Fall 2013 prior to first flush rain fall	PCC010, PGC019*, PGC040, FOL2, FOL3, FOL5, TRP1, TPR2	8	$587	$4696	
Fall 2013 after first flush rain fall	PCC010, PGC019*, PGC040, FOL2, FOL3, FOL5	6	$587	$3522	
Winter 2014	FOL2, FOL3, FOL5	3	$587	$1761	
Spring 2014 after ~ last rainfall of water year	PCC010, PGC019*, PGC040, FOL2, FOL3, FOL5, TRP1, TPR2	8	$587	$4696	
Field duplicates (various timing)	Selected sites	3	$587	$1761	$16,436

*A combination of PGC021 and PGC022
[§]Includes 29% overhead

Table 6. Modifications for FY13-14 monitoring in northern California. Listed below are modifications from FY 12-13 Study 269 protocol (http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study269protocol2012.pdf).

Change from FY 12-13	Justification
Add dinitroaniline herbicides, photosynthetic inhibitor herbicides, oxyfluorfen, and carbaryl to Roseville sites PGC010, PGC021, PGC022, PGC040.	Diuron, oxyfluorfen, pendimethalin, prodiamine, oryzalin, simazine, and trifluralin identified as high priority pesticides in northern California; these are long term monitoring sites.
Monitor only two rainstorm events (not three). Dry (non-rainstorm) sampling at the CWQTPs four times a year) will be maintained.	Free up resource for additional monitoring at CWQTPs and to add analytes mentioned above.
Limit toxicity testing to dry (non-rainstorm) monitoring.	Initial data indicates the small CWQTPs are more effective during non-rainstorm urban runoff.
Drop sites FOL6 and FOL100.	Folsom area will just concentrate on the effectiveness of the CWQTPs.
Add sampling sites TRP1 and TRP2 at a second CWQTP in Folsom (non-rainstorm sampling).	Initial data indicates that small CWQTPs are more effective mitigating non-rainstorm pesticide urban runoff.
Drop chlorothalonil from monitoring.	Chlorothalonil is a top priority pesticide but 94% of urban use is on golf courses and sod/professional fields (Kelly 2012) which are not in the sampling areas, so detections of chlorothalonil are unlikely.
Continue sediment sampling at FOL2, FOL3, FOL5, PGC010, PGC021/022, and PGC040.	Not specifically listed in FY 12-13 protocol due to analysis by CDFW but sediments were collected at these sites in FY12-13.

