Index for the Supporting Information (FY12-13)

Appendix I. Protocol Study 269

Appendix II. Sampling Site Information

Appendix III. Water Quality Data

Appendix IV. Water and Sediment Monitoring Data

Appendix V. Aquatic Toxicity Data

Appendix VI. Analytical Methods

Determination of bensulide and imidacloprid in surface water (CDFA)

Determination of chlorothalonil in ground and surface water (CDFA)

Determination of ethalfluralin, trifluralin, benfluralin, prodiamine, pendimethalin, oxyfluorfen, and oryzalin in surface water (CDFA)

Determination of fipronil and metabolites in surface water using gas chromatography/mass spectrometry (CDFA)

Determination of n-methylcarbamate pesticides in surface water using high performance liquid chromatography and post-column derivatization (CDFA)

Determination of organophosphate pesticides in surface water using gas chromatography with mass selective detection (MSD) (CDFA)

Determination of phenoxy herbicides in surface water using gas chromatography/MSD (CDFA)

Determination of pyrethroids in sediment water using triple quadrupole (GC/MS/MS) (CDFA)

Determination of pyrethroid pesticides in sediment (CDFW)

Fipronil and degradates by LC/MS/MS (CDFW)

Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812

STUDY 269. Surface Water and Sediment Monitoring in a Constructed Water Quality Pond in Folsom, CA, 2012-2013

Michael Ensminger
June 2012

I. INTRODUCTION

The California Department of Pesticide Regulation (CDPR) Surface Water Program has been monitoring urban pesticide runoff in northern and southern California since 2008. The specific focus of Study 269 is surface water monitoring in the Sacramento area of northern California, where 24 different urban use pesticides have been detected (Table 1). The objectives of recent monitoring has been to: 1) identify the types of pesticides and their concentrations in urban runoff from selected sites in Roseville and Folsom, CA, and 2) to determine the magnitude of concentration decreases as runoff progresses through urban tributary streams and constructed water quality ponds (Ensminger 2011). Preliminary data indicate that water quality ponds have more promise than tributary streams to mitigate insecticide concentrations in urban runoff (Figure 1). For FY 2012-2013 we will further determine the effectiveness of the Folsom water quality pond in mitigating pesticide runoff. Monitoring in Roseville will be put on a six month hiatus to devote resources to this objective.

II. OBJECTIVES

For FY 2012–2013, the objectives of this Study 269 are four-fold:
1) Determine the presence and concentrations of selected pesticides in two urban storm drain outfalls which are at inlets to a water quality pond in Folsom, CA;
2) Compare the presence and concentrations of selected pesticides at the water quality pond inlet to the pesticide concentrations at a) the water quality pond outlet, and b) at the water quality pond outlet after it passes through a streamed area;
3) Determine the presence and concentrations of selected pesticides exiting from the entire neighborhood in Folsom CA;
4) 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 2011a, 2011b).

III. 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 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, Department of Food and Agriculture (CDFA)
- Analytical Chemistry, sediment: Department of Fish and Game
- Collaborator: Lorence Oki, Ph.D., University of California at Davis, CE Associate 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

Sampling will occur in Folsom, CA, located in the greater Sacramento area. Water samples will be collected at five different sites (Table 2 and Figure 2). FOL002 and FOL003 are outfalls from specific neighborhood areas and are a measure of the runoff from urban homes. FOL002 and FOL003 are inputs to a water quality pond in Folsom, CA. FOL005 is the water quality pond output and sampling at this outfall will determine the effectiveness of the water quality pond to remove pesticide concentrations from the urban runoff. FOL006 receives the water from FOL005 without any further direct inputs but is buffered by additional water quality ponds which feed into FOL006. FOL100 is at the end of the Folsom, CA neighborhood with other inputs after the water quality pond (*i.e.*, FOL006). FOL100 will measure the total output the Folsom neighborhood is contributing to the environment. Additional monitoring in Roseville CA will be conducted at selected sites for long term monitoring (Ensminger 2011).

V. SAMPLING METHODS

There will be four dry season and three rainstorm sampling events (Table 3). Water samples will be collected generally as grab samples. However, some of the storm runoff samples will be composite samples collected by automated sampling equipment. Sediment samples will also be collected quarterly (Table 4).

VI. 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 six different analyte groups which will include 23 pesticides (Table 5). The California Department of Fish and Game (CDFG) will conduct pesticide analyses for pyrethroids in sediments (Table 6).

VII. 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. The data collected from this project may be used to develop or calibrate an urban pesticide runoff model.

VIII. TIMETABLE

Field Sampling:	July 2012 – June 2013
Chemical Analysis:	July 2012 – October 2013
Draft Report:	April 2014

IX. LABORATORY BUDGET

The total cost for the CDFA chemical analyses is $140,820 (water samples; Table 3) and $9100 (sediment samples; Table 4) from CDFG. This cost includes field QC sample analysis (field blanks and field duplicates).

X. LITERATURE CITED

Ensminger, M. 2011. Study 269: Further characterization of Sacramento, California area urban neighborhoods. Addendum for Fiscal Year 2011-2012. http://cdpr.ca.gov/docs/emon/pubs/protocol/study269protocol_add.pdf. Accessed 22 June 2012.

Fojut, T. J., Palumbo, A. J., Tjeerdema, R. S. (2012a). Aquatic life water quality criteria derived via the UC Davis method: II Pyrethroid Insecticides. In R.S. Tjeerdema (Ed.), Aquatic life water quality criteria for selected pesticides (pp. 51-103). Reviews of Environmental Contamination and Toxicology 216, doi:10.1007/978-1-4614-2260-0_3

Fojut, T. J., Palumbo, A. J., Tjeerdema, R. S. (2012b). Aquatic life water quality criteria derived via the UC Davis method: III. Diuron. In R.S. Tjeerdema (Ed.), Aquatic life water quality criteria for selected pesticides (pp. 105-141). Reviews of Environmental Contamination and Toxicology 216, doi:10.1007/978-1-4614-2260-0_3

U.S. Environmental Protection Agency (2012). Office of Pesticide Programs. Aquatic life benchmarks. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm. Accessed 22 June 2012.

Table 1. Pesticides detected in the Sacramento area during CDPR urban monitoring, 2008-2012.

Pesticide	Number of Detections[a]		Pesticide	Number of Detections	
	Folsom	Roseville		Folsom	Roseville
2,4-D	20	56	Fipronil desulfinyl	1	13
Bifenthrin	20	78	Fipronil sulfone	2	20
Carbaryl	2	13	Imidacloprid[b]	4	9
Chlorothalonil[b]	1	0	Lambda-cyhalothrin	0	2
Chlorpyrifos	0	1	Malathion	3	16
Cyfluthrin	2	21	MCPA	3	16
Cypermethrin	2	18	Oryzalin[c]	--	3
Diazinon	1	3	Pendimethalin[c]	--	15
Dicamba	12	50	Permethrin	1	13
Diuron	4	19	Prodiamine[c]	--	5
Fipronil	4	44	Prometon	2	3
Fipronil amide	1	1	Triclopyr	10	31

[a]Folsom, 24 sampling events at 6 sites; Roseville, 104 sampling events at 15 sites

[b]Chlorothalonil and imidacloprid added July 2011

[c]Oryzalin, pendimethalin, and prodiamine were not monitored for in Folsom and discontinued monitoring for in Roseville after May 2009.

Table 2. Sampling sites in Folsom CA.

Site	Type/Describe	No. Homes[§]	Area[§] (Acres)	Sampling Type (Matrix)	GPS Coordinates (WGS84)	
					Latitude	Longitude
FOL002	Stormdrain outfall; input into water quality pond at Brock Circle	252	58	Sediment Water	38.65030	-121.14494
FOL003	Stormdrain outfall; input into water quality pond via (lower) Marsh Hawk Dr.	91	21	Sediment Water	38.64938	-121.14494
FOL005	Outflow from FOL002 and FOL003, through water quality pond			Sediment Water	38.64969	-121.14459
FOL006	Outflow fromWillow Springs Reservoir and water quality pond (FOL005) at (lower) Marsh Hawk Dr.			Sediment Water	38.649253	-121.144276
FOL100	Receiving water at Iron Point Rd., near Buckingham Way			Water	38.64559	-121.14442

[§]Approximate number of homes and area.

Table 3. Analytical cost estimates for urban water samples collected in Study 269, FY 2012-2013, and analyzed by CDFA

Sampling Date	Analyte Screen*						Grand Total
	CT	FP/OP	IMD	PD	PX	PY-6	
Aug 1, 2012 (dry season)	6	6	6	6	6	6	
Sept 5, 2012 (dry season)	0	6	6	6	6	6	
First Flush Rain, Oct/Nov 2012	0	6	6	6	6	6	
Winter Rain, Feb 2013	0	6	6	6	6	6	
Spring Rain Mar/April 2013	0	6	6	6	6	6	
May 29, 2013 (dry season)	0	6	6	6	6	6	
June 26, 2013(dry season)	0	6	6	6	6	6	
Total Number of Chemical Analyses	6	42	42	42	42	42	
Cost per Screen	$550	$840	$600	$540	$690	$600	
Total Analyte Screen Costs	$3,300	$35,280	$25,200	$22,680	$28,980	$25,200	$140,820

*CT = chlorothalonil; FP/OP = fipronil and organophosphates (chlorpyrifos, diazinon, and malathion); IMD = imidacloprid; PD = pendimethalin; PX = synthetic auxin; PY-6 = pyrethroid

Table 4. Analytical cost estimates for urban sediment samples collected in Study 269, FY 2012-2013, and analyzed by CDFG

	Quarterly Samples	Total Samples	Cost per Sample	Total Cost
Number of Chemical Analysis	5	20	$455	$9100

Table 5. 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 Detection Limit (µg L^{-1})	Reporting Limit (µg L^{-1})
Fipronil	Fipronil (FP) + Organophosphate (OP)	0.004	0.05
Fipronil sulfide		0.003	0.05
Fipronil sulfone		0.005	0.05
Desulfinyl fipronil		0.003	0.05
Desulfinyl fipronil 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
Chlorothalonil	Chlorothalonil (CT)	0.0111	0.05
Imidacloprid	Imidacloprid (IMD)	0.0101	0.05
Pendimethalin	Pendimethalin (PD)	0.019	0.05
2,4-D	Synthetic Auxin (PX)	0.015	0.05
Dicamba		0.017	0.05
MCPA		0.022	0.05
Triclopyr		0.020	0.05
		Pyrethroid units in ng L^{-1}	
Bifenthrin	Pyrethroid (PY-6)	1.76	5.0
Lambda-cyhalothrin		1.15	15.0
Permethrin cis		3.52	15.0
Permethrin trans		7.68	15.0
Cyfluthrin		1.73	15.0
Cypermethrin		1.75	15.0
Fenvalerate/Esfenvalerate		1.75	15.0

Table 6. Chemical analysis of pesticides in the Northern California urban monitoring Study 269. All samples collected in sediments and the Department of Fish and Game (DFG) will conduct the analyses.

Pesticide	Method Detection Limit (ng g^{-1} dry wt)	Reporting Limit (ng g^{-1} dry wt)
Bifenthrin	0.5	1
Cyfluthrin	2	4
Cypermethrin	2	4
Deltamethrin	2	4
Esfenvalerate/Fenvalerate	1	2
Fenpropathrin	2	4
Lambda cyhalothrin	1	2
Permethrin, cis	4	8
Permethrin, trans	4	8

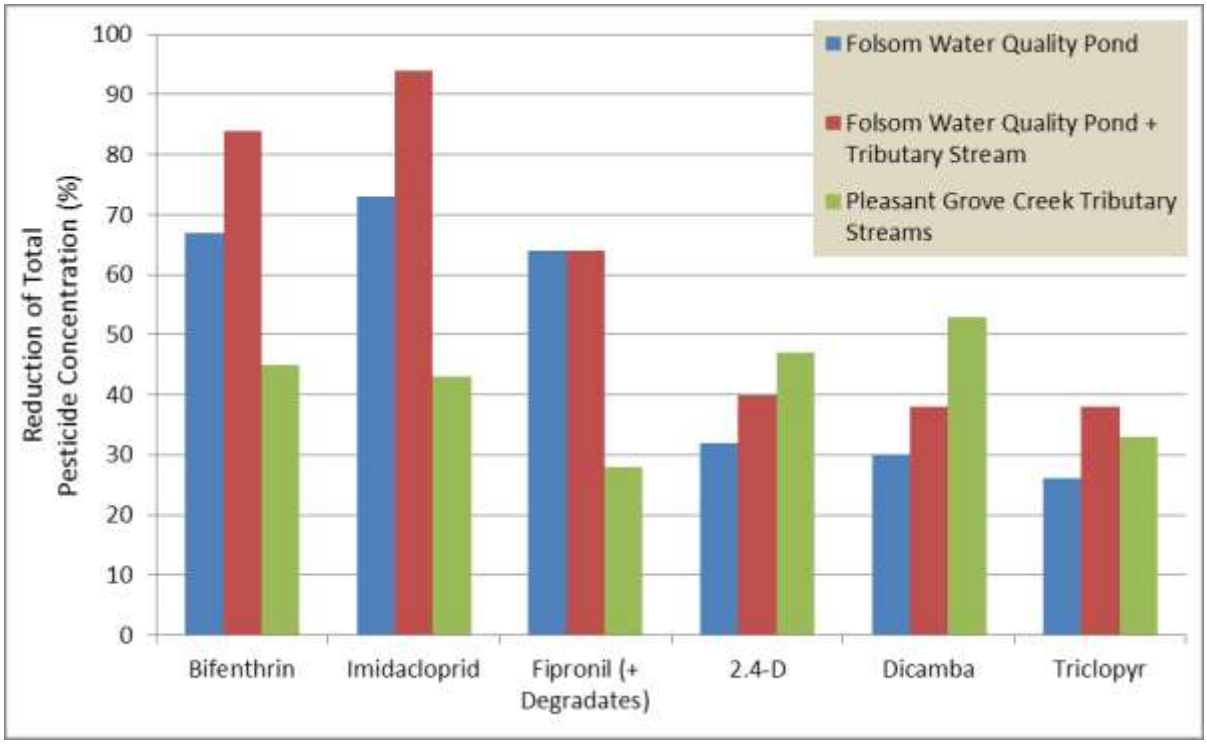

Figure 1. Comparison of the effectiveness of tributary streams in Roseville, CA to the constructed water quality pond in Folsom, CA in removing pesticide concentrations from urban runoff.

Figure 2. The five sampling sites in Folsom CA. Drainage area for FOL002 (F2) and FOL003 (F3) are outlined in same color as the marker.

Appendix II. Sampling Site Information, Study 269 FY2-12-13

Site ID	County	Watershed	Latitude	Longitude	Site Type	Description
FOL002	Sacramento	Upper American River	38.6503	-121.14494	Stormdrain	Storm Drain outfall at Brock Circle
FOL003	Sacramento	Upper American River	38.6494	-121.14494	Stormdrain	Outfall at Marsh Hawk Dr between Donnelly Cir & Widgeon Ct
FOL100	Sacramento	Upper American River	38.6456	-121.14442	Receiving Water	Receiving Water at Iron Pt Rd. near Penrod Ct.
PGC010	Placer	Pleasant Grove Creek	38.8048	-121.32733	Stormdrain	Storm drain at Dr. Paul J. Dugan Park, 1432 Diamond Woods Circle
PGC019	Placer	Pleasant Grove Creek	38.8025	-121.3386	Stormdrain	Conflucence of two Storm Drain outlfows at Opal and Parkside Way
PGC021	Placer	Pleasant Grove Creek	38.8027	-121.33855	Stormdrain	Single Storm Drain at Opal and Parkside Way
PGC022	Placer	Pleasant Grove Creek	38.8026	-121.33881	Stormdrain	Dual Storm Drain at Opal and Parkside Way
PGC040	Placer	Pleasant Grove Creek	38.7986	-121.34802	Receiving Water	Pleasant Grove Creek Receiving Water at Veteran's Memorial Park
TRP1	Sacramento	Upper American River	38.6498	-121.18014	Stormdrain	Wetland at Natoma and Turn Pike Drive

FOL002

FOL003

F100

TRP1

TRP1

PGC010

PGC021

PGC022

PGC040

PGC040

Appendix III. Water quality data for Study 269, FY2012-13

Site ID	Sample Date	Site Type	Event Type*	Water Flow	Temp (oC)	pH	DO (mg/L)**	Cond (mS/cm)	TDS (g/L)	Salinity (ppt)	TSS (mg/L)	Water TOC (ppm)
FOL002	31-Jul-12	Stormdrain	Nonstorm	Flowing	22.64	7.46	7.09	0.124	0.08	0.06	8.59	10.85
FOL003	31-Jul-12	Stormdrain	Nonstorm	Flowing	24.54	7.31	7.548	0.247	0.162	0.12	11.98	6.534
FOL100	31-Jul-12	Receiving Water	Nonstorm	Flowing	24.02	7.33	5.7	0.275	0.136	0.13	3.05	4.512
FOL002	05-Sep-12	Stormdrain	Nonstorm	Flowing	19.31	7.05	7.7	0.28	0.184	0.13	7.48	6.876
FOL003	05-Sep-12	Stormdrain	Nonstorm	Flowing	22.72	7.37	MV	0.526	0.342	0.25	5.07	3.57
FOL100	05-Sep-12	Receiving Water	Nonstorm	Flowing	19.1	7.12	7.65	0.513	0.33	0.25	1.97	3.164
FOL002	22-Oct-12	Stormdrain	Storm	Flowing	14.61	7.19	9.52	0.237	0.153	0.11	7.34	8.381
FOL003	22-Oct-12	Stormdrain	Storm	Flowing	15.26	8.21	9.38	0.217	0.176	0.13	5.72	8.063
FOL100	22-Oct-12	Receiving Water	Storm	Flowing	13.9	6.72	7.9	0.297	0.192	0.14	6.66	8.477
FOL002	19-Feb-13	Stormdrain	Storm	Flowing	8.96	7.83	95.4	0.036	0.056	0.04	16.20	5.35
FOL003	19-Feb-13	Stormdrain	Storm	Flowing	8.57	7.69	10.83	0.078	0.051	0.04	23.30	3.51
PGC010	19-Feb-13	Stormdrain	Storm	Flowing	8.25	7.12	11.53	0.078	0.051	0.04	1.28	4.28
PGC019	19-Feb-13	Stormdrain	Storm	Flowing	9.08	7.88	11.25	0.124	0.081	0.06	9.81	7.94
PGC021	19-Feb-13	Stormdrain	Storm	Flowing	9.43	7.47	11.03	0.117	0.076	0.06	3.86	7.46
PGC022	19-Feb-13	Stormdrain	Storm	Flowing	9.07	8.05	11.92	0.112	0.073	0.05	1.76	8.29
PGC040	19-Feb-13	Receiving Water	Storm	Flowing	8.09	8.08	11.14	0.499	0.318	0.24	4.74	4.82
PGC010	30-Apr-13	Stormdrain	Nonstorm	Ponded	18.63	7.16	4.27	0.314	0.204	0.15	0.70	13.39
PGC019	30-Apr-13	Stormdrain	Nonstorm	Ponded	19.85	7.19	6.95	0.292	0.19	0.14	8.73	14.79
PGC021	30-Apr-13	Stormdrain	Nonstorm	Flowing	17.87	7.48	9.71	0.235	0.153	0.11	-2.23	12.74
PGC022	30-Apr-13	Stormdrain	Nonstorm	Flowing	17.28	7.28	7.49	0.32	0.208	0.15	2.07	17.06
PGC040	30-Apr-13	Receiving Water	Nonstorm	Flowing	20.8	8.69	10.21	0.554	0.36	0.27	2.05	8.0965
FOL002	01-May-13	Stormdrain	Nonstorm	Flowing	18.28	7.7	8.49	0.237	0.154	0.11	2.12	16.54
FOL003	01-May-13	Stormdrain	Nonstorm	Flowing	18.92	7.99	8.87	0.336	0.218	0.16	6.76	7.453
FOL002	17-May-13	Stormdrain	Nonstorm	Flowing	17.29	7.53	9.48	0.236	0.153	0.11	MV	MV
FOL003	17-May-13	Stormdrain	Nonstorm	Flowing	19.18	7.93	8.06	0.367	0.28	0.18	MV	MV
TRP1	17-May-13	Stormdrain	Nonstorm	Flowing	20.16	6.69	5.57	0.312	0.203	0.15	MV	MV
FOL002	04-Jun-13	Stormdrain	Nonstorm	Flowing	18.55	7.48	8.73	0.207	0.136	0.1	3.11	11.23
FOL003	04-Jun-13	Stormdrain	Nonstorm	Flowing	19.93	7.94	8.42	0.187	0.121	0.09	2.01	6.664

Appendix III. Water quality data for Study 269, FY2012-13

Site ID	Sample Date	Site Type	Event Type*	Water Flow	Temp (oC)	pH	DO (mg/L)**	Cond (mS/cm)	TDS (g/L)	Salinity (ppt)	TSS (mg/L)	Water TOC (ppm)
PGC010	04-Jun-13	Stormdrain	Nonstorm	Ponded	20.25	6.96	1.08	0.3	0.195	0.14	2.63	11.33
PGC019	04-Jun-13	Stormdrain	Nonstorm	Flowing	19.25	7.29	6.97	0.266	0.173	0.13	4.41	9.506
PGC021	04-Jun-13	Stormdrain	Nonstorm	Flowing	20.78	7.46	6.26	0.281	0.183	0.13	21.61	14.52
PGC022	04-Jun-13	Stormdrain	Nonstorm	Flowing	19.97	8.3	9.12	0.23	0.15	0.11	4.40	9.323
PGC040	04-Jun-13	Receiving Water	Nonstorm	Ponded	21.24	7.87	6.76	0.643	0.418	0.31	3.65	10.83
FOL002	13-Jun-13	Stormdrain	Nonstorm	Flowing	20.34	7.8	8.35	3.6	1.65	1.32	MV	MV
FOL003	13-Jun-13	Stormdrain	Nonstorm	Flowing	21.53	7.97	7.9	0.303	0.197	0.14	MV	MV
TRP1	13-Jun-13	Stormdrain	Nonstorm	Flowing	21.8	6.78	6.27	0.281	0.183	0.13	MV	MV

*Nonstorm, dry season monitoring; Storm, rain storm monitoring; **MV, missing value

Appendix IV. Sediment monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Analyte Name	Result (ug/kg dry wt)*	RL (ug/kg)	MDL (ug/kg)	Sediment TOC (%)	Sediment Moisture (%)	LC50 (ug/g OC)	Toxicity Unit
FOL002	Stormdrain	05-Sep-12	Bifenthrin	310.89	6.906	0.25	6.16	63.8	0.52	9.70
FOL002	Stormdrain	05-Sep-12	Cyfluthrin	61.29	3.453	0.2	6.16	63.8	1.08	0.92
FOL002	Stormdrain	05-Sep-12	Cypermethrin	474.95	3.453	0.3	6.16	63.8	0.38	20.28
FOL002	Stormdrain	05-Sep-12	Deltamethrin/Tralomethrin	365.66	2.762	0.2	6.16	63.8	0.79	7.51
FOL002	Stormdrain	05-Sep-12	Fenpropathrin	2.07	0.691	0.8	6.16	63.8	None	--
FOL002	Stormdrain	05-Sep-12	Fenvalerate/Esfenvalerate	18.11	1.381	0.2	6.16	63.8	1.54	0.19
FOL002	Stormdrain	05-Sep-12	Lambda-cyhalothrin	27.07	1.381	0.15	6.16	63.8	0.45	0.98
FOL002	Stormdrain	05-Sep-12	Permethrin	237.34	10.36	1.90	12.32	63.8	21.66	0.36
FOL003	Stormdrain	05-Sep-12	Bifenthrin	345.11	6.793	0.25	8.17	63.2	0.52	8.12
FOL003	Stormdrain	05-Sep-12	Cyfluthrin	137.66	3.397	0.2	8.17	63.2	1.08	1.56
FOL003	Stormdrain	05-Sep-12	Cypermethrin	45.61	3.397	0.3	8.17	63.2	0.38	1.47
FOL003	Stormdrain	05-Sep-12	Deltamethrin/Tralomethrin	9.65	2.717	0.2	8.17	63.2	0.79	0.15
FOL003	Stormdrain	05-Sep-12	Fenpropathrin	nd	0.679	0.8	8.17	63.2	None	--
FOL003	Stormdrain	05-Sep-12	Fenvalerate/Esfenvalerate	6.54	1.359	0.2	8.17	63.2	1.54	0.05
FOL003	Stormdrain	05-Sep-12	Lambda-cyhalothrin	145.80	1.359	0.15	8.17	63.2	0.45	3.97
FOL003	Stormdrain	05-Sep-12	Permethrin	89.01	10.19	1.90	16.34	63.2	21.66	0.10
FOL002	Stormdrain	26-Oct-12	Bifenthrin	202.42	5.23	0.25	5.55	52.2	0.52	7.01
FOL002	Stormdrain	26-Oct-12	Cyfluthrin	60.52	2.615	0.2	5.55	52.2	1.08	1.01
FOL002	Stormdrain	26-Oct-12	Cypermethrin	215.74	2.615	0.3	5.55	52.2	0.38	10.22
FOL002	Stormdrain	26-Oct-12	Deltamethrin/Tralomethrin	133.00	2.092	0.2	5.55	52.2	0.79	3.03
FOL002	Stormdrain	26-Oct-12	Fenpropathrin	nd	0.523	0.8	5.55	52.2	None	--
FOL002	Stormdrain	26-Oct-12	Fenvalerate/Esfenvalerate	9.24	1.046	0.2	5.55	52.2	1.54	0.11
FOL002	Stormdrain	26-Oct-12	Lambda-cyhalothrin	19.73	1.046	0.15	5.55	52.2	0.45	0.79
FOL002	Stormdrain	26-Oct-12	Permethrin	251.06	7.85	1.90	11.11	52.2	21.66	0.42
FOL003	Stormdrain	26-Oct-12	Bifenthrin	162.39	5.176	0.25	5.12	51.7	0.52	6.10
FOL003	Stormdrain	26-Oct-12	Cyfluthrin	273.44	2.588	0.2	5.12	51.7	1.08	4.94
FOL003	Stormdrain	26-Oct-12	Cypermethrin	8.23	2.588	0.3	5.12	51.7	0.38	0.42
FOL003	Stormdrain	26-Oct-12	Deltamethrin/Tralomethrin	4.13	2.07	0.2	5.12	51.7	0.79	0.10
FOL003	Stormdrain	26-Oct-12	Fenpropathrin	nd	0.518	0.8	5.12	51.7	None	--
FOL003	Stormdrain	26-Oct-12	Fenvalerate/Esfenvalerate	3.52	1.035	0.2	5.12	51.7	1.54	0.04
FOL003	Stormdrain	26-Oct-12	Lambda-cyhalothrin	26.06	1.035	0.15	5.12	51.7	0.45	1.13

Appendix IV. Sediment monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Analyte Name	Result (ug/kg dry wt)*	RL (ug/kg)	MDL (ug/kg)	Sediment TOC (%)	Sediment Moisture (%)	LC50 (ug/g OC)	Toxicity Unit
FOL003	Stormdrain	26-Oct-12	Permethrin	49.96	7.76	1.90	10.24	51.7	21.66	0.09
FOL002	Stormdrain	21-Feb-13	Bifenthrin	44.65	2.7	0.25	5.82	54.5	0.52	1.48
FOL002	Stormdrain	21-Feb-13	Cyfluthrin	9.35	2.71	0.2	5.82	54.5	1.08	0.15
FOL002	Stormdrain	21-Feb-13	Cyhalothrin	1.73	1.08	0.2	5.82	54.5	0.45	0.07
FOL002	Stormdrain	21-Feb-13	Cypermethrin	3.62	2.71	0.3	5.82	54.5	0.38	0.16
FOL002	Stormdrain	21-Feb-13	Deltamethrin/Tralomethrin	7.29	2.17	0.2	5.82	54.5	0.79	0.16
FOL002	Stormdrain	21-Feb-13	Fenpropathrin	nd	0.54	0.8	5.82	54.5	None	--
FOL002	Stormdrain	21-Feb-13	Fenvalerate/Esfenvalerate	trace	1.08	0.2	5.82	54.5	1.54	0
FOL002	Stormdrain	21-Feb-13	Permethrin	47.51	8.13	1.90	11.63	54.5	21.66	0.08
FOL003	Stormdrain	21-Feb-13	Bifenthrin	276.24	11.43	0.25	5.72	57.3	0.52	9.29
FOL003	Stormdrain	21-Feb-13	Cyfluthrin	138.19	57.13	0.2	5.72	57.3	1.08	2.24
FOL003	Stormdrain	21-Feb-13	Cyhalothrin	trace	22.85	0.2	5.72	57.3	0.45	0
FOL003	Stormdrain	21-Feb-13	Cypermethrin	trace	57.13	0.3	5.72	57.3	0.38	0
FOL003	Stormdrain	21-Feb-13	Deltamethrin/Tralomethrin	trace	45.7	0.2	5.72	57.3	0.79	0
FOL003	Stormdrain	21-Feb-13	Fenpropathrin	nd	11.43	0.8	5.72	57.3	None	--
FOL003	Stormdrain	21-Feb-13	Fenvalerate/Esfenvalerate	nd	22.85	0.2	5.72	57.3	1.54	0
FOL003	Stormdrain	21-Feb-13	Permethrin	0.00	171.39	1.90	11.44	57.3	21.66	0.00
PGC010	Stormdrain	25-Feb-13	Bifenthrin	550.42	10.01	0.25	3.82	50.9	0.52	27.69
PGC010	Stormdrain	25-Feb-13	Cyfluthrin	53.19	50.07	0.2	3.82	50.9	1.08	1.29
PGC010	Stormdrain	25-Feb-13	Cyhalothrin	trace	20.03	0.2	3.82	50.9	0.45	0
PGC010	Stormdrain	25-Feb-13	Cypermethrin	trace	50.07	0.3	3.82	50.9	0.38	0
PGC010	Stormdrain	25-Feb-13	Deltamethrin/Tralomethrin	trace	40.06	0.2	3.82	50.9	0.79	0
PGC010	Stormdrain	25-Feb-13	Fenpropathrin	nd	10.01	0.8	3.82	50.9	None	--
PGC010	Stormdrain	25-Feb-13	Fenvalerate/Esfenvalerate	trace	20.03	0.2	3.82	50.9	1.54	0
PGC010	Stormdrain	25-Feb-13	Permethrin	0.00	150.21	1.90	7.65	50.9	21.66	0.00
PGC019	Stormdrain	25-Feb-13	Bifenthrin	188.42	8.21	0.25	3.06	39.7	0.52	11.83
PGC019	Stormdrain	25-Feb-13	Cyfluthrin	trace	41.05	0.2	3.06	39.7	1.08	0
PGC019	Stormdrain	25-Feb-13	Cyhalothrin	trace	16.42	0.2	3.06	39.7	0.45	0
PGC019	Stormdrain	25-Feb-13	Cypermethrin	trace	41.05	0.3	3.06	39.7	0.38	0
PGC019	Stormdrain	25-Feb-13	Deltamethrin/Tralomethrin	nd	32.84	0.2	3.06	39.7	0.79	0
PGC019	Stormdrain	25-Feb-13	Fenpropathrin	nd	8.21	0.8	3.06	39.7	None	--

