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Study 282. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2013

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February 27, 2013

I. INTRODUCTION

As part the California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program, surface water monitoring for pesticides is conducted in agricultural areas of the state. A wide variety of agricultural pesticides are applied in California throughout the year. In 2011, over 300 pesticide active ingredients (AIs) were applied in agricultural areas (CDPR 2013). Many pesticide AIs with significant use in California agriculture are toxic to aquatic organisms (US EPA 2013). Surface water monitoring data for these pesticides are needed in order to assess the potential impacts of California pesticide use on aquatic systems.

For CDPR's 2013 agricultural surface water monitoring project, potential monitoring candidates were identified using DPR's Draft Pesticide Prioritization for Surface Water Monitoring Program ("Prioritization Program"). This is a computer program recently developed by CDPR (Luo 2012) which automates the process of identifying potential monitoring candidates based on their use amounts in California and their toxicity to aquatic organisms. The program uses CDPR's Pesticide Use Reporting (PUR) data (CDPR 2013) in conjunction with US EPA Aquatic Life Benchmarks (US EPA 2013) to develop a rank of AIs. The candidates identified in this way are then further screened individually for appropriateness as monitoring candidates. The primary elements of this additional assessment include consideration of chemical-physical properties, environmental fate data, any available recent monitoring data, and existing analytical methodology, as well as the completion of a more detailed assessment of spatial and temporal use patterns.

Based on a statewide assessment using the Prioritization Program, the top 10 state-wide priority AIs were identified. Of these, seven were selected for inclusion in this project: chlorpyrifos, malathion, permethrin, trifluralin, pendimethalin, chlorothalonil, and oxyfluorfen. These seven AIs were also identified as monitoring candidates in a previous assessment (Starner 2008), and analytical methods are available for all of them.

Three of the top 10 AIs from the assessment that are not included in the current project are paraquat dichloride, copper (copper sulfate), and ziram; these AIs were not identified in the previous assessment from 2008. The analytical lab used by CDPR for sample analysis does not currently have analytical methods for these AIs. Additional factors will be assessed to determine if monitoring, and therefore the development of analytical methods, is warranted for these AIs. Factors to be considered should include any available recent monitoring results, the chemical/physical properties and environmental fate, and detailed use patterns of these AIs.

For the seven AIs, areas with periods of intensive use in the vicinity of surface water were identified through spatial/temporal analysis of PUR data (CDPR 2012). Chlorpyrifos, malathion and permethrin use is very high in the Salinas and Santa Maria Valleys throughout the irrigation season as well as in Imperial Valley in the fall (Figure 1). DPR has previously designated these three geographic areas as high priority areas for long-term surface water monitoring, largely due to the high use of these AIs (Starner 2010). This

assessment supports that designation as well. For permethrin analysis, the analytical method includes five additional pyrethroids (Table 2). As such, monitoring for permethrin will provide data for these other commonly used pyrethoids as well. Use of trifluralin and pendimethalin is very high in Imperial Valley, as well as in the Palo Verde area in Riverside County, in the spring (Figure 1). Monitoring for these AIs will be conducted in these areas; DPR has not recently conducted surface water monitoring in Palo Verde. Chlorothalonil use is high in several areas of the Central Valley, as well as in Salinas, Santa Maria, and Imperial Valleys. Monitoring will be included in two areas of the Central Valley (Figure 1) where use is high on tomatoes, as well as in the three high priority monitoring regions. DPR has not previously monitored for chlorothalonil in agricultural areas in any part of the state. Oxyfluorfen use is highest in California during the winter months (CDPR 2013); winter season monitoring is not included in the current study. However, oxyfluorfen use is also high during the irrigation season in Salinas and Santa Maria Valleys; some oxyfluorfen monitoring will be included in those regions.

For each of the regions selected above for inclusion in the project, an additional region-specific assessment was conducted using the Prioritization Program. The goal of these assessments was to identify AIs that have significant aquatic toxicity and high use within a specific geographic region, but for which use was not high enough on a statewide basis to rank in the statewide analysis. The regional assessment for Salinas Valley (Monterey County) resulted in the addition of diazinon, methomyl and imidacloprid for monitoring in that area. Significant use of pendimethalin and malathion in Palo Verde concurrent with the high trifluralin use was also identified in this way; those AIs will be included in the monitoring there.

