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Environmental Monitoring Branch
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STUDY 270: URBAN PESTICIDE MONITORING IN SOUTHERN CALIFORNIA

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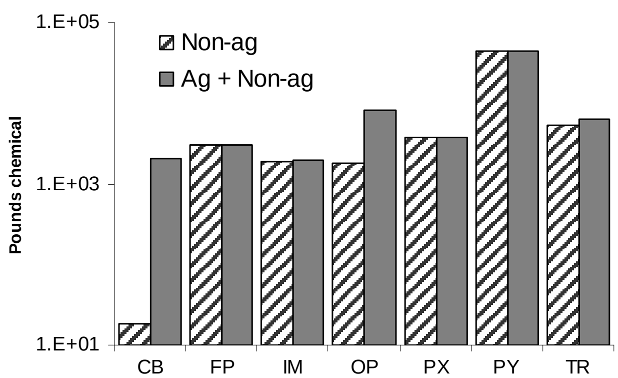
1.0 INTRODUCTION

Urban runoff is an important source of pesticide loading into surrounding waterways and validates monitoring efforts to characterize composition. 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). Figure 1 below shows the reported agricultural and non-agricultural usage of selected pesticide active ingredients within Orange County, CA, for the year 2008 (CDPR 2010b). There were a total of 59,724 pounds of selected active ingredients (a.i.) used for non-agricultural use in 2008, with pyrethroids making up 74% of total usage.



	Non-Ag
Carbamates (CB)	19
Fipronil + Met. (FP)	3053
Imidacloprid (IM)	1864
Organophosphates (OP)	1816
Phenoxy herbicides (PX)	3764
Pyrethroids (PY)	43949
Triazine herbicides (TR)	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, 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 (Appendix 1). Study 270 will additionally monitor imidacloprid, which is a moderately toxic and persistent (>30 d) neonicotinoid insecticide.

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.

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) 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). 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 2. 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 dry season and two storm sampling events. Dry season sampling will occur in September, 2010 and May, 2011. We will conduct storm sampling with the first major storm (rain) event of the 2010-2011 season (average highest precipitation is December – March) and with a major storm in the winter or early spring of 2011 (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	Sept 2010	May 2011	Nov-Dec 2010	Jan-Mar 2011
Event	Dry season		Stormwater	
Water Samples				
Number of sites	9	8	9	8
Number of samples	90	80	90	80
Sediment Samples				
Number of sites	7	7	2	2
Number of samples	1	1	2	2

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) (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 32 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})
Carbamate Insecticides	Water	HPLC	0.01 – 0.02	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
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})
Triazine Herbicides	Water	LC-MS/MS	0.01 – 0.031	0.05

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 2010 – June 2011
Chemical Analysis: July 2010 – October 2011
Draft Report: December 2011

8.0 LABORATORY BUDGET

The total cost for the CDFA chemical analyses is $141,050 (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	Carbaryl	W	8	2	2	400	**12,800**
	Fipronil	W	8	2	2	500	**16,000**
	OP (short)	W	8	2	2	500	**16,000**
	Phenoxy Herbicides	W	8	2	2	575	**18,400**
	Triazines (short)	W	8	2	2	450	**14,400**
	Imidacloprid	W	8	2	2	500	**16,000**
	Pyrethroids	W	8	2	2	800	**25,600**
WC3	CB- Carbaryl	W	1	1	1	400	**800**
	Fipronil	W	1	1	1	500	**1,000**
	OP (short)	W	1	1	1	500	**1,000**
	Phenoxy Herbicides	W	1	1	1	575	**1,150**
	Pyrethroids	W	1	1	1	800	**1,600**
	Triazines (short)	W	1	1	1	450	**900**
	Imidacloprid	W	1	1	1	500	**1,000**
SC2, SC4, SC5, SC6, SC7	Pyrethroids	S	5	0	2	800	**8,000**
WC1, WC2	Pyrethroids	S	2	2	2	800	**6,400**
						Total	**$141,050**

OP = organophosphate, W = water, S = sediment

9.0 LITERATURE CITED

Bennett, K. 1997. California Department of Pesticide Regulation SOP FSWA002.00: Conducting surface water monitoring for pesticides. Accessed at http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa002.pdf on December 10, 2009.

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. 2009. Central Valley Regional Water Quality Control Board. Accessed at http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/impaired_waters_list/index.shtml on December 8, 2009.

CDPR. 2009a. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed at http://www.cdpr.ca.gov/docs/pur/purmain.htm on December 8, 2009.