Appendix IV. Sediment monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Analyte Name	Result (ug/kg dry wt)*	RL (ug/kg)	MDL (ug/kg)	Sediment TOC (%)	Sediment Moisture (%)	LC50 (ug/g OC)	Toxicity Unit
PGC019	Stormdrain	25-Feb-13	Fenvalerate/Esfenvalerate	nd	16.42	0.2	3.06	39.7	1.54	0
PGC019	Stormdrain	25-Feb-13	Permethrin	0.00	123.15	1.90	6.13	39.7	21.66	0
TRP1	Stormdrain	25-Feb-13	Bifenthrin	106.15	4.26	0.25	4.53	42.4	0.52	4.51
TRP1	Stormdrain	25-Feb-13	Cyfluthrin	trace	21.32	0.2	4.53	42.4	1.08	0
TRP1	Stormdrain	25-Feb-13	Cyhalothrin	trace	8.53	0.2	4.53	42.4	0.45	0
TRP1	Stormdrain	25-Feb-13	Cypermethrin	trace	21.32	0.3	4.53	42.4	0.38	0
TRP1	Stormdrain	25-Feb-13	Deltamethrin/Tralomethrin	trace	34.12	0.2	4.53	42.4	0.79	0
TRP1	Stormdrain	25-Feb-13	Fenpropathrin	nd	4.26	0.8	4.53	42.4	None	--
TRP1	Stormdrain	25-Feb-13	Fenvalerate/Esfenvalerate	trace	8.53	0.2	4.53	42.4	1.54	0
TRP1	Stormdrain	25-Feb-13	Permethrin	0.00	63.97	1.90	9.05	42.4	21.66	0
TRP1	Stormdrain	27-Mar-13	Bifenthrin	103.92	1.96	0.25	6.62	36.9	0.52	3.02
TRP1	Stormdrain	27-Mar-13	Cyfluthrin	13.23	9.78	0.2	6.62	36.9	1.08	0.19
TRP1	Stormdrain	27-Mar-13	Cyhalothrin	8.55	3.91	0.2	6.62	36.9	0.45	0.29
TRP1	Stormdrain	27-Mar-13	Cypermethrin	14.48	9.78	0.3	6.62	36.9	0.38	0.58
TRP1	Stormdrain	27-Mar-13	Deltamethrin/Tralomethrin	trace	7.83	0.2	6.62	36.9	0.79	0
TRP1	Stormdrain	27-Mar-13	Fenpropathrin	nd	1.96	0.8	6.62	36.9	None	--
TRP1	Stormdrain	27-Mar-13	Fenvalerate/Esfenvalerate	4.76	3.91	0.2	6.62	36.9	1.54	0.05
TRP1	Stormdrain	27-Mar-13	Permethrin	17.49	29.35	1.90	13.24	36.9	21.66	0.02
TRP1	Stormdrain	03-Jun-13	Bifenthrin	206.01	1.599	0.25	19.10	85.0	0.52	2.07
TRP1	Stormdrain	03-Jun-13	Cyfluthrin	31.77	7.997	0.2	19.10	85.0	1.08	0.15
TRP1	Stormdrain	03-Jun-13	Cyhalothrin	15.84	3.199	0.2	19.10	85.0	0.45	0.18
TRP1	Stormdrain	03-Jun-13	Cypermethrin	20.81	7.997	0.3	19.10	85.0	0.38	0.29
TRP1	Stormdrain	03-Jun-13	Deltamethrin/Tralomethrin	9.46	6.398	0.2	19.10	85.0	0.79	0.06
TRP1	Stormdrain	03-Jun-13	Fenpropathrin	trace	1.599	0.8	19.10	85.0	None	--
TRP1	Stormdrain	03-Jun-13	Fenvalerate/Esfenvalerate	3.90	3.199	0.2	19.10	85.0	1.54	0.01
TRP1	Stormdrain	03-Jun-13	Permethrin	24.15	23.99	1.90	38.21	85.0	21.66	0.01
FOL002	Stormdrain	04-Jun-13	Bifenthrin	268.64	0.954	0.25	13.36	74.1	0.52	3.87
FOL002	Stormdrain	04-Jun-13	Cyfluthrin	41.08	4.771	0.2	13.36	74.1	1.08	0.28
FOL002	Stormdrain	04-Jun-13	Cyhalothrin	49.47	1.908	0.2	13.36	74.1	0.45	0.82
FOL002	Stormdrain	04-Jun-13	Cypermethrin	59.22	4.771	0.3	13.36	74.1	0.38	1.17
FOL002	Stormdrain	04-Jun-13	Deltamethrin/Tralomethrin	51.20	3.817	0.2	13.36	74.1	0.79	0.49

Appendix IV. Sediment monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Analyte Name	Result (ug/kg dry wt)*	RL (ug/kg)	MDL (ug/kg)	Sediment TOC (%)	Sediment Moisture (%)	LC50 (ug/g OC)	Toxicity Unit
FOL002	Stormdrain	04-Jun-13	Fenpropathrin	trace	0.954	0.8	13.36	74.1	None	--
FOL002	Stormdrain	04-Jun-13	Fenvalerate/Esfenvalerate	9.28	1.908	0.2	13.36	74.1	1.54	0.05
FOL002	Stormdrain	04-Jun-13	Permethrin	138.42	14.31	1.90	26.72	74.1	21.66	0.10
FOL003	Stormdrain	04-Jun-13	Bifenthrin	168.42	0.519	0.25	5.08	52.0	0.52	6.38
FOL003	Stormdrain	04-Jun-13	Cyfluthrin	34.36	2.593	0.2	5.08	52.0	1.08	0.63
FOL003	Stormdrain	04-Jun-13	Cyhalothrin	13.94	1.037	0.2	5.08	52.0	0.45	0.61
FOL003	Stormdrain	04-Jun-13	Cypermethrin	19.35	2.593	0.3	5.08	52.0	0.38	1.00
FOL003	Stormdrain	04-Jun-13	Deltamethrin/Tralomethrin	3.33	2.075	0.2	5.08	52.0	0.79	0.08
FOL003	Stormdrain	04-Jun-13	Fenpropathrin	trace	0.519	0.8	5.08	52.0	None	--
FOL003	Stormdrain	04-Jun-13	Fenvalerate/Esfenvalerate	2.13	1.037	0.2	5.08	52.0	1.54	0.03
FOL003	Stormdrain	04-Jun-13	Permethrin	22.31	7.78	1.90	10.15	52.0	21.66	0.04
PGC010	Stormdrain	05-Jun-13	Bifenthrin	934.69	52.966	0.25	12.39	77.6	0.52	14.51
PGC010	Stormdrain	05-Jun-13	Cyfluthrin	94.96	264.831	0.2	12.39	77.6	1.08	0.71
PGC010	Stormdrain	05-Jun-13	Cyhalothrin	70.51	2.119	0.2	12.39	77.6	0.45	1.26
PGC010	Stormdrain	05-Jun-13	Cypermethrin	143.57	5.297	0.3	12.39	77.6	0.38	3.05
PGC010	Stormdrain	05-Jun-13	Deltamethrin/Tralomethrin	29.45	4.237	0.2	12.39	77.6	0.79	0.30
PGC010	Stormdrain	05-Jun-13	Fenpropathrin	trace	1.059	0.8	12.39	77.6	None	--
PGC010	Stormdrain	05-Jun-13	Fenvalerate/Esfenvalerate	28.35	2.119	0.2	12.39	77.6	1.54	0.15
PGC010	Stormdrain	05-Jun-13	Permethrin	178.25	15.89	1.90	24.77	77.6	21.66	0.13
PGC019	Stormdrain	05-Jun-13	Bifenthrin	170.36	0.565	0.25	4.34	57.4	0.52	7.55
PGC019	Stormdrain	05-Jun-13	Cyfluthrin	22.78	2.824	0.2	4.34	57.4	1.08	0.49
PGC019	Stormdrain	05-Jun-13	Cyhalothrin	11.55	1.129	0.2	4.34	57.4	0.45	0.59
PGC019	Stormdrain	05-Jun-13	Cypermethrin	18.42	2.824	0.3	4.34	57.4	0.38	1.12
PGC019	Stormdrain	05-Jun-13	Deltamethrin/Tralomethrin	6.83	2.259	0.2	4.34	57.4	0.79	0.20
PGC019	Stormdrain	05-Jun-13	Fenpropathrin	trace	0.565	0.8	4.34	57.4	None	--
PGC019	Stormdrain	05-Jun-13	Fenvalerate/Esfenvalerate	3.18	1.129	0.2	4.34	57.4	1.54	0.05
PGC019	Stormdrain	05-Jun-13	Permethrin	105.71	8.47	1.90	8.67	57.4	21.66	0.23
PGC022	Stormdrain	05-Jun-13	Bifenthrin	80.44	0.464	0.25	2.78	50.7	0.52	5.56
PGC022	Stormdrain	05-Jun-13	Cyfluthrin	8.95	2.319	0.2	2.78	50.7	1.08	0.30
PGC022	Stormdrain	05-Jun-13	Cyhalothrin	5.59	0.928	0.2	2.78	50.7	0.45	0.45
PGC022	Stormdrain	05-Jun-13	Cypermethrin	8.20	2.319	0.3	2.78	50.7	0.38	0.78

Appendix IV. Sediment monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Analyte Name	Result (ug/kg dry wt)*	RL (ug/kg)	MDL (ug/kg)	Sediment TOC (%)	Sediment Moisture (%)	LC50 (ug/g OC)	Toxicity Unit
PGC022	Stormdrain	05-Jun-13	Deltamethrin/Tralomethrin	3.05	1.855	0.2	2.78	50.7	0.79	0.14
PGC022	Stormdrain	05-Jun-13	Fenpropathrin	trace	0.464	0.8	2.78	50.7	None	--
PGC022	Stormdrain	05-Jun-13	Fenvalerate/Esfenvalerate	1.63	0.928	0.2	2.78	50.7	1.54	0.04
PGC022	Stormdrain	05-Jun-13	Permethrin	34.09	6.96	1.90	5.56	50.7	21.66	0.11
PGC040	Receiving Water	05-Jun-13	Bifenthrin	21.94	0.444	0.25	1.35	44.3	0.52	3.13
PGC040	Receiving Water	05-Jun-13	Cyfluthrin	2.24	2.22	0.2	1.35	44.3	1.08	0.15
PGC040	Receiving Water	05-Jun-13	Cyhalothrin	1.66	0.888	0.2	1.35	44.3	0.45	0.27
PGC040	Receiving Water	05-Jun-13	Cypermethrin	trace	2.22	0.3	1.35	44.3	0.38	0
PGC040	Receiving Water	05-Jun-13	Deltamethrin/Tralomethrin	trace	1.776	0.2	1.35	44.3	0.79	0
PGC040	Receiving Water	05-Jun-13	Fenpropathrin	nd	0.444	0.8	1.35	44.3	None	--
PGC040	Receiving Water	05-Jun-13	Fenvalerate/Esfenvalerate	trace	0.888	0.2	1.35	44.3	1.54	0
PGC040	Receiving Water	05-Jun-13	Permethrin	2.57	6.66	1.90	2.70	44.3	21.66	0.02

*nd, not detected; trace, trace detection, > MDL and < RL

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL002	Stormdrain	31-Jul-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348
FOL002	Stormdrain	31-Jul-12	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL002	Stormdrain	31-Jul-12	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL002	Stormdrain	31-Jul-12	Nonstorm	Fipronil	FP	nd	0.02	0.004
FOL002	Stormdrain	31-Jul-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	31-Jul-12	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
FOL002	Stormdrain	31-Jul-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	31-Jul-12	Nonstorm	Imidacloprid	IM	0.102	0.05	0.0394
FOL002	Stormdrain	31-Jul-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL002	Stormdrain	31-Jul-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL002	Stormdrain	31-Jul-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL002	Stormdrain	31-Jul-12	Nonstorm	2,4-D	PX	0.146	0.05	0.015
FOL002	Stormdrain	31-Jul-12	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL002	Stormdrain	31-Jul-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL002	Stormdrain	31-Jul-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL002	Stormdrain	31-Jul-12	Nonstorm	Bifenthrin	PY	0.0137	0.001	0.0009
FOL002	Stormdrain	31-Jul-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL002	Stormdrain	31-Jul-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	31-Jul-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	31-Jul-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL002	Stormdrain	31-Jul-12	Nonstorm	Permethrin	PY	0.0045	0.002	0.002
FOL003	Stormdrain	31-Jul-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348
FOL003	Stormdrain	31-Jul-12	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL003	Stormdrain	31-Jul-12	Nonstorm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	31-Jul-12	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL003	Stormdrain	31-Jul-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	31-Jul-12	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL003	Stormdrain	31-Jul-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL003	Stormdrain	31-Jul-12	Nonstorm	Imidacloprid	IM	0.227	0.05	0.0394
FOL003	Stormdrain	31-Jul-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL003	Stormdrain	31-Jul-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL003	Stormdrain	31-Jul-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL003	Stormdrain	31-Jul-12	Nonstorm	2,4-D	PX	0.189	0.05	0.015
FOL003	Stormdrain	31-Jul-12	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL003	Stormdrain	31-Jul-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	31-Jul-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL003	Stormdrain	31-Jul-12	Nonstorm	Bifenthrin	PY	0.0025	0.001	0.0009
FOL003	Stormdrain	31-Jul-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL003	Stormdrain	31-Jul-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	31-Jul-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	31-Jul-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	31-Jul-12	Nonstorm	Permethrin	PY	0.005	0.002	0.002
FOL100	Receiving Water	31-Jul-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL100	Receiving Water	31-Jul-12	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL100	Receiving Water	31-Jul-12	Nonstorm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	31-Jul-12	Nonstorm	Fipronil	FP	nd	0.02	0.004
FOL100	Receiving Water	31-Jul-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	31-Jul-12	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
FOL100	Receiving Water	31-Jul-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL100	Receiving Water	31-Jul-12	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
FOL100	Receiving Water	31-Jul-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL100	Receiving Water	31-Jul-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL100	Receiving Water	31-Jul-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL100	Receiving Water	31-Jul-12	Nonstorm	2,4-D	PX	trace	0.05	0.015
FOL100	Receiving Water	31-Jul-12	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL100	Receiving Water	31-Jul-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL100	Receiving Water	31-Jul-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL100	Receiving Water	31-Jul-12	Nonstorm	Bifenthrin	PY	0.0034	0.001	0.0009
FOL100	Receiving Water	31-Jul-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL100	Receiving Water	31-Jul-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL100	Receiving Water	31-Jul-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL100	Receiving Water	31-Jul-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL100	Receiving Water	31-Jul-12	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	05-Sep-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348
FOL002	Stormdrain	05-Sep-12	Nonstorm	Desulfinyl fipronil	FP	nd	0.02	0.003
FOL002	Stormdrain	05-Sep-12	Nonstorm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	05-Sep-12	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL002	Stormdrain	05-Sep-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	05-Sep-12	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL002	Stormdrain	05-Sep-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	05-Sep-12	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
FOL002	Stormdrain	05-Sep-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL002	Stormdrain	05-Sep-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL002	Stormdrain	05-Sep-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL002	Stormdrain	05-Sep-12	Nonstorm	2,4-D	PX	0.087	0.05	0.015
FOL002	Stormdrain	05-Sep-12	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL002	Stormdrain	05-Sep-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL002	Stormdrain	05-Sep-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL002	Stormdrain	05-Sep-12	Nonstorm	Bifenthrin	PY	0.0033	0.001	0.0009
FOL002	Stormdrain	05-Sep-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL002	Stormdrain	05-Sep-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	05-Sep-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	05-Sep-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL002	Stormdrain	05-Sep-12	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL003	Stormdrain	05-Sep-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348
FOL003	Stormdrain	05-Sep-12	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL003	Stormdrain	05-Sep-12	Nonstorm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	05-Sep-12	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL003	Stormdrain	05-Sep-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	05-Sep-12	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL003	Stormdrain	05-Sep-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL003	Stormdrain	05-Sep-12	Nonstorm	Imidacloprid	IM	0.058	0.05	0.0394
FOL003	Stormdrain	05-Sep-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL003	Stormdrain	05-Sep-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL003	Stormdrain	05-Sep-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL003	Stormdrain	05-Sep-12	Nonstorm	2,4-D	PX	2.82	0.05	0.015
FOL003	Stormdrain	05-Sep-12	Nonstorm	Dicamba	PX	0.274	0.05	0.017
FOL003	Stormdrain	05-Sep-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	05-Sep-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL003	Stormdrain	05-Sep-12	Nonstorm	Bifenthrin	PY	0.0042	0.001	0.0009
FOL003	Stormdrain	05-Sep-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL003	Stormdrain	05-Sep-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	05-Sep-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	05-Sep-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	05-Sep-12	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL100	Receiving Water	05-Sep-12	Nonstorm	Chlorothalonil	CT	nd	0.05	0.0348
FOL100	Receiving Water	05-Sep-12	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL100	Receiving Water	05-Sep-12	Nonstorm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	05-Sep-12	Nonstorm	Fipronil	FP	nd	0.02	0.004
FOL100	Receiving Water	05-Sep-12	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	05-Sep-12	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
FOL100	Receiving Water	05-Sep-12	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL100	Receiving Water	05-Sep-12	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
FOL100	Receiving Water	05-Sep-12	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL100	Receiving Water	05-Sep-12	Nonstorm	Diazinon	OP	nd	0.01	0.0012
FOL100	Receiving Water	05-Sep-12	Nonstorm	Malathion	OP	nd	0.05	0.0117
FOL100	Receiving Water	05-Sep-12	Nonstorm	2,4-D	PX	0.13	0.05	0.015
FOL100	Receiving Water	05-Sep-12	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL100	Receiving Water	05-Sep-12	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL100	Receiving Water	05-Sep-12	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL100	Receiving Water	05-Sep-12	Nonstorm	Bifenthrin	PY	0.001	0.001	0.0009
FOL100	Receiving Water	05-Sep-12	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL100	Receiving Water	05-Sep-12	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL100	Receiving Water	05-Sep-12	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL100	Receiving Water	05-Sep-12	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL100	Receiving Water	05-Sep-12	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	22-Oct-12	Storm	Pendimethalin	DN	nd	0.05	0.012
FOL002	Stormdrain	22-Oct-12	Storm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL002	Stormdrain	22-Oct-12	Storm	Desulfinyl fipronil amide	FP	trace	0.03	0.005

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL002	Stormdrain	22-Oct-12	Storm	Fipronil	FP	0.026	0.02	0.004
FOL002	Stormdrain	22-Oct-12	Storm	Fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	22-Oct-12	Storm	Fipronil sulfide	FP	nd	0.02	0.003
FOL002	Stormdrain	22-Oct-12	Storm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	22-Oct-12	Storm	Imidacloprid	IM	0.3	0.05	0.0394
FOL002	Stormdrain	22-Oct-12	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL002	Stormdrain	22-Oct-12	Storm	Diazinon	OP	nd	0.01	0.0012
FOL002	Stormdrain	22-Oct-12	Storm	Malathion	OP	nd	0.05	0.0117
FOL002	Stormdrain	22-Oct-12	Storm	2,4-D	PX	1.335	0.05	0.015
FOL002	Stormdrain	22-Oct-12	Storm	Dicamba	PX	1.077	0.05	0.017
FOL002	Stormdrain	22-Oct-12	Storm	MCPA	PX	3.664	0.05	0.022
FOL002	Stormdrain	22-Oct-12	Storm	Triclopyr	PX	0.268	0.05	0.02
FOL002	Stormdrain	22-Oct-12	Storm	Bifenthrin	PY	0.0149	0.001	0.0009
FOL002	Stormdrain	22-Oct-12	Storm	Cyfluthrin	PY	nd	0.002	0.0015
FOL002	Stormdrain	22-Oct-12	Storm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	22-Oct-12	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	22-Oct-12	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL002	Stormdrain	22-Oct-12	Storm	Permethrin	PY	0.0025	0.002	0.002
FOL003	Stormdrain	22-Oct-12	Storm	Pendimethalin	DN	nd	0.05	0.012
FOL003	Stormdrain	22-Oct-12	Storm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL003	Stormdrain	22-Oct-12	Storm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	22-Oct-12	Storm	Fipronil	FP	0.039	0.02	0.004
FOL003	Stormdrain	22-Oct-12	Storm	Fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	22-Oct-12	Storm	Fipronil sulfide	FP	nd	0.02	0.003
FOL003	Stormdrain	22-Oct-12	Storm	Fipronil sulfone	FP	0.03	0.03	0.005
FOL003	Stormdrain	22-Oct-12	Storm	Imidacloprid	IM	0.082	0.05	0.0394
FOL003	Stormdrain	22-Oct-12	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL003	Stormdrain	22-Oct-12	Storm	Diazinon	OP	nd	0.01	0.0012
FOL003	Stormdrain	22-Oct-12	Storm	Malathion	OP	nd	0.05	0.0117
FOL003	Stormdrain	22-Oct-12	Storm	2,4-D	PX	1.249	0.05	0.015
FOL003	Stormdrain	22-Oct-12	Storm	Dicamba	PX	0.436	0.05	0.017
FOL003	Stormdrain	22-Oct-12	Storm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	22-Oct-12	Storm	Triclopyr	PX	0.095	0.05	0.02
FOL003	Stormdrain	22-Oct-12	Storm	Bifenthrin	PY	0.013	0.001	0.0009
FOL003	Stormdrain	22-Oct-12	Storm	Cyfluthrin	PY	nd	0.002	0.0015
FOL003	Stormdrain	22-Oct-12	Storm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	22-Oct-12	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	22-Oct-12	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	22-Oct-12	Storm	Permethrin	PY	nd	0.002	0.002
FOL100	Receiving Water	22-Oct-12	Storm	Pendimethalin	DN	nd	0.05	0.012
FOL100	Receiving Water	22-Oct-12	Storm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL100	Receiving Water	22-Oct-12	Storm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	22-Oct-12	Storm	Fipronil	FP	0.026	0.02	0.004

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL100	Receiving Water	22-Oct-12	Storm	Fipronil amide	FP	trace	0.03	0.005
FOL100	Receiving Water	22-Oct-12	Storm	Fipronil sulfide	FP	nd	0.02	0.003
FOL100	Receiving Water	22-Oct-12	Storm	Fipronil sulfone	FP	trace	0.03	0.005
FOL100	Receiving Water	22-Oct-12	Storm	Imidacloprid	IM	0.166	0.05	0.0394
FOL100	Receiving Water	22-Oct-12	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
FOL100	Receiving Water	22-Oct-12	Storm	Diazinon	OP	nd	0.01	0.0012
FOL100	Receiving Water	22-Oct-12	Storm	Malathion	OP	nd	0.05	0.0117
FOL100	Receiving Water	22-Oct-12	Storm	2,4-D	PX	1.35	0.05	0.015
FOL100	Receiving Water	22-Oct-12	Storm	Dicamba	PX	0.689	0.05	0.017
FOL100	Receiving Water	22-Oct-12	Storm	MCPA	PX	2.34	0.05	0.022
FOL100	Receiving Water	22-Oct-12	Storm	Triclopyr	PX	0.151	0.05	0.02
FOL100	Receiving Water	22-Oct-12	Storm	Bifenthrin	PY	0.0101	0.001	0.0009
FOL100	Receiving Water	22-Oct-12	Storm	Cyfluthrin	PY	nd	0.002	0.0015
FOL100	Receiving Water	22-Oct-12	Storm	Cypermethrin	PY	nd	0.005	0.0015
FOL100	Receiving Water	22-Oct-12	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL100	Receiving Water	22-Oct-12	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL100	Receiving Water	22-Oct-12	Storm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	nd	0.02	0.003
FOL002	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL002	Stormdrain	19-Feb-13	Storm	Fipronil	FP	trace	0.02	0.004
FOL002	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	nd	0.03	0.005
FOL002	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	nd	0.02	0.003
FOL002	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	0.185	0.05	0.0394
FOL002	Stormdrain	19-Feb-13	Storm	2,4-D	PX	0.626	0.05	0.015
FOL002	Stormdrain	19-Feb-13	Storm	Dicamba	PX	trace	0.05	0.017
FOL002	Stormdrain	19-Feb-13	Storm	MCPA	PX	nd	0.05	0.022
FOL002	Stormdrain	19-Feb-13	Storm	Triclopyr	PX	0.378	0.05	0.02
FOL002	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.0598	0.001	0.0009
FOL002	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	0.0033	0.002	0.0015
FOL002	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	0.0061	0.002	0.0017
FOL002	Stormdrain	19-Feb-13	Storm	Permethrin	PY	0.0106	0.002	0.002
FOL003	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	0.05	0.02	0.003
FOL003	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL003	Stormdrain	19-Feb-13	Storm	Fipronil	FP	0.13	0.02	0.004
FOL003	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	nd	0.03	0.005
FOL003	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	trace	0.02	0.003
FOL003	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	0.043	0.03	0.005
FOL003	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
FOL003	Stormdrain	19-Feb-13	Storm	2,4-D	PX	2.09	0.05	0.015
FOL003	Stormdrain	19-Feb-13	Storm	Dicamba	PX	0.163	0.05	0.017

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL003	Stormdrain	19-Feb-13	Storm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	19-Feb-13	Storm	Triclopyr	PX	trace	0.05	0.02
FOL003	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.0172	0.001	0.0009
FOL003	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	0.0042	0.002	0.0015
FOL003	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	19-Feb-13	Storm	Permethrin	PY	nd	0.002	0.002
PGC010	Stormdrain	19-Feb-13	Storm	Carbaryl	CB	nd	0.05	0.011
PGC010	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	0.05	0.02	0.003
PGC010	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC010	Stormdrain	19-Feb-13	Storm	Fipronil	FP	0.106	0.02	0.004
PGC010	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	trace	0.03	0.005
PGC010	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	trace	0.02	0.003
PGC010	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	0.07	0.03	0.005
PGC010	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
PGC010	Stormdrain	19-Feb-13	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC010	Stormdrain	19-Feb-13	Storm	Diazinon	OP	nd	0.01	0.0012
PGC010	Stormdrain	19-Feb-13	Storm	Malathion	OP	0.416	0.05	0.0117
PGC010	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.141	0.001	0.0009
PGC010	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	0.0043	0.002	0.0015
PGC010	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	0.0113	0.005	0.0015
PGC010	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC010	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	0.009	0.002	0.0017
PGC010	Stormdrain	19-Feb-13	Storm	Permethrin	PY	0.0097	0.002	0.002
PGC019	Stormdrain	19-Feb-13	Storm	Carbaryl	CB	nd	0.05	0.011
PGC019	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	0.036	0.02	0.003
PGC019	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC019	Stormdrain	19-Feb-13	Storm	Fipronil	FP	0.117	0.02	0.004
PGC019	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	trace	0.03	0.005
PGC019	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	trace	0.02	0.003
PGC019	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	0.05	0.03	0.005
PGC019	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
PGC019	Stormdrain	19-Feb-13	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC019	Stormdrain	19-Feb-13	Storm	Diazinon	OP	0.032	0.01	0.0012
PGC019	Stormdrain	19-Feb-13	Storm	Malathion	OP	nd	0.05	0.0117
PGC019	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.0427	0.001	0.0009
PGC019	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	nd	0.002	0.0015
PGC019	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
PGC019	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC019	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	0.0023	0.002	0.0017
PGC019	Stormdrain	19-Feb-13	Storm	Permethrin	PY	nd	0.002	0.002
PGC021	Stormdrain	19-Feb-13	Storm	Carbaryl	CB	0.086	0.05	0.011

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC021	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC021	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	trace	0.03	0.005
PGC021	Stormdrain	19-Feb-13	Storm	Fipronil	FP	0.038	0.02	0.004
PGC021	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	trace	0.03	0.005
PGC021	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	trace	0.02	0.003
PGC021	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	0.053	0.03	0.005
PGC021	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
PGC021	Stormdrain	19-Feb-13	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC021	Stormdrain	19-Feb-13	Storm	Diazinon	OP	nd	0.01	0.0012
PGC021	Stormdrain	19-Feb-13	Storm	Malathion	OP	trace	0.05	0.0117
PGC021	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.0363	0.001	0.0009
PGC021	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	0.0033	0.002	0.0015
PGC021	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
PGC021	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC021	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	0.0028	0.002	0.0017
PGC021	Stormdrain	19-Feb-13	Storm	Permethrin	PY	0.0114	0.002	0.002
PGC022	Stormdrain	19-Feb-13	Storm	Carbaryl	CB	nd	0.05	0.011
PGC022	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil	FP	0.041	0.02	0.003
PGC022	Stormdrain	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC022	Stormdrain	19-Feb-13	Storm	Fipronil	FP	0.135	0.02	0.004
PGC022	Stormdrain	19-Feb-13	Storm	Fipronil amide	FP	trace	0.03	0.005
PGC022	Stormdrain	19-Feb-13	Storm	Fipronil sulfide	FP	trace	0.02	0.003
PGC022	Stormdrain	19-Feb-13	Storm	Fipronil sulfone	FP	0.048	0.03	0.005
PGC022	Stormdrain	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
PGC022	Stormdrain	19-Feb-13	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC022	Stormdrain	19-Feb-13	Storm	Diazinon	OP	0.039	0.01	0.0012
PGC022	Stormdrain	19-Feb-13	Storm	Malathion	OP	nd	0.05	0.0117
PGC022	Stormdrain	19-Feb-13	Storm	Bifenthrin	PY	0.0499	0.001	0.0009
PGC022	Stormdrain	19-Feb-13	Storm	Cyfluthrin	PY	nd	0.002	0.0015
PGC022	Stormdrain	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
PGC022	Stormdrain	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC022	Stormdrain	19-Feb-13	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC022	Stormdrain	19-Feb-13	Storm	Permethrin	PY	0.0024	0.002	0.002
PGC040	Receiving Water	19-Feb-13	Storm	Carbaryl	CB	nd	0.05	0.011
PGC040	Receiving Water	19-Feb-13	Storm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC040	Receiving Water	19-Feb-13	Storm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC040	Receiving Water	19-Feb-13	Storm	Fipronil	FP	trace	0.02	0.004
PGC040	Receiving Water	19-Feb-13	Storm	Fipronil amide	FP	nd	0.03	0.005
PGC040	Receiving Water	19-Feb-13	Storm	Fipronil sulfide	FP	nd	0.02	0.003
PGC040	Receiving Water	19-Feb-13	Storm	Fipronil sulfone	FP	trace	0.03	0.005
PGC040	Receiving Water	19-Feb-13	Storm	Imidacloprid	IM	nd	0.05	0.0394
PGC040	Receiving Water	19-Feb-13	Storm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC040	Receiving Water	19-Feb-13	Storm	Diazinon	OP	nd	0.01	0.0012