II. OBJECTIVE

The objective of the study is to provide data for a long-term assessment of surface water pesticide contamination in agricultural areas of California.
Results will provide useful data on the environmental fate of current-use pesticides under a variety of conditions for use in the development of management responses.

III. PERSONNEL

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

Project Leader:	Keith Starner
Field Coordinator:	Kevin Kelley
Laboratory Liaison:	Sue Peoples
Chemists:	California Department of Food and Agriculture, Center for Analytical Chemistry Staff Chemists

Questions concerning this monitoring project should be directed to Keith Starner at (916) 324-4167 or by email at kstarner@cdpr.ca.gov.

IV. STUDY PLAN

Monitoring in each area will be conducted for the appropriate AIs during the season or seasons of historically high pesticide use (CDPR 2013, Table 1). Sampling will commence in March 2013 and continue through October 2013.

V. SAMPLING METHODS

At each sampling site, surface water grab samples for chemical analysis will be collected into 1-liter amber glass bottles. Grab samples will be collected using either a grab pole consisting of a glass bottle at the end of an extendable pole. Glass bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at $4^{o}C$ until extraction for chemical analysis. Appropriate DPR QA/QC Standard Operating Procedures will be followed.

Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site during each sampling period. Flow data will be collected using a digital flow meter.

VI. CHEMICAL ANALYSIS

Chemical analysis will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Analytical method analytes, method detection limits, and reporting limits for this study are given in Table 2. Details of the chemical analysis methods will be provided in the final report. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa 1995).

VII. DATA ANALYSIS

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L) / parts per billion (ppb) or nanograms per liter (ng/L) / parts per trillion (ppt). Resulting data will be analyzed and reported as appropriate, potentially including the following:

Comparison of pesticide concentrations to aquatic toxicity benchmarks, water quality limits and other toxicity data (CCVRWQCB 2012, US EPA 2012); spatial analysis of data in order to identify correlations between observed pesticide concentrations and region-specific pesticide use and geographical features; assessment of multiple years of data to characterize patterns and trends in detection frequencies; assessment of results to determine potential additional monitoring in regions with similar pesticide use patterns.

VIII. TIMETABLE

Field Sampling:	March 2013 through October 2013
Chemical Analysis:	March 2013 through December 2013
Draft Report:	September 2014

IX. BUDGET

Organophosphate	85	600	$51,000
Diazinon	45	510	22950
Chlorothalonil	35	660	23100
Pyrethroids	30	960	28800
Dinitroanilines	30	960	28800
Methomyl	18	480	8640
Imidicaloprid	30	720	21600
Diacylhydrazines	17	720	12240
Subtotal Analysis			**$197,130**

Continuing QC	**Samples**	**Cost/sample**	**Cost Estimate**
Organophosphate	9	600	$5,400
Diazinon	5	510	2550
Chlorothalonil	4	660	2640
Pyrethroids	3	960	2880
Dinitroanilines	3	960	2880
Methomyl	2	480	960
Imidicaloprid	3	720	2160
Diacylhydrazines	2	720	1440
Subtotal QC			**$20,910**

Total	**$218,040**

X. REFERENCES

CCVRWQCB (California Central Valley Regional Water Quality Control Board) 2012. Criteria reports. Accessed January 10 2013. http://www.swrcb.ca.gov/rwqcb5/water_issues/tmdl/central_valley_projects/central_valley_pesticides/criteria_method/index.shtml

CDPR (California Department of Pesticide Regulation) 2013. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. http://calpip.cdpr.ca.gov/

Luo, Y. 2012. Documentation, Pesticide Prioritization for Surface Water Monitoring Program. Software documentation,, Draft December 2012.

Segawa, R. 1995. Chemistry Laboratory Quality Control. Environmental Hazards Assessment Program QAQC001.00. Department of Pesticide Regulation, Sacramento, CA.