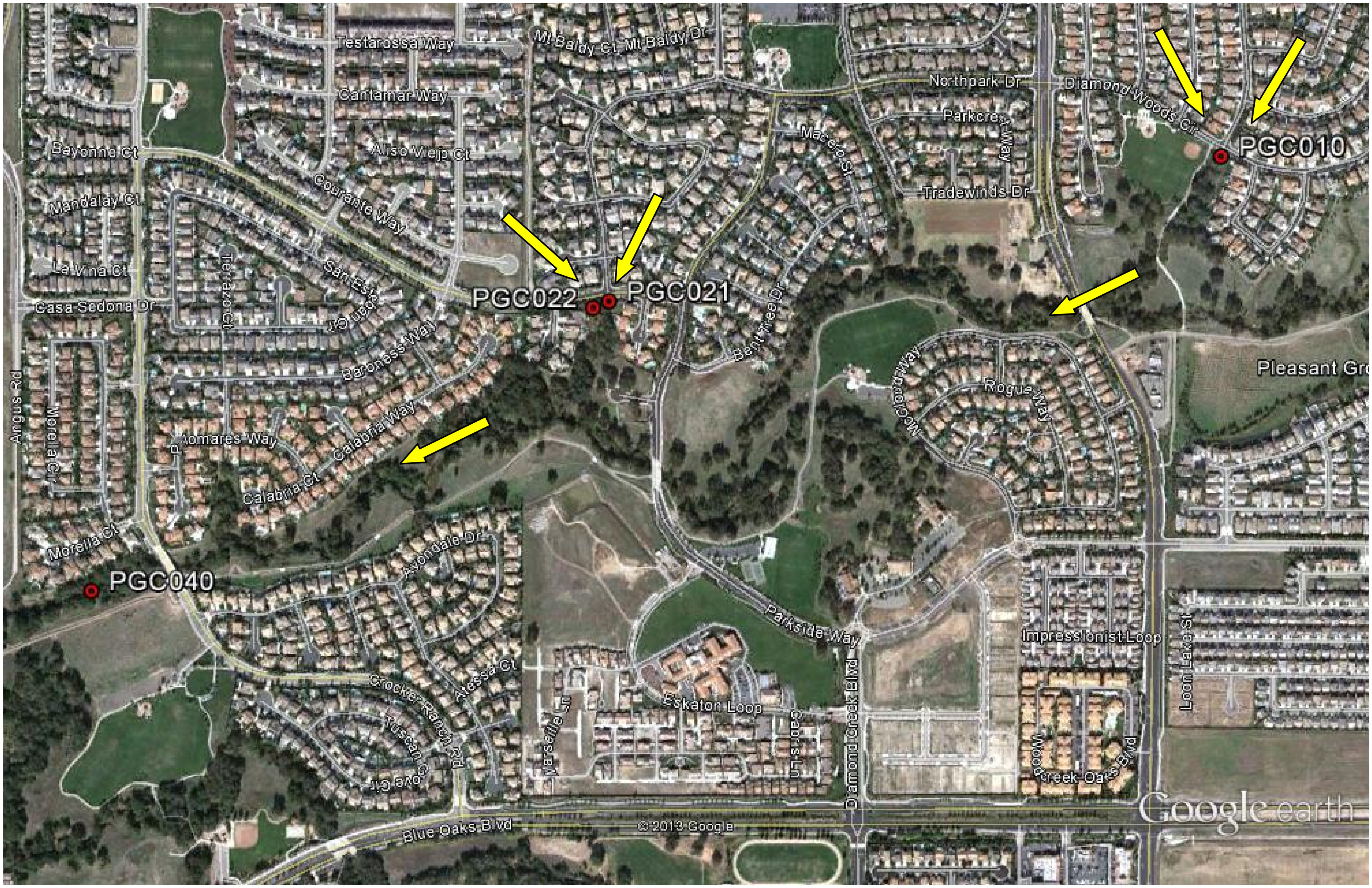

Figure 1. Long-term monitoring sites in Roseville, California. Arrows indicate water flow direction. PGC040 is the downstream sampling site.