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC040	Receiving Water	19-Feb-13	Storm	Malathion	OP	nd	0.05	0.0117
PGC040	Receiving Water	19-Feb-13	Storm	Bifenthrin	PY	0.0066	0.001	0.0009
PGC040	Receiving Water	19-Feb-13	Storm	Cyfluthrin	PY	nd	0.002	0.0015
PGC040	Receiving Water	19-Feb-13	Storm	Cypermethrin	PY	nd	0.005	0.0015
PGC040	Receiving Water	19-Feb-13	Storm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC040	Receiving Water	19-Feb-13	Storm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC040	Receiving Water	19-Feb-13	Storm	Permethrin	PY	nd	0.002	0.002
PGC010	Stormdrain	30-Apr-13	Nonstorm	Carbaryl	CB	trace	0.05	0.011
PGC010	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC010	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC010	Stormdrain	30-Apr-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
PGC010	Stormdrain	30-Apr-13	Nonstorm	Fipronil amide	FP	nd	0.03	0.005
PGC010	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
PGC010	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC010	Stormdrain	30-Apr-13	Nonstorm	Imidacloprid	IM	0.164	0.05	0.0394
PGC010	Stormdrain	30-Apr-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC010	Stormdrain	30-Apr-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC010	Stormdrain	30-Apr-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC010	Stormdrain	30-Apr-13	Nonstorm	Bifenthrin	PY	0.019	0.001	0.0009
PGC010	Stormdrain	30-Apr-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC010	Stormdrain	30-Apr-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC010	Stormdrain	30-Apr-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC010	Stormdrain	30-Apr-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC010	Stormdrain	30-Apr-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC019	Stormdrain	30-Apr-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC019	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil	FP	0.0303	0.02	0.003
PGC019	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC019	Stormdrain	30-Apr-13	Nonstorm	Fipronil	FP	0.0596	0.02	0.004
PGC019	Stormdrain	30-Apr-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC019	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC019	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfone	FP	0.0369	0.03	0.005
PGC019	Stormdrain	30-Apr-13	Nonstorm	Imidacloprid	IM	0.077	0.05	0.0394
PGC019	Stormdrain	30-Apr-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC019	Stormdrain	30-Apr-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC019	Stormdrain	30-Apr-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC019	Stormdrain	30-Apr-13	Nonstorm	Bifenthrin	PY	0.0095	0.001	0.0009
PGC019	Stormdrain	30-Apr-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC019	Stormdrain	30-Apr-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC019	Stormdrain	30-Apr-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC019	Stormdrain	30-Apr-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC019	Stormdrain	30-Apr-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC021	Stormdrain	30-Apr-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC021	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC021	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC021	Stormdrain	30-Apr-13	Nonstorm	Fipronil	FP	0.0206	0.02	0.004
PGC021	Stormdrain	30-Apr-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC021	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC021	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC021	Stormdrain	30-Apr-13	Nonstorm	Imidacloprid	IM	0.11	0.05	0.0394
PGC021	Stormdrain	30-Apr-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC021	Stormdrain	30-Apr-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC021	Stormdrain	30-Apr-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC021	Stormdrain	30-Apr-13	Nonstorm	Bifenthrin	PY	0.0079	0.001	0.0009
PGC021	Stormdrain	30-Apr-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC021	Stormdrain	30-Apr-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC021	Stormdrain	30-Apr-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC021	Stormdrain	30-Apr-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC021	Stormdrain	30-Apr-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC022	Stormdrain	30-Apr-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC022	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil	FP	0.0282	0.02	0.003
PGC022	Stormdrain	30-Apr-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC022	Stormdrain	30-Apr-13	Nonstorm	Fipronil	FP	0.0446	0.02	0.004
PGC022	Stormdrain	30-Apr-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC022	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC022	Stormdrain	30-Apr-13	Nonstorm	Fipronil sulfone	FP	0.0403	0.03	0.005
PGC022	Stormdrain	30-Apr-13	Nonstorm	Imidacloprid	IM	0.051	0.05	0.0394
PGC022	Stormdrain	30-Apr-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC022	Stormdrain	30-Apr-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC022	Stormdrain	30-Apr-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC022	Stormdrain	30-Apr-13	Nonstorm	Bifenthrin	PY	0.0099	0.001	0.0009
PGC022	Stormdrain	30-Apr-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC022	Stormdrain	30-Apr-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC022	Stormdrain	30-Apr-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC022	Stormdrain	30-Apr-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC022	Stormdrain	30-Apr-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC040	Receiving Water	30-Apr-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC040	Receiving Water	30-Apr-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC040	Receiving Water	30-Apr-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC040	Receiving Water	30-Apr-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
PGC040	Receiving Water	30-Apr-13	Nonstorm	Fipronil amide	FP	nd	0.03	0.005
PGC040	Receiving Water	30-Apr-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
PGC040	Receiving Water	30-Apr-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC040	Receiving Water	30-Apr-13	Nonstorm	Imidacloprid	IM	0.05	0.05	0.0394
PGC040	Receiving Water	30-Apr-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC040	Receiving Water	30-Apr-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC040	Receiving Water	30-Apr-13	Nonstorm	Malathion	OP	nd	0.05	0.0117

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC040	Receiving Water	30-Apr-13	Nonstorm	Bifenthrin	PY	nd	0.001	0.0009
PGC040	Receiving Water	30-Apr-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC040	Receiving Water	30-Apr-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC040	Receiving Water	30-Apr-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC040	Receiving Water	30-Apr-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC040	Receiving Water	30-Apr-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	01-May-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL002	Stormdrain	01-May-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL002	Stormdrain	01-May-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL002	Stormdrain	01-May-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	01-May-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL002	Stormdrain	01-May-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	01-May-13	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
FOL002	Stormdrain	01-May-13	Nonstorm	2,4-D	PX	0.064	0.05	0.015
FOL002	Stormdrain	01-May-13	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL002	Stormdrain	01-May-13	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL002	Stormdrain	01-May-13	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL002	Stormdrain	01-May-13	Nonstorm	Bifenthrin	PY	0.0019	0.001	0.0009
FOL002	Stormdrain	01-May-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL002	Stormdrain	01-May-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	01-May-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	01-May-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL002	Stormdrain	01-May-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL003	Stormdrain	01-May-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL003	Stormdrain	01-May-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL003	Stormdrain	01-May-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL003	Stormdrain	01-May-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	01-May-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL003	Stormdrain	01-May-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL003	Stormdrain	01-May-13	Nonstorm	Imidacloprid	IM	0.148	0.05	0.0394
FOL003	Stormdrain	01-May-13	Nonstorm	2,4-D	PX	0.057	0.05	0.015
FOL003	Stormdrain	01-May-13	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL003	Stormdrain	01-May-13	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	01-May-13	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL003	Stormdrain	01-May-13	Nonstorm	Bifenthrin	PY	0.0117	0.001	0.0009
FOL003	Stormdrain	01-May-13	Nonstorm	Cyfluthrin	PY	0.0036	0.002	0.0015
FOL003	Stormdrain	01-May-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	01-May-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	01-May-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	01-May-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil	FP	0.0171	0.01	0.0005
FOL002	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
FOL002	Stormdrain	17-May-13	Nonstorm	Fipronil	FP	trace	0.01	0.0005

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL002	Stormdrain	17-May-13	Nonstorm	Fipronil amide	FP	nd	0.02	0.0016
FOL002	Stormdrain	17-May-13	Nonstorm	Fipronil sulfide	FP	nd	0.01	0.0005
FOL002	Stormdrain	17-May-13	Nonstorm	Fipronil sulfone	FP	0.0219	0.01	0.0005
FOL003	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil	FP	0.0144	0.01	0.0005
FOL003	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
FOL003	Stormdrain	17-May-13	Nonstorm	Fipronil	FP	0.0402	0.01	0.0005
FOL003	Stormdrain	17-May-13	Nonstorm	Fipronil amide	FP	nd	0.02	0.0016
FOL003	Stormdrain	17-May-13	Nonstorm	Fipronil sulfide	FP	nd	0.01	0.0005
FOL003	Stormdrain	17-May-13	Nonstorm	Fipronil sulfone	FP	0.0507	0.01	0.0005
TRP1	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil	FP	nd	0.01	0.0005
TRP1	Stormdrain	17-May-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
TRP1	Stormdrain	17-May-13	Nonstorm	Fipronil	FP	nd	0.01	0.0005
TRP1	Stormdrain	17-May-13	Nonstorm	Fipronil amide	FP	0.02	0.02	0.0016
TRP1	Stormdrain	17-May-13	Nonstorm	Fipronil sulfide	FP	nd	0.01	0.0005
TRP1	Stormdrain	17-May-13	Nonstorm	Fipronil sulfone	FP	nd	0.01	0.0005
FOL002	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL002	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL002	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL002	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL002	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
FOL002	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL002	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
FOL002	Stormdrain	04-Jun-13	Nonstorm	2,4-D	PX	0.644	0.05	0.015
FOL002	Stormdrain	04-Jun-13	Nonstorm	Dicamba	PX	0.097	0.05	0.017
FOL002	Stormdrain	04-Jun-13	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL002	Stormdrain	04-Jun-13	Nonstorm	Triclopyr	PX	nd	0.05	0.02
FOL002	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0039	0.001	0.0009
FOL002	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL002	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL002	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL002	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL002	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	0.0107	0.002	0.002
FOL003	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
FOL003	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
FOL003	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
FOL003	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
FOL003	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
FOL003	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
FOL003	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	0.1075	0.05	0.0394
FOL003	Stormdrain	04-Jun-13	Nonstorm	2,4-D	PX	nd	0.05	0.015
FOL003	Stormdrain	04-Jun-13	Nonstorm	Dicamba	PX	nd	0.05	0.017
FOL003	Stormdrain	04-Jun-13	Nonstorm	MCPA	PX	nd	0.05	0.022
FOL003	Stormdrain	04-Jun-13	Nonstorm	Triclopyr	PX	nd	0.05	0.02

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
FOL003	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0068	0.001	0.0009
FOL003	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
FOL003	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
FOL003	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
FOL003	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
FOL003	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC010	Stormdrain	04-Jun-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC010	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC010	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC010	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	0.032	0.02	0.004
PGC010	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	nd	0.03	0.005
PGC010	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC010	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC010	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	0.347	0.05	0.0394
PGC010	Stormdrain	04-Jun-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC010	Stormdrain	04-Jun-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC010	Stormdrain	04-Jun-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC010	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0116	0.001	0.0009
PGC010	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC010	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC010	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC010	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC010	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC019	Stormdrain	04-Jun-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC019	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	0.025	0.02	0.003
PGC019	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC019	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	0.089	0.02	0.004
PGC019	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC019	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC019	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	0.044	0.03	0.005
PGC019	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	0.386	0.05	0.0394
PGC019	Stormdrain	04-Jun-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC019	Stormdrain	04-Jun-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC019	Stormdrain	04-Jun-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC019	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0067	0.001	0.0009
PGC019	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	0.0058	0.002	0.0015
PGC019	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC019	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC019	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC019	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
PGC021	Stormdrain	04-Jun-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC021	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC021	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC021	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	0.022	0.02	0.004
PGC021	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC021	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC021	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	0.037	0.03	0.005
PGC021	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	0.0685	0.05	0.0394
PGC021	Stormdrain	04-Jun-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC021	Stormdrain	04-Jun-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC021	Stormdrain	04-Jun-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC021	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0388	0.001	0.0009
PGC021	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC021	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	0.0199	0.005	0.0015
PGC021	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC021	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC021	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	0.0104	0.002	0.002
PGC022	Stormdrain	04-Jun-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC022	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC022	Stormdrain	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC022	Stormdrain	04-Jun-13	Nonstorm	Fipronil	FP	0.04	0.02	0.004
PGC022	Stormdrain	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC022	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.02	0.003
PGC022	Stormdrain	04-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC022	Stormdrain	04-Jun-13	Nonstorm	Imidacloprid	IM	0.3115	0.05	0.0394
PGC022	Stormdrain	04-Jun-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC022	Stormdrain	04-Jun-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC022	Stormdrain	04-Jun-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC022	Stormdrain	04-Jun-13	Nonstorm	Bifenthrin	PY	0.009	0.001	0.0009
PGC022	Stormdrain	04-Jun-13	Nonstorm	Cyfluthrin	PY	0.0074	0.002	0.0015
PGC022	Stormdrain	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC022	Stormdrain	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC022	Stormdrain	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC022	Stormdrain	04-Jun-13	Nonstorm	Permethrin	PY	0.0021	0.002	0.002
PGC040	Receiving Water	04-Jun-13	Nonstorm	Carbaryl	CB	nd	0.05	0.011
PGC040	Receiving Water	04-Jun-13	Nonstorm	Desulfinyl fipronil	FP	trace	0.02	0.003
PGC040	Receiving Water	04-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.03	0.005
PGC040	Receiving Water	04-Jun-13	Nonstorm	Fipronil	FP	trace	0.02	0.004
PGC040	Receiving Water	04-Jun-13	Nonstorm	Fipronil amide	FP	trace	0.03	0.005
PGC040	Receiving Water	04-Jun-13	Nonstorm	Fipronil sulfide	FP	nd	0.02	0.003
PGC040	Receiving Water	04-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.03	0.005
PGC040	Receiving Water	04-Jun-13	Nonstorm	Imidacloprid	IM	nd	0.05	0.0394
PGC040	Receiving Water	04-Jun-13	Nonstorm	Chlorpyrifos	OP	nd	0.01	0.0008
PGC040	Receiving Water	04-Jun-13	Nonstorm	Diazinon	OP	nd	0.01	0.0012
PGC040	Receiving Water	04-Jun-13	Nonstorm	Malathion	OP	nd	0.05	0.0117
PGC040	Receiving Water	04-Jun-13	Nonstorm	Bifenthrin	PY	0.0012	0.001	0.0009

Appendix IV. Water monitoring data for Study 269, FY2012-13

Site ID	Site Type	Sample Date	Event Type*	Analyte Name	Analyte Group**	Result (ug/L)*	RL (ug/L)	MDL (ug/L)
PGC040	Receiving Water	04-Jun-13	Nonstorm	Cyfluthrin	PY	nd	0.002	0.0015
PGC040	Receiving Water	04-Jun-13	Nonstorm	Cypermethrin	PY	nd	0.005	0.0015
PGC040	Receiving Water	04-Jun-13	Nonstorm	Fenvalerate/Esfenvalerate	PY	nd	0.005	0.0017
PGC040	Receiving Water	04-Jun-13	Nonstorm	Lambda-cyhalothrin	PY	nd	0.002	0.0017
PGC040	Receiving Water	04-Jun-13	Nonstorm	Permethrin	PY	nd	0.002	0.002
FOL002	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil	FP	0.0154	0.01	0.0005
FOL002	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
FOL002	Stormdrain	13-Jun-13	Nonstorm	Fipronil	FP	0.0118	0.01	0.0005
FOL002	Stormdrain	13-Jun-13	Nonstorm	Fipronil amide	FP	nd	0.02	0.0016
FOL002	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.01	0.0005
FOL002	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfone	FP	0.0419	0.01	0.0005
FOL003	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil	FP	0.0114	0.01	0.0005
FOL003	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
FOL003	Stormdrain	13-Jun-13	Nonstorm	Fipronil	FP	trace	0.01	0.0005
FOL003	Stormdrain	13-Jun-13	Nonstorm	Fipronil amide	FP	nd	0.02	0.0016
FOL003	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.01	0.0005
FOL003	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfone	FP	0.0264	0.01	0.0005
TRP1	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil	FP	nd	0.01	0.0005
TRP1	Stormdrain	13-Jun-13	Nonstorm	Desulfinyl fipronil amide	FP	nd	0.01	0.0008
TRP1	Stormdrain	13-Jun-13	Nonstorm	Fipronil	FP	nd	0.01	0.0005
TRP1	Stormdrain	13-Jun-13	Nonstorm	Fipronil amide	FP	nd	0.02	0.0016
TRP1	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfide	FP	trace	0.01	0.0005
TRP1	Stormdrain	13-Jun-13	Nonstorm	Fipronil sulfone	FP	trace	0.01	0.0005

*nd, not detected; trace, trace detection, > MDL and < RL; nonstorm, dry season monitoring; storm, rain storm monitoring

**CB, carbamate; CT, chlorothalonil; FP, fipronil; IM, imidacloprid; OP, organophosphate; PX, synthetic auxin herbicide; PY, pyrethroid

Appendix V. Aquatic toxicity data for Study 269, FY2012-13

Region	Area	Sample Date	Event Type	Site ID	Site Type	24 hr Survival	48 hr Survival	72 hr Survival	96 hr Survival
NorCal	SAC	7/31/2012	Nonstorm	FOL002	Stormdrain	100	77.38*	4*	2*
NorCal	SAC	7/31/2012	Nonstorm	FOL003	Stormdrain	100	100	100	100
NorCal	SAC	10/22/2012	Storm	FOL002	Stormdrain	58*	2*	0*	0*
NorCal	SAC	10/22/2012	Storm	FOL003	Stormdrain	44.72*	4.22*	0*	0*
NorCal	SAC	6/4/2013	Nonstorm	FOL002	Stormdrain	98	96	85.78	69.3*
NorCal	SAC	6/4/2013	Nonstorm	FOL003	Stormdrain	100	84	40*	24*

*Highlighted, significantly different than the control

Appendix VI. Analytical Methods used in Study 269 FY2012-13

Title: Determination of Bensulide and Imidacloprid in Surface Water

1. Scope:

This section method (SM) documents Bensulide and Imidacloprid pesticide Residue analysis in surface water. It is to be followed by all authorized section personnel.

2. Principle:

The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with methanol. The extract is then analyzed by an Ultra Performance Liquid Chromatography (UPLC) coupled to a triple quadrupole using electrospray ionization in positive ion mode.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

There is no known interference for this analysis.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Balance (Mettler PC 4400) or equivalent
5.5 Liquid Chromatograph equipped with an ion trap mass spectrometer

6. Reagents and Supplies

6.1 Methylene Chloride, nanograde or equivalent pesticide grade
6.2 Methanol, nanograde or equivalent pesticide grade
6.3 Anhydrous Sodium Sulfate, granular
6.4 Bensulide CAS# 741-58-2
6.5 Imidacloprid CAS# 138261-41-3
6.6 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.7 Separatory funnel, 2 L
6.8 Boiling flask, 500 mL
6.9 Funnel, long stem, 10 mm diameter
6.10 Disposable Pasteur pipettes, and other laboratory ware as needed
6.11 Recommended analytical columns: Waters Symmetry HSS T3 1.8µm 2.1x100 mm column

7. Standards Preparation:

7.1 The individual bensulide and Imidacplorid stock standards of 1.0mg/mL were obtained from the CDFA/CAC Environmental Analysis Standards Repository. The standards were diluted to 10 µg/mL with methanol for identification purposes. A combination standard of 10 µg/mL was prepared from the individual mg/mL standards in methanol. The combination 10 µg/mL standard was used to dilute the following concentrations: 0.025, 0.05, 0.1, 0.25, 0.5, 1.0 µg/mL in methanol.

7.2 Store standards according to manufacturing requirement. Keep all standards in designated refrigerator for storage.

7.3 The expiration date of working standard is six months from the preparation date of the stock standard

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulations (DPR) provided the background water for matrix blank and spikes.

9.1.2.1 Matrix blank: Weigh out approximate 1000 g of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out approximate 1000 g of background water. Spike a client requested amount of bensulide/imidacloprid into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Record the weight of the whole bottle water sample to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.2.2 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glasswool, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 80 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.2.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 - 20 inch Hg vacuum. Add 2 - 4 mL of methanol and rotoevaporate to 1 - 2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 3 more times with 2 - 4 mL of methanol and transfer each rinse to the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 1.0 mL with methanol, mix well and transfer into two autosampler vials.

9.2.9 Submit extract for LC-MS analysis.

10. Instrument Calibration:

10.1 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.025, 0.05, 0.1, 0.25, 0.5 or 1.0 ηg/µL are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

11. Analysis:

11.1 UPLC-MS/MS

11.1.1 UPLC instrument: Waters Acquity Ultra Performance LC
Column: Waters Acquity HSS T3 1.8µm 2.1x100 mm
ColumnTemperature: 50°C
Mobile Phase: Gradient
Solvent 1: Water + 4% acetic acid
Solvent 2: Methanol + 4% acetic acid
Gradient:

Time (min)	Flow rate	Solvent 1	Solvent 2
0	0.50	90.0	10.0
0.5	0.50	90.0	10.0
3.5	0.50	10.0	90.0
4.5	0.50	10.0	90.0
5.0	0.50	90.0	10.0
6.0	0.50	90.0	10.0

Injection Volume: 1.0 µL

11.1.2 Mass Spectrometry and Operating Parameters
Model: Waters Xevo Triple Quadrupole
Ion ProbeType: Electrospray Ionization (ES)
Ion Mode: ESI (+)
Desolvation Temp: 500 °C
Source Temp: 150 °C

Compound	Retention Time (min)	Precursor ion	Product Ion	Dwell (s)	Cone(V)	Collision Energy/-ev
Imidacloprid	2.51	256.08	**175.02**	0.025	24.0	16.0
		256.08	209.1	0.025	24.0	16.0
Bensulide	3.94	398.16	**158.01**	0.061	14.0	34.0
		398.16	314	0.061	46.0	30.0

Quantitation ions are in bold.

12. Quality Control:

12.1 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.10 ppb. The standard deviation from the spiked sample recoveries are used to calculate the MDL for the analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client agreement, the RL is chosen in a range 1-5 times the MDL. The reporting limit for Bensulide is 0.04ppb and Imidacloprid is 0.05ppb

12.3 Method Validation

The method validation for bensulide and Imidachloprid consisted of three sample sets. Each set included five levels of fortification and a method blank. All spikes

and method blanks were processed through the entire analytical method. Spikes levels and recoveries for bensulide and Imidacloprid are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation. The upper and lower control limits are set at ± 3 standard deviation of the % recovery, shown in Appendix 2. The control chart range generated from this validation data was narrower than that of the previous method for Bensulide. It was decided that the control charts would be used but the upper and lower control limits would be set with the limits from the previous methods Bensulide 56.7 – 130.6 and Imidacloprid 77.2-121.9. The new data for Bensulide fit within these limits and the data for Imidacloprid was almost the same as the old control limits.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time should be within ± 2 per cent of that of the standards.

12.5.3 The recoveries of the matrix spikes shall be within the control limits.

12.5.4 The sample shall be diluted if results fall outside of the calibration curve.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, results may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{(\text{sample peak ht. or area})\,(\text{std. conc.})\,(\text{std. vol. injected})\,(\text{sample final vol., (mL)})(1000\ \mu\text{L/mL})}{(\text{std. peak ht. or area})\,(\text{sample vol. injected})\,(\text{sample wt., g})}$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specifications sheets.

15. Discussion:

This SOP combines the analysis of bensulide and Imidacloprid into a single method. In the past both compounds were extracted and analyzed separately.

16. References:

16.1. Lee, Paul; *Determination of Bensulide in Surface Water Using Liquid Chromatography Mass Spectrometry,* 2002, Environmental Monitoring method, Center for Analytical Chemistry, CDFA.

16.2 Hernandez, Jorge; *HPLC Determination of Imidacloprid in Surface and Well Water,* 2001, Environmental Monitoring method, Center for Analytical Chemistry, CDFA.

APPENDIX I

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL) for Bensulide and Imidacloprid in surface water:

Spk\Analyte	Bensulide ppb	Imidacloprid ppb
0.1 ppb spk 1	0.105	0.112
0.1 ppb spk 2	0.107	0.094
0.1 ppb spk 3	0.190	0.100
0.1 ppb spk 4	0.105	0.093
0.1 ppb spk 5	0.106	0.080
0.1 ppb spk 6	0.097	0.095
0.1 ppb spk 7	0.097	0.073
SD	0.00629	0.00125
MDL	0.0198	0.0394
RL	0.04	0.05

APPENDIX II

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	%	%
Bensulide	0.1	109	112	92.2	Mean:	102
	0.2	113	104	106	SD:	7.43
	0.5	106	89.2	97.4	UCL:	124.4
	1.0	103	108	102	UWL:	117
	2.0	95.0	103	92.0	LWL:	87.3
					LCL:	79.8
Imidacloprid	0.1	103	97.0	105	Mean:	100
	0.2	108	104	103	SD:	7.78
	0.5	104	87.0	103	UCL:	123.5
	1.0	104	108	108	UWL:	115.7
	2.0	90.0	93.0	84.9	LWL:	84.6
					LCL:	76.8

Written BY:

Original Signed by _____ 9/25/2013 _____

Jean Hsu
Environmental Scientist

Date

Written BY:

Original Signed by _____ 9/25/2013 _____

Jane White
Staff Environmental Scientist

Date

Approved By:

Original Signed by _____ 9/25/2013 _____

Steve Siegel
Sr. Environmental Scientist

Date

Approved By:

Original Signed by _____ 9/25/2013 _____

Elaine Wong
Environmental Program Manager I

Date

Revision Log:

Date	What was revised? Why?

Title: Determination of Chlorothalonil in Ground and Surface Water

1. Scope:

This section method (SM) provides stepwise procedure for chlorothalonil analysis in ground and surface water. It is followed by all authorized EA personnel.

2. Principle:

The chlorothalonil is extracted from the acidified ground water and surface water samples with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated on a rotary evaporator and then a solvent exchange is performed with methanol. The extract is concentrated to a final volume of 1 mL and then vialed into 2 autosampler vials for analysis on an Ultra Performance Liquid Chromatography (UPLC) coupled to a negative atmosphere pressure chemical ionization triple quadrupole mass spectrometry (APCI-LC/MS/MS).

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

4. Interferences:

There were no matrix interferences for chlorothalonil at the time of method development.

5. Apparatus and Equipment:

5.1 Rotary Evaporator (Buchi/Brinkman or equivalent)
5.2 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.3 Balance (Mettler PC 4400 or equivalent)
5.4 Vortex-vibrating mixer
5.5 UPLC equipped with a triple quadrupole mass spectrometry and APCI ion source.

6. **Reagents and Supplies**:

6.1 Chlorothalonil CAS#1897-45-6
6.2 Methylene Chloride, nanograde or equivalent pesticide grade
6.3 Sulfuric Acid, Conc. ACS Grade
6.4 Water, MS grade, Burdick & Jackson or equivalent
6.5 Methanol, MS grade, Burdick & Jackson or equivalent
6.6 Separatory funnel, 2 L
6.7 Boiling flask, 500 mL
6.8 Sodium Sulfate, ACS grade
6.9 Funnels, long stem, 60°, 10 mm diameter
6.10 Graduated conical tubes with glass stopper, 15 mL
6.11 Glass wool, Pyrex® fiber glass slivers 8 microns
6.12 Disposable Pasteur pipettes, and other laboratory ware as needed
6.13 Recommended analytical column:
Waters Acquity BEH 1.7µm, 2.1 x 50 mm

7. **Standards Preparation:**

7.1 An individual stock standard of 1.0 mg/mL was obtained from the CDFA/CAC Standards Repository. The standard was diluted to 10 µg/mL with methanol for identification purposes.

The following concentrations: 1, 0.5, 0.25, 0.1, 0.05, 0.025, µg/mL were prepared in methanol for LC instrument calibration.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 The expiration date of each standard is six months from the preparation date.

8. **Sample Preservation and Storage**:

Store all samples waiting for extraction in a separate refrigerator (4±3°C).

9. **Test Sample Preparation**:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the ground water and surface water for background to be used in method validation and QC.

9.2 Preparation of blank and spike

Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of fungicide into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Record the weight of water samples to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a funnel.

9.3.2 Add 2.5 mL of sulfuric acid to each separatory funnel and mix well.

9.3.3 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.3.4 After phases have separated, drain the lower methylene chloride layer through 25 ± 4 g of anhydrous sodium sulfate and glass wool into a 500 mL boiling flask.

9.3.5 Repeat steps 9.3.3 & 9.3.4 two more times using 80 ± 5 mL of methylene chloride for 1 minute each time. Combine the extracts in the same boiling flask.

9.3.6 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.7 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inch Hg vacuum. Add 2-4 mL of methanol and rotoevaporate to 1-2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.3.8 Rinse flask 3 more times with 2 - 4 mL of methanol and transfer each rinse to the same test tube.

9.3.9 Evaporate the sample extract to a volume slightly less than 1 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 1.0 mL with methanol, mix well and transfer to 2 autosampler vials with inserts.

10. **Instrument Calibration**:

10.1 The calibration standard curve consists of a minimum of three levels. The lowest level must be at or below the corresponding reporting limits.

10.2 The calibration curve for the LCMS instrument was obtained using Linear fit.

11. **Analysis:**

11.1 UPLC-MS/MS

11.1.1 UPLC Instrument: Waters Acquity Ultra Performance LC
Column: Waters Acquity BEH 1.7µm, 2.1 x 50 mm
Column Temperature: 60 °C
Mobile Phase: Gradient
Solvent 1: Water
Solvent 2: Methanol
Gradient:

Time(min)	Flow rate	Solvent 1	Solvent 2
0	0.50	90.0	10.0
1.0	0.50	90.0	10.0
1.5	0.50	5.0	95.0
3.5	0.50	5.0	95.0
3.55	0.50	90.0	10.0
5.0	0.50	90.0	10.0

Injection Volume:2.0 µL

11.1.2 Mass Spectrometry and Operating Parameters
Model: Waters Xevo Triple Quadrupole
Ion ProbeType: Atmospheric Pressure Chemical Ionization (APCI)
Ion Mode: APCI-
APCI Probe Temp: 500 °C
Source Temp: 150 °C

Compound	Retention Time (min)	Precursor ion	Product Ion	Dwell (s)	Cone(V)	Collision Energy/-ev
Chlorothalonil	1.90	244.95	174.95	0.061	46.0	28.0
		244.95	**181.91**	0.061	46.0	30.0

Quantitation ions are in bold.

Note: The column conditions, temperature, mobile phase, etc. may slightly shift retention time.

12. **Quality Control**:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 well water samples and 7 surface water samples are spiked at 0.1ppb and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following equation:

MDL = tS

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL, as per client agreement. The reporting limit for Chlorothalonil in well water and surface water is 0.05 ppb.

12.3 Method Validation

The method validation consisted of five sample sets. Each set included five levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the analytes are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the % recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.
12.5.2 The retention time should be within ± 2 per cent of that of the standards.
12.5.3 The recoveries of the matrix spikes shall be within the control limits.
12.5.4 The sample shall be diluted if results fall outside of the calibration curve.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The LCMS software used a linear curve fit, with all levels weighted 1/x.

$$\text{ppb} = \frac{(\text{sample peak area or ht}) \times (\text{std conc}) \times (\text{std vol. Injected}) \times (\text{final vol of sample})(1000\ \mu\text{L/mL})}{(\text{std.peak area or ht}) \times (\text{sample vol injected}) \times (\text{sample wt (g)})}$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

15. Discussion and References:

15.1 Upon infusion of chlorothalonil, we found the principal ion to be 245 ion rather than the anticipated molecular ion at 264. This is consistent with substitution of the chlorine by hydroxyl within the source.

15.2 Acid is not necessary for the extraction of chlorothalonil but was added with the intent of including its metabolites at a later date.

15.3 A storage stability study was done with this project for well water only. The storage stability study consisted of a 1.0 ppb spike level and 2 replicates over a 28 day period. Fourteen liters of background well water were spiked and then transferred to fourteen one liter amber bottles. These spiked samples were stored in the refrigerator until analyzed at 0, 2, 5, 7, 14, 21 and 28 days. Along with the storage spikes a blank and method control spike were also extracted. This storage study showed no degradation for the chlorothalonil within the 28 days. Results for the storage studies are shown in Appendix 3.

15.4 We have observed gradual losses in sensitivity and peak tailing caused by the sample matrix. We recommend cleaning the cones when this occurs.

