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STUDY 270: URBAN PESTICIDE MONITORING IN SOUTHERN CALIFORNIA DURING FISCAL YEAR 2011-2012

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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. Yearly, applicators generally report over 12 million pounds active ingredient (a.i.) of urban pesticide use in California (CDPR, 2009a). 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, watershed) applications. Non-agricultural use includes applications by a licensed pesticide applicator for residential, industrial, institutional, structural, or vector control purposes (CDPR, 2010a). 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). Appendix 1 shows the 2009 reported use of selected pesticides for non-agricultural purposes within Orange County, CA (CDPR 2010b). There were a total of 70,386 pounds of selected active ingredients (a.i.) used for non-agricultural use in 2009, with pyrethroids making up 63% of total usage.

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, OPs, and fipronil. 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). During the 2008-2009 monitoring events, CDPR detected carbaryl, diuron, simazine, triclopyr, dicamba, 2,4-D, and MCPA in addition to those mentioned above.

Study 270, which is a continuation of monitoring efforts of Studies 249 and 265, will provide data used to evaluate urban pesticide water quality trends. With new surface water regulations being proposed in California, long term (approximately 5 years) 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. A summary of results from 2010-2011 fiscal year (FY) sampling efforts and modifications from the previous sampling plan is presented in section 5.1.

2.0 OBJECTIVE

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

1) Determine presence and concentrations of selected pesticides in urban runoff under dry season and stormwater conditions;
2) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity benchmarks;
3) Observe the mitigation effects of a small constructed wetland on pesticide concentrations in receiving waters;
4) Observe the mitigation effects of a small water treatment facility receiving dry season flow;
5) Monitor downstream transport of pyrethroids bound to sediments throughout watershed during various flow conditions.

3.0 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.

4.0 STUDY PLAN

4.1 Monitoring Sites

Water quality monitoring will be conducted at 10 sites within Orange County, California (Table 1). Details of site descriptions are provided in Appendix 2. There are eight sampling locations within the Salt Creek watershed (Figure 1) and three within the Wood Creek watershed (Figure 2).

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, schools, and a golf course.

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

Area	Stormdrain Outfall	Receiving Water	Total Sites
Salt Creek	5	3	7
Wood Creek	2	1	3
Total	6	4	10

4.2 Sampling

Water sampling. Samples will be collected during two dry season and two storm sampling events. Dry season sampling will occur between August - September, 2011 and April-June, 2012. We will conduct storm sampling with the first major storm (rain) event of the 2011-2012 season (average highest precipitation is December – March) and with a major storm in the winter or early spring of 2012 (Table 2).

CDPR staff will collect water samples for chemical analysis and for determining total suspended solids (TSS) and total organic carbon (TOC). During creek sampling, CDPR will collect samples from the center channel 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. Water 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. Where applicable, sediment samples will be collected in 1 quart glass Mason Jars using passive sediment collection samplers (Budd, 2009) and analyzed for pyrethroids.

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	**Aug-Sept 2011**	**Apr-Jun 2012**	**Nov-Dec 2011**	**Jan-Mar 2012**
Event	Dry season		Storm Events	
Water Samples				
Number of sites	10	10	9	9
Number of samples	90	90	81	81
Sediment Samples				
Number of sites	6	6	2	0
Number of samples	6	6	2	0

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, 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. 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) (Puckett, 2002) will be consulted where applicable.

5.0 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 seven different analyte groups which will include up to 28 chemical compounds for analysis (Table 3, Appendix 3).

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	Media	Analytical Method	Method Detection Limit (µg L^{-1})	Reporting Limit (µg L^{-1})
Chlorthalonil	Water	LC-MS/MS	0.0348	0.05
Fipronil & Degradates	Water	GC-MSD (SIM)	0.003 – 0.005	0.05
Imidacloprid	Water	GC-MS	0.01	0.05
Organophosphorus Insecticides	Water	GC-FPD	0.008 – 0.0142	0.05
	Water	GC-MS	0.0012 – 0.0079	0.01
Pendimethalin	Water	LC-MS/MS	0.012	0.05
Phenoxy 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	0.07 – 0.87	1 (µg Kg^{-1})

5.1 Analytical Justification

The current sampling plan is an extension of sampling conducted during fiscal year 2010-2011. The details of the previous sampling is described in the document titled Study 270: Urban pesticide monitoring in southern California, available at: http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study270protocol.pdf. Sampling locations and scheduling will remain consistent during the 2011-2012 fiscal year. The current sampling plan has several modifications to the pesticides monitored however. Decisions to keep, add, or delete pesticide analysis from the current monitoring plan were based on a review of current pesticide use (Appendix 1), as well as frequency of detections (Figure 4) and potential toxicity (Appendix 4-5) of samples collected during previous monitoring. Table 4 below is a summary of discrepancies between the current and the 2010-2011 FY monitoring plan.