Starner, K. 2008. Review of the Environmental Protection Agency Aquatic Life Benchmarks, with Monitoring Recommendations. CDPR Technical Memorandum. http://www.cdpr.ca.gov/docs/emon/pubs/analysmemos.htm?filter=surfwater

Starner, K. 2010. Long-term Pesticide Monitoring in High-Use Agricultural Areas.

http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study262protocol.pdf

US EPA 2013. Aquatic Life Benchmark Table.
http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Table 1. Monitoring Plan, 2013

Region	Season	Analytical Screen	Events
Salinas	spring through fall	Organophosphate	6
		Diazinon	6
		Chlorothalonil	3
		Pyrethroids	3
		Dinitroanilines	2
		Methomyl	3
		Imidicaloprid	2
		Diacylhydrazines	3
Santa Maria	spring through fall	Organophosphate	3
		Chlorothalonil	1
		Pyrethroids	1
		Dinitroanilines	1
		Imidicaloprid	2
Imperial	spring	Organophosphate	1
		Diazinon	1
		Chlorothalonil	1
		Dinitroanilines	1
Imperial	fall	Organophosphate	1
		Diazinon	1
		Pyrethroids	1
		Imidicaloprid	1
Palo Verde	spring	Organophosphate	1
		Dinitroanilines	1
Los Banos/SJ Delta	fall	Chlorothalonil	1

Table 2. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Organophosphate (OP) Insecticides in Surface Water by GC/FPD (Short)

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorpyrifos	0.0008	0.01
Diazinon	0.0012	0.01
Dimethoate	0.0079	0.04
Malathion	0.0117	0.04
Methidathion	0.0111	0.05

Dinitroaniline (DN) Herbicides/ Oxyfluorfen in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Oryzalin	0.01	0.05
Ethalfluralin	0.01	0.05
Trifluralin	0.01	0.05
Benfluralin	0.01	0.05
Prodiamine	0.01	0.05
Pendimethalin	0.01	0.05
Oxyfluorfen	0.01	0.05

Chlorothalonil in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Chlorothalonil	0.0348	0.05

Diacylhydrazine Insecticides in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Methoxyfenozide	0.00641	0.05
Tebufenozide	0.00573	0.05

Pyrethroid Insecticides (PY) in Water

Chemical	***Method Detection Limit (µg/kg)***	***Reporting Limit (µg/L)***
Bifenthrin	0.00176	0.005
Lambda-cyhalothrin	0.00115	0.015
Permethirn (cis)	0.00352	0.015
Permethrin (trans)	0.00352	0.015
Cyfluthrin	0.0173	0.015
Cypermethrin	0.00175	0.015
Fenvalerate/esfenvalerate	0.00175	0.015

Imidacloprid (IMD) in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Imidacloprid	0.0101	0.05

Methomyl in Surface Water

Chemical	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Methomyl	0.0265	0.05

Figure 1. California agricultural monitoring regions, 2013.

Appendix II. Sampling Sites, Water Quality Data, and Aquatic Life Benchmarks

Table 1. Sampling Site Information for Study 282

SURF code	Site ID	Site Location	County	Watershed	Latitude	Longitude	Site Type
13_10	Imp_Garst	Alamo River at Garst	Imperial	Alamo River	33.199	-115.59696	Receiving Water
13_22	Imp_Holtville	Holtville Main Drain at 115	Imperial	Alamo River	32.93092	-115.406109	Ag Drain
13_23	Imp_Malva	Malva Drain nr. Park	Imperial	Alamo River	33.05179	-115.488615	Ag Drain
13_24	Imp_Young	Vail Drain nr Young	Imperial	New River	33.13279	-115.666463	Ag Drain
13_25	Imp_Verde	Verde Drain at Bonds Corner Rd	Imperial	Alamo River	32.75552	-115.33697	Ag Drain
13_26	Imp_Clark	Palo Verde Outfall Drain (PVOD2) - Colorado River Region - SWAMP station code 715CPVOD2	Imperial	Colorado River	33.428	-114.73	Ag Drain
13_56	Imp_Rutherford	Alamo River at Rutherford Rd (upstream of Imperial State Wildlife Area)	Imperial	Alamo River	33.04468	-115.488291	Receiving Water
13_58	Imp_Butte	Salton Sea at Obsidian Butte	Imperial	Salton Sea	33.17473	-115.64069	Receiving Water
13_69	Imp_Rice3	Rice Drain III at Weinert	Imperial	New River	32.86905	-115.650998	Ag Drain
13_71	Imp_NewRiv27	New River at HWY S27/Keystone Rd	Imperial	New River	32.91362	-115.606457	Receiving Water
13_81	Imp_OFD78	Outfall Drain-78	Imperial	Colorado River	33.36126	-114.722993	Ag Drain
24_32	CV_Henry	Boundary Drain at Henry Miller Ave; Regional Board Irr. Lands Mon. site code: 541XSSJ07	Merced	San Joaquin River	37.09916	-120.7789	Ag Drain
24_50	CV_Camp	Los Banos Ck at China Camp Rd; Regional Board Irr. Lands Mon. site code: 541XLBCCC	Merced	San Joaquin River	37.11451	-120.8893	Receiving Water
24_61	CV_Lander	Salt Slough at Lander Ave; Regional Board Irr. Lands Mon. site code: 541XSSALA	Merced	San Joaquin River	37.24764	-120.851973	Receiving Water
24_62	CV_SandDam	Salt Slough at Sand Dam; Regional Board Irr. Lands Mon. site code: 541XSSASD	Merced	San Joaquin River	37.1366	-120.7619	Receiving Water
24_83	CV_Belmont	Belmont Drain at Palazzo Rd	Merced	San Joaquin River	37.13098	-120.74311	Ag Drain
24_84	CV_Midway1	Boundary Drain No 1 at Midway Rd	Merced	San Joaquin River	37.06945	-120.744055	Ag Drain