15.5 References:

15.51 Wakefield, Mike (Principal MS Applications Specialist); UPLC-MS/MS conditions for Chlorothalonil, Waters Corporation

15.52 Hsu, J. and White, J.; *Determination of Azoxystrobin, Azoxystrobin Acid, Azoxystrobin Z-metabolite,Dicloran, Iprodione,Isoiprodione,Vinclozalin and 3,5-Dichloroaniline in Well Water*, 2010, Environmental Analysis Section Method, Center for Analytical Chemistry, CDFA

Appendix 1

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Results:	Well Water	Surface Water
Spk\Analyte	Chlorothalonil	Chlorothalonil
	Spike Level: 0.1 ppb	Spike Level: 0.1 ppb
Spike 1	0.0919	0.0898
Spike 2	0.127	0.0959
Spike 3	0.0958	0.102
Spike 4	0.106	0.0797
Spike 5	0.104	0.115
Spike 6	0.107	0.101
Spike 7	0.106	0.0928
SD	0.0112	0.0111
MDL	0.0351	0.0348
RL	0.05	0.05

Appendix 2

Results: Well Water

Analyte	Spike ppb	Recovery (%) Set 1	(%) set 2	(%) set 3	(%) set 4	(%) set 5	%	%
Chlorothalonil	0.1	113	100	95.8	111	85.4	Mean:	93.2
	0.2	98.3	110	79.7	115	84.0	SD:	12.4
	0.5	73.2	116	78.3	91.8	79.1	UCL:	130.4
	1.0	93.3	91.6	87.7	89.0	82.9	UWL:	118.0
	2.0	83.0	101	85.8	99.5	86.2	LWL:	68.5
							LCL:	56.1

Results:Surface Water

Analyte	Spike ppb	Recovery (%) Set 1	(%) set 2	(%) set 3	(%) set 4	(%) set 5	%	%
Chlorothalonil	0.1	95.2	79.7	76.2	94.3	100	Mean:	93.3
	0.2	103	89.8	81.8	102	110	SD:	9.9
	0.5	101	92.4	74.9	102	97.6	UCL:	123.0
	1.0	90.8	92.7	81.8	104	90.7	UWL:	113.1
	2.0	106	91.8	79.3	104	90.5	LWL:	73.4
							LCL:	63.5

Appendix 3 Storage Stability Study

Spike Level: 1.0ppb

Chlorothalonil Results:

Storage Day	EMON Lab#	Sample	1st injection result ppb	2nd injection result ppb	Avgerage ppb	% Recovery
Day 0						
	2010-1618	Blank	ND	ND	ND	N/A
	2010-1619	SPK 1	0.785	0.676	0.731	73.1%
	2010-1620	Spk 2	0.765	0.721	0.743	74.3%
Day 2	2010-1621	Blank	ND	ND	ND	N/A
	2010-1622	QC spk	0.887	0.844	0.866	86.6%
	2010-1623	SPK 1	1.04	1.07	1.055	106%
	2010-1624	Spk 2	1.02	0.931	0.976	97.6%
Day 5	2010-1625	Blank	ND	ND	ND	N/A
	2010-1626	QC spk	0.783	0.718	0.751	75.1%
	2010-1627	SPK 1	0.810	0.764	0.787	78.7%
	2010-1628	Spk 2	0.882	0.718	0.800	80.0%
Day 7	2010-1629	Blank	ND	ND	ND	N/A
	2010-1630	QC spk	0.902	0.907	0.905	90.5%
	2010-1631	SPK 1	0.889	0.842	0.866	86.6%
	2010-1632	Spk 2	0.903	0.848	0.876	87.6%
Day 14	2010-1633	Blank	ND	ND	ND	N/A
	2010-1634	QC spk	1.21	1.23	1.22	122%
	2010-1635	SPK 1	0.984	0.849	0.917	91.7%
	2010-1636	Spk 2	0.968	0.878	0.923	92.3%

Appendix 3 Storage Stability Study continued:

Day 21	2010-1637	Blank	ND	ND	ND	N/A
	2010-1638	QC spk	0.977	0.959	0.968	96.8%
	2010-1639	SPK 1	0.766	0.739	0.753	75.3%
	2010-1640	Spk 2	0.834	0.787	0.811	81.1%
Day 28	2010-1641	Blank	ND	ND	ND	N/A
	2010-1642	QC spk	0.953	0.899	0.926	92.6%
	2010-1643	SPK 1	0.887	0.875	0.881	88.1%
	2010-1644	Spk 2	0.994	0.914	0.954	95.4%

Written By:

Original signed by: 1/11/2011

Jean Hsu
Environmental Scientist

Date

Written By:

Original signed by: 1/11/2011

Jane White
Environmental Scientist

Date

Approved By:

Original signed by: 1/10/2011

Stephen Siegel
Senior Environmental Scientist

Date

Approved By:

Original signed by: 1/10/2011

Elaine Wong
Environmental Program Manager I

Date

Revision Log:

Date	What was revised? Why?

Title: Determination of Ethalfluralin, Trifluralin, Benfluralin, Prodiamine, Pendimethalin, Oxyfluorfen, and Oryzalin in Surface Water

1. Scope:

This section method (SM) provides stepwise procedure for selective Dinitroaniline compounds and Oxyfluorfen analysis in surface water. It is followed by all authorized EA personnel.

2. Principle:

The dinitroanilines and oxyfluorfen are extracted from surface water samples with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated on a rotary evaporator and then a solvent exchange is performed with acetone. The extract is concentrated to a final volume of 1 mL where 0.5 mL is removed and vialed for GCMS-SIM (Gas Chromatography with Mass Spectrometer operated in the Single Ion Monitoring mode) or GCMS/MS analysis. The remaining 0.5mL is evaporated to just dryness and then brought up to a final volume of 0.5mL with methanol for analysis of oryzalin on LCMS.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

4. Interferences:

There were no matrix interferences that caused quantitative problems during method development and validation.

5. Apparatus and Equipment:

5.1 Rotary Evaporator (Buchi/Brinkman or equivalent)
5.2 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.3 Balance (Mettler PC 4400 or equivalent)
5.4 Vortex-vibrating mixer

5.5 Gas Chromatograph equipped with a mass selective detector (MSD)
5.6 Gas Chromatograph equipped with a triple stage quadropole detector (MS/MS)
5.7 Liquid Chromatograph equipped with an ion trap (LCMS)

6. **Reagents and Supplies**:

6.1	Ethalfluralin	CAS#55283-68-6
6.2	Trifluralin	CAS#1582-09-8
6.3	Benfluralin	CAS#1861-40-1
6.4	Prodiamine	CAS#29091-21-2
6.5	Pendimethalin	CAS#40487-42-1
6.6	Oxyfluorfen	CAS#42874-03-3
6.7	Oryzalin	CAS#19044-88-3

6.8 Methylene Chloride, nanograde or equivalent pesticide grade
6.9 Acetone, nanograde or equivalent pesticide grade
6.10 Water, MS grade, Burdick & Jackson or equivalent
6.11 Methanol, MS grade, Burdick & Jackson or equivalent
6.12 Formic Acid, HPLC grade
6.13 Ammonium formate, reagent grade or equivalent
6.10 Separatory funnel, 2 L
6.11 Boiling flask, 500 mL
6.12 Sodium Sulfate, ACS grade
6.13 Funnels, long stem, 60°, 10 mm diameter
6.14 Volumetric Pipette, 0.5 mL
6.15 Graduated conical tubes with glass stopper, 15 mL
6.16 Glass wool, Pyrex® fiber glass slivers 8 microns
6.17 Disposable Pasteur pipettes, and other laboratory ware as needed
6.18 Recommended analytical columns:

For MSD - 5% (Phenyl)-methylpolysiloxane (HP-5MS or equivalent) fused silica column, 30 m x 0.25 mm id x 0.25 µm film thickness.

For HPLC/MS – Waters SymmetryShieldRP$_{18}$ 5 µm, 3.9 x 150 mm cartridge
Guard column: Waters SymmetryShieldRP$_{18}$ 5 µm, 3.9 x 20 mm cartridge
Guard column holder: Waters Sentry guard holder universal.

7. Standards Preparation:

7.1 The individual dinitroaniline and oxyfluorfen stock standards of 1.0 mg/mL were obtained from the CDFA/CAC Standards Repository. The standards were diluted

to 10 µg/mL with acetone for identification purposes. Oryzalin was prepared in methanol at a concentration of 10 µg/mL for infusion into the LCMS.

A combination standard of 10 µg/mL was prepared from the individual mg/mL standards with acetone. The standard was also used to dilute the following concentrations: 0.025, 0.05, 0.1, 0.2, 0.5, and 1 µg/mL in acetone for GC instrument calibration. The 10 µg/mL of oryzalin in methanol was diluted to the same concentrations as above for LC instrument calibration.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 The expiration date of each standard is six months from the preparation date.

8. **Sample Preservation and Storage**:

Store all samples waiting for extraction in a separate refrigerator (0 - 5 °C).

9. **Test Sample Preparation**:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the surface water for background to be used in method validation and QC.

9.2 Preparation of blank and spike

Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of herbicides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Record the weight of water samples to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.3.2 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.3.3 After phases have separated, drain lower the methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glass wool, into a 500 mL boiling flask.

9.3.4 Repeat steps 9.3.1 & 9.3.2 two more times using 80 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.3.5 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inch Hg vacuum. Add 2-4 mL of acetone and rotoevaporate to 1-2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.3.7 Rinse flask 3 more times with 2 - 4 mL of acetone and transfer each rinse to the same test tube.

9.3.8 Evaporate the sample extract to a volume slightly less than 1 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 1.0 mL with acetone, mix well and transfer 0.5mL to two autosampler vials with inserts. Submit extract for GCMS-Triple Stage quadrapole analysis.

9.3.9 The remaining 0.5 mL sample extract is placed back in the water bath and evaporated to just dryness. Pipet 0.5 mL of methanol into the test tube and vortex well. Transfer extract to an autoampler vial to analyze on LCMS for oryzalin.

10. **Instrument Calibration**:

10.1 The calibration standard curve consists of a minimum of three levels. The lowest level must be at or below the corresponding reporting limits.

10.2 The calibration curves for the GCMS and Triple Quad were obtained using quadratic fit. The LCMS calibration curves were obtained using linear regression.

11. Analysis:

11.1 HPLC-MS

11.1.1 HPLC Instrument: Waters model 2695 HPLC and auto-sampler with column heater and remote control through Thermo Finnigan Xcalibur system.

Column: Waters SymmetrySheid RP_{18} 5 µm, 3.9 x 150 mm column
Column Temperature: 40 °C
Mobile Phase: Gradient
Solvent 1: 3762 mL water, 200 mL methanol, 38 mL 1M ammonium formate and 4.0 mL formic acid.
Solvent 2: 3600 mL methanol, 360 mL water, 36 mL 1.0 M ammonium formate, 4 mL formic acid.
Gradient:

Time(min)	Flow rate	Mobile Phase 1	Mobile Phase 2
0	0.75	85.0	15.0
3.0	0.75	85.0	15.0
4.0	0.75	50.0	50.0
10.0	0.75	50.0	50.0
14.0	0.75	40.0	60.0
16.0	0.75	5.0	95.0
22.0	0.75	5.0	95.0
24.5	0.75	85.0	15.0
27.0	0.75	85.0	15.0

Injection Volume:20 µL

11.1.2 Liquid Chromatograph Mass spectrometer (LC-MS) and Operating Parameters

Model:	Finnigan Model DECA ion trap MS
Ion Source Type:	Atmospheric pressure Ionization (APCI)
Source Polarity:	Positive
APCI Vaporizer Temp:	450 °C
Capillary Temperature:	220 °C
Sheath Gas:	60
Auxiliary Gas:	10
Mode of operation:	MS/MS

Compound Name	Retention Time (min.)	Molecular Weight	Mass Range	Product Ions
Oryzalin	18.96	346.36	95-400	288, 305

Note:The column conditions, temperature, mobile phase, etc. may slightly shift retention time.

11.1.3 Operating parameter

Parent Mass(m/z)	Isolation Width (m/z)	Normalized Collision Energy (%)	Activation Q	Activation Time (msec.)
347	2.0	30.0	0.250	30.0

11.2 GC-Triple Quad Instrumentation:

11.2.1 Model: Varian Triple Quad 320-MS
Column: Varian Factor Four VF-5ms x 0.25mm x0.25µm

Temperature Program: initial column temperature 80 °C, hold 1 min., ramp at 15 °C/min. to temperature of 180 °C and hold for 3 min. ramp at 15 °C/min. to final temperature of 300°C and hold for 3 min.;

Injector Temperature: 250 °C
Injection volume: 1 uL.

Compound	Retention Time (min)	Precursor ion	Product Ion	Collison Energy/-ev
Ethalfluralin	10.28	333	316	-10
Trifluralin	10.52	335	290	-15
Benfluralin	10.62	335	276	-15
Prodiamine	13.91	350	275	-10
Pendimethalin	14.86	281	252	-10
Oxyfluorfen	15.97	361	300	-15

11.3 GCMS Instrumentation:

11.3.1Model: Agilent GCMS

Column: 5% (Phenyl)-methylpolysiloxane (HP-5MS or equivalent) fused silica column, 30 m x 0.25 mm id x 0.25 µm film thickness.

Temperature Program: initial column temperature 80 °C, hold 1 min., ramp at 15 °C/min. to temperature of 180 °C and hold for 3 min. ramp at 15 °C/min. to final temperature of 300°C and hold for 3 min.;

Injector Temperature: 250 °C
Transfer line Temperature: 280 °C

Compound	Retention Time (min.)	Selected ions	Starting time (min.)
Ethalfluralin	9.41	**276**, 316, 333	6.00
Trifluralin	9.62	264, **306**, 335	9.52
Benfluralin	9.69	264, **292**, 335	9.52
Prodiamine	13.27	279, **321**, 333	12.50
Pendimethalin	14.23	**252**, 253, 281	13.85
Oxyfluorfen	15.38	**252**, 300, 361	14.85

Quantitation ions are in bold.

12. **Quality Control**:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 surface water samples are spiked at 0.05ppb and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL, as per client agreement. The reporting limit for the dinitroanilines and oxyfluorfen is 0.05 ppb.

12.3 Method Validation

The method validation consisted of four sample sets. Each set included five levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the selective dinitroaniline and oxyfluorfen are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each analyte. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the % recovery, respectively, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.
12.5.2 The retention time should be within ± 2 per cent of that of the standards.
12.5.3 The recoveries of the matrix spikes shall be within the control limits.
12.5.4 The sample shall be diluted if results fall outside of the calibration curve.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The LCMS software used a linear curve fit, with all levels weighted equally. The software for the triple quadrapole uses a quadratic curve fit, with all levels weighted 1/nx and the GCMS uses quadratic curve fit, with all levels weighted equally. Alternatively, at the chemist's discretion, sample results may be calculated using the response factor for the standard.

$$\text{ppb} = \frac{(\text{sample peak area or ht}) \times (\text{std conc}) \times (\text{std vol. Injected}) \times (\text{final vol of sample})(1000\ \mu\text{L/mL})}{(\text{std.peak area or ht}) \times (\text{sample vol injected}) \times (\text{sample wt (g)})}$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

15. Discussion and References:

15.1 The triple quadrapole will used as the primary instrument for the analysis of the dinitroanalines and oxyfluorfen. The MSD will be used as a backup instrument. The LCMS is used for the analysis of oryzalin since it wasn't very sensitive on the GC.

15.2 A storage stability study was done with this project. The storage stability study consisted of a 5 ppb spike level and 3 replicates over a 28 day period. Fifteen bottles containing backgrouond water were spiked and stored in the refrigerator until analyzed on 0, 4, 7, 14, and 28 days. Along with the storage spikes a blank and method control spike were also extracted. This storage study showed no degradation for the dinitroaniline compounds or oxyfluorfen. The results are shown in Appendix 3.

15.3 We have observed gradual losses in sensitivity caused by the sample matrix. We recommend changing the injector liner and trimming the column when this occurs.

15.4 Solid phase extraction has been tried for sample preparation as part of our method development. The recoveries were low and inconsistent for some compounds.

15.5 GC-Triple Quad analysis of the samples produced a sample response and quantitation varied depending on matrix background in the samples. Therefore the calibration standards were added to a matrix blank extract to correct for matrix background interference. This is unnecessary for LCMS analysis.

15.6 References:

15.61 J.L Kish, E.M. Thruman, E.A. Scribner, and L.R. Zimmerman; *Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of Selected Herbicides Metabolites and Their Degradaion Products in Water Using Solid-Phase Extraction and Gas*

Chromatography/Mass, U.S. Geological Survey Kansas Water Science Center

15.62 Hsu, J. and Feng, H.; *Determination of Organophosphate Pesticides in the surface water using Gas Chromatography*, 2004, Environmental monitoring method, Center for Analytical Chemistry, CDFA

Appendix 1

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Results: Varian GC/TQMS

Spk\Analyte	Ethalfluralin	Trifluralin	Benfluralin	Prodiamine	Pendimethalin	Oxyfluorfen
0.05ppb spk 1	0.0366	0.0410	0.0384	0.0375	0.0358	0.0332
0.05ppb spk 2	0.0463	0.0402	0.0387	0.0384	0.0359	0.0369
0.05ppb spk 3	0.0416	0.0399	0.0451	0.0414	0.0377	0.0343
0.05ppb spk 4	0.05	0.0478	0.0465	0.0427	0.0464	0.0403
0.05ppb spk 5	0.0479	0.0398	0.0433	0.0391	0.0385	0.0375
0.05ppb spk 6	0.0461	0.0408	0.0437	0.0415	0.0394	0.0381
0.05ppb spk 7	0.0495	0.0512	0.0487	0.0493	0.0425	0.0425
SD	0.00479	0.00460	0.00382	0.00395	0.00382	0.00322
MDL	0.0150	0.0144	0.0120	0.0124	0.0120	0.0101
RL	0.05	0.05	0.05	0.05	0.05	0.05

Appendix 1: continued

Results: Agilent GC/MSD

Spk\Analyte	Ethalfluralin	Trifluralin	Benfluralin	Prodiamine	Pendimethalin	Oxyfluorfen
0.05ppb spk 1	0.044	0.040	0.038	0.051	0.045	0.052
0.05ppb spk 2	0.052	0.047	0.044	0.060	0.054	0.061
0.05ppb spk 3	0.048	0.044	0.041	0.057	0.051	0.059
0.05ppb spk 4	0.059	0.054	0.051	0.069	0.062	0.070
0.05ppb spk 5	0.047	0.044	0.041	0.054	0.048	0.052
0.05ppb spk 6	0.049	0.045	0.042	0.057	0.051	0.056
0.05ppb spk 7	0.056	0.052	0.049	0.066	0.059	0.068
SD	0.00528	0.0049	0.0047	0.0064	0.0059	0.0072
MDL	0.017	0.015	0.015	0.020	0.019	0.023
RL	0.05	0.05	0.05	0.05	0.05	0.05

Results: Finningan LCQ Deca

Spk\Analyte	Oryzalin
0.05ppb spk 1	0.057
0.05ppb spk 2	0.057
0.05ppb spk 3	0.057
0.05ppb spk 4	0.056
0.05ppb spk 5	0.055
0.05ppb spk 6	0.057
0.05ppb spk 7	0.053
SD	0.001528
MDL	0.021
RL	0.05

Appendix 2

Method Validation Data

Results: **Varian GC/TQMS**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	%	%
Ethalfluralin	0.15	110	97.7	101	97.9	Mean:	98.7
	0.3	108	107	86.2	96.4	SD:	6.4
	1	94.7	94	98.9	93.9	UCL:	117.9
	2	94.7	105	108	96.7	UWL:	111.5
	5	90.0	95.9	102	95.0	LWL:	85.9
						LCL:	79.5
Trifluralin	0.15	109	91.4	103	89.8	Mean:	97.4
	0.3	108	104	88.5	92.7	SD:	6.6
	1	96.5	92	97.6	95.2	UCL:	117.2
	2	96.8	106	106	91.5	UWL:	110.6
	5	92.6	89.9	102	95.6	LWL:	84.2
						LCL:	77.6
Benfluralin	0.15	103	86	101	87.7	Mean:	96.7
	0.3	107	104	83.5	92.6	SD:	7.0
	1	98.3	92.5	101	93.6	UCL:	117.7
	2	94.9	108	104	95.1	UWL:	110.7
	5	91	90.4	102	97.3	LWL:	82.7
						LCL:	75.7
Prodiamine	0.15	120	95.1	112	99.0	Mean:	101
	0.3	117	113	77.6	97.2	SD:	11.4
	1	102	93.7	113	90.2	UCL:	135.2
	2	92.6	108	115	92.5	UWL:	123.8
	5	90.1	93.9	100.9	91.0	LWL:	78.2
						LCL:	66.8

Results: **Varian GC/TQMS**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	%	%
Pendimethlin	0.15	109	94.4	109	95.3	Mean:	98.0
	0.3	112	106	85.1	98.0	SD:	8.9
	1	101	91.6	105	90.2	UCL:	124.7
	2	94.2	99.6	115	92.2	UWL:	115.8
	5	86.6	88.3	99.3	88.5	LWL:	80.2
						LCL:	71.3
Oxyfluorfen	0.15	114	96.5	112.4	95.3	Mean:	100.4
	0.3	115	113	75.2	101	SD:	12.8
	1	105	90.7	107	91.3	UCL:	138.8
	2	97.6	109	128	91.9	UWL:	126.0
	5	84.1	89.8	106	85.7	LWL:	74.8
						LCL:	62.0

Results: **Agilent GC/MSD**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Ethalfluralin	0.15	94.3	84.9	95.9	91.2	Mean:	99.6
	0.3	104	114	105	90.6	SD:	9.6
	1	123	107	100	106	UCL:	128.4
	2	96.3	114	103	89.2	UWL:	118.8
	5	96.9	92.9	92.7	92.6	LWL:	80.4
						LCL:	70.8
Trifluralin	0.15	91.3	82	91.3	87.3	Mean:	97.1
	0.3	101	111	102	87.7	SD:	9.4
	1	119	104	96.5	102	UCL:	125.3
	2	94.6	112	102	88.0	UWL:	115.9
	5	95.8	92.4	91.4	92.0	LWL:	78.3
						LCL:	68.9

Results: **Agilent GC/MSD**

Benfluralin	0.15	90.0	80.0	89.3	84.7	Mean:	96.0
	0.3	99.7	110	99.1	85.7	SD:	9.5
	1	118	103	96.1	101	UCL:	124.5
	2	94.0	111	101	87.5	UWL:	115.0
	5	95.8	92.0	91.4	91.6	LWL:	77.0
						LCL:	67.5
Prodiamine	0.15	116	96.7	117	108	Mean:	112
	0.3	121	135	121	102	SD:	11.0
	1	130	116	113	115	UCL:	145.0
	2	106	121	120	97.5	UWL:	134.0
	5	105	103	99.2	98.8	LWL:	90.0
						LCL:	79.0
Pendimethlin	0.15	112	89.6	106	98.1	Mean:	108
	0.3	117	126	120	95.5	SD:	10.6
	1	123	111	108	111	UCL:	139.8
	2	105	120	119	95.0	UWL:	129.2
	5	106	100	97.6	97.9	LWL:	86.8
						LCL:	76.2
Oxyfluorfen	0.15	124	87.3	111	103	Mean:	113
	0.3	125	131	134	102	SD:	12.1
	1	123	120	115	118	UCL:	149.6
	2	110	120	123	102	UWL:	137.2
	5	114	105	99.9	100	LWL:	88.8
						LCL:	76.7

Results: **Finningan LCQ Deca**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Oryzlin	0.15	92.7	96.0	73.3	84.0	Mean:	83.6
	0.3	86.0	91.7	100	77.7	SD:	9.3
	1	87.2	91.2	77.9	68.0	UCL:	111.5
	2	93.0	70.6	80.5	68.5	UWL:	102.2
	5	90.4	81.8	79.6	81.0	LWL:	65.0
						LCL:	55.7

Appendix 3 Storage Stability Study

		Day 0		Day 4		Day 7		Day 14		Day 28	
Analyte		ppb	%R	ppb	%R	ppb	%R	ppb	%R	ppb	%R
Ethalfluralin	blk	nd		nd		nd		nd		nd	
	spk	0.836	83.6%	0.875	87.5%	0.849	84.9%	0.796	79.6%	0.804	80.4%
	spk 1	0.865	86.5%	0.894	89.4%	0.877	87.7%	0.961	96.1%	1.00	100%
	spk 2	0.873	87.3%	0.857	85.7%	0.858	85.8%	1.03	103%	1.04	104%
	spk 3	0.831	83.1%	0.821	82.1%	0.895	89.5%	0.941	94.1%	0.872	87.2%
Trifluralin	blk	nd		nd		nd		nd		nd	
	spk	0.795	79.5%	0.851	85.1%	0.877	87.7%	0.818	81.8%	0.83	83.0%
	spk 1	0.825	82.5%	0.862	86.2%	0.828	82.8%	0.948	94.8%	0.964	96.4%
	spk 2	0.734	73.4%	0.838	83.8%	0.88	88.0%	1.06	106.0%	1.03	103%
	spk 3	0.797	79.7%	0.833	83.3%	0.913	91.3%	0.94	94.0%	0.832	83.2%
Benfluralin	blk	nd		nd		nd		nd		nd	
	spk	0.840	84.0%	0.827	82.7%	0.859	85.9%	0.806	80.6%	0.838	83.8%
	spk 1	0.875	87.5%	0.854	85.4%	0.858	85.8%	0.983	98.3%	0.962	96.2%
	spk 2	0.853	85.3%	0.874	87.4%	0.878	87.8%	1.03	103%	1.06	106%
	spk 3	0.856	85.6%	0.828	82.8%	0.879	87.9%	0.930	93.0%	0.885	88.5%
Prodiamine	blk	nd		nd		nd		nd		nd	
	spk	0.858	85.8%	0.852	85.2%	0.899	89.9%	0.832	83.2%	0.813	81.3%
	spk 1	0.906	90.6%	0.881	88.1%	0.834	83.4%	1.02	102%	0.97	97.0%
	spk 2	0.905	90.5%	0.910	91.0%	0.953	95.3%	1.09	109%	1.10	110%
	spk 3	0.899	89.9%	0.851	85.1%	0.908	90.8%	0.979	97.9%	0.907	90.7%
Pendimethlin	blk	nd		nd		nd		nd		nd	
	spk	0.82	82.0%	0.825	82.5%	0.881	88.1%	0.796	79.6%	0.802	80.2%
	spk 1	0.898	89.8%	0.836	83.6%	0.785	78.5%	0.948	94.8%	0.953	95.3%
	spk 2	0.900	90.0%	0.875	87.5%	0.871	87.1%	1.02	102%	1.04	104%
	spk 3	0.868	86.8%	0.783	78.3%	0.857	85.7%	0.906	90.6%	0.868	86.8%

Oxyfluorfen	blk	nd		nd		nd		nd		nd	
	spk	0.775	77.5%	0.824	82.4%	0.884	88.4%	0.819	81.9%	0.726	72.6%
	spk 1	0.889	88.9%	0.810	81.0%	0.788	78.8%	0.984	98.4%	0.977	97.7%
	spk 2	0.857	85.7%	0.849	84.9%	0.913	91.3%	0.991	99.1%	1.04	104%
	spk 3	0.838	83.8%	0.752	75.2%	0.869	86.9%	0.867	86.7%	0.837	83.7%
Oryzalin	blk	nd		nd		nd		nd		nd	
	spk	0.900	90.0%	0.963	96.3%	0.95	95.0%	0.960	96.0%	0.795	79.5%
	spk 1	0.963	96.3%	0.929	92.9%	0.937	93.7%	0.918	91.8%	0.881	88.1%
	spk 2	0.898	89.8%	0.824	82.4%	0.867	86.7%	1.02	102%	0.884	88.4%
	spk 3	0.999	99.9%	0.997	99.7%	0.803	80.3%	1.03	103%	0.870	87.0%

Written By:

Original signed by : 3/17/2009

Jean Hsu
Chemist

Date

Written By:

Original signed by : 3/17/2009

Jane White
Chemist

Date

Approved By:

Original signed by : 3/17/2009

Steve Siegel
Section Supervisor

Date

Approved By:

Original signed by : 3/19/2009

Elaine Wong
Program Supervisor

Date

Revision Log:

Date	What was revised? Why?

Title: Determination of Fipronil and Metabolites in Surface Water using Gas Chromatography/Mass spectrometry

1. Scope:

This section method (SM) documents the procedure for Fipronil pesticide analysis in surface water by all authorized section personnel.

2. Principle:

The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 0.5mL with methylene chloride. The extract is then analyzed by a gas chromatograph/ mass selective detector (MSD) in selected ion monitoring (SIM) mode.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Balance (Mettler PC 4400) or equivalent
5.5 Gas Chromatograph equipped with mass selective detector (MSD)

6. Reagents and Supplies

6.1 Methylene Chloride, nanograde or equivalent pesticide grade
6.2 Acetone, nanograde or equivalent pesticide grade
6.3 Anhydrous Sodium Sulfate, granular
6.4 Fipronil CAS# 120068-37-3
6.5 Fipronil Amide CAS#
6.6 Fipronil DeSulfinyl CAS#
6.7 Fipronil DeSulfinylamide CAS#
6.8 Fipronil Sulfide CAS#
6.9 Fipronil Sulfone CAS# 120068-36-2
6.10 Phenanthrene-d10 CAS# 1517-22-2
6.11 Conical tube with glass stopper, 15-mL graduated, 0.1mL subdivision
6.12 Separatory funnel, 1 L
6.13 Boiling flask, 500mL
6.14 Funnel, long stem, 10 mm diameter
6.15 Disposable Pasteur pipettes, and other laboratory ware as needed
6.16 Recommended analytical columns:

For MSD - 5% phenyl Methyl silicone (HP-5ms or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 μm film thickness.

7. Standards Preparation:

7.1 Dilute the 1 mg/mL Fipronil standards obtained from the CDFA/CAC Environmental Analysis Standards Repository with acetone to make up a series of mixed working standards (see 10.2). These standards shall be prepared to cover the linear range from 0.025 ηg/μL to 1.0 ηg/μL.

7.2 Prepare the Phenanthrene-d10 internal standard at 20μg/mL from the stock standard.

7.3 The calibration standards are diluted with matrix blank extracts (9.1.2.1) to correct for matrix background interference.

7.4 Store standards according to manufacturing requirement. Keep all standards in designated refrigerator for storage.

7.5 The expiration date of each mixed working standard is six months from the preparation date or same as stock standards, if sooner.

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulations (DPR) provides the background water for matrix blank and spikes.

9.1.2.1 Matrix blank: Weigh out approximately 500 g of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out approximate 500 g of background water. Spike a client requested amount of Fipronil pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Shake sample bottle before making sample aliquot. Measure 500mL of sample into a graduated cylinder then transfer sample into a separatory funnel. Add 5 ± 1 grams sodium chloride and shake to dissolve.

9.2.2 Shake with 60 ± 5mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glass wool, into a 500mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 60 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.2.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 - 20 inch Hg vacuum. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 3 times with 2 - 4 mL of acetone and transfer each rinse to the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 0.4 mL in a water bath at 35 ± 4 °C under a gentle stream of nitrogen. Then bring to a final volume of 0.5mL with acetone. Add 10µL of the 20.0µg/mL Phenanthrene-d10 standard, mix well and transfer into auto sampler vials.

9.2.9 Submit extract for GC/MSD analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background interference.

10.2 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.025, 0.10, 0.25, 0.50, 1.0µg/mL are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995. All standards, samples and quality control samples have the internal standard, Phenanthrene-d10, added at 1.0µg/mL final concentration.

11. Analysis:

11.1 Injection Scheme

Recommended injection scheme: Calibration standards, Solvent, Matrix Bank, Matrix Spike, Test Samples (maximum of 10-12 samples) and Calibration standards. Injection of an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC/MSD Instrumentation

11.2.1 Recommended instrument (GC/MSD) parameters: Injector 230 °C; MSD transfer line heater 280 °C; initial oven temperature 50 °C, hold 2 min., ramp @ 25 °C/min. to 200 °C hold 1 min. and then ramp @ 5 °C/min. to 275 °C, hold 8 min; Injection volume 2 or 3 µL.

Ions Selected for SIM Acquisition: (in retention time order)

Phenanthrene-d10	**188**	Group 1
Desulfinyl Fipronil	333, 369, **388**, 390	Group 1
Fipronil Sulfide	255, **351**, 353, 420	Group 2
Fipronil	213, **367**, 369	Group 2
Desulfinyl Fipronil amide	308, 390, **406**	Group 3
Fipronil Sulfone	213, 365, **383**	Group 3
Fipronil amide	255, 368, **385**, 387	Group 4

(Quantitation ions are in bold)

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank should be free of target compounds above the MDL.

12.3 The recoveries of the matrix spike shall be within the control limits.

12.3.1 When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples may be re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.3.2 If the spike recoveries still fall outside the control limits, the client will be notified. The backup samples may need to be re-extracted for analysis.

12.4 The retention time should be within ± 2 percent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard should have a percent change less than 25%.

12.7 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.025 ppb for Fipronil and metabolites. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.8 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client agreement, the RL is chosen in a range 1-5 times the MDL.

MDL data and the RL are tabulated in Appendix IA and IB.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of three sample sets. Each set included 5 levels of fortification (0.025, 0.05, 0.10, 0.2, and 1.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.9.2 Upper and lower warning and control limits are set at $\pm$ 2 and $\pm$ 3 standard deviations of the average % recovery, respectively.