Table 4. Justification for modifications to analytical schedule from FY 2010-2011 sampling plan.

Analyte	Addition/ Deletion from SP	Justification
Chlorothalonil	Addition	High* use, very low aquatic benchmark (0.6 ppb)
Pendimethalin	Addition	Moderate use, low aquatic benchmark (5.2 ppb)
Carbaryl	Deletion	Low use, low detection frequency (17%), 3% above benchmark in Salt Creek, 0% in Wood Creek
‘Triazine’ screen – bromacil, diuron, haxazinon, simazine	Deletion	Low -moderate use, diuron moderate detection frequency (50%), others not detected, no detects above aquatic benchmarks
Deltamethrin, Fenpropathrin, Resemethrin	Deletion	Deltamethrin – moderate use, low detection frequency (<10%), others low use and no detections

* Use Rating based on 2009 use in Orange County, CA: High = >10,000 lbs, Moderate = 1,000-10,000 lbs, Low = <1,000 lbs

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. 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.

7.0 TIMELINE

Field Sampling: July 2011 – June 2012
Chemical Analysis: July 2011 – October 2012
Draft Report: December 2012

8.0 LABORATORY BUDGET

The total cost for the CDFA chemical analyses is $142,850 (Table 4).

Table 4. Analytical yearly cost estimates for urban samples collected in Southern California based on 2010 per sample costs.

Site Location	Analytical Suite	Matrix	# Sites	Storm Samples	Dry Season Samples	Cost/ Sample	**Cost**
SC1, SC2, SC3, SC4, SC6, SC7, WC1, WC2, WC3	Chlorothalonil	W	9	2	2	550	**19,800**
	Fipronil	W	9	2	2	500	**18,000**
	Imidacloprid	W	9	2	2	500	**18,000**
	OP (short)	W	9	2	2	500	**18,000**
	Pendimethalin	W	9	2	2	450	**16,200**
	Phenoxy Herbicides	W	9	2	2	575	**20,700**
	Pyrethroids-6	W	9	2	2	500	**18,000**
SC7A	Chlorothalonil	W	1		2	550	**1,100**
	Fipronil	W	1		2	500	**1,000**
	Imidacloprid	W	1		2	500	**1,000**
	OP (short)	W	1		2	500	**1,000**
	Pendimethalin	W	1		2	450	**900**
	Phenoxy Herbicides	W	1		2	575	**1,150**
	Pyrethroids-6	W	1		2	500	**1,000**
SC2, SC5, SC6, SC7	Pyrethroids-6	S	4	0	2	500	**4,000**
WC1, WC2	Pyrethroids-6	S	2	1	2	500	**3,000**
						Total	**$142,850**