24_85	CV_Midway7	Boundary Drain No 7 at Midway Rd	Merced	San Joaquin River	37.05844	-120.748586	Ag Drain
24_86	CV_Devon	Devon Drain at Henry Miller Rd	Merced	San Joaquin River	37.09895	-120.765732	Ag Drain
24_87	CV_PasoSlough	Paso Slough/Belmont Drain (Herford Rd)	Merced	San Joaquin River	37.1436	-120.753599	Receiving Water
24_88	CV_SandSlough	Unnamed Drain at Sand Slough Rd	Merced	San Joaquin River	37.1791	-120.726	Ag Drain
24_89	CV_Hereford	Salt Slough @ Hereford Rd	Merced	San Joaquin River	37.13653	-120.762034	Receiving Water
24_94	CV_Wolfsen	Salt Slough @ (Wolfsen)	Merced	San Joaquin River	37.15913	-120.81264	Receiving Water
27_10	Sal_Rec3	Reclamation Ditch Site 3	Monterey	Salinas River	36.65922	-121.615668	Ag Drain
27_11	Sal_Potrero	Old Salinas R @ Potrero	Monterey	Old Salinas River	36.79056	-121.790637	Receiving Water
27_12	Sal_SanJon	Reclamation Ditch at San Jon Road	Monterey	Old Salinas River	36.70487	-121.70506	Ag Drain
27_13	Sal_Davis	Salinas River at Davis Rd	Monterey	Salinas River	36.64698	-121.702185	Receiving Water
27_14	Sal_Monte	Salinas River at Del Monte Road	Monterey	Salinas River	36.7319	-121.7824	Receiving Water
27_50	Sal_Dunes	Old Salinas R. at Monterey Dunes Way	Monterey	Old Salinas River	36.7719	-121.78971	Receiving Water
27_58	Sal_Molera	Tembladero Sl. at Molera	Monterey	Old Salinas River	36.77211	-121.787632	Receiving Water
27_66	Sal_Haro	Tembladero Sl. at Haro Street	Monterey	Old Salinas River	36.75955	-121.75433	Receiving Water
27_7	Sal_Quail	Quail Creek at HWY 101, btwn Spence and Potter Roads (trib. to Salinas R.)	Monterey	Salinas River	36.60922	-121.562694	Receiving Water
27_70	Sal_Hartnell	Alisal Creek at Hartnell Rd	Monterey	Old Salinas River	36.6435	-121.57836	Receiving Water
27_8	Sal_Chualar	Chualar Creek at Chualar River Rd., ca. 1.2 mi. from HWY 101 (trib. to Salinas R.)	Monterey	Salinas River	36.55835	-121.52964	Receiving Water
27_86	Sal_Natividad	Natividad Ck nr Rhode Island Cir	Monterey	Old Salinas River	36.70172	-121.604162	Receiving Water
27_87	Sal_Gablilan	Gabilan Ck near Boronda Rd	Monterey	Old Salinas River	36.71479	-121.61684	Receiving Water