12.10 Estimated Measurement Uncertainty:
Total uncertainty for this method is 13.9% based on the method validation.

12.11 Trend Identification

12.11.1 All matrix spike recoveries for this analysis will be put into control charts and monitored for trends. Three trend characteristics will be evaluated at least bi-yearly by the supervisor or designee.
2 of 3 points above or below 2/3 of the UCL or LCL.
7 continuous points above or below the center line (CL)
14 points alternating above and below the CL.

12.11.2 When results indicate an out of control situation the supervisor or designee will indicate this on the control chart and take appropriate corrective action, which may include monitoring the results more closely to initiating a formal corrective action with root cause investigation.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{(\text{sample peak ht. or area})\ (\text{std. conc.})\ (\text{std. vol. injected})\ (\text{sample final vol., (mL)})(1000\ \mu\text{L/mL})}{(\text{std. peak ht. or area})\ (\text{sample vol. injected})\ (\text{sample wt., g})}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 Sample results are reported out according to the client's analytical laboratory specifications.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards are diluted with a matrix blank extract to correct for matrix background interference.

16. References:

16.1 *EPA Method 507, Pesticides, Capillary Column*. EPA Test Method for Drinking Water and Raw Source Water, 1987.

16.2 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography*, 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

APPENDIX IA

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

Seven replicates of a 0.025µg/mL spike (25.00 µg/L)

Sample #	Desulfinyl Fipronil	Fipronil sulfide	Fipronil	Desulfinyl fipronil amide	Fipronil sulfone	Fipronil amide	
	ng/L	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	
1	26.39	26.94	28.44	28.40	26.68	24.63	
2	25.30	26.24	29.20	28.53	26.14	22.40	
3	24.79	25.73	31.52	30.22	27.26	25.61	
4	26.45	26.67	30.94	31.32	29.32	25.84	
5	24.84	25.28	29.06	28.13	24.47	23.95	
6	24.30	25.23	29.09	27.10	25.26	23.09	
7	25.93	26.13	29.25	28.40	26.17	23.30	
Std. Dev	0.84	0.66	1.13	1.42	1.55	1.30	
3.14*SD	2.65	2.06	3.55	4.45	4.87	4.09	
MDL **(ng/L)**	2.650	2.060	3.550	4.450	4.870	4.090	MDL in ng/L
MDL (µg/L)	**0.003**	**0.003**	**0.004**	**0.005**	**0.005**	**0.005**	**MDL in ppb**

Spiked water sample with 0.5mL of a 0.025µg/mL fipronil and metabolites standard.
The extraction is 1:1000 concentration.
The MDL then is spiked at 0.025µg/L (ppb)
The results are reported in ng/L, which is 1000 times the ppb value.
The MDL is reported in µg/L (ppb)

APPENDIX IB

Method Validation and Control Limit

Compound	Mean	Std. Dev.	Control limit
Desulfinyl Fipronil	100.4	13.9	UCL: 142.2 UWL: 128.3 LWL: 72.6 LCL: 58.5
Fipronil Sulfide	97.3	16.8	UCL: 147.6 UWL: 130.8 LWL: 63.8 LCL: 46.9
Fipronil	103.3	12.0	UCL: 139.4 UWL: 127.4 LWL: 79.2 LCL: 67.1
Desulfinyl Fipronil amide	110.7	16.2	UCL: 159.2 UWL: 143.0 LWL: 78.3 LCL: 62.2
Fipronil Sulfone	106.1	15.0	UCL: 151.2 UWL: 136.2 LWL: 76.1 LCL: 60.9
Fipronil amide	92.4	9.1	UCL: 119.6 UWL: 110.5 LWL: 74.2 LCL: 65.1

Written BY:

Original signed by: 3/17/2009

Wei Cui
Chemist

Date

Approved By:

Original signed by: 3/17/2009

Stephen Siegel
Section Supervisor

Date

Approved By:

Original signed by: 3/19/2009

Elaine Wong
Program Supervisor

Date

Revision Log:

Date	What was Revised? Why?

Title: Determination of N-methylcarbamate Pesticides in Surface Water using High Performance Liquid Chromatography and Post-column derivatization

1. Scope:

This section method (SM) documents the selected N-methylcarbamate pesticides analysis in surface water by all authorized section personnel.

2. Principle:

The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness then diluted to a final volume of 0.40 mL with methanol. The extract is then analyzed by HPLC. The analytes are derivatized with OPA (ortho-phthaladehyde) in a post column reaction and detected with a fluorescence detector. The reporting limit for this method is 0.05 ppb for all compounds.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Balance (Mettler PC 4400) or equivalent

5.5 HPLC with post column derivatization system and fluorescence detector.

6. Reagents and Supplies

6.3 Methylene Chloride, nanograde or equivalent pesticide grade
6.4 Methanol, nanograde or equivalent pesticide grade
6.5 Anhydrous Sodium Sulfate, granular
6.6 Aldicarb Sulfoxide CAS# 1646-87-3
6.7 Aldicarb Sulfone CAS# 1646-88-4
6.8 Oxamyl CAS# 23135-22-0
6.9 Methomyl CAS# 16752-775
6.10 3-OH-Carbofuran CAS# 16655-82-6
6.11 Aldicarb CAS# 116-06-3
6.12 Carbofuran CAS# 1563-66-2
6.13 Carbaryl CAS# 63-25-2
6.14 Methiocarb CAS# 2032-65-7
6.15 Hydrolysis reagent (Pickering Laboratories CB130 or equivalent)
6.16 O-phthaladehyde (Pickering Laboratories 012 or equivalent)
6.17 O-phthaladehyde diluent (Pickering Laboratories CB910 or equivalent)
6.18 2-mercaptoethanol
6.19 OPA Reagent- Dissolve 100mg O-Phthaladehyde in 10mL methanol. Add this mixture to 950 mL O-Phthaladehyde diluent and mix well. Add 1 mL 2-mercaptoethanol and pour solution into reagent reservoir.
6.20 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.21 Separatory funnel, 250 mL
6.22 Boiling flask, 500 mL
6.23 Funnel, long stem, 10 mm diameter
6.24 Nitrogen Evaporator, Organomation
6.25 Disposable Pasteur pipettes, and other laboratory ware as needed
6.26 0.2µ nylon filters (Acrodisc 28143-274 or equivalent)
6.27 Recommended analytical columns:
Carbamate analysis C18 4.6mm ID X 250 mm. (Pickering Laboratories 1846250 or equivalent)

7. Standards Preparation:

7.1 Dilute the 1 mg/mL Carbamate standards obtained from the CDFA/CAC Environmental Analysis Standards Repository with methanol to make up a series of

mixed working standards (see 10.2). These standards shall be prepared to cover the linear range from 0.0125 ηg/μL to 0.5 ηg/μL for the carbamate screen.

7.2 Store standards according to manufacturing requirement. Keep all standards in designated refrigerator for storage.

7.3 The expiration date of each mixed working standard is six months from the preparation date or same as stock standards, if sooner.

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulations (DPR) provides the background water for matrix blank and spikes.

9.1.2.1 Matrix blank: Weigh out 100 grams of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out 100 grams of background water. Spike a client requested amount of carbamate pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Shake each sample then weigh out 100 grams of sample and transfer to a separatory funnel.

9.2.2 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glasswool, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 100 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.2.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 - 20 inch Hg vacuum. Pass sample through 0.2µ filter into a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 2-3 more times with 2 - 4 mL of methylene chloride and filter the rinse into the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 0.5 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Add in approx. 1 mL methanol. Evaporate the extract to less than 300 µL. Transfer extract to a calibrated vial insert. Wash the tube with a few drops of Methanol and add to insert. Adjust the final volume of 0.4 mL with methanol.

9.2.9 Submit extract for HPLC analysis.

10. Instrument Calibration:

10.1 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.0125, 0.025, 0.05, 0.1, and 0.5 ηg/µL are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

10.2 Compositions of calibration mixed standards are as follows:

CB-A Mixed Standard
Aldicarb Sulfoxide
Aldicarb Sulfone
Methomyl
3-Hydroxycarbofuran
Aldicarb
Carbofuran
Carbaryl

CB-B Mixed Standard
Oxamyl
Methiocarb

11. Analysis:

11.1 Injection Scheme

Follow the sequence of calibration standards, QC samples, test samples (maximum of 10-12 samples) and final calibration standards.

11.2 HPLC Instrumentation

11.2.1 Analyze carbamate pesticides by HPLC equipped with post column reaction module and a fluorescence detector.

11.2.2 Recommended instrument HPLC gradient::
A= 1% methanol in water B= acetonitrile

Time (min)	% A	%B
0.00	98.0	2.0
1.00	98.0	2.0
16.00	30.0	70.0
18.00	30.0	70.0
22.00	100.0	0.0
25.00	100.0	0.0
25.10	98.0	2.0
30.00	98.0	2.0

11.2.3 Injection volume 25 µL.

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank should be free of target compounds.

12.3 The recoveries of the matrix spike shall be within the control limits.

12.3.1 When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples is re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.3.2 If the spike recoveries still fall outside the control limits, the client will be notified. The backup samples will be re-extracted for analysis.

12.4 The retention time should be within ± 2 percent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard curves should have a percent change less than 20 % for all compounds.

12.7 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyteI that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.05 ppb for OP screen and 7 replicate water samples are spiked at 10 ppt for low level diazinon and chloripyrifos. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.8 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client agreement, the RL is chosen in a range 1-5 times the MDL except in special cases. (See 15.5)

MDL data and the RL are tabulated in Appendix IA and IB.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of three sample sets. Each set included five levels of fortification (0.0125, 0.025, 0.05, 0.1, 1.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.9.2 Upper and lower warning and control limits are set at ± 2 and ± 3 standard deviations of the average % recovery, respectively.

12.10 Estimated Measurement Uncertainty:

12.11 Trend Identification

12.11.1 All matrix spike recoveries for carbamate analysis will be put into control

Charts and monitored for trends. Three trend characteristics will be evaluated at least bi-yearly by the supervisor or designee.

2 of 3 points above or below 2/3 of the UCL or LCL.

7 continuous points above or below the center line (CL)

14 points alternating above and below the CL.

12.11.2 When results indicate an out of control situation the supervisor or designee will indicate this on the control chart and take appropriate corrective action, which may include monitoring the results more closely to initiating a formal corrective action with root cause investigation.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{(\text{sample peak ht. or area})\ (\text{std. conc.})\ (\text{std. vol. injected})\ (\text{sample final vol., (mL)})(1000\ \mu\text{L/mL})}{(\text{std. peak ht. or area})\ (\text{sample vol. injected})\ (\text{sample wt., g})}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 Sample results are reported out according to the client's analytical laboratory specifications.

15. References:

Muth, G.L., Erro, F. A Rapid Carbamate Multiresidue Procedure of Vegetable Crops Environmental Contamination & Toxicology, 1980, 24, 759-765

Keith, Lawrence H., Principles of Environmental Analysis, Anal Chem, 1983, 55, 2210-2218

APPENDIX IA

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

	Aldicarb sulfoxide	Aldicarb sulfone/Oxamyl	Methomyl	3-OH Carbofuran	Aldicarb	Carbofuran	Carbaryl	Methiocarb
MDL#1	0.02433	0.06784	0.02939	0.0322165	0.024847	0.02892	0.03208	0.03113
MDL#2	0.02126	0.05778	0.02545	0.02704	0.02244	0.0267	0.02718	0.02444
MDL#3	0.0248	0.06608	0.02709	0.03169	0.02316	0.02691	0.02924	0.02875
MDL#4	0.02172	0.05155	0.02367	0.02685	0.02164	0.02417	0.0245	0.03718
MDL#5	0.01686	0.05218	0.02204	0.02594	0.01776	0.02235	0.02388	0.02301
MDL#6	0.02388	0.05906	0.029	0.03161	0.02579	0.02815	0.02841	0.02617
MDL#7	0.026	0.06423	0.03	0.035	0.0245	0.03114	0.03286	0.02866
SD	0.00307	0.00651	0.00306	0.00343	0.00268	0.00294	0.00344	0.00473
3.1416 xSD	0.01026	0.01882	0.00967	0.01133	0.00871	0.00964	0.01038	0.01578
MDL	0.011	0.020	0.010	0.011	0.010	0.010	0.011	0.016

All concentrations are expressed in ppb.

APPENDIX IIA

Method Validation Data and Control Limit for Carbamates Table 1

Level **µg/L** (ppb)	Aldicarb Sulfoxide	Percent recovery	Aldicarb Sulfone	Percent recovery	Methomyl	Percent recovery	3-OH-Carbofuran	Percent recovery
0.0125	0.0089	71.2	0.0114	91.2	0.0070	88.8	0.0144	115
	0.0093	74.4	0.0109	87.6	0.0140	84.4	0.0123	98.4
	0.0108	86.2	0.0115	91.8	0.0114	86.4	0.0124	99.2
0.025	0.0196	78.5	0.0211	84.2	0.0201	78.1	0.0214	85.7
	0.0216	86.6	0.0232	92.8	0.0268	90.4	0.0231	92.5
	0.0238	95.2	0.0274	110	0.0213	97.6	0.0303	121
0.05	0.0495	99.2	0.0470	94.0	0.0438	87.2	0.0541	108
	0.0467	93.6	0.0459	91.8	0.0404	87.4	0.0481	96.2
	0.0248	85.7	0.0439	87.7	0.0440	85.0	0.0440	87.9
0.10	0.0944	94.4	0.0978	97.8	0.0948	94.8	0.0954	95.4
	0.0904	90.4	0.1031	103	0.0928	92.8	0.1097	110
	0.0896	89.6	0.1033	103	0.0996	99.6	0.1102	110
1.00	0.8064	80.6	0.9223	92.2	0.8858	88.6	0.9238	92.4
	0.8259	82.6	0.9318	93.2	0.8752	87.5	0.9300	93.0
	0.8578	85.8	0.9842	98.4	0.9673	96.7	0.9859	98.6
SD		7.88		6.79		5.73		10.30
SD X 3		23.64		20.38		17.19		30.89

Table 2

Level **µg/L** (ppb)	Aldicarb	Percent recovery	Carbofuran	Percent recovery	Carbaryl	Percent recovery
0.0125	0.0119	95.2	0.0138	110	0.0132	106
	0.0108	86.4	0.0119	95.2	0.0119	95.6
	0.0107	85.8	0.0118	94.4	0.0119	95.2
0.025	0.0188	75.3	0.0208	83.0	0.0213	85.1
	0.0222	88.9	0.0234	93.5	0.0234	93.6
	0.0252	101	0.0284	114	0.0276	110
0.05	0.0416	83.2	0.0488	97.6	0.0480	96.0
	0.0418	83.6	0.0462	92.4	0.0454	90.8
	0.0397	79.4	0.0436	87.2	0.0435	86.9
0.10	0.0886	88.6	0.0956	95.6	0.0946	94.6
	0.0984	98.4	0.1018	102	0.1023	102
	0.1038	102	0.1063	106	0.1049	105
1.00	0.8776	87.8	0.9238	92.4	0.9178	91.8
	0.8309	83.1	0.9122	91.2	0.9267	92.7
	0.9291	92.9	0.9743	97.4	0.9711	97.1
SD		7.79		8.26		6.97
3 X SD		23.38		24.79		20.90

Table 3

Level **µg/L** (ppb)	Oxamyl	Percent recovery	Methiocarb	Percent recovery
0.0125	0.0116	92.8	0.0124	99.2
	0.0118	94.8	0.0124	99.2
	0.0103	82.4	0.0105	83.6
0.025	0.0242	96.9	0.0247	98.9
	0.0233	93.2	0.0237	94.7
	0.0248	99.2	0.0232	92.8
0.05	0.0462	92.4	0.0424	84.8
	0.0449	89.8	0.0412	82.4
	0.0458	91.5	0.0442	88.3
0.10	0.0940	94.0	0.0949	94.9
	0.0848	84.8	0.0992	99.2
	0.0964	96.4	0.1042	104
1.00	0.9099	91.0	0.9043	90.4
	0.8909	89.1	0.8887	88.9
	0.9159	91.6	0.9263	92.6
SD		4.37		6.50
3 X SD		13.12		19.50

Written BY:

Original Copy Signed by 6/11/2009

_____ _____
Vincent Quan Date
Chemist

Revised By:

Original Signed by 3/3/2011

_____ _____
Steve Siegel Date
Sr. Environmental Scientist

Approved By:

Original Signed by 3/3/2011

_____ _____
Steve Siegel Date
Sr. Environmental Scientist

Approved By:

Original Signed by 3/5/2011

_____ _____
Elaine Wong Date
Environmental Program Manager I

Revision Log:

Date	What was Revised? Why?
3/11/09	Changed method validation results to the validation results done in June 2007.
3/3/2011	Change validation results to the validation done in November 2007.

Determination of Organophosphate Pesticides in Surface water using Gas Chromatography with mass selective detection (MSD).

1. Scope:

This section method (SM) documents the selected organophosphate pesticides analysis in surface water by all authorized section personnel. This method is not applicable for Ethoprop, Azinphos-methyl and Profenofos.

2. Principle:

The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed by a gas chromatograph equipped with a mass selective detector (MSD).

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer

5.4 Balance (Mettler SM-L) or equivalent
5.5 Gas Chromatograph equipped with a mass selective detector (MSD)

6. Reagents and Supplies

6.1 Methylene Chloride, nanograde or equivalent pesticide grade
6.2 Acetone, nanograde or equivalent pesticide grade
6.3 Anhydrous Sodium Sulfate, granular
6.4 Diazinon CAS# 333-41-5
6.5 Disulfoton CAS# 298-04-4
6.6 Chlorpyrifos CAS# 2921-88-2
6.7 Malathion CAS# 121-75-5
6.8 Methidation CAS# 950-37-8
6.9 Fenamiphos CAS# 22224-92-6
6.10 Dichlorvos CAS# 62-73-7
6.11 Phorate CAS# 298-02-2
6.12 Fonofos CAS# 66767-39-3
6.13 Dimethoate CAS# 60-51-5
6.14 Parathion methyl CAS# 298-00-0
6.15 Tribufos (DEF) CAS# 78-48-8
6.16 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.17 Separatory funnel, 2 L
6.18 Boiling flask, 500 mL
6.19 Funnel, long stem, 10 mm diameter
6.20 Disposable Pasteur pipettes, and other laboratory ware as needed
6.21 Recommended analytical columns:

For MSD - 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane (Restek Rxi-5Sil MS or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 μm film thickness.

7. Standards Preparation:

7.1 Dilute the 1 mg/mL Organophosphate standards obtained from the CDFA/CAC Environmental Analysis Standards Repository with acetone to make up a series of mixed working standards (see 10.2). These standards shall be prepared to cover the linear range from 0.025 ηg/μL to 0.5 ηg/μL for OP screen and 0.01 ηg/μL to 0.5 ηg/μL for low level diazinon and chlorpyrifos.

7.2 The calibration standards are added to matrix blank extracts (9.1.2.1) to correct for matrix background interference.

7.3 Store standards according to manufacturing requirement. Keep all standards in designated refrigerator for storage.

7.4 The expiration date of each mixed working standard is six months from the preparation date or same as stock standards, if sooner.

7.5 A portion of the new standard will be vialed and set aside in the refrigerator. This will be used when doing the intermediate check and the check for a new set of standards. The intermediate check will be performed before the standard is 3 months old and be documented along with the comparison for that set of standards. There should be <20% difference between the response of the new standard or the intermediate check standard and the response of the vialed standard.

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulations (DPR) provides the background water for matrix blank and spikes.

9.1.2.1 Matrix blank: Weigh out approximate 1000 g of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out approximate 1000 g of background water. Spike a client requested amount of organophosphate pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Record the weight of the whole bottle water sample to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.2.2 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glass wool, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 80 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.2.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 - 20 inch Hg vacuum. Add 2 - 4 mL of acetone and rotoevaporate to 1 - 2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 3 more times with 2 - 4 mL of acetone and transfer each rinse to the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 1.0 mL with acetone, mix well and transfer into two autosampler vials.

9.2.9 Submit extract for GC/MS analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background.

10.2 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.01, 0.025, 0.05, 0.1, 0.25 and 0.5 ηg/µL are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

11.1 Injection Scheme

Follow the sequence of Solvent, Calibration standards, Solvent, Matrix Blank, Matrix Spike, Test Samples (maximum of 10-12 samples) and Calibration standards. Injection of an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC Instrumentation

11.2.1 Recommended instrument (GC/MSD) parameters: Injector 250 °C; MSD transfer line heater 280 °C; oven temperature 80 °C, hold 2 min., ramp @ 20 °C/min. to 250 °C, hold 4 min.; injection volume 2 or 3 µL.

Ions Selected for SIM Acquisition:

Diazinon	137, 152, 179, **304**,	Retention time: 11.9 min
Disulfoton	**88**, 97, 142, 274,	Retention time: 12.2 min
Malathion	93, 125, 127, **173**,	Retention time: 14.1 min
Chlorpyrifos	125, **197**, 258, 314,	Retention time: 11.2 min
Methidathion	58, 85, 93, **145**,	Retention time: 9.88 min
Fenamiphos	154, 217, 288, **303**,	Retention time: 9.26 min
DDVP	79, **109**, 185,	Retention time: 11.2 min
Phorate	**75**, 97, 121, 260,	Retention time: 9.72 min
Dimethoate	**87**, 93, 125, 126,	Retention time: 12.0 min
Fonofos	**109**, 137, 246,	Retention time: 10.7 min
Me Parathion	63, 109, 125, **263**,	Retention time: 9.94 min
DEF	**169**, 202,	Retention time: 9.73 min

(Quantitation ions are in bold)

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank should be free of target compounds.

12.3 The recoveries of the matrix spike shall be within the control limits.

12.3.1 When spike recoveries fall outside the control limits, the chemist must

investigate the cause. The entire extraction set of samples is re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.3.2 If the spike recoveries still fall outside the control limits, the client will be notified. The backup samples will be re-extracted for analysis.

12.4 The retention time should be within ± 2 percent of that of the standard.

12.5 All calibration standards analyzed for a sample set will be used in the calibration curve. If the calibration curve does not meet the acceptance criteria the samples shall be re-run. If the calibration criteria are met the sample results will be reported. If the calibration criteria are still not met a method deviation will be prepared and approved by the supervisor or designee. The client will be notified of the deviation and a copy of the method deviation detailing what was changed and why it was changed will be included with the sample results and the data will be flagged to let the data user know of the deviation.

12.6 The sample must be diluted if results fall outside the linear range of the standard curve.

12.7 Bracketing standard curves should have a percent change less than 20%.

12.8 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.05 ppb for OP screen and 7 replicate water samples are spiked at 10 ppt for low level diazinon and chlorpyrifos and 7 replicates were spikes at 0.02 ppb for malathion. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.9 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client

agreement, the RL is chosen in a range 1-5 times the MDL except in special cases. (See 15.5)

MDL data and the RL are tabulated in Appendix IA and IB.

12.10 Method Validation Recovery Data and Control Limits:

12.10.1 The method validation consisted of five sample sets. Each set included seven levels of fortification (0.01, 0.025, 0.05, 0.10, 0.25, 0.5 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.10.2 Upper and lower warning and control limits are set at ± 2 and ± 3 standard deviations of the average % recovery, respectively.

12.10.3 The method validation consisted of five sample sets. Each set included six levels of fortification and a method blank. All spikes and method blank samples were processed through the entire analytical method.

Method validation results and control limits are tabulated in Appendix IB.

12.11 Estimated Measurement Uncertainty:
Total uncertainty for this method is 17% at 95% confidence interval.

12.12 Trend Identification

12.12.1 All matrix spike recoveries for OP analysis will be put into control charts and monitored for trends. Three trend characteristics will be evaluated at least bi-yearly by the supervisor or designee.
2 of 3 points above or below 2/3 of the UCL or LCL.
7 continuous points above or below the center line (CL)
14 points alternating above and below the CL.

12.12.2 When results indicate an out of control situation the supervisor or designee will indicate this on the control chart and take appropriate corrective action, which may include monitoring the results more closely to initiating a formal corrective action with root cause investigation.

13. Calculations:
Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted
equally. Alternatively, at chemist discretion, concentrations may be calculated using

the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{(\text{sample peak ht. or area})\ (\text{std. conc.})\ (\text{std. vol. injected})\ (\text{sample final vol., (mL)})(1000\ \mu\text{L/mL})}{(\text{std. peak ht. or area})\ (\text{sample vol. injected})\ (\text{sample wt., g})}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 Sample results are reported out according to the client's analytical laboratory specifications.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards were added to a matrix blank extract to correct for matrix background interference.

15.2 Some of the late eluting compounds were observed to suffer gradual losses in sensitivity. We recommend changing the injector liner and trimming the column when this occurs.

15.3 The client requested a lower reporting limit for both diazinon and chlorpyrifos. We re-validated this method using GC/MSD as the analysis instrument to achieve the lower reporting limit for those two compounds.

16. References:

16.1 *EPA Method 507, Pesticides, Capillary Column*. EPA Test Method for Drinking
Water and Raw Source Water, 1987.

16.2 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography*, 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

Appendix IA

Determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Spike/analyte	Diazinon		Avg.	Disulfoton		Avg.	Chlorpyrifos		Avg.
0.05/ ppb Spk 1	0.04709	0.04664	0.04687	0.04203	0.04528	0.04366	0.04784	0.04804	0.04794
0.05/ ppb Spk 2	0.04901	0.04975	0.04938	0.03938	0.03474	0.03706	0.04991	0.05010	0.05001
0.05/ ppb Spk 3	0.04465	0.04871	0.04668	0.04050	0.03653	0.03852	0.04580	0.04566	0.04573
0.05/ ppb Spk 4	0.04851	0.05026	0.04939	0.04640	0.04365	0.04503	0.04775	0.04768	0.04772
0.05/ ppb Spk 5	0.04405	0.04447	0.04426	0.04774	0.04583	0.04679	0.04459	0.04420	0.04440
0.05/ ppb Spk 6	0.04154	0.04181	0.04168	0.04740	0.04446	0.04593	0.04222	0.04262	0.04242
0.05/ ppb Spk 7	0.03949	0.04188	0.04069	0.03821	0.03487	0.03654	0.04093	0.04070	0.04082
		SD	0.00348			0.00441			0.00326
MDL= 3.14 * SD		MDL	0.01093			0.01384			0.01024
		RL	0.01			0.04			0.01
Spike/analyte	Malathion		Avg.	Methidathion		Avg.	Fenamiphos		Avg.
0.05/ ppb Spk 1	0.04549	0.04553	0.04551	0.03980	0.04117	0.04049	0.04614	0.04229	0.04422
0.05/ ppb Spk 2	0.04877	0.04895	0.04886	0.04612	0.04541	0.04577	0.04490	0.04879	0.04685
0.05/ ppb Spk 3	0.04489	0.04101	0.04295	0.03971	0.03883	0.03927	0.04202	0.04175	0.04189
0.05/ ppb Spk 4	0.04693	0.04568	0.04631	0.04224	0.04092	0.04158	0.04880	0.04839	0.04860
0.05/ ppb Spk 5	0.04169	0.04129	0.04149	0.03380	0.03328	0.03354	0.04403	0.04333	0.04368
0.05/ ppb Spk 6	0.04208	0.04177	0.04193	0.03967	0.03922	0.03945	0.04305	0.04289	0.04297
0.05/ ppb Spk 7	0.04121	0.04039	0.04080	0.04004	0.03957	0.03981	0.04196	0.03691	0.03944
		SD	0.00298			0.00362			0.00305
MDL= 3.14 * SD		MDL	0.00935			0.01136			0.00957
		RL	0.02			0.05			0.05

Determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Spike/analyte	Malathion		Avg.
0.02/ ppb Spk 1	0.02160	0.02590	0.02375
0.02/ ppb Spk 2	0.01830	0.02260	0.02045
0.02/ ppb Spk 3	0.01690	0.02170	0.01930
0.02/ ppb Spk 4	0.01850	0.02230	0.02040
0.02/ ppb Spk 5	0.01710	0.02340	0.02025
0.02/ ppb Spk 6	0.01410	0.01960	0.01685
0.02/ ppb Spk 7	0.01830	0.02220	0.02025
Standard deviation		SD	0.00203
MDL= 3.14 * SD		MDL	0.00638
Reporting limit		RL	0.02

Appendix IB

Spike/analyte	DDVP		Avg.	Phorate		Avg.	Fonofos		Avg.
0.05/ ppb Spk 1	0.04130	0.04339	0.04235	0.04292	0.04329	0.04311	0.04369	0.04362	0.04366
0.05/ ppb Spk 2	0.04210	0.04447	0.04329	0.04396	0.04350	0.04373	0.04652	0.04794	0.04723
0.05/ ppb Spk 3	0.04034	0.04069	0.04052	0.04084	0.04006	0.04045	0.04155	0.04126	0.04141
0.05/ ppb Spk 4	0.03780	0.04184	0.03982	0.04263	0.04252	0.04258	0.04368	0.04409	0.04389
0.05/ ppb Spk 5	0.03835	0.03789	0.03812	0.04031	0.03962	0.03997	0.04167	0.04151	0.04159
0.05/ ppb Spk 6	0.03834	0.03724	0.03779	0.03725	0.03734	0.03730	0.03935	0.03893	0.03914
0.05/ ppb Spk 7	0.03534	0.03528	0.03531	0.03577	0.03555	0.03566	0.03822	0.03774	0.03798
		SD	0.00276			0.00305			0.00343
MDL= 3.14 * SD		MDL	0.00868			0.00959			0.01076
		RL	0.05			0.05			0.04
Spike/analyte	Dimethoate		Avg.	Methyl Parathion		Avg.	DEF		Avg.
0.05/ ppb Spk 1	0.03922	0.03874	0.03898	0.04111	0.04046	0.04079	0.04293	0.04358	0.04326
0.05/ ppb Spk 2	0.04397	0.04344	0.04371	0.04610	0.04631	0.04621	0.04628	0.04591	0.04610
0.05/ ppb Spk 3	0.03692	0.03638	0.03665	0.03906	0.04019	0.03963	0.04186	0.04259	0.04223
0.05/ ppb Spk 4	0.03869	0.03900	0.03885	0.04044	0.03966	0.04005	0.04388	0.04400	0.04394
0.05/ ppb Spk 5	0.03068	0.03089	0.03079	0.03278	0.03343	0.03311	0.03993	0.04046	0.04020
0.05/ ppb Spk 6	0.03617	0.03964	0.03791	0.03637	0.03720	0.03679	0.03932	0.03886	0.03909
0.05/ ppb Spk 7	0.03801	0.03736	0.03769	0.03748	0.03708	0.03728	0.03696	0.03786	0.03741
		SD	0.00383			0.00406			0.00301
MDL= 3.14 * SD		MDL	0.01202			0.01276			0.00946
		RL	0.04			0.03			0.05