CDPR. 2009b. Surface water protocols: Study 249a and 249b. Accessed at http://www.cdpr.ca.gov/docs/emon/surfwtr/protocol.htm December 8, 2009.

CDPR. 2009c. Surface water regulations. Accessed at http://www.cdpr.ca.gov/docs/emon/surfwtr/regulatory.htm December 8, 2009.

CDPR 2010a. Department of Pesticide Regulation's Agricultural and Non-Agricultural Pest Control Use. Bulletin number ENF-003. Accessed at http://www.cdpr.ca.gov/docs/enforce/enf_003_rev_5-09.pdf on August 31, 2010.

CDPR. 2010b. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed at http://www.cdpr.ca.gov/docs/pur/purmain.htm on January 21, 2010.

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. Accessed at http://www.cdpr.ca.gov/docs/emon/pubs/sopequip.htm on December 9, 2009.

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. Accessed at http://www.cdpr.ca.gov/docs/emon/pubs/sopfield.htm on December 9, 2009.

Oki, L. and D. Haver. 2009. Monitoring pesticides in runoff in Northern and Southern California neighborhoods. Accessed at http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations.htm on December 8, 2009.

Jones, D. 1999. California Department of Pesticide Regulation SOP QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory. Accessed at http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc0401.pdf on December 10, 2009.

Kelley, K. and K. Starner. 2004. Preliminary results for Study 219: Monitoring surface waters and sediments of the Salinas and San Joaquin River Basins for organophosphate and pyrethroid pesticides. Accessed at http://www.cdpr.ca.gov/docs/emon/surfwtr/swmemos.htm on December 10, 2009.

Puckett, M. 2002. Quality assurance management plan for the state of California's surface water ambient monitoring program (SWAMP). California Department of Fish and Game, Monterey, CA. Accessed at http://www.waterboards.ca.gov/water_issues/programs/swamp/qamp.shtml on December 10, 2009.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry Laboratory Quality Control. Accessed at http://www.cdpr.ca.gov/docs/emon/pubs/sop.htm on December 9, 2009.

UP3 Project. 2007. Pesticide Sales and Use Information. Pesticides in urban surface water: Urban pesticide use trends report 2007. Accessed at http://www.up3project.org/up3_use.shtml on December 9, 2009.

USEPA. 1971. National Exposure Research Laboratory (NERL), Microbiological and Chemical Exposure Assessment Research Division (MCEARD). Method 160.2, Residue, Non-Filterable (Gravimetric, Dried at 103 – 105° C). Accessed at http://www.caslab.com/EPA-Method-160_2/ on December 10, 2009.

USEPA. 2002. Guidance for quality assurance project plans (QA/G-5), EPA/240/R-02/009. Accessed at http://www.epa.gov/quality/qs-docs/g5-final.pdf on December 10, 2009.

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.