27_9	Sal_Blanco	Blanco Drain at Cooper Rd, ca 0.2 mi. S of Nashua Rd, drains to Salinas R.	Monterey	Salinas River	36.6987	-121.735167	Ag Drain
33_11	Riv_LG	Palo Verde Lagoon (LG1) - Colorado River Region - SWAMP station code 715CPVLG1	Riverside	Colorado River	33.43595	-114.7162	Receiving Water
33_30	Riv_PVL	Palo Verde Lagoon @ 35th	Riverside	Colorado River	33.4559	-114.705511	Receiving Water
33_31	Riv_South	South End Drain @Palo Verde Lagoon	Riverside	Colorado River	33.45619	-114.705008	Ag Drain
39_100	CV_Grimes	Ag Drain on Grimes Rd	San Joaquin	San Joaquin River	37.8185	-121.48225	Ag Drain
39_101	CV_Inland	Unnamed Drain on S. Inland Dr	San Joaquin	San Joaquin River	37.91952	-121.48225	Ag Drain
39_14	CV_Fabian	Fabian Tract Drain, 2nd drain to Fabian and Bell Canal	San Joaquin	San Joaquin River	37.78906	-121.485	Ag Drain
39_42	CV_Wing	Ag Drain Wing Levee @ W. Howard	San Joaquin	San Joaquin River	37.85659	-121.378232	Ag Drain
39_44	CV_GLC	Grant Line Canal off Wind Levee Rd	San Joaquin	San Joaquin River	37.82017	-121.405728	Receiving Water
39_51	CV_Clifton	Grant Line Canal @ Clifton	San Joaquin	San Joaquin River	37.842	-121.538	Receiving Water
39_6	CV_Tracy	Grant Line Canal @ Tracy Blvd	San Joaquin	San Joaquin River	37.81992	-121.448282	Receiving Water
39_75	CV_Howard	Unnamed Canal @ Howard Rd.	San Joaquin	San Joaquin River	37.87696	-121.37645	Receiving Water
39_99	CV_Canal	Grant Line Canal	San Joaquin	San Joaquin River	37.8189	-121.48671	Receiving Water
40_13	SM_OFC	Oso Flaco Creek @ OFL Rd	San Luis Obispo	Santa Maria River	35.01639	-120.58755	Receiving Water
40_23	SM_LOFC	Little Oso Flaco Creek	San Luis Obispo	Santa Maria River	35.02283	-120.587	Receiving Water
42_48	SM_Solomon	Solomon Creek @ Hwy 1	Santa Barbara	Santa Maria River	34.9414	-120.5742	Receiving Water
42_50	SM_Orcutt	Orcutt Creek @ Main	Santa Barbara	Santa Maria River	34.95755	-120.63244	Receiving Water
42_53	SM_Brown	Orcutt Creek @ Brown	Santa Barbara	Santa Maria River	34.93393	-120.55793	Receiving Water
42_71	SM_MainDitch	Main St Ditch @ Main	Santa Barbara	Santa Maria River	34.95474	-120.48501	Ag Drain
42_72	SM_Simas	Green Valley Creek @ Simas	Santa Barbara	Santa Maria River	34.9423	-120.5563	Receiving Water

Appendix II. (continuing)

Table 2. Water Quality Data for Study 282

SURF code	Sample Date	Site ID	Sample Time	pH (units)	Conductivity (µS/cm)	DO (mg/L)	Temp (^{o}C)	Salinity (ppt)
13_10	3/5/2013	Imp_Garst	13:45	7.49	2911	7.38	16.8	1.5
13_10	10/9/2013	Imp_Garst	14:50	-	-	-	-	-
13_22	10/9/2013	Imp_Holtville	12:37	-	-	-	-	-
13_22	3/5/2014	Imp_Holtville	11:30	7.62	3418	8.38	15.9	1.8
13_23	3/5/2013	Imp_Malva	12:25	7.75	2067	7.73	15.6	1.1
13_23	10/9/2013	Imp_Malva	13:20	-	-	-	-	-
13_24	3/5/2013	Imp_Young	15:30	7.