Method Validation Data

Analyte	Spike ppb	Set 1		Avg.	Set 2		Avg.	Set 3		Avg.		
Diazinon	0.01	83.4	82.7	83.1	90.1	90.4	90.3	94.5	107.0	100.8	SD	6.082
	0.025	89.2	90.9	90.1	85.6	91.3	88.5	93.6	85.2	89.4	Mean	90.2
	0.05	101.0	94.6	97.8	90.0	89.8	89.9	89.3	93.4	91.4	UCL	108.5
	0.1	85.0	85.5	85.3	86.2	87.9	87.1	89.3	89.4	89.4	UWL	102.4
	0.25	92.9	93.5	93.2	80.4	81.0	80.7	88.3	86.3	87.3	LWL	78.1
	0.5	93.7	93.7	93.7	98.1	98.8	98.5	89.4	87.0	88.2	LCL	72.0
Disulfoton	0.01	84.1	83.1	83.6	112.0	105.0	108.5	114.0	114.0	114.0	SD	10.855
	0.025	73.6	72.3	73.0	80.5	78.4	79.5	85.2	83.8	84.5	Mean	85.4
	0.05	74.1	73.2	73.7	84.6	86.0	85.3	90.7	87.4	89.1	UCL	117.9
	0.1	85.3	85.7	85.5	81.2	79.2	80.2	85.0	83.1	84.1	UWL	107.1
	0.25	79.8	78.7	79.3	76.1	74.7	75.4	83.5	82.4	83.0	LWL	63.7
	0.5	79.7	78.1	78.9	95.2	94.6	94.9	85.0	84.2	84.6	LCL	52.8
Chlorpyrifos	0.01	111.0	109.0	110.0	98.5	101.0	99.8	102.0	102.0	102.0	SD	7.133
	0.025	98.1	97.6	97.9	89.4	90.4	89.9	86.1	87.6	86.9	Mean	92.9
	0.05	97.7	98.4	98.1	90.7	93.9	92.3	89.8	90.0	89.9	UCL	114.3
	0.1	88.1	88.4	88.3	87.2	87.4	87.3	87.3	86.8	87.1	UWL	107.2
	0.25	93.8	94.0	93.9	81.0	81.2	81.1	87.0	86.4	86.7	LWL	78.6
	0.5	94.8	93.8	94.3	98.9	99.6	99.3	88.0	87.1	87.6	LCL	71.5
Malathion	0.01	88.0	87.8	87.9	90.6	94.4	92.5	99.4	97.0	98.2	SD	4.642
	0.025	93.0	96.8	94.9	91.6	90.3	91.0	89.2	88.4	88.8	Mean	91.8
	0.05	99.0	98.9	99.0	91.7	92.8	92.3	90.3	89.1	89.7	UCL	105.7
	0.1	89.0	91.2	90.1	88.2	86.6	87.4	91.2	88.0	89.6	UWL	101.1
	0.25	95.7	95.7	95.7	81.8	82.3	82.1	89.8	88.2	89.0	LWL	82.5
	0.5	97.3	96.0	96.7	99.0	99.1	99.1	89.0	87.3	88.2	LCL	77.8

Method Validation Data (continued)

Methidathion	0.01	97.3	91.2	94.3	81.2	81.7	81.5	92.1	95.1	93.6	SD	8.648
	0.025	107.0	103.0	105.0	84.4	81.5	83.0	90.4	83.6	87.0	Mean	91.6
	0.05	107.0	101.0	104.0	88.7	86.2	87.5	83.3	81.9	82.6	UCL	117.6
	0.1	103.0	99.6	101.3	85.0	83.9	84.5	87.9	87.7	87.8	UWL	108.9
	0.25	106.0	104.0	105.0	80.1	80.5	80.3	93.0	92.0	92.5	LWL	74.3
	0.5	101.0	100.0	100.5	95.5	95.8	95.7	84.4	82.5	83.5	LCL	65.7

Fenamiphos	0.01	75.7	73.1	74.4	77.3	78.6	78.0	77.6	76.9	77.3	Sd	6.793
	0.025	86.5	85.6	86.1	78.3	77.0	77.7	77.4	78.4	77.9	Mean	84.4
	0.05	93.0	90.7	91.9	90.3	82.1	86.2	84.5	79.2	81.9	UCL	104.8
	0.1	93.0	91.4	92.2	83.8	82.8	83.3	81.3	83.5	82.4	UWL	98.0
	0.25	96.3	94.0	95.2	77.8	77.2	77.5	85.5	86.3	85.9	LWL	70.8
	0.5	94.8	92.8	93.8	95.1	94.9	95.0	82.7	82.2	82.5	LCL	64.0

	ppb	Set 1		Avg.	Set 2		Avg.	Set 3		Avg.		
DDVP	0.01	86.0	74.8	80.4	81.3	80.1	80.7	77.3	93.9	85.6	SD	7.765
	0.025	90.9	89.3	90.1	74.6	81.7	78.2	89.3	81.8	85.6	Mean	86.4
	0.05	84.0	85.6	84.8	81.6	81.2	81.4	81.7	82.3	82.0	UCL	109.7
	0.1	109.0	107.0	108.0	85.0	84.1	84.6	86.0	89.0	87.5	UWL	101.9
	0.25	99.2	91.7	95.5	76.6	76.5	76.6	85.2	85.4	85.3	LWL	70.8
	0.5	92.4	89.0	90.7	94.4	96.4	95.4	84.1	81.0	82.6	LCL	63.1

Fonofos	0.01	95.5	89.9	92.7	92.2	87.6	89.9	108.0	84.3	96.2	SD	4.794
	0.025	90.3	92.8	91.6	82.6	82.2	82.4	85.6	84.2	84.9	Mean	88.6
	0.05	86.4	84.9	85.7	85.8	83.4	84.6	87.0	82.8	84.9	UCL	103.0
	0.1	86.5	87.2	86.9	86.6	85.5	86.1	89.3	88.0	88.7	UWL	98.2
	0.25	92.5	91.1	91.8	80.3	85.6	83.0	87.1	86.4	86.8	LWL	79.0
	0.5	91.7	90.4	91.1	101.0	101.0	101.0	88.8	86.3	87.6	LCL	74.3

Dimethoate	0.01	97.5	87.7	92.6	72.0	74.7	73.4	106.0	97.2	101.6	SD	14.969
	0.025	137.0	136.0	136.5	84.3	82.5	83.4	79.9	83.8	81.9	Mean	90.2
	0.05	102.0	98.7	100.4	79.1	80.2	79.7	73.7	73.6	73.7	UCL	135.1
	0.1	105.0	101.0	103.0	81.4	81.6	81.5	83.9	84.3	84.1	UWL	120.1
	0.25	99.7	97.8	98.8	76.0	76.4	76.2	88.9	88.3	88.6	LWL	60.3
	0.5	93.8	92.9	93.4	94.2	92.6	93.4	82.6	80.7	81.7	LCL	45.3

Methyl Parathion	0.01	89.3	81.8	85.6	82.3	76.5	79.4	93.9	82.3	88.1	SD	12.244
	0.025	106.0	99.0	102.5	80.5	81.0	80.8	83.5	81.0	82.3	Mean	89.4
	0.05	103.0	96.9	100.0	76.7	78.7	77.7	74.4	75.3	74.9	UCL	126.1
	0.1	120.0	116.0	118.0	79.9	80.0	80.0	86.1	88.8	87.5	UWL	113.9
	0.25	108.0	105.0	106.5	75.6	75.6	75.6	90.3	91.5	90.9	LWL	64.9
	0.5	104.0	104.0	104.0	92.9	94.1	93.5	82.8	82.1	82.5	LCL	52.7

DEF	0.01	82.6	76.6	79.6	76.2	78.8	77.5	83.2	82.9	83.1	Sd	6.175
	0.025	91.5	93.5	92.5	93.8	83.5	88.7	82.9	83.6	83.3	Mean	88.0
	0.05	94.8	92.5	93.7	83.5	82.8	83.2	83.4	83.3	83.4	UCL	106.5
	0.1	91.6	91.9	91.8	88.7	87.6	88.2	87.1	87.8	87.5	UWL	100.4
	0.25	98.2	97.1	97.7	83.9	83.2	83.6	88.4	87.7	88.1	LWL	75.7
	0.5	96.5	94.9	95.7	99.4	99.9	99.7	88.5	86.6	87.6	LCL	69.5

Written By:

Original Signed by 1/7/2014

Stephen Siegel Date

Sr. Environmental Scientist

Approved By:

Original Signed by 1/7/2014

Stephen Siegel Date

Sr. Environmental Scientist

Approved By:

Original Signed by 1/8/2014

Elaine Wong Date
EPM I

Revision Log:

Date	What was Revised. Why?

Title: Determination of Phenoxy Herbicides in Surface water using Gas Chromatography/MSD

1. Scope:

This section method (SM) documents the selected phenoxy herbicide analysis in surface water by all authorized section personnel.

2. Principle:

The surface water sample is extracted with methyl tertiary butyl ether. The extract is evaporated on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed by a gas chromatograph equipped with a mass selective detector (MSD).

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.
3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Stir plate
5.5 Balance (Mettler PC 4400) or equivalent
5.6 Gas Chromatograph equipped with a mass selective detector (MSD)

6. Reagents and Supplies

6.1 Methyl tertiary butyl ether (MTBE), nanograde or equivalent pesticide grade
6.2 Methylene Chloride, nanograde or equivalent pesticide grade
6.3 Acetone, nanograde or equivalent pesticide grade
6.4 Sodium Hydroxide, ACS grade
6.5 Hydrochloric acid, ACS grade
6.6 Diazomethane – prepared from Diazald
6.7 2,4-D CAS# 94-75-7
6.8 MCPA CAS# 94-74-6
6.9 Dicamba CAS# 1918-00-9
6.10 Triclopyr CAS# 55335-06
6.11 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.12 Separatory funnel, 1 L
6.13 Boiling flask, 250 mL
6.14 Disposable Pasteur pipettes, and other laboratory ware as needed
6.15 Recommended analytical column:

For MSD - 5% phenyl Methylsilicone (HP-5ms or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 μm film thickness.

7. Standards Preparation:

7.1 Dilute the 1 mg/mL phenoxy herbicide standards obtained from the CDFA/CAC Environmental Analysis Standards Repository with acetone to make up a series of mixed working standards (see 10.2). These standards shall be prepared to cover the linear range from 0.02 µg/mL to 1.0 µg/mL for all phenoxy herbicides.

7.2 The calibration standards are added to matrix blank extracts (9.1.2.1) to correct for matrix background interference.

7.3 Store standards according to manufacturing requirement. Keep all standards in designated refrigerator for storage.

7.4 The expiration date of each mixed working standard is six months from the preparation date or same as stock standards, if sooner.

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulation (DPR) provides the background water for matrix blank and spikes.

9.1.2.1 Matrix blank: Weigh out 400 g of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out 400 g of background water. Spike a client requested amount of phenoxy herbicides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Weight out 400 g of the sample and transfer into a 600mL beaker.

9.2.2 Adjust the pH of the sample to above pH=12 with conc. Sodium hydroxide. Add 100 ± 10 g sodium chloride. Stir the sample and allow 1 hour for the sample to hydrolyze at room temperature converting all forms of the herbicides to the parent acid.

9.2.3 Stir rapidly on a stir plate with 75 ± 5 mL of methylene chloride for 2 minutes.

9.2.4 Transfer contents of beaker to a 1 liter separatory funnel.

9.2.5 After phases have separated, drain lower methylene chloride layer and discard. Return the water layer to the beaker.

9.2.6 Repeat steps 9.2.3 to 9.2.5 two more times using 60 ± 5 mL of methylene chloride each time. Discarding the methylene chloride.

9.2.7 Adjust the pH of the sample to less than pH=2 with conc. Hydrochloric acid.

9.2.8 Stir rapidly on a stir plate with 75 ± 5 mL of MTBE for 2 minutes.

9.2.9 Transfer contents of beaker to a 1 liter separatory funnel.

9.2.10 After phases have separated, drain lower water layer back into beaker. Transfer the organic layer into a 250mL boiling flask

9.2.11 Repeat steps 9.2.8 to 9.2.10 two more times using 60 ± 5 mL of MTBE each time.

9.2.12 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 40 ± 2 °C and 15 - 20 inch Hg vacuum. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.13 Rinse flask 3 more times with 2 - 4 mL of MTBE and transfer each rinse to the same test tube. Let the tubes sit for several hours in a refrigerator to allow the remaining water in the extract to settle on the bottom of the tube.

9.2.14 Remove the tubes from the refrigerator and remove remaining water from the tube using a disposable pipette.

9.2.15 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 40 ± 5 °C under a gentle stream of nitrogen.

9.2.16 Add approxametly 1 mL of diazomethane to each sample, spike, blank and standards. Allow to sit for 15 to 20 minutes to methylate the herbicides. The yellow color of the diazomethane should be evident and persist for this period.

9.2.17 Evaporate the extract to approximately about 0.5 mL in a water bath at 35 ± 5 °C under a gentle stream of nitrogen to remove any remaining diazomethane. Then bring to a final volume of 1.0 mL with acetone, mix well and transfer into an auto sampler vial.

9.2.18 Submit extract for GC/MS analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background interference.

10.2 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.02, 0.10, 0.20, 0.50, and 1.00 µg/µL are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

11. Analysis:

11.1 Injection Scheme

Recommended injection scheme: calibration standards, Solvent, QC samples, Test Samples (maximum of 10-12 samples) and Calibration standards. Injection an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC Instrumentation

11.2.1 Analyze phenoxy herbicides by a gas chromatograph equipped with mass selective detector.

11.2.2 Recommended instrument (GC/MSD) parameters: Injector 250 °C; detector 250 °C; oven temperature 80 °C (hold 2 min.) to 180 °C @ 20 °C/min. to 280 °C @ 6 °C/min. (hold 6 min.); injection volume 3 µL.

Ions Selected for SIM Acquisition:

Dicamba	**203**, 205, 234, 236
MCPA	**141,** 143, 214
2,4-D	**234**, 236, 199
Triclopyr	**210**, 212, 269

(Quantitation ions are in bold)

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank should be free of target compounds above the MDL.

12.3 The recoveries of the matrix spike shall be within the control limits.

12.3.1 When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples may be re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.3.2 If the spike recoveries still fall outside the control limits, the client will be notified. The backup samples will be extracted and analyzed.

12.4 The retention time should be within $\pm$ 2 percent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard curves should have a percent change less than 20 %.

12.7 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.05 pp. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.8 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Per client agreement, the RL is chosen in a range 1-5 times the MDL except in special cases.
MDL data and the RL are tabulated in Appendix IA and IB.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of three sample sets. Each set included five levels of fortification (0.02, 0.1, 0.2, 0.5, and 1.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.9.2 Upper and lower warning and control limits are set at ± 2 and ± 3 standard deviations of the average % recovery, respectively

Method validation results and control limits are tabulated in Appendix IIA and IIB.

12.10 Estimated Measurement Uncertainty:
Total uncertainty for this method is 16% at 95% confidence interval.

12.11 Trend Identification

12.11.1 All matrix spike recoveries for phenoxy herbicides analysis will be put into control charts and monitored for trends. Three trend characteristics will be evaluated at least bi-yearly by the supervisor or designee.
2 of 3 points above or below 2/3 of the UCL or LCL.
7 continuous points above or below the center line (CL)
14 points alternating above and below the CL.

12.11.2 When results indicate an out of control situation the supervisor or designee will indicate this on the control chart and take appropriate corrective action, which may include monitoring the results more closely to initiating a formal corrective action with root cause investigation.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{(\text{sample peak ht. or area})\ (\text{std. conc.})\ (\text{std. vol. injected})\ (\text{sample final vol., (mL)})(1000\ \mu\text{L/mL})}{(\text{std. peak ht. or area})\ (\text{sample vol. injected})\ (\text{sample wt., g})}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 Sample results are reported out according to the client's analytical laboratory specifications.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards were added to a matrix blank extract to correct for matrix background interference.

16. References:

16.1 *EPA Method 8151A, Chlorinated Herbicides By GC using Methylation Derivatization*. Test methods for Evaluating Solid Waste, 1986

APPENDIX IA

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

Sample ID	Dicamba	MCPA	2,4-D	Triclopyr
MDL #1	0.059	0.049	0.052	0.054
MDL #2	0.057	0.051	0.048	0.049
MDL #3	0.056	0.050	0.049	0.052
MDL #4	0.069	0.061	0.056	0.062
MDL #5	0.065	0.061	0.058	0.064
MDL #6	0.066	0.067	0.061	0.065
MDL #7	0.067	0.060	0.055	0.058
SD	0.005251	0.006952	0.004741	0.006237
SD* 3.143	0.016503	0.021851	0.014901	0.019604
MDL	**0.017**	**0.022**	**0.015**	**0.020**
RL	0.050	0.050	0.050	0.050

APPENDIX IIA

Sample ID	Spike level	Set 1	% Rec.	Set 2	% Rec.	Set 3	% Rec	Control Limit
Dicamba	0.0200	0.0209	**104.5**	0.0224	**112.0**	0.0175	**87.5**	Mean:100.9 SD 21.9
	0.1000	0.1241	**124.1**	0.1415	**141.5**	0.1277	**127.7**	UCL: 166.6
	0.2000	0.1729	**86.5**	0.1966	**98.3**	0.1905	**95.3**	UWL: 144.7
	0.5000	0.4032	**80.6**	0.4724	**94.5**	0.4191	**83.8**	LWL: 57.1
	1.0000	0.6894	**68.9**	1.3210	**132.1**	0.7731	**77.3**	LCL: 35.2

Sample ID	Spike level							Control Limit
MCPA	0.0200	0.0229	**114.5**	0.0206	**103.0**	0.0189	**94.5**	Mean:98.0 SD 19.9
	0.1000	0.1164	**116.4**	0.1307	**130.7**	0.1223	**122.3**	UCL: 157.6
	0.2000	0.1649	**82.5**	0.1848	**92.4**	0.1913	**95.7**	UWL: 137.7
	0.5000	0.3878	**77.6**	0.4505	**90.1**	0.4091	**81.8**	LWL: 60.2
	1.0000	0.6698	**67.0**	1.2674	**126.7**	0.7586	**75.9**	LCL: 40.4

Sample ID	Spike level							Control Limit
2,4-D	0.0200	0.0232	**116.0**	0.0238	**119.0**	0.0204	**102.0**	Mean:97.2 SD 21.2
	0.1000	0.1087	**108.7**	0.1335	**133.5**	0.1176	**117.6**	UCL: 170.0
	0.2000	0.1601	**80.1**	0.1652	**82.6**	0.1649	**82.5**	UWL: 139.7
	0.5000	0.3448	**69.0**	0.4097	**81.9**	0.3849	**77.0**	LWL: 54.85
	1.0000	0.6906	**69.1**	1.2182	**121.8**	0.8035	**80.4**	LCL: 33.5

Sample ID	Spike level							Control Limit
Triclopyr	0.0200	0.0238	119.0	0.0224	112.0	0.0201	**100.5**	Mean: 99.2 SD 22.1
	0.1000	0.1189	118.9	0.1379	137.9	0.1283	**128.3**	UCL: 165.5
	0.2000	0.1625	81.3	0.1752	87.6	0.1850	**92.5**	UWL: 143.4
	0.5000	0.3882	77.6	0.4298	86.0	0.4071	**81.4**	LWL: 55.0
	1.0000	0.6565	65.7	1.2182	121.8	0.7772	**77.7**	LCL: 32.9

Written BY:

Original signed by: 3/17/2009

Wei Cui
Chemist

Date

Approved By:

Original signed by: 3/17/2009

Stephen Siegel
Section Supervisor

Date

Approved By:

Original signed by: 3/19/2009

Elaine Wong
Program Supervisor

Date

Revision Log:

Date	What was Revised? Why?

Title: Determination of Pyrethroids in Sediment Water Using Triple Quadrupole GC/MS/MS

1. Scope:

This section method (SM) documents a selective pyrethroid analysis in sediment water and is followed by all authorized EMON personnel. This method uses the triple quadrupole to improve sensitivity and enables the lowering of the reporting limit over the previous method which used the ECD and MSD.

2. Principle:

The SM describes the method for determination of resmethrin, bifenthrin, fenpropathrin, lambda cyhalothrin epimer, lambda cyhalothrin, permethin cis, permethrin trans, cyfluthrin, cypermethrin, fenvalerate/ esfenvalerate and deltamethrin in sediment water. The pyrethroids are extracted from the sediment water using liquid-liquid extraction with hexane. The extracts are concentrated and then cleaned up with florisil before being analyzed with a gas chromatography equipped with triple quadrupole detector. The reporting limit is 10 ppt for resmethrin, 2 ppt for bifenthrin and 5 ppt for all the rest of the compounds.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 Hexane is a flammable and toxic solvent; it should be handled with care in a ventilated area.

4. Interferences:

There were no interferences at the time of validation for the background water provided.

5. Apparatus and Equipment:

5.1 Rotary Evaporator (Buchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.3 Balance, (Mettler PC 4400 or equivalent)
5.4 Vortex-vibrating mixer
5.5 Gas Chromatograph equipped with a triple quadrupole

6. Reagents and Supplies:

6.1	Bifenthrin	CAS#42576-02-3
6.2	Fenpropathrin	CAS#39515-41-8
6.3	Lambda cyhalothrin epimer	CAS# unknown
6.4	Lambda cyhalothrin	CAS#91465-08-06
6.5	Permethrin cis	CAS#54774-45-7
6.6	Permethrin trans	CAS#51877-74-8
6.7	Cyfluthrin	CAS#68369-37-5
6.8	Cypermethrin	CAS#52315-07-8
6.9	Fenvalerate	CAS#51630-58-1
6.10	Deltamethrin	CAS#52918-63-5
6.11	Resmethrin	CAS#10453-86-8

6.12 Hexanes, nanograde or equivalent pesticide grade
6.13 Diethylether, nanograde or equivalent pesticide grade
6.14 Separatory funnel, 2 L
6.15 Boiling flask, 500 mL
6.16 Sodium Sulfate, ACS grade
6.17 Funnels, short stem, 60°, 10 mm diameter
6.18 Glass wool, Pyrex® fiberglass slivers 8 microns
6.19 Beaker, 1 L
6.20 Florisil SPE cartridge, 2 grams with 20 mL reservoir
6.21 Volumetric Pipette, 1 mL
6.22 Test tube, 50 mL
6.23 Test tube, 15 mL
6.24 Disposable Pasteur pipettes, and other laboratory ware as needed
6.25 Recommended analytical columns:
Varian –VF-5ms arylene stabilized phase equivalent to 5% phenyl, 95% dimethylpolysiloxane fused silica column, 30 m x 0.25 mm id x 0.25 um film thickness.

7. Standards Preparation:

7.1 The individual pyrethroid stock standards of 1.0 mg/mL were obtained from the CDFA/CAC Standards Repository. The standards were diluted to 10 µg/mL with hexanes for identification purposes.

A combination standard of 10 µg/mL was prepared from individual mg/mL standards with acetone to be used for fortification. Another 10 µg/mL combination standard was prepared in hexanes and was diluted to the following

concentrations: 0.005, 0.01, 0.025, 0.05, 0.1, 0.2, 0.5 µg/mL in hexanes for instrument calibration. The calibration standards are added to blank matrix extracts to correct for matrix background response enhancement.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 The expiration date of each standard is six months from the preparation date.

8. Sample Preservation and Storage:

Store all samples waiting for extraction in a separate refrigerator (32-40 °F)

9. Test Sample Preparation:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the sediment water for background to be used in method validation and QC. The sediment water was prepared by adding 5 g of soil to approximately a liter of American river water.

9.2 Spike

Take a liter of background sediment water from refrigerator and allow it to come to room temperature. Fortify at a level requested by client. After fortification mix well and process same as samples.

9.3 Test Sample Extraction

9.3.1 Remove water samples from refrigerator and allow samples to come to room temperature before weighing them. Record weight.

9.3.2 Transfer the water sample to a 2 L separatory funnel leaving as much of the sediment as possible in the sample bottle.

9.3.3 Add 60 mL of hexanes to the sample bottle and manually shake for 30 seconds.

9.3.4 Transfer hexane and sediment into the separatory funnel and shake for 2 min., venting frequently.

9.3.5 Allow the layers to separate, drain the lower aqueous layer into a 1L beaker. Pour the hexane layer through a funnel containing a plug of glasswool and approximately 40 g sodium sulfate into a 500 mL boiling flask.

9.3.6 Transfer the water from the beaker into the separatory funnel and repeat steps 9.3.3 – 9.3.6 two more times shaking for 1 min. Combine the extracts in the same boiling flask. Record sample bottle weight.

9.3.7 Rotory evaporate to ~ 5 mL under vacuum at approximately 20-24 inch Hg in a water bath at 42-45° C.

9.3.8 Transfer the extract to a 15 mL test tube. Rinse flask 3 times with approximately 2 mL of hexane and transfer each rinsate to the same test tube.

9.3.9 Place the test tube on a nitrogen evaporator under a gentle stream of nitrogen with water bath set at 40-45° C and concentrate to ~ 2 mL final volume.

Cleanup

9.3.10 Condition a 2 g florisil SPE cartridge with 10 mL of 15% diethylether in hexane followed by 20 mL hexane. Do not allow cartridges to go to dryness.

9.3.11 Carefully load the sample extract onto the conditioned florisil SPE cartridge. Rinse the tube that previously contained the extract twice with 2 mL hexane. Add rinses to florisil cartridge.

9.3.12 Elute the pesticides from the cartridge with 30 mL of 15% diethylether in hexane and collect in a 50 mL tube.

9.3.13 Evaporate the sample eluants to dryness under a gentle stream of nitrogen in a 40-45° C water bath.

9.3.14 Pipet 1mL of hexane into the test tube and vortex well. Vial extract into 2 autosampler vials with inserts.

10. Instrument Calibration:

10.1 The calibration standards are added to blank matrix extracts to correct for matrix background response enhancement.

10.2 The calibration standard curve consists of a minimum of three levels. The recommended concentrations levels of standards are 0.001, 0.005, 0.01, 0.025, 0.05, 0.1, 0.2, or 0.5 µg/mL. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

11. Analysis:

11.1 Injection Scheme

The instrument may need to be conditioned with a matrix blank or old sample before running the following sequence of Standard Curve, Hexane, Matrix Blank, Matrix Spike, Test Samples (maximum of 10 – 12) and Standard Curve.

11.2 GC-Triple Quadrupole Instrumentation

11.2.1 Gas Chromatograph: Varian CP-3800
Column: Varian Factor Four VF-5ms 30M x 0.25mm x 0.25um.

Temperature Program: initial column temperature 80 °C, hold 1 min., ramp at 40 °C/min. to 180 °C hold for 0 min., ramp at 5 °C/min. to 305 °C hold for 0.5 min..

Injector Temperature: 250°C
Injection Volume: 1 µL
Carrier Gas:Helium 1mL/min.

Triple Quadrupole: Varian Triple Quad 320-MS
Ionization: Positive Electron Impact
Transfer Line: 300°C
Source Temp: 200°C
Collision Gas: Argon @ 1.8 mTorr

Compound	Retention Time (min.)	Precursor Ion	Product Ion	Collision Energy/-ev
Resmethrin 1	16.3	171	128,143	12
Resmethrin 2	16.5	171	128,143	12
Bifenthrin	17.3	181	166	15
Fenpropathrin	17.6	265	210	15
λ Cyhalothrin epimer	18.8	208	181	10
λ Cyhalothrin	19.2	208	181	10
Permethrin cis	20.7	183	168	23
Permethrin trans	20.9	183	168	23
Cyfluthrin 1,	21.7	226	206	15
Cyfluthrin 2	21.9	226	206	15
Cyfluthrin 3	22.0	226	206	15
Cyfluthrin 4	22.1	226	206	15
Cypermethrin 1,	22.3	181	152	20
Cypermethrin 2	22.5	181	152	20
Cypermethrin 3	22.6	181	152	20
Cypermethrin 4	22.7	181	152	20
Fenvalerate	24.2	167	125	15
Esfenvalerate	24.4	167	125	15
Deltamethrin	25.5	253	174	10

12. Quality Control:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 sediment water samples are spiked at 5 ppt except resmethrin, which was spiked at 10 ppt and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for each analyte using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143. The results for the standard deviations and MDL are in Appendix 1.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The reporting limit for resmethrin is 10 ppt, bifenthrin is 2 ppt and for all other compounds is 5ppt.

12.3 Method Validation

The method validation consisted of three sample sets. Each set included three levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the pyrethroids are tabulated in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each analyte. The upper and lower control limits are set at ± 3 standard deviations of the % recovery, shown in Appendix 2.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time should be within ± 2 per cent of that of the standards.

12.5.3 The recoveries of the matrix spikes shall be within the control limits.

12.5.4 The sample shall be diluted if results exceed the calibration curve.

13. Calculations:

Lambda cyhalothrin/epimer, cyfluthrin, cypermethrin and fenvalerate are expressed as the sum of their isomers. Therefore, the total residues should be calculated using the sum of their peak responses.

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The MSD uses linear regression fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppt} = \frac{(\text{sample peak area or ht}) \times (\text{std conc}) \times (\text{std vol. Injected}) \times (\text{final vol of sample})(1000)(1000)}{(\text{std.peak area or ht}) \times (\text{sample vol injected}) \times (\text{sample wt (g)})}$$

14. Reporting Procedure:

Sample results are reported in accordance with the client's analytical laboratory specification sheets.

15. Discussion:

15.1 This method was developed to lower the reporting limit for the pyrethroids by using triple quadrupole mass spectrometry. The only change from the previous method EMON-SM-05-003 is the instrumentation. Since the extraction procedure is the same as the previous method a reduced number of spikes were analyzed for validation.

15.2 Negative chemical ionization (NCI) in selected ion monitor mode was also tried for the pyrethroids and showed some promise for all compounds except resmethrin which provided no signal. Method detection limits and validation resembled those found in EI mode. Future samples that have high background noise will be analyzed by both techniques since in chemical ionization mode the background noise has a different chemical origin and might offer some improvement. In the case of the background matrix provided for the QC there was little benefit observed by running samples under CI mode.

15.3 The sample matrix may require that the injector liner be changed more frequently and the column trimmed to maintain sensitivity. The ion volume and the source may also need to be cleaned more frequently.