OP = organophosphate, W = water, S = sediment

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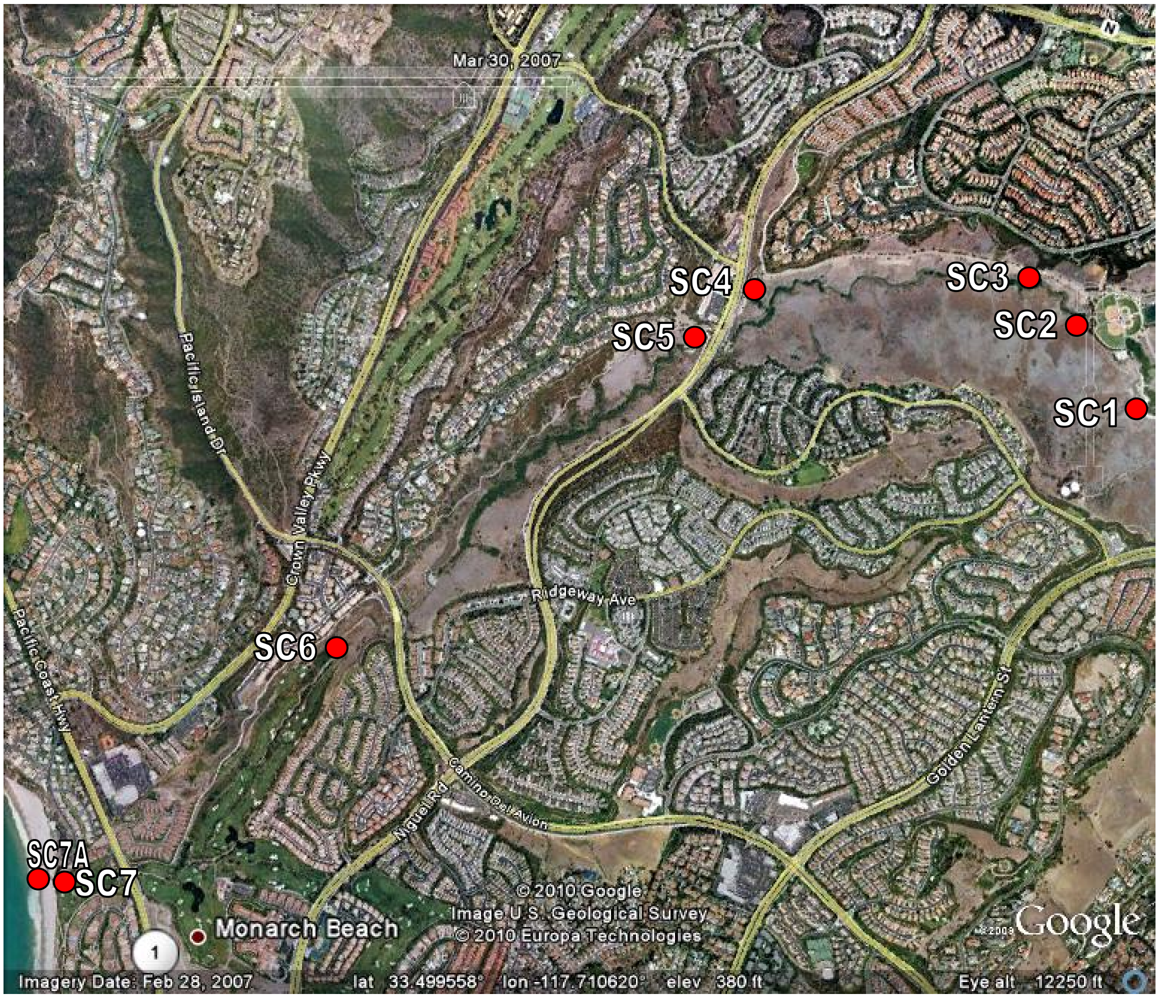