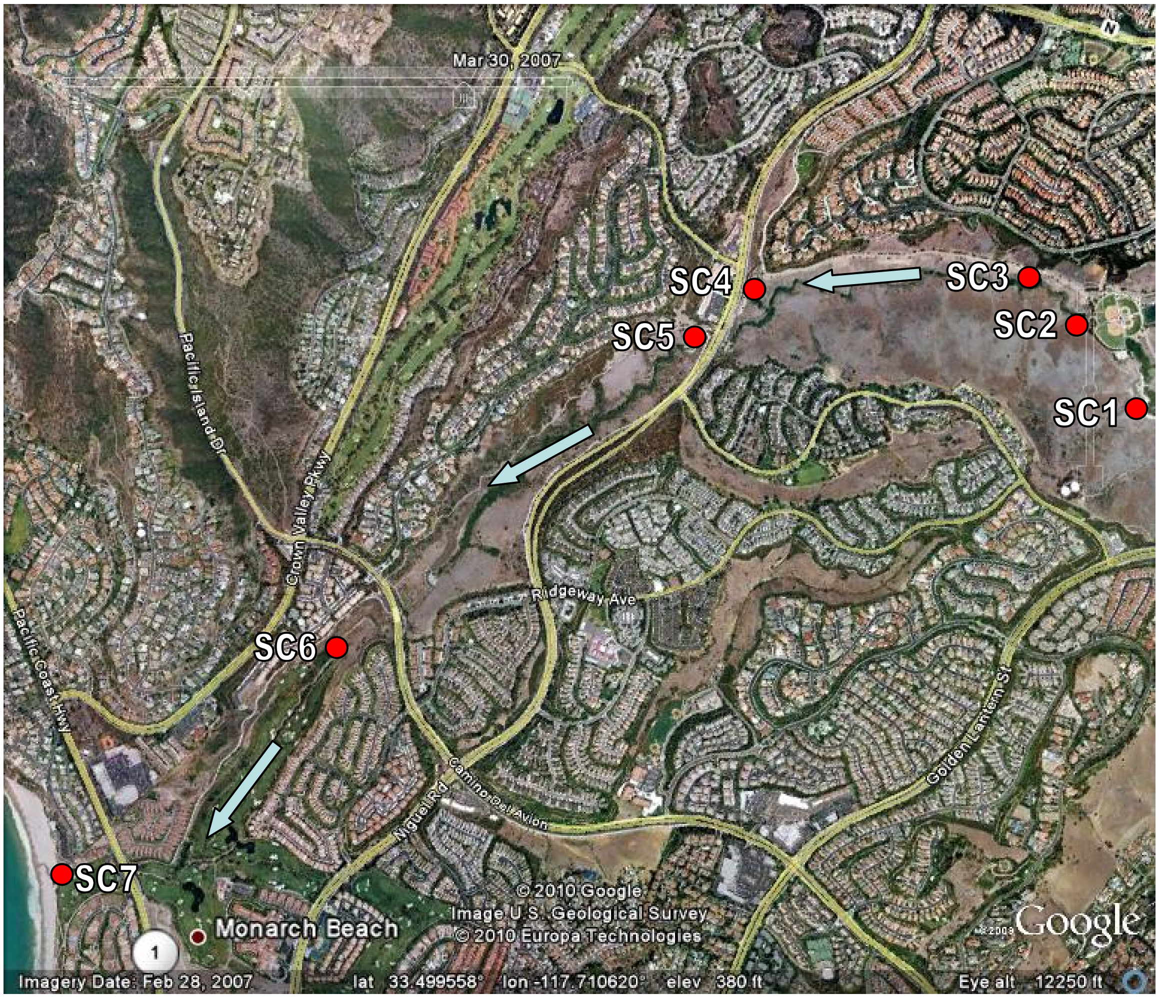


Figure 2. Sampling locations within Salt Creek watershed, Orange County, CA

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

Appendix 1. Analytes detected above minimum detection limit during 2008-2009 sampling events

AnalyteGroup	AnalyteName	Max Concentration (ug/L)	% >MDL
Carbamates	Aldicarb	0.17	2
Carbamates	Carbaryl	0.68	48
Carbamates	Oxymyl	0.11	2
Fipronil	Fipronil+ met.	2.11	100
Organophosphates	Diazinon	0.12	12
Organophosphates	Malathion	0.24	31
Phenoxy	2,4-D	2.37	87
Phenoxy	Dicamba	1.16	65
Phenoxy	MCPA	7.30	22
Phenoxy	Triclopyr	1.33	97
Pyrethroids*	Bifenthrin	0.05 / 81.9	41 / 83
Pyrethroids	Cyfluthrin	nd / 22.6	0 / 75
Pyrethroids	Cypermethrin	0.02 / 5.34	5 / 17
Pyrethroids	Deltamethrin	nd / 4.2	0 / 75
Pyrethroids	Fenvalerate/esfenvalerate	0.03 / 4.9	5 / 33
Pyrethroids	Lambda-cyhalothrin epimer	0.02 / 5.6	5 / 69
Pyrethroids	Permethrin cis	0.26 / 41.5	18 / 92
Pyrethroids	Permethrin trans	0.35 / 52.3	14 / 100
Pyrethroids	Resmethrin	nd / 5.7	0 / 8
Triazines	Diuron	0.44	79
Triazines	Prometon	< RL	3
Triazines	Simazine	0.10	38

*First value represents water samples (ug/L), second value represents sediment samples

Appendix 2. 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 3. Active ingredient chemical analysis lists

Carbamates	**Organophosphates**	**Pyrethroids**
Carbaryl	Chlorpyrifos	Bifenthrin
	Diazinon	Cyfluthrin
Fipronil + Metabolites	Dimethoate	Cypermethrin
Desulfinyl fipronil	Malathion	Deltamethrin
Desulfinyl fipronil amide	Methidathion	Fenopropathrin
Fipronil		Fenvalerate/esfenvalerate
Fipronil amide		λ-cyhalothrin/epimer
Fipronil sulfide		cis-Permethrin
Fipronil sulfone		trans-Permethrin
		Resmethrin
Neonicotinoids	**Phenoxy Herbicides**	**Triazine Herbicides**
Imidacloprid	2,4-D	Bromacil
	Dicamba	DACT
	MCPA	Diuron
	Triclopyr	Hexazinone
		Simazine