15.4 This method was adapted from the methods listed in the references below.

16. References:

16.1 J. White, *Analysis of Pyrethroids in Sediment Water* Emon-SM-05-003, 2006, California Department of Food and Agriculture, Center for Analytical Chemistry, Environmental Analysis Section, 3292 Meadowview Road, Sacramento, California 95832

16.2 J. You, D.P. Weston, M. J. Lydy, *A Sonication Extraction Method for the Analysis of Prethroid, Organophosphate, and Organchlorine Pesticides from Sediment by Gas Chromatography with Electron-Capture Detection,* Archives Environmental Contamination and Toxicology 47, 141-147 (2004)

16.3 J. You, M. J. Lydy, *Evaluation of Desulfuration Methods for Pyrethroid, Organophosphate, and Organochloride Pesticides in Sediment with High Sulfur Content,* Archives Environmental Contamination and Toxicology 47, 148 -153 (2004)

16.4 J. White, H. Feng, Determination of Pyrethroids in Sediment Water, EMON-SM-52-7.1, 2004, California Department of Food and Agriculture, Center for Analytical Chemistry, Environmental Monitoring Laboratory, 3292 Meadowview Road, Sacramento, California 95832

Appendix 1

The determination of Method Detection Limit (MDL) and Reporting Limit (RL)

Spike level is 5 ppt for all compounds except Resmethrin, which is 10 ppt

	Bifenthrin	Fenopropathrin	λcyhalothrin Epimer/ λcyhalothrin	Permethrin cis	Permethrin trans	Cyfluthrin
	ppt	ppt	ppt	ppt	ppt	ppt
blk sed	n/d	n/d	n/d	n/d	n/d	n/d
spk1	5.74	5.51	5.87	5.72	4.10	5.68
spk2	4.98	4.57	5.23	6.04	4.06	5.23
spk 3	5.57	5.00	5.46	5.54	4.39	5.46
spk 4	5.36	4.71	5.71	5.40	3.85	5.53
spk 5	5.46	5.58	6.76	6.01	4.75	6.32
spk 6	5.02	4.42	5.93	5.29	4.24	5.90
spk 7	4.86	5.07	5.39	5.36	3.92	5.04
Std dev	0.29	0.42	0.55	0.34	0.33	0.47
MDL	0.91	1.32	1.74	1.05	1.05	1.46
RL	**2 ppt**	**5 ppt**	**5 ppt**	**5 ppt**	**5 ppt**	**5 ppt**

	Cypermethrin	Fenvalerate/ Esfenvalerate	Deltamethrin	Resmethrin
	ppt	ppt	ppt	ppt
blk sed	n/d	n/d	n/d	n/d
spk1	6.27	5.11	4.86	9.22
spk2	4.99	4.44	5.29	8.68
spk 3	6.31	5.92	4.50	10.70
spk 4	5.02	4.75	4.93	10.20
spk 5	5.71	5.41	6.29	10.19
spk 6	5.45	4.99	5.14	12.79
spk 7	5.65	4.82	5.36	9.56
Std dev	0.49	0.53	0.56	1.33
MDL	1.54	1.66	1.77	4.18
RL	**5 ppt**	**5 ppt**	**5 ppt**	**10 ppt**

Appendix 2

Method Validation Data and Control Limits

Analyte	Spike ppt	Recovery % set 1	set 2	set 3		
Bifenthrin	5	88.6	93.0	75.8	Mean:	80.2
	10	79.9	83.3	75.7	SD:	6.81
	25	72.8	75.6	76.8	UCL:	101
					LCL:	59.7
Fenpropathrin	5	91.0	91.6	108	Mean:	91.0
	10	83.8	86.9	76.1	SD:	9.39
	25	88.8	102	90.8	UCL:	119
					LCL:	62.8
λ cyhalothrin /epimer	5	97.2	101	76.2	Mean:	87.4
	10	84.4	92	76.2	SD:	8.59
	25	90.4	85.2	83.6	UCL:	113
					LCL:	61.6
Permethrin cis	5	98.2	132	71.2	Mean:	93.9
	10	95.7	85.0	93.5	SD:	16.8
	25	82.4	88.4	98.8	UCL:	144
					LCL:	43.6
Permethrin trans	5	91.8	129	78.4	Mean:	96.2
	10	108	87.4	92.6	SD:	14.5
	25	92.8	91.6	94.0	UCL:	140
					LCL:	52.7
Cyfluthrin	5	105	120	103	Mean:	102
	10	101	103	89.4	SD:	8.43
	25	95.2	103	96.8	UCL:	127
					LCL:	76.5
Cypermethrin	5	102	113	74.6	Mean:	95.8
	10	101	96.1	101	SD:	10.7
	25	90.0	96.4	88.4	UCL:	128
					LCL:	63.5
Fenvalerate / Esf	5	96.8	122	93.8	Mean:	95.2
	10	90.7	100	89.9	SD:	11.0
	25	86.8	90.0	86.4	UCL:	128
					LCL:	62.2

Appendix 2 continued

Method Validation Data and Control Limits

Analyte	Spike ppt	Recovery % set 1	set 2	set 3		
Deltamethrin	5	110	104	95.6	Mean:	96.4
	10	93.5	99.0	64.5	SD:	13.4
	25	95.2	109	96.4	UCL:	137
					LCL:	56.2
Resmethrin	15	85.3	74.0	69.3	Mean:	74.5
	25	80.7	63.7	67.0	SD:	8.4
	50	79.8	65.7	84.8	UCL:	99.7
					LCL:	49.3

Written By:

Original signed by 5/9/2011

Jean Hsu Date
Environmental Scientist

Written By:

Original signed by 5/9/2011

Jane White Date
Environmental Scientist

Approved By:

Original signed by 5/10/2011

Steve Siegel Date
Senior Environmental Scientist

Approved By:

Original signed by 5/11/2011

Elaine Wong Date
Environmental Program Manager I

Revision Log:

Date	What was Revised? Why?

Determination of Pyrethroid Pesticides in Sediment

1.0 Scope and Application

1.1 This method describes the sample preparation using an automated extraction system for the determination of trace residue levels of a selected list of pyrethroid pesticides in sediment. Dual column gas chromatography with dual electron capture detectors (GC-ECD) and/or gas chromatography with triple quadrupole mass spectrometry (GC-MSMS) are used for analysis. Table 1 lists the target pyrethroid compounds currently analyzed with their method detection limits (MDL) and reporting limits (RL), based on dry weight. Detection limits were calculated using USEPA procedures found in Title 40 Code of Federal Regulations Part 136 (40CFR 136, Appendix B, revision 1.11). Sediment results can be found in Appendix A. The average percent recoveries, amount recovered and standard deviations are listed in Table 5.

These procedures are applicable when low parts per billion analyses are required to monitor differences between burdens in soils and sediment from relatively uncontaminated reference areas and contaminated areas.

Table 1. Pyrethroid Compounds Analyzed, CAS Numbers, Minimum Detection Limits (MDL) and Reporting Limits (RL) in Sediment, Based on 50 % Moisture.

		GC-ECD		GC-MSMS	
Target Analytes	CAS#	MDL, ng/g dry wt.	RL, ng/g dry wt.	MDL, ng/g dry wt.	RL, ng/g dry wt.
Allethrin	584-79-2	1.0	2.0	1.5	3.0
Bifenthrin	82657-04-3	0.50	1.0	0.25	0.50
Cyfluthrin	68359-37-5	2.0	4.0	0.20	0.40
Cypermethrin	52315-07-8	2.0	4.0	0.30	0.60
Deltamethrin/ Tralomethrin	52918-63-5/ 66841-25-6	2.0	4.0	0.20	0.40
Esfenvalerate/ Fenvalerate	66230-04-4/ 51630-58-1	1.0	2.0	0.20	0.40
Fenpropathrin	64257-84-7	2.0	4.0	0.80	1.6
Flucythrinate	70124-77-5	5.0	10	NA	NA
Lambda- cyhalothrin	91465-08-6	1.0	2.0	0.15	0.30
Permethrin, cis	54774-45-7	4.0	8.0	0.70	1.40
Permethrin, trans	51877-74-8	4.0	8.0	1.20	2.40
Phenothrin	26002-80-2	5.0	10	0.11	0.22
Prallethrin	23031-36-9	1.0	2.0	0.40	0.80
Resmethrin	10453-86-8	NA	NA	0.40	0.80
Tetramethrin	7696-12-0	5.0	10	0.30	0.60

UNOFFICIAL COPY - FINAL

2.0 Summary of Method

2.1 Sets of 12-18 homogenized sediment samples are scheduled for extraction by the project lead chemist. Extraction method employed was developed and validated by the Water Pollution Control Laboratory (WPCL) and is a modification of EPA Method 3545A Pressurized Fluid Extraction (PFE). Extract cleanup and partitioning methods are modifications of EPA Methods 3640A Gel Permeation Cleanup and 3620C Florisil Cleanup and the multi-residue methods for fatty and non-fatty foods described in the U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, 3rd Edition 1994, Chapter 3, Multi-residue Methods, Section 303-C1.

Sediment samples are removed from the freezer and allowed to thaw.

2.2 A 1-5 g sample is weighed into a pre-weighed aluminum planchet and placed in a 70°C oven for 24 hours to determine moisture content. A 10 g sample is mixed using a clean glass stirring rod with approximately 7 g of pre-extracted Hydromatrix® (Varian Corp) in a 250 mL Trace Clean Wide Mouth Jar until the mixture is free flowing. The mixture is then poured into a 33 mL stainless steel Dionex Accelerated Solvent Extractor (ASE 200) extractor cell and packed by tamping the mixture. A solution containing cis-permethrin (C^{13}) surrogate is added to the cell and the cap is screwed onto the cell. The extractor cells (maximum of 24) are placed on the ASE 200 autosampler rack and the samples are extracted twice with a 50/50 mixture of acetone/dichloromethane (DCM) using heat and pressure. The extracts are automatically collected in 60 mL VOA vials.

2.3 The combined extracts are dried using sodium sulfate, evaporated to approximately 0.5-1.0 mL using Kuderna-Danish (K-D) glassware equipped with 3-ball Snyder columns and micro-Snyder apparatus and diluted to 10 mL using DCM. The extracts are then filtered through a 0.45 µm syringe filter into 12 mL culture tubes fitted with Teflon-septa open style caps.

2.4 The culture tubes are then placed on the GPC autosampler for initial sample cleanup.

2.5 The cleaned-up extracts are evaporated using K-D apparatus and solvent exchanged into petroleum ether. The extracts are then further cleaned using Florisil® in a 22 mm x 300 mm column. The Florisil® columns are eluted with 70% diethyl ether/petroleum ether. The extracts are concentrated to an appropriate volume using K-D/micro K-D apparatus prior to analysis by GC-ECD and/or GC-MSMS.

UNOFFICIAL COPY - FINAL

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may cause GC artifacts and/or elevated baselines, resulting in the misinterpretation of chromatograms. All materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks initially and with each sample lot. Specific selection of reagents and purification of solvents by distillation in all-glass systems are required. High-purity, distilled-in-glass solvents are commercially available.

An effective way of cleaning laboratory glassware is by rinsing with polar and non-polar solvents before use. The cleaning procedure used must be tested by analyzing procedural blanks prior to analyzing samples.

3.2 Phthalates are common laboratory contaminants that are used widely as plasticizers. Sources of phthalate contamination include plastic lab-ware, plastic tubing, plastic gloves, plastic coated glassware clamps, and have been found as a contaminant in Na_2SO_4. Polytetrafluoroethylene (PTFE) can be used instead of polypropylene or polyethylene to minimize this potential source of contamination. However, use of PTFE lab-ware will not necessarily preclude all phthalate contamination.

3.3 Interferences co-extracted from tissue and sediment samples limit the method detection and quantitation limits. For this reason, sample extract cleanup is necessary to yield reproducible and reliable analyses of low level contaminants.

4.0 Apparatus and Materials

4.1 Wide mouth, borosilicate glass, pre-cleaned and certified, 250 mL, Qorpak or equivalent.

4.2 Chromatographic Column - (300 mm x 11 mm) borosilicate glass chromatography column with a Teflon stopcock.

4.3 Glass wool, Pyrex - solvent washed prior to use.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 mL, graduate (Kontes K0570050-1025, or equivalent). A ground stopper, 19/22 joint, is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500 mL (Kontes K-570050-0500, or equivalent), attached

UNOFFICIAL COPY - FINAL

to concentrator tube with blue clamp (Kontes K-662750-0012).

4.4.3 Snyder column - three ball (Kontes K-503000-0121, or equivalent).

4.4.4 Micro-Snyder column - (Kontes VWR KT569261-0319 or equivalent).

4.4.5 Boiling chips, Chemware® Ultra-pure PTFE, extracted with acetone and petroleum ether. Note that boiling chips can be a significant source of contamination if not properly cleaned.

4.5 Water bath, Organomation Assoc. Inc. (OA-SYS/S-EVAP-KD), 115 V, thermostatically controlled with stainless steel cover to fit 5 K-D apparatus, installed in a fume hood.

4.6 Extractor, automated, Dionex Accelerated Solvent Extractor (ASE 200), Dionex P/N 047046.

4.6.1 Extraction Cells, 33 mL, Dionex P/N 049562

4.6.2 Filters, cellulose for ASE extraction cells, Dionex P/N 049458.

4.6.3 VOA Vials, 60 mL, pre-cleaned and certified.

4.7 Sample vials - glass, 2 mL with PTFE-lined screw cap.

4.8 Analytical balance - capable of weighing 0.1 mg.

4.9 Drying oven.

4.10 Balance - capable of 100 g to the nearest 0.01 g.

4.11 Disposable Pasteur Pipettes - (rinsed with solvents before use).

4.12 Aluminum dishes for moisture determination.

4.13 Desiccator with indicating desiccant.

4.14 Glass funnel, 75 mm.

4.15 Graduated cylinder, 250 mL and 100 mL.

4.16 Culture tubes, 13 x 100 mm and 16 x 100 mm, with PTFE lined cap.

UNOFFICIAL COPY - FINAL

4.17 Gas chromatographs: 1) Agilent 6890*plus*, equipped with two micro ECD detectors with EPC, split-splitless injector with EPC, and autosampler. Capillary columns, 60 meter DB5 and 60 meter DB17MS (J&W Scientific) (0.25 mm I.D. and 25 µm film thickness) connected to a single injection port using a "Y" press fit connector. 2) Gas chromatograph-mass spectrometer (triple quadrupole), Varian Model 1200L with Varian Model 3800 gas chromatograph, split-splitless injector with EPC and Combi-Pal autosampler. The capillary column is a XLB (Waters) 60 m x 0.25 mm I.D. x 0.25 µm film thickness.

4.18 Data Systems (Agilent and Varian Workstations) to collect and record GC data, generate reports, and compute and record response factors for multi-level calibrations. Data system should be capable of calibrating a method using a minimum of 5 concentrations of analytical standards.

4.19 Homogenizer, Bucchi Model B-400 (Brinkman P/N 16-07-200-1) or equivalent equipped with titanium knife assembly (Brinkman P/N 16-07-222-2) and glass sample vessel (Brinkman P/N 16-07-245-1).

4.20 Homogenizer, Brinkman Polytron or equivalent equipped Teflon and titanium generator assembly (for homogenization of small sample amounts).

4.21 Gel Permeation (size exclusion) Chromatograph, automated, J_2 Scientific AccuPrep 170, equipped with 70 g S-X3 BioBeads J_2 Scientific P/N C0070G (100% DCM).

5.0 Reagents

5.1 Petroleum ether (PE), Burdick and Jackson, distilled in glass and pesticide residue or HRGC grade or equivalent.

5.2 Acetone. (Same as above).

5.3 Iso-Octane. (Same as above).

5.4 Diethyl ether preserved with 2% ethanol. (Same as above).

5.5 Dichloromethane (DCM). (Same as above).

5.6 Chem Elut-Hydromatrix®, Varian P/N 0019-8003. Pre-extracted on ASE-200 with acetone/DCM prior to use.

5.7 Sodium sulfate. Anhydrous granular reagent grade, rinsed with PE prior to use.

UNOFFICIAL COPY - FINAL

5.8 Florisil®, 60/100 mesh, PR grade, U. S. Silica.

5.9 Nitrogen, pre-purified grade (99.9999%) or better (used for ASE and GPC.)

5.10 Nitrogen, ultra-pure (99.99999%) for ECD makeup and blowdowns.

5.11 Helium, ultra-pure (99.99999%) for GC carrier gas.

5.12 Air, compressed, breathing quality, for ASE pneumatics.

5.13 Pyrethroid Surrogate Solution containing 20 ppb of cis-permethrin (C^{13}) obtained from Cambridge Isotope Laboratories (Andover, MA). P/N CLM-7322-1.2.

5.14 Pyrethroid Spiking Solution Mix A (for GC/ECD): Individual compounds obtained from Chem Service, Inc., West Chester, PA. Solution made in iso-octane.

Compound	P/N	Concentration (ppb)
Bifenthrin	PS2003	50
Cyfluthrin	F2460	200
Cypermethrin	PS1068	200
Deltamethrin	PS2071	200
Es-fenvalerate	PS2004	100
Fenpropathrin	PS2002	200
Lambda-cyhalothrin	PS2018	100
Permethrin, cis	PS758-1	250
Permethrin, trans	PS758-2	250

Pyrethroid Spiking Solution Mix B (for GC/MSMS): Individual compounds obtained from Chem Service, Inc., West Chester, PA except for tetramethrin, which was purchased from AccuStandard, New Haven, CT. Solution made in iso-octane.

Compound	P/N	Concentration (ppb)
Allethrin	PS791	25
Bifenthrin	PS2003	5
Cyfluthrin	F2460	25
Cypermethrin	PS1068	25
Deltamethrin	PS2071	25
Es-fenvalerate	PS2004	10
Fenpropathrin	PS2002	50
Lambda-cyhalothrin	PS2018	10

UNOFFICIAL COPY - FINAL

Permethrin, cis	PS758-1	5
Permethrin, trans	PS758-2	5
Phenothrin	PS1030	5
Prallethrin	PS2109	25
Resmethrin	F2293	25
Tetramethrin	P-406	25

5.15 Pyrethroid Instrument Calibration Standards: Individual compounds obtained from Chem Service (see 5.14) are mixed in iso-octane with concentrations ranging from 0.50 ppb to 500 ppb (based on bifenthrin).

5.16 Second Source Standards: Pyrethroid analytes were obtained from AccuStandard, New Haven, CT (P/N AE-00023, Pesticide Mix 14 - components include cyfluthrin, cypermethrin, deltamethrin, fenvalerate, L-cyhalothrin, and permethrin and P-5252 (esfenvalerate)) and Ultra Scientific, North Kingstown, RI (P/N PST-1915 (bifenthrin) for verification of calibration standards.

CAUTION

The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined. However, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling Material Safety Data Sheets should also be made available to all personnel involved in these analyses.

6.0 Sample Collection, Preparation, and Storage

6.1 In the field, sources of contamination include sampling gear, grease from ship winches or cables, ship and/or motor vehicle engine exhaust, dust, and ice used for cooling. Efforts should be made to minimize handling and to avoid sources of contamination.

6.2 To avoid cross-contamination, all equipment used in sample handling should be thoroughly cleaned before each sample is processed. All instruments must be of a material that can be easily cleaned (e.g., stainless steel, anodized aluminum, or borosilicate glass). Before the next sample is processed, instruments should be washed with a detergent solution, rinsed with tap water, rinsed with a high-purity acetone, and finally rinsed with Type II water.

UNOFFICIAL COPY - FINAL

6.3 Sediment samples are collected in wide-mouth glass jars and must be frozen if not extracted within 14 days.

7.0 Sample Extraction

7.1 Frozen sediment samples are removed from the freezer and allowed to thaw. Prior to extraction, sediment samples are thoroughly mixed by hand using a clean glass rod or may be homogenized using a Polytron homogenizer equipped with stainless steel generator equipped with Teflon bearings. Sample sets of 12-18 should be extracted when possible. The ASE-200 extractor will extract 24 cells. Be sure to reserve enough cells for method blanks, matrix spikes and duplicates, laboratory control spikes and sample duplicates.

7.2 Prepare a glass rod or Teflon spatula for each sample to be weighed by rinsing 3 times with petroleum ether using a Teflon wash bottle.

7.3 Label 60 mL VOA vials for the collection of the sample extract. The labels must be placed between 1.5" and 3" from the top of the VOA cap; if they are placed outside of this area, they will interfere with the ASE optical sensor. Use two VOA vials for each sample. Label the first VOA vial with the ASE position number, bench sheet number and the sample name. Label the second VOA vial the same but add “RE” to distinguish between the two vials. Label and weigh aluminum planchets for moisture determinations (samples ID can be made on the bottom of planchets using a ball point pen.

7.4 Tare a 250 mL glass jar. Using a clean (solvent rinsed) glass rod, stir the sediment so that the mixture is homogeneous. Weigh 10 g of sample into the jar, record the weight on the bench sheet, and add the twice-extracted Hydromatrix® from one ASE cell. Stir the mixture thoroughly and go on to the next sample. After approximately 15 minutes stir the sample again. Repeat this at 15 minute intervals two more times or until the sample mixture is free flowing.

7.5 Weigh 1-5 g of additional sample into a pre-weighed and tared aluminum planchet for % moisture analysis. Place planchets in 70°C oven for 24 hours and re-weigh dry weight.

7.6 Place a pre-rinsed powder funnel on top of a 33 mL ASE cell containing a pre-extracted cellulose filter *(the filter is the one that was used to pre-extract the Hydromatrix®)*.

7.7 Pour the sediment/Hydromatrix® mixture through the powder funnel back into the extraction cell that the Hydromatrix® was poured from. Tap the cell against the counter top to settle the contents. The mixture will fill the cell and it may be

UNOFFICIAL COPY - FINAL

necessary to pack it slightly using the glass rod and the end of the powder funnel. The cells used for the method blank and laboratory control spike and its duplicate *(if used)* will contain only Hydromatrix®.

7.8 **All** of the extraction cells are spiked with the pyrethroid surrogate standard. Spike each cell with exactly 1.0 mL of the pyrethroid surrogate solution (20 ng/mL). Surrogate spikes must be witnessed, recorded and dated on the extraction bench sheet.

7.9 The extraction cells used for the matrix spike (MS) and matrix spike duplicate (MSD) and laboratory control spike (LCS) and its duplicate (LCSD) (if used) are spiked with exactly 1.0 mL of the pyrethroid matrix spike solution (20 ng/mL). Matrix spikes must be witnessed, recorded and dated on the extraction bench sheet.

7.10 The extraction cells are capped *(Firmly tightened but do not over tighten)* and placed on the ASE 200 carrousel. The first set of labeled VOA collection vials are placed on the ASE 200 collection carrousel with the position numbers corresponding to the position numbers of the extraction cells. Make sure that the solvent reservoir contains enough solvent for the extraction.

7.11 Samples are extracted with acetone/methylene chloride (DCM) 50:50 using the following conditions:

Pre-heat	0 min.
Heat	5 min.
Static	5 min.
Flush	60%
Purge	300 sec.
Cycles	1
Pressure	1500 psi
Temp	100 ^{o}C
Sol A Other	100%

7.12 After the initial extraction is complete, remove full VOA vials and place in a Wheaton rack. Place the second set of collection VOA vials labeled “RE” on the ASE carrousel. Check each of the extraction cells to make sure that the caps are *(firmly tightened)* as they tend to loosen with the first extraction. Make sure that the replacement vials are in the correct order. Make sure that the solvent reservoir contains enough solvent for the re-extraction. Re-start the ASE-200.

7.13 When extraction is completed, place VOA vials in a Wheaton rack with the “RE” vials next to the vials from the first extraction. The extracts should be re-capped with solid green caps (Qorpak) and placed in a refrigerator for storage until they

UNOFFICIAL COPY - FINAL

are removed for the GPC cleanup procedure.

8.0 Gel Permeation Chromatography

IMPORTANT: ***All glassware, glass wool, and sodium sulfate must be triple-rinsed with petroleum ether before they are used for this procedure.***

8.1 Remove VOA vials containing the sample extracts from the refrigerator. Make sure the vials are capped with the green Qorpak caps. Allow them to sit out until they are at room temperature.

8.2 Set up and label pre-cleaned K-D flasks (4-6) with concentrator tubes attached on ring stands in the fume hood. Place a funnel containing a plug of pre-cleaned glass wool in the bottom of the funnel and place the funnel in the top of the K-D flask. Add about two inches of pre-rinsed sodium sulfate to the funnel. Make sure that the level of the sodium sulfate is uniform across the funnel to prevent any possible splashing out.

8.3 Pour sample extracts from the VOA vials through sodium sulfate into the K-D flask. Add about 10 mL of DCM to the VOA vial, cap and shake and add this rinse to the sodium sulfate. Repeat with another 10 mL DCM rinse. Rinse the sodium sulfate with an additional portion of DCM (~50 mL) by pouring from a clean and rinsed 400 mL beaker. After the solvent has completely drained through the sodium sulfate add one more additional rinse of DCM (~50 mL) from the beaker of clean DCM. Allow the DCM to completely drain through the sodium sulfate (~3-5 minutes).

8.4 Add 0.5 mL Iso-Octane using a macro-pipette and a solvent rinsed boiling chip to each K-D flask. Place a Snyder column on the K-D flask and place the flask on the hot water bath set at 80-82°C. Evaporate the solvent until the apparent volume is 2-5 mL. Remove the inverted Hopkins condenser and secure using the set clamps so that it is out of the way. At this point there should be between 2-5 mL visible in the concentrator tube while the K-D apparatus is still on the hot water bath and 10 mL or less of the solvent remaining after the K-D flask is removed from the hot water bath and the solvent drains from the Snyder column. Dry off the water using a WyPall X60 towel to remove any water from around the ground glass union of the concentrator tube and the K-D flask to prevent any of it from entering the concentrator tube upon removal.

8.5 After the K-D apparatus has cooled and all of the solvent has drained from the Snyder column, remove the Snyder column, label the concentrator tube and then remove the concentrator tube from the flask and place the tube in a test tube rack and cover with pre-rinsed aluminum foil. Rinse the Snyder column with petroleum ether and place back in the column rack for storage. After all of the flasks have

UNOFFICIAL COPY - FINAL

been removed from the hot water bath, repeat steps 2-5 for the remaining samples extracted with this set.

8.6 Add a new micro-boiling stone and place a clean micro-Snyder column on the concentrator tube with a blue clamp and place in a 400 mL beaker containing hot water heated to approximately 75°C on a hot plate. If the solvent does not begin to boil, remove the tube from the bath immediately, allow it to cool slightly, add a new micro boiling stone to prevent it from bumping and place it back in the bath. Evaporate the solvent until only 0.5-1.0 mL remains in the concentrator tube. Four or five tubes can be evaporated at one time.

8.7 When the solvent has been evaporated to 1.0 mL remove the tube from the bath and allow it to cool in a test tube rack. Remove the micro-Snyder column and add DCM to the concentrator tube to reach a final volume of 10.0 mL.

8.8 Gelman filter (0.45 µm) the sample into a 12 mL culture tube. Using a volumetric pipette remove 2.0 mL of the filtered sample and place it in a pre-weighed aluminum planchet if lipid determination is needed. Cap the culture tube with the Teflon-insert style caps. Mark the bottom of the meniscus with a pen in case of evaporation before clean-up on GPC.

8.9 All samples are cleaned using a J_2 Scientific GPC (Autoinject 110, AccuPrep 170, DFW-20 Fixed Wavelength Detector, 1" ID glass column with 70g Bio-Beads SX-3 in 100% DCM)

8.9.1 From the desktop double click on the AccuPrep.exe shortcut to open the program. Click on the Use Injector button and allow the instrument time to initialize. Activate the pump by using the top left hand button. A solvent Control Pump window will open up. Click on the Apply Defaults button and then OK on the Selected Pressure Limit 30 psi. The pump should audibly be heard coming on and the green light should show that the system is on line and status flowing. Make sure that the bottle of clean DCM is full and the waste bottle is empty. Allow the system to pump for about 5 minutes before switching the column in-line (gray button next to Column that has 'Put in line' on it). The pressure will be observed to normally go up to the 12-16 psi range. Turn the power on to the detector to allow it at least 30 minutes of time to warm up before use. Because the scale is auto-adjusted in the software now it is no longer necessary to manually adjust the range on the unit itself.

8.9.2 While the system is equilibrating, the sequence can be entered. Click on the Seq button next to the Pump button. An 'Editing new sequence' window will pop up. This gives a view of the instrument which clearly shows the sample tray locations and the corresponding sample collection locations. By clicking on the sample tray position, a new window 'Adding sample at tray position #' will pop up.

UNOFFICIAL COPY - FINAL

This allows information to be included about each specific sample. Sample position 1 will always be a calibration standard (CLP-340) which is run prior to any sequence of runs to verify instrument integrity. In the Sample ID field just type in 'CLP-340'. In the Descrip (optional), information pertaining to the project, laboratory control number, bench sheet number and date are typically added. The Method File needs to be changed to 'GPC-Sed' for only this sample and in the Sample Type field the 'Calibration' type can be chosen. After this information is completed click on the OK to continue. This returns you back to the main sequence window but now the first position will be highlighted in green. Continue by adding the next sample information to tray position 2, again following the same steps as before. The Method File name to be used is 'Sed-Pest'. Also by default, the Sample Type field will already be set at 'Sample'. This will not need to be changed until a duplicate sample (Duplicate), matrix spike (Matrix Spike), matrix spike duplicate (Spike Duplicate) and laboratory control spike (Spiked Blank) are encountered. After all the samples have been added to the sequence, save it as the WPCL log-in number (L-###-##). From the Editing sequence window print out the sample list. Compare the information to your original bench sheet to insure there are no mistakes. Make sure the GPC-Sed method is being used for the calibration standard and 'Sed-Pest' method is being used for the samples. Next verify that the samples are still at the marked line on the culture tubes (add DCM to the marked line if they are not). Place a tube with the GPC Calibration Standard Solution (CLP-340) in sample tray position 1 and then follow as the sequence was made in the remaining positions.

8.9.3 Get two boxes of the 125 mL Trace Clean amber bottles for sample collection. A bottle does not need to be placed in collection position #1 because that is the GPC Calibration Std (all goes to waste). Remove the white caps from the bottles and place them on top of the detector (so that Teflon side is not exposed to possible contamination). Label the boxes with laboratory control numbers and keep them for the post-GPC samples to be stored in. Now that the pump has had plenty of time to equilibrate the system and the detector has had plenty of time to warm up, in the Signal field click to adjust the setting to 'Absorbance Units' and click on the 'Zero Signal' button to set the baseline.

8.9.4 If the pressure seems to be pretty stable between the 12-16 psi range and all the samples positions and collection positions have been loaded, then click on the large button with the stop watch to begin the program. A window will pop up asking if the correct column method is loaded (100%DCM). Click on 'yes' to engage the syringe pump to begin priming. The sample probe will move over to sample position #1 and aspirate the sample. After the samples have all been processed (~1 hour per sample), remove the label from the sample position and place it on the bottle in corresponding collection position. Cap the bottle and place it back in the box that was retained for their storage. At the end of the sequence there will be a window that pops up saying that the 'Sequence has been

UNOFFICIAL COPY - FINAL

successfully completed'. The column will switch offline and the pump will automatically shut down. The only thing that has to manually be turned off is the power to the detector.

8.10 Pour the GPC eluate into a rinsed K-D flask. Rinse the bottle with some DCM and add that to the K-D flask. Add 0.5 mL Iso-Octane and a micro boiling chip to each K-D flask. Attach a Snyder column to the flask and place in the hot water bath. When the volume of the solvent in the concentrator tube is level with the base of the K-D flask, lift the K-D apparatus up enough to be able to angle it slightly and add 40-50 mL Petroleum Ether through the top of the Snyder column. By holding the K-D apparatus at an angle, it allows the solvent to more easily drain back into the flask. Return to the K-D apparatus back into the hot water bath. Repeat this step 2 more times to successfully solvent exchange the sample from DCM to Petroleum Ether. When the apparent volume in the concentrator tube is 5-10 mL remove it from the hot water bath. Wipe down the K-D apparatus with a WyPall X60 towel especially around the ground glass junction. Remove the Snyder column from the K-D apparatus and allow to completely drain into the concentrator tube. After it has finished cooling, remove the concentrator tube and place a micro-Snyder column on it. Add a new micro boiling chip and place it in a 400 mL beaker containing water heated to approximately 75°C on a hot plate (4-5 tubes can be evaporated at one time). Evaporate the solvent down to 1-2 mL. Remove it from the water bath and allow it to cool.

8.11 Transfer the solution to a 13 x 100 culture tube with a Pasteur pipette; rinse the concentrator tube with 0.5 mL of Petroleum Ether, vortex, and transfer the rinse to the culture tube. Repeat the rinse step two more times and add each rinse to the culture tube. Cap the culture tube with a Teflon faced cap. Place extracts in a refrigerator for storage until the final Florisil® column cleanup is done.

8.12 Add acid rinsed copper to all culture tubes to remove any residual sulfur from the extract.

9.0 Florisil® Column Fractionation

IMPORTANT: All glassware, glass wool, and sodium sulfate must be triple-rinsed with petroleum ether (PE) before they are used for this procedure. Florisil® must be activated in an oven at 130°C for at least 24 hours prior to use.

9.1 This procedure is performed after the GPC cleanup procedure for all sediment samples analyzed for pyrethroid pesticides.

9.2 Prepare the reagent to be used for Florisil® cleanup: 70% ethyl ether in petroleum ether (EE/PE). Make an amount slightly in excess of what is actually needed to

UNOFFICIAL COPY - FINAL

allow for any loss which may occur during solvent transfer. The required volume is 280 mL per sample.

9.3 Prepare the chromatography columns. Place a small piece of PE rinsed glass wool in the bottom of the 22 x 300 mm column and tap into place with a PE rinsed glass rod. Cover with a small portion (0.5 inch) of sodium sulfate. Fill the column with four inches of Florisil®. Tap column with rubber "mallet" to firmly settle the Florisil®. Top the column with 3/4-1 inch of sodium sulfate. This will prevent the column from being disrupted when solvent is added and will remove any residual water.

9.4 Place a 600 mL beaker under the column and pre-wet the column with about 25 mL of 70% EE/PE.

IMPORTANT: From this point and through the elution process, the solvent level should never be allowed to go below the top of the sodium sulfate layer.