Figure 1. Sampling locations within Salt Creek watershed, Orange County, CA

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

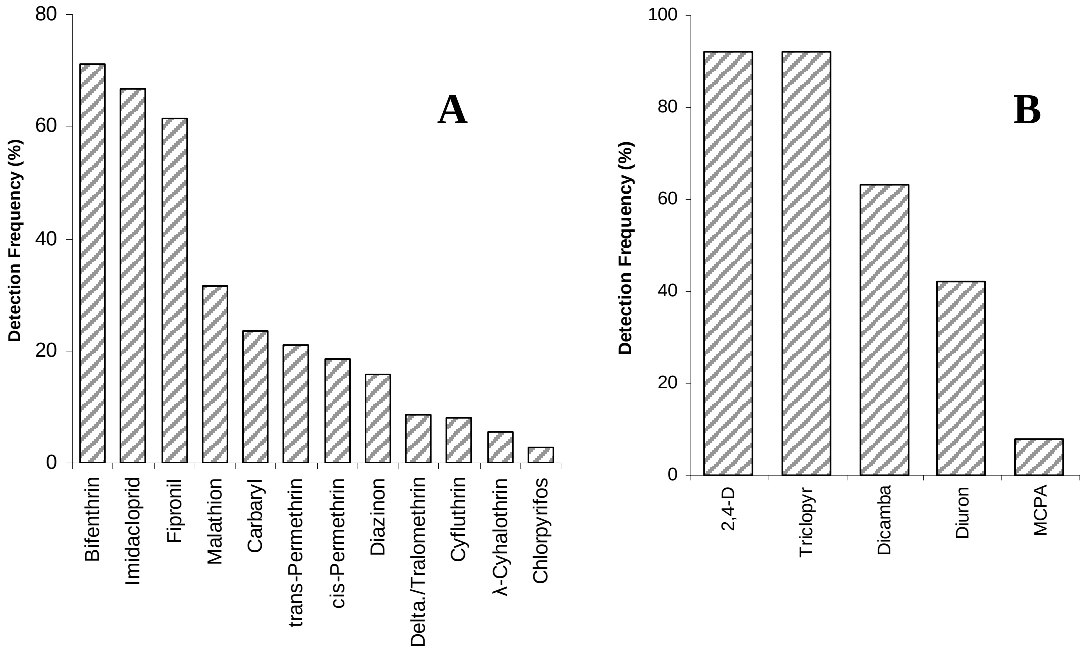

Figure 3. Frequency of detections of insecticides (A) and herbicides (B) within Salt Creek watershed between December, 2009 and February 2011.

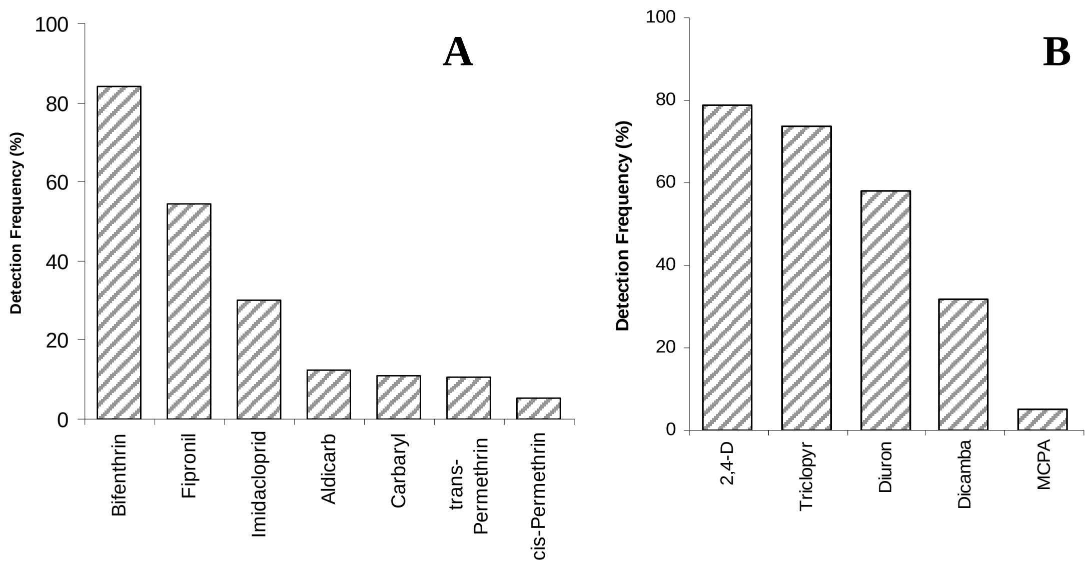

Figure 4. Frequency of detections of insecticides (A) and herbicides (B) within Wood Creek watershed between December, 2009 and February 2011.

Appendix 1: Non-agricultural pesticide usage (lbs) in Orange County, CA

Analyte	2009 Use	2005-2009 Total	2005-2009 Average
Carbamates			
Carbaryl	49	559	112
Chloronitrils			
Chlorothalonil	14,726	69,829	13,966
Dinitoanalines			
Pendamethalin	1,779	7,185	1,437
Fipronil + Degradates			
Fipronil	3,968	38,842	7,768
Neonicotinoids			
Imidacloprid	1,000	41,283	8,257
Organophosphates			
Chlorpyrifos	263	6,312	1,262
Diazinon	15	565	113
Dimethoate	18	77	15
Malathion	1,134	8,755	1,751
Total Organophosphates		15,709	
Phenoxy			
2,4-D	7	179	36
Dicamba	132	727	145
Triclopyr	2,891	26,679	5,336
Total Phenoxy		27,585	
Pyrethroids			
Bifenthrin	3,489	39,729	7,946
Cyfluthrin	1,508	7,663	1,533
Cypermethrin	2,673	16,386	3,277
Deltamethrin	317	2,219	444
Esfenvalerate	28	108	22
Fenpropathrin		0	0
λ-Cyhalothrin	490	5,255	1,051
Permethrin	35,801	203,636	40,727
Resmethrin	98	346	69
Total Pyrethroids		275,341	
Triazines			
Bromacil	597	2,980	596
Diuron	4,979	22,028	4,406
Hexazinone	920	2,036	407
Simazine	91	6,304	1,261
Total Triazines		33,348	