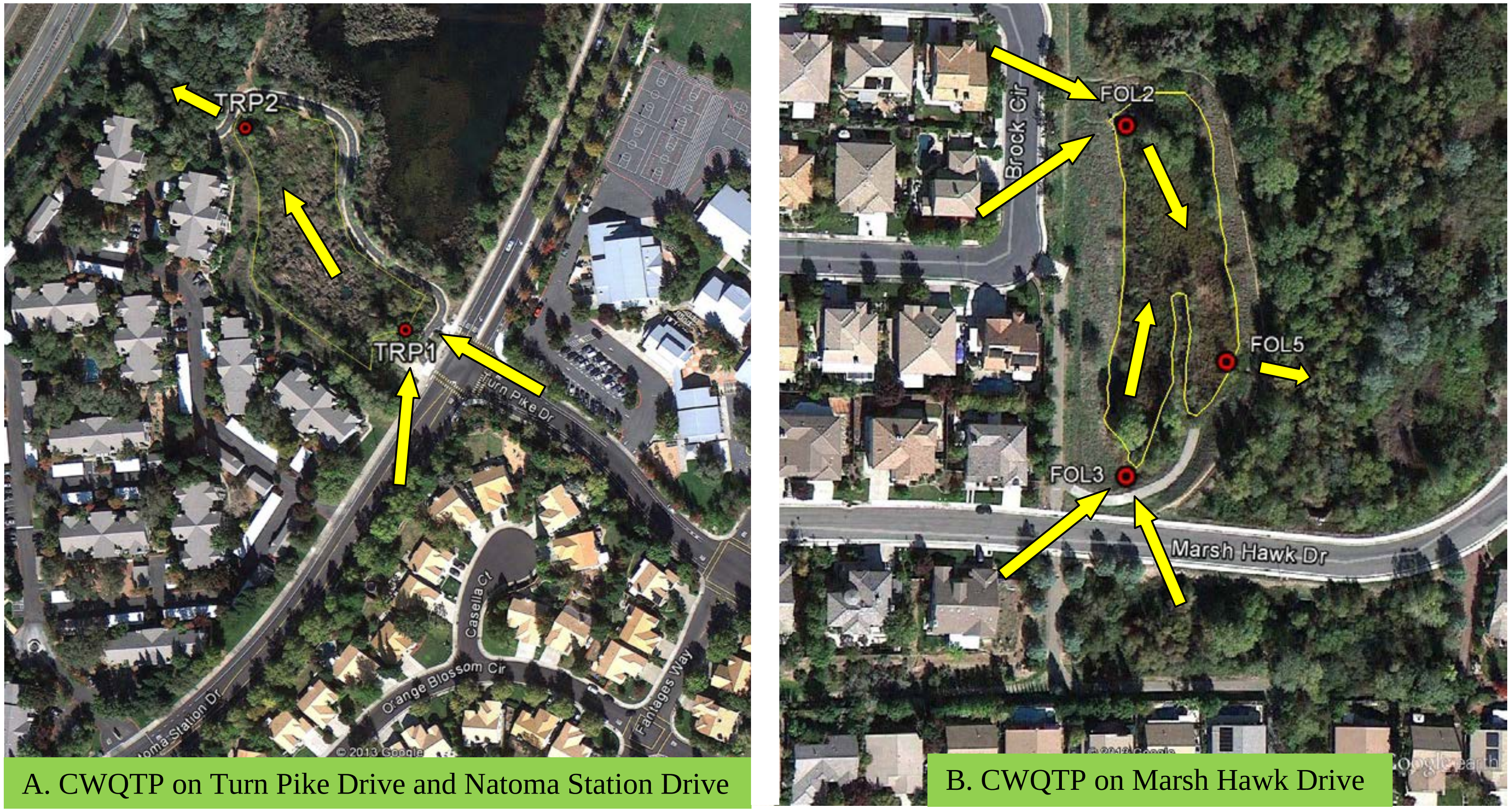

Figure 2. Two constructed water quality treatment ponds (CWQTP) in Folsom California. The CWQTPs are outlined in yellow with arrows indicating water flow direction (inputs at TRP1, FOL2, and FOL3; outfalls at TRP2 and FOL5).

Appendix. Priority model pesticides based on Sacramento and Placer Counties urban usage (2009-2011). Pesticides with priorities greater or equal to the priority score of 6 are listed.

Pesticide	Priority Score	Pesticide	Priority Score
Bifenthrin	30	Triclopyr, butoxyethyl ester	9
Permethrin	28	Mancozeb	9
Copper	20	Chlorfenapyr	8
Chlorothalonil	20	Oxadiazon	8
Cypermethrin	20	S-Metolachlor	8
Fipronil	20	Cyhalothrin (gamma)	8
Cyfluthrin	18	Diflubenzuron	7
Pendimethalin	16	Isoxaben	6
Prodiamine	16	Thiophanate-methyl	6
Oryzalin	15	Tebuthiuron	6
Diquat dibromide	15	Propiconazole	6
Malathion	15	Simazine	6
Sulfometuron-methyl	15	2,4-D, 2-ethylhexyl ester	6
Oxyfluorfen	15	Iprodione	6
Flumioxazin	15	Azoxystrobin	6
Cyhalothrin (lambda)	14	2,4-D	6
Imidacloprid	12	PCNB	6
Dithiopyr	12	MCPP-P, dimethylamine salt	6
Halosulfuron-methyl	12	Esfenvalerate	6
Acrolein	12	Chlorpyrifos	6
Diuron	12	Endosulfan	6
Trifluralin	12	DDVP	6
Cyfluthrin (beta)	12	Fenvalerate	6
Deltamethrin	12	Abamectin	6
Chlorsulfuron	12	Tralomethrin	6
Carbaryl	10		

Yellow = in current monitoring plan, green = previously monitored, blue= monitored as part of isomer mixture.