9.5 When approximately 1 inch of solvent remains above the surface of the column, place a K-D flask under column making sure that the stopcock is in the full open position. This will allow for a flow rate of about 2 to 3 mL/min. When the meniscus of the solvent rinse reaches the column bed surface, decant the sample onto the column. Immediately add approximately 0.5 mL of 70% EE/PE to the tube, vortex, and add the rinse to the sample extract on the column. Add another 0.5 ml of 70% EE/PE to the tube, vortex, and add this final rinse to the sample extract on the column. Start the columns in a sequential fashion, and the lag time will be adequate to perform the necessary tasks for up to six columns.

9.6 When the combined sample and rinses reach the sodium sulfate layer, add 280 mL of 70% EE/PE that has been carefully measured out using a graduated cylinder to the column. Make sure that the stopcock is fully open in order to achieve the desired flow rate of 5 mL per minute. Collect directly into a clean PE rinsed 500 mL KD flask.

9.7 After all of the solvent drains through the column, add a micro boiling stone and attach a Snyder column with a green clamp to the K-D flask and place vessel in the hot water bath with the temperature set at 80-82°C and reduce volume to an apparent volume of 1 mL. Tap the Snyder column to make sure solvent is not trapped between the balls then remove the vessel from the bath and place in the vessel stand to cool.

9.8 When the vessels are cool, remove the concentrator tube from the K-D flask add a new micro boiling stone and attach a clean micro-Snyder column to the concentrator tube with a blue clamp and place in a 400 mL beaker containing hot water heated to approximately 75°C on a hot plate. Evaporate the solvent until

UNOFFICIAL COPY - FINAL

only 0.5 mL remains in the concentrator tube. Four or five tubes can be evaporated at one time.

9.9 Final preparation procedures:

9.9.1 PYR Mix A by GC/ECD: When the solvent has been evaporated to 1 mL remove the tube from the bath and allow it to cool in a test tube rack. Remove the micro-Snyder column and add iso-octane to the concentrator tube to reach a final volume of 0.5 mL. Mix the tube contents by tapping the bottom of the tube causing a vortex which will rinse the sides of the tube. A Vortex Genie mixer may be used for this step. Transfer the extract to a labeled amber GC vial. The extracts are ready for analysis.

9.9.2 PYR Mix B by GC/MSMS: When the solvent has been evaporated to 1 mL remove the tube from the bath. Remove the micro-Snyder column and reduce the volume to 0.500 mL using nitrogen (Ultra-high purity). Transfer the extract to a labeled amber GC vial. The extracts are ready for analysis.

10.0 Analytical Procedure

10.1 Before the sample extracts can be analyzed by the GC-ECD or GC-MSMS, a sequence listing the order of calibration standards, second source check standards, initial and continuing calibration blanks, initial and continuing calibration verification standards and sample extracts is written using Agilent Chemstation Software or Varian Workstation (GC/MS/MS) software.

10.2 Each GC sequence includes a minimum of seven calibration standards. The calibration curve concentration for pyrethroids differs for different analytes, but in general the range is 0.1 ppb to 500 ppb.

10.3 To verify the calibration standards, second source check standards (see 5.16) are analyzed. No second source existed. We have purchased individual analytes and a mix from AccuStd and UltraSci to be used in the future.

10.4 An initial calibration blank and initial calibration verification standard is analyzed after the calibration standards and prior to the first sample extract. Continuing calibration blanks (CCBs) and calibration verification standards (CCVs) are analyzed after ten sample extracts have been analyzed. If a CCV fails, the five samples prior to the failed CCV and the five samples after the failed CCV are re-analyzed after a new calibration curve is analyzed.

10.5 The CCV analyte concentrations are mid-range of the calibration curve (20-60 ppb).

UNOFFICIAL COPY - FINAL

10.6 As the run proceeds, sample extracts are monitored for analyte concentrations that are greater than the calibration curve and need dilution.

10.7 Instrumentation – GC-ECD

10.7.1 Agilent 6890*plus* gas chromatograph equipped with two ^{63}Ni micro-electron capture detectors with EPC and autosampler. Two 60 meter, 0.25 mm ID, 0.25 µm (film thickness) fused silica columns (J&W) are used. A 5 meter length of DB-5 column is connected to a press fit "Y" union which splits the column effluent into two 60 m columns, a DB-5 and a DB-17MS. The injector is a split-splitless injector with EPC.

10.7.2 Chromatograph conditions: The injector is operated isothermal at 240°C. The oven has an initial temperature of 130°C which is held for 1 minute and then temperature programmed to 240°C at a rate of 20°C/min and held for 7 min. It is then programmed to 290°C at a rate of 2°C/min and is held for 16.50 min. Helium is used as the carrier gas at a linear velocity of 33 cm/sec. Nitrogen is used for the detector makeup at 30 mL/min.

10.7.3 Sample volume: Three microliters of samples and standards are injected and split approximately 50/50 onto the 60 m DB-5 and the 60 m DB-17MS.

10.7.4 Data processing: An Agilent 3365 Series II Chemstation is used for detector signal acquisition and analysis.

10.8 Instrumentation – GC-MS QqQ

10.8.1 Varian GC-MS 1200L Triple Quadrupole: set-up and optimum operating parameters are listed in Table 2. Parent (Q1)-daughter (Q3) ion transitions and optimum Q2-collision voltages for EI-MSMS analysis to achieve maximum instrument sensitivity for each analyte are listed in Table 3 and signal to noise estimates were established for low ppb concentrations of these analytes (Table 4).

Table 2. GC-MS/MS Operating Parameters

- Instrument: Varian 1200L GC-MS -Triple quadrupole Detector
- Carrier gas: Helium
- Columns: XLB, 60 m x 0.25 mm I.D. x 0.25 µm film thickness
- Varian 1078 Inlet: Isocratic temp @ 240 ºC
- Injection Volume: 2 µL
- Oven: Initial temperature: 80 ºC Initial time: 1.00 min
  Ramp 1: 15.0 deg/min, final temp 210 ºC,
  hold time 10.00 min
  Ramp 2: 2.0 deg/min, final temp 280 ºC,

UNOFFICIAL COPY - FINAL

hold time 0.50 min

- MS-MS Operating Conditions

Ion source temperature:	200 ºC	Ionization pressure:	45 mTorr
Manifold temperature:	40 ºC	Ion preparation:	MS/MS
Transferline temperature:	280 ºC	Collision gas:	Argon
		Filament delay:	5 min

Table 3. Retention times, parent (Q1)-daughter (Q3) ion transitions and Collision Energy for selected pyrethroids.

	Segment	Q1	Q3	Collision Energy	Internal Standard
Allethrin	1	123	81	-10	permethrin,transC^{13}
Paralethrin	1	123	81	-10	permethrin,transC^{13}
Resmethrin	1	123	81	-10	permethrin,transC^{13}
Bifenthrin	2	181	166	-15	permethrin,transC^{13}
Fenpropathrin	2	181	152	-25	permethrin,transC^{13}
Tetramethrin	2	164	107	-20	permethrin,transC^{13}
Phenothrin	3	123	81	-15	permethrin,transC^{13}
Lambda-cyhalothrin	4	181	152	-25	permethrin,transC^{13}
Permethrin, cis	5	183	153	-10	permethrin,transC^{13}
Permethrin, cisC^{13}-(surrogate)	5	189	159	-15	permethrin,transC^{13}
Permethrin, trans	5	183	153	-10	permethrin,transC^{13}
Permethrin, trans C^{13}	5	189	159	-15	Internal std
Cyfluthrin	6	163	127	-10	permethrin,transC^{13}
Cypermethrin	6	163	127	-10	permethrin,transC^{13}
Esfenvalerate-Fenvalerate	7	167	125	-10	permethrin,transC^{13}
Deltamethrin	8	181	152	-20	permethrin,transC^{13}

Table 4. Concentrations and Signal to Noise (S/N-RMS) Results for Selected Pyrethroids Using EI-MSMS

UNOFFICIAL COPY - FINAL

	Pyreth 0.1 Std conc (ppb)	Conc in sediment Mult=0.2	Signal to Noise
permethrin, trans-L (int std)			416
allethrin	0.5	0.1	18
bifenthrin	0.1	0.02	109
cyfluthrin 1-4	0.5	0.1	94
cyfluthrin 1	0.5	0.1	81
cyfluthrin-2	0.5	0.1	80
cyfluthrin-3	0.5	0.1	50
cyfluthrin-4	0.5	0.1	77
cypermethrin 1-4	0.5	0.1	118
cypermethrin 1	0.5	0.1	77
cypermethrin-2	0.5	0.1	125
cypermethrin-3	0.5	0.1	197
cypermethrin-4	0.5	0.1	93
deltamethrin	0.5	0.1	22
esfenvalerate_fenvalerate-1	0.2	0.04	22
esfenvalerate_fenvalerate-2	0.2	0.04	124
fenpropathrin	1.0	0.2	73
lambda-cyhalothrin-2	0.2	0.04	37
paralethrin	0.5	0.1	54
permethrin-cis	0.1	0.02	19
permethrin-trans	0.1	0.02	24
phenothrin	0.1	0.02	18
resmethrin	0.5	0.1	55
tetramethrin	0.5	0.1	34

11.0 Method Performance

11.1 Pyrethroid analyte average percent recoveries, amount recovered and standard deviations in American River sediment are listed in Table 5.

Table 5. Summary of method validation results for pyrethroids in American River sediment; spike level at 5-20 ng/g by GC/ECD.

Pyrethroids by GC/ECD	Average % Recovery	Average Amount Recovered	Standard Deviation (n=8)

UNOFFICIAL COPY - FINAL

Bifenthrin	106	5.30	0.14
Cyfluthrin	108	10.4	0.85
Cypermethrin	108	11.1	0.81
Deltamethrin	62.0	3.10	0.69
Es/Fenvalerate	107	5.39	0.27
Lambda- cyhalothrin	104	5.17	0.38
Permethrin	99.0	16.2	1.27

12.0 References

U.S. Food and Drug Administration. 1994. Pesticide Analytical Manual. Volume 1, Chapter 3, Multiclass Multiresidue Methods. U.S. Food and Drug Administration, Rockville, MD.

U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 On-Line, Method 3545A, *Pressurized Fluid Extraction*, Revision 1, February 2007, http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf [11/10/08]
Method 3620C, *Florisil Cleanup*, Revision 3, February 2007, http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3620c.pdf [11/10/08]
Method 3640A, *Gel Permeation Cleanup*, Revision 1, September 1994, http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3640a.pdf [03/29/07]

SOP Section Approval: _____ Date: _____

SOP Final Approval: _____ Date: _____

SOP QA Officer Approval: _____ Date:_____

UNOFFICIAL COPY - FINAL

APPENDIX A

METHOD DETECTION LIMIT VALIDATION FOR PYRETHROIDS IN SEDIMENT BY GC/ECD

Pyrethroid Pesticides	Spike Amount Expected (ng/g)	Average Amount Recovered (ng/g)	Average Percent Recovery	Variance Amount Recovered (ng/g)	Standard Deviation Amount Recovered	MDL=t*Stdev (ng/g)
Bifenthrin	5.00	5.30	106	0.021	0.143	0.43
Cyfluthrin-1	10.0	10.4	104	0.723	0.850	2.55
Cyfluthrin-2	10.0	10.8	108	1.16	1.08	3.23
Cyfluthrin-3	10.0	10.6	106	0.421	0.649	1.94
Cyfluthrin-4	10.0	11.2	112	1.47	1.21	3.64
Cypermethrin-1	10.0	11.1	111	0.662	0.814	2.44
Cypermethrin-2	10.0	10.9	109	0.916	0.957	2.87
Cypermethrin-3	10.0	10.4	104	0.665	0.815	2.44
Cypermethrin-4	10.0	11.0	110	0.467	0.683	2.05
Deltamethrin	5.00	3.10	62	0.481	0.693	2.08
Esfenvalerate/Fenvalerate-1	5.00	5.39	108	0.072	0.268	0.80
Esfenvalerate/Fenvalerate-2	5.00	5.31	106	0.126	0.355	1.06
Lambda-cyhalothrin-1	5.00	5.17	103	0.147	0.384	1.15
Lambda-cyhalothrin-2	5.00	5.26	105	0.070	0.265	0.79
Permethrin-cis	15.0	16.2	108	1.60	1.27	3.80
Permethrin-trans	15.0	13.5	90	9.28	3.05	9.13

American River sediment was used for validation (29.2 % moisture)

Students' t value for 99% confidence, where n=8, is 2.998

UNOFFICIAL COPY - FINAL

METHOD DETECTION LIMIT VALIDATION FOR PYRETHROIDS IN SEDIMENT BY GC/MSMS					
	RSD	Average	STD DEV	Std Dev x Student's T (7 Deg of Freedom) 2.998	MDL Dry Wt mult=0.2
permethrin, trans-L					
allethrin	13	18.6	2.48	7.43	1.486
paralethrin	9	7.6	0.65	1.95	0.391
resmethrin	8	8.1	0.64	1.93	0.386
tetramethrin	10	4.3	0.44	1.31	0.262
Bifenthrin	18	2.2	0.41	1.24	0.247
Fenpropathrin	12	11.3	1.33	4.00	0.799
phenothrin	12	1.5	0.19	0.56	0.113
lambda-cyhalothrin-2		2.1	0.25	0.75	0.150
permethrin-cis	32	3.8	1.22	3.67	0.734
permethrin-trans	44	4.5	2.01	6.03	1.205
Cyfluthrin 1-4	6	5.8	0.35	1.06	0.211
Cyfluthrin 1	6	6.0	0.34	1.02	0.205
Cyfluthrin-2	5	6.0	0.32	0.97	0.195
Cyfluthrin-3	7	6.0	0.40	1.19	0.237
Cyfluthrin-4	8	5.9	0.45	1.36	0.271
cypermethrin 1-4	8	6.9	0.53	1.59	0.318
Cypermethrin 1	6	7.2	0.40	1.21	0.242
Cypermethrin-2	10	6.7	0.69	2.06	0.411
Cypermethrin-3	10	7.6	0.74	2.22	0.445
Cypermethrin-4	7	6.8	0.46	1.38	0.276
Esfenvalerate_Fenvalerate-1	12	4.6	0.56	1.68	0.335
Esfenvalerate_Fenvalerate-2	10	2.8	0.27	0.82	0.163
Deltamethrin	11	2.7	0.31	0.92	0.184

UNOFFICIAL COPY - FINAL

SURF ID: 83

STANDARD OPERATING PROCEDURE
TITLE: FIPRONIL AND DEGRADATES BY LC/MS/MS

REVISION HISTORY		
Revision #	**Summary of Changes**	**Date**
0	Initial release.	Unknown.

DRAFT

Author:	*Cindy Tsai, Ph.D*		Date: 09/09/13
Approved:	Laboratory Director *Pete Ode, Ph.D*		Date:
Approved:	Section Leader *Martice Vasquez, Ph.D*		Date:
Approved:	Quality Assurance *Gail Cho*		Date:
Approved:	Health and Safety *Thomas Lew*		Date:

STANDARD OPERATING PROCEDURE

TITLE: Fipronil and Degradates by LCMSMS

1.0 Scope and Application

1.1 This procedure describes the analysis of extracts by liquid chromatography, tandem mass spectroscopy for fipronil and fipronil degradates.

1.2 This method applies to the analysis of sediment and water extracts. This method may be used to analyze +extracts of other media for which an extraction procedure has been validated.

1.3 Refer to Table 1 for the analytes, reporting limits, and method detection limits.

1.4 This analysis should only be performed by personnel qualified in spectral interpretation and in the use of a LC/MS/MS. Analysts must meet training requirements specified in WPCL-QA-003 Training.

2.0 Summary of Method.

2.1 Water samples are processed by passing an aliquot of 500 mLs through a pre-conditioned solid-phase extraction (SPE) cartridge. The loaded cartridge is dried under vacuum, then eluted with acetonitrile/water (50%/50% v/v) and methanol/formic acid (99.9%/0.1%). The final extract is evaporated under nitrogen and brought up to a final volume of 2 mLs with acetonitrile/water/formic acid (10%/90%/0.1% v/v/v). The extracts are filtered prior to the addition of internal standard and instrument analysis.

2.2 Sediment samples are processed by extracting a 10 g sample with methylene chloride using pressurized fluid extraction. The resulting extract is brought up to volume with methanol and water then loaded onto a pre-conditioned solid phase extraction cartridge. Methanol is used to elute the compounds from the column, then the eluate is filtered prior to the addition of internal standard and instrument analysis.

2.3 The analysis is performed on an Agilent 1200 series LC system with a G6410A QQQ Mass Spectrometer (Agilent Technologies, Inc., Santa Clara, California) with electrospray ionization (ESI). The controlled computer is installed with Windows 7 Professional (64-bit) operating system and MassHunter programs including Acquisition with Optimizer program plus Offline utilities, Qualitative Analysis program, and Quantitative Analysis program. The analyzed compounds are optimized using Optimizer. The data are acquired using MassHunter Workstation LC/QQQ

DRAFT

Acquisition program and quantified using MassHunter Workstation Quantitative Analysis program. All data files are saved on the hard drive (D:/) of local computer and backup on the portable hard drive and on-line shared drive.

3.0 Interferences and Comments.

3.1 Turbid samples or samples with high solids content may cause column clogging. A smaller sample size may be necessary. Adjust reporting limits and method detection limits accordingly.

4.0 Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined. However, each chemical compound and sample should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should be made available to all personnel involved in this procedure. It is the responsibility of the analyst to read the MSDS as part of the training process.

4.2 Wear gloves, lab coats, safety glasses while processing samples. All processes must be performed in an operating hood.

4.3 Wear a face shield while performing any operations involving vacuum.

4.4 Dispose of waste solvents and spiking solutions according to WPCL-EH-049 “Disposal of Hazardous Wastes.”

4.5 The following chemicals have the potential to be highly toxic or hazardous. For details, read the MSDS associated with each chemical.

4.5.1 Acetonitrile.

4.5.2 Dichloromethane (AKA methylene chloride, DCM)

4.5.3 Methanol.

4.5.4 Formic acid.

5.0 Equipment and Supplies

5.1 Agilent 1200 Series Liquid Chromatography System with G6410A QQQ Mass Spectrometer with electrospray ionization, positive mode, or equivalent.

5.2 Agilent MassHunter including Acquistion with Optimizer, Qualitative Analysis, Quantitative Analysis programs or equivalent

DRAFT

5.3 Agilent Zorbax Column, PN 993967-906 or equivalent.

5.4 Gas-tight glass syringes.

5.5 Autosampler vials.

6.0 Reagents and Standards

6.1 Water: HPLC-grade or Ultra-Pure HPLC water (18MΩ resistivity).

6.2 Methylene chloride, HPLC-grade.

6.3 Methanol, HPLC-grade.

6.4 Acetonitrile, HPLC-grade.

6.5 Formic acid, HPLC-grade.

6.6 Solvent A: HPLC-water/0.1% Formic Acid.

6.7 Solvent B: Acetonitrile/0.1% Formic Acid.

6.8 Calibration Standards: See Table 2.

6.9 Internal standards.

6.10 Initial Calibration Verification standard**.**

6.10.1 Must be from a source different than used for the calibration standard curve. Obtain from a second vendor, different lot number, or prepared independently from a neat solution.

7.0 Preservation and Holding Times

7.1 Store samples at < 6°C. Extract samples within 7 days of collection. Analyze extracts within 40 days of extraction.

8.0 Calibration and Standardization/Instrument Set Up.

8.1 Instrument parameters and operating conditions. See Table 3.

8.2 Initial calibration or other initialization. See Table 2.

8.2.1 Only first-order or second-order curves are permitted.

8.2.2 Correlation coefficient r^2 >= 0.99, not forced through the origin.

8.3 Continuing calibration.

8.3.1 Analyze the Initial Calibration Verification (ICV) immediately after the calibration curve. All compound identification criteria must be met and the concentration should be within ± 20% of the expected value.

8.3.2 Analyze the Continuing Calibration Verification (CCV) after 10 samples and at the end of the analytical run. The concentration should be within ± 20% of the expected value.

8.3.3 See Table 4 for Corrective Actions.

DRAFT

9.0 Procedure

9.1 Liquid chromatograph preparation.

9.1.1 Use only HPLC grade solvents and water. The HPLC grade water can be replaced with ultra-pure HPLC water (18MΩ resistivity). Purge the system with mobile phases (50% Solvent A/50% Solvent B) at a flow rate of 5 mL/min for 5 minutes. Condition the LC column with mobile phase at start-running percentage till the instrument shows stable system pressure (pressure difference < 1%; take 5-10 minutes). If there is a contamination, the system can be washed with HPLC flushing solvent (Agilent Technologies, Inc., Santa Clara, California) or DCM/Isopropanol/Acetonitrile (1/2/1) solution at flow rate of 0.1 mL/min overnight. If the reverse phase HPLC column is not used for a period of time, flush the column with a solvent mix that contains 50% organic in water and cap the column tight.

9.2 Instrument Preparation-MS/MS

9.2.1 For the mass spectrometer, clean the spray chamber, the spray shield, and the end of the capillary cap with methanol weekly or once per two weeks. Use abrasive paper (p/n 8660-0852; Agilent Technologies, Inc.) to gently clean the end of the capillary cap and the spray shield. Dampen a clean cloth (p/n 05980-60051; lint-free) or Kimwipes with methanol and wipe the end of the capillary cap, the spray shield, and the spray chamber. Do not spray directly toward the tip of the capillary. This can cause pressure surges in the vacuum system. Do a Checktune (step for mass calibration) regularly (once per week) to ensure accurate assignments of m/z's by the instrument. If Checktune fails, need to do an Autotune. If the instrument is shut down and restarted, do an Autotune before starting analysis. This calibration must be performed to maintain instrument sensitivity and accuracy. The tune condition will be saved automatically.

9.3 Optimization of MS/MS Parameters

9.3.1 Prior to measurement, the target compounds must be optimized to maximize the response of the protonated [M+H]+ or deprotonated [M-H]- molecule ion and daughter-ion transitions for each compound. Check and confirm the EXACT molecule mass of each compound and the information is needed for setting up Optimizer methods. Prepare 10 mM solution of the individual

DRAFT

compound in methanol and determine the MRM transition parameters with Optimizer. The MS/MS source and MRM transition parameters are optimized for each com¬pound by injecting 1 uL of 10 mM solution with 50-200V Fragmentor and 0-50 Collision Energy.

9.4 Evaluation of Instrument Performance

9.4.1 The LC/MS/MS method is checked before each sample run by injecting the mid-level calibration standard. If the peak shape deteriorates (diminished response and peak tailing), the columns may need to be cleaned or replaced. If the pressure reading is high (overpressures), there may be a clog in the mobile-phase flow path. If the retention time moves, the LC/MS/MS method needs to be modified. After setting up the method, the low-level calibration standard is injected to assess the instrument sensitivity.

10.0 Data Analysis and Calculations.

10.1 All results will be reported as µg/L in a sample.

Concentration, µg/L =

(ng/mLinstrument) x (final extract volume, mL) x dilution ÷ (init. sample vol, mLs).

10.2 % Recovery = 100 x (Spiked sample conc – Native conc) ÷ (Conc. Spiked).

11.0 Quality Control

11.1 A batch is comprised of 20 or fewer samples of the same matrix processed concurrently. All samples and QC in the batch share the same reagent lots, procedure, and processing time period.

11.2 A method blank, laboratory blank, laboratory control spike and/or laboratory control duplicate, matrix spike, matrix spike duplicate should be analyzed for every 20 samples, sample batch or unique sample matrix. Refer to the attachments for acceptance criteria and corrective actions.

11.2.1 **Method Blank**: An extraction blank is included with the batch to demonstrate freedom from contamination during the extraction procedure. The blank undergoes all of the same processes as the samples including any clean ups and addition of surrogates and/or internal standards.

11.2.2 **Laboratory Control Spike:** A laboratory control spike is required as verification of the preparation method (LCS/LCSD). In conjunction with an MS/MSD pair, the LCS helps to differentiate bias from the method versus interferences introduced by a field sample. The LCS is an aliquot of a clean

DRAFT

lab matrix spiked with the target analytes and surrogates then extracted as a sample. Recovery of compounds are calculated and compared to acceptance limits.

11.2.3 **Matrix Spike and Spike Duplicate:** A matrix spike and spike duplicate are required to demonstrate method accuracy and precision and to monitor matrix interferences (MS/MSD). A MS is a subsample of a field sample spiked with the target analytes and surrogates then extracted with the samples in the batch. Recovery of the compounds are calculated and compared to acceptance limits.

11.2.4 **Surrogates:** A surrogate is a compound similar in chemistry to the target analytes that is not expected to be found in samples. Surrogates are added to all QC and samples prior to extraction. Surrogates are usually labeled or deuterated compounds when used in mass spectroscopic techniques.

11.2.5 **Internal Standard:** An internal standard is added to each QC extract, sample extract, and calibration standard prior to instrument analysis to monitor instrument changes.

11.3 Method Detection Limits (MDL)

11.3.1 Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 lab Milli-Q water samples are spiked and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries were used to calculate the MDL for each analyte using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

11.4 Reporting Limit (RL).

11.4.1 Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is typically chosen in a range 1-10 times the MDL.

11.5 Method Validation

DRAFT

11.5.1 Refer to WPCL-QA-006 Validation and Method Detection Limit Studies.

11.6 Control Charts and Limits

11.6.1 Control charts are generated initially using the data from the method validation. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average percent recovery**.**

12.0 References

12.1 WPCL-EH-049 Disposal of Hazardous Wastes

12.2 WPCL-QA-003 Training

12.3 WPCL-QA-006 Validation and Method Detection Limit Studies.

12.4 USEPA, SW846, Method 8000B, Revision 2, 1996.

12.5

13.0 Attachments

13.1 Table 1: Analyte list.

13.2 Table 2: Calibration Curve Standard Concentrations.

13.3 Table 3: Instrument Parameters

13.4 Table 4: Gradient Conditions

13.5 Table 5: MRM Parameters.

13.6 Table 6: Corrective Actions.

DRAFT

Table 1: Fipronil and Degradates Method Detection Limits and Reporting Limit

CAS Number	Analyte	Water, µg/L Effective 01/2013		Solid, ng/g Effective 09/2013	
		MDL*	Reporting Limit	MDL*	Reporting Limit
205650-65-3	Desulfinyl fipronil	0.0005	0.0020	0.124	0.500
120068-37-3	Fipronil	0.0005	0.0020	0.119	0.500
120067-83-6	Fipronil sulfide	0.0005	0.0020	0.086	0.500
120068-36-2	Fipronil sulfone	0.0005	0.0020	0.120	0.500
NA	Desulfinyl fipronil amide	0.0008	0.0040	0.264	1.00
NA	Fipronil amide	0.0016	0.0080	0.477	2.00

* Method detection limit. MDLs may be updated at the discretion of the lab.

DRAFT

Table 2: Calibration Curve Standards

Analyte	STD1 ng/mL	STD2 ng/mL	STD3 ng/mL	STD4 ng/mL	STD5 ng/mL	STD6 ng/mL	STD7 ng/mL
Desulfinyl fipronil	0.5	1	2	5	10	20	50
Fipronil	0.5	1	2	5	10	20	50
Fipronil sulfide	0.5	1	2	5	10	20	50
Fipronil sulfone	0.5	1	2	5	10	20	50
Desulfinyl fipronil amide	1.25	2.5	5	12.5	25	50	250
Fipronil amide	2.5	5	10	25	50	100	500
Surrogate							
Warfarin-d_5 (ASE)	2	4	8	20	40	80	200
2,4,5-T-d_2 (SPE)	1	2	4	10	20	40	100

DRAFT

Table 3: Instrument Parameters

Method Name:	Fipronil and Metabolites
Ion Mode:	ESI-negative
Scan Type:	Dynamic MRM
Source Parameters:	
Gas Temp (°C)	350
Gas Flow (L/min)	11
Nebulizer (psi)	40
Capillary (V)	4000
Column:	
Column Temp:	40°C
Injection Volume:	5 µL
Mobile Phase:	
A:	HPLC H_2O with 0.1% formic acid
B:	Methanol with 0.1% formic acid

Table 4: Gradient conditions used for separation

Step	Time (min)	B%	Flow rate (ml/min)
1	0	45	0.3
2	2	45	0.3
3	8	80	0.3
4	13	80	0.3
5	14	45	0.3

DRAFT

Table 5: MRM parameters

Compound	Precursor	Product	Fra (V)	CE (V)	RT (min)
Desulfinyl Fipronil Amide	405	368.9	90	4	4.02
Desulfinyl Fipronil Amide	405	328.9	90	16	4.02
Fipronil Amide	452.9	303.9	100	24	7.44
Fipronil Amide	452.9	271.9	100	24	7.44
Desulfinyl fipronil	387	351	90	8	10
Desulfinyl fipronil	387	282	90	32	10
Fipronil	434.9	330	110	12	10.29
Fipronil	434.9	249.9	110	28	10.29
Fipronil sulfide	418.9	261.9	110	28	10.51
Fipronil sulfide	418.9	382.9	110	8	10.51
Fipronil Sulfone	450.9	415	130	12	10.83
Fipronil Sulfone	450.9	281.9	130	28	10.83
Surrogate					
Warfarin-d_5 (ASE)	312.1	255	140	16	8.76
Warfarin-d_5 (ASE)	312.1	161	140	16	8.76
2,4,5-T-d_2 (SPE)	256.9	196.9	70	8	9.02
Internal Standard					
Diclofenac-d_4	298	254	90	4	10.26
Diclofenac-d_4	298	217	90	16	10.26

DRAFT

Table 6: Corrective Actions

QC TYPE	CONTROL	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Batch	Unit of sample processing.	Up to 20 samples of similar matrix, same reagents, equipment, techniques.	Batch is comprised of 20 or fewer field samples.	Include additional controls during processing or reextract.
Method blank.	Indicator of contamination that may be introduced by reagents, equipment during processing.	Every batch.	Must be less than reporting limit or project requirements, whichever is more stringent.	Reanalyze blank to confirm result. Evaluate impact on sample results. Re-extract affected samples as needed.
LCS	Accuracy and recovery of target analytes from a clean, lab matrix.	Every batch.	Must be within control limits.	Reanalyze LCS to confirm result. Evaluate impact on sample results. Low recoveries require re-extraction of the batch.
LCS Duplicate	Accuracy and reproducibility of target analyte recovery in a clean lab matrix	Every batch where a MS/MSD is not processed.	Recoveries must be within control limits. RPD must be within control limits.	Reanalyze LCSD to confirm result. Evaluate impact on sample results. Low recoveries require re-extraction of the batch.
MS	Accuracy and recovery of target analytes in a field sample.	Every batch (assumes sufficient sample).	Recoveries should be within control limits.	Reanalyze MS to confirm result. Review against LCS.
MSD	Accuracy and reproducibility of target analytes in a field sample.	Every batch (assumes sufficient sample).	Recoveries should be within control limits. RPD should be within control limits.	Reanalyze MSD to confirm result. Review against LCS/LCSD.
Surrogates	Accuracy and recovery of chemically similar compounds in field samples.	Every sample.	Should be within limits.	Reanalyze sample to confirm result. Review against LCS.
ICV/CCV	Instrument drift.	After multipoint calibration, prior to sample analysis after every 10 samples, and end of run.	± 20% from expected concentration.	If exceeds acceptance criteria, verify that the standard was not mis-injected, then review bracketed sample results. If CCV response is higher than expected, reanalyze samples with positive detections and surrogate failures. Analyze samples back to the last acceptable CCV. Document decisions with reported results. Recalibrate if ICV/CCV fails.
Internal standard	Instrument drift, matrix effects.	Every sample and QC.	Factor of 2x of the initial calibration average.	Guideline to assist analyst in troubleshooting. Reanalyze if needed.
Ions	Compound identification and quantitation.	Every sample.	Compare with standard for retention time, precursor ion, product ion (if available), ratio.	Criteria not met, compound is considered “not detected.”

DRAFT