Appendix 2. Detailed sampling site information

Watershed	Site ID	Northing	Easting	Site type
Salt Creek	SC-1	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	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	33 30 20.23	117 42 30.87	Receiving water
Salt Creek	SC-6	33 29 31.91	117 43 02.68	Stormdrain
Salt Creek	SC-7	33 28 53.97	117 43 26.55	Receiving water
Salt Creek	SC-7A	33 28 54.12	117 43 27.37	Receiving water
Wood Creek	WC-1	33 34.56.56	117 44 43.02	Stormdrain
Wood Creek	WC-2	33 34 53.70	117 44 44.65	Receiving water
Wood Creek	WC-3	33 34 53.69	117 44 44.60	Stormdrain

Appendix 3. Active ingredient chemical analysis lists

Fipronil + Metabolites	Organophosphates	Pyrethroids
Desulfinyl fipronil	Chlorpyrifos	Bifenthrin
Desulfinyl fipronil amide	Diazinon	Cyfluthrin
Fipronil	Dimethoate	Cypermethrin
Fipronil amide	Malathion	Fenvalerate/esfenvalerate
Fipronil sulfide	Methidathion	λ-cyhalothrin/epimer
Fipronil sulfone		cis-Permethrin
		trans-Permethrin
Chloronitriles	**Neonicotinoids**	**Phenoxy Herbicides**
Chlorothalonil	Imidacloprid	2,4-D
		Dicamba
Dinitroanalines		MCPA
Pendamethalin		Triclopyr

Appendix 4. Detections above aquatic benchmarks of samples collected within Salt Creek Watershed

Analyte	Minimum Benchmark*	Median Concentration*	Maximum Concentration*	% Above Benchmark
Carbamates				
Carbaryl	0.5	nd	0.5	3
Fipronil + Degredates				
Fipronil	0.011	0.07	0.6	82
Fipronil Sulfide	0.11	trace	0.01	0
Fipronil sulfone	0.037	0.07	0.3	77
Neonicotinoids				
Neonicotinoids				
Imidacloprid	1.05	0.06	0.7	0
Organophosphates				
Chlorpyrifos	0.04	nd	0.1	3
Diazinon	0.11	nd	0.1	3
Malathion	0.035	nd	4.1	34
Phenoxy				
Dicamba	61	0.07	1.2	0
MCPA	170	nd	7.3	0
Triclopyr	100	0.15	1.1	0
Pyrethroids				
Bifenthrin	1.3	8.1	70	76
Cyfluthrin	7	nd	27	16
λ-Cyhalothrin	2	nd	15	8
cis-Permethrin	1.4	nd	260	29
trans-Permethrin	1.4	nd	351	29
Triazines				
Diuron	2.4	nd	0.3	0

*Concentrations in ppb except pyrethroids (ppt)

Appendix 5. Detections above aquatic benchmarks of samples collected within Wood Creek watershed

Analyte	Minimum Benchmark*	Median Concentration*	Maximum Concentration*	% Above Benchmark
Carbamates				
Carbaryl	0.5	nd	0.4	0
Fipronil + Degredates				
Fipronil	0.011	0.1	0.3	73
Fipronil Sulfide	0.11	trace	0.01	0
Fipronil Sulfone	0.037	0.1	0.1	68
Neonicotinoids				
Imidacloprid	1.05	trace	0.1	0
Phenoxy				
Dicamba	61	nd	0.1	0
MCPA	170	nd	0.1	0
Triclopyr	100	0.1	0.9	0
Pyrethroids				
Bifenthrin	1.3	14	134	89
Cyfluthrin	7	nd	3	0
λ-cyhalothrin	2	nd	7	11
cis-Permethrin	1.4	nd	217	6
trans-Permethrin	1.4	nd	311	17
Triazines				
Diuron	2.4	0.07	0.4	0

*Concentrations in ppb except pyrethroids (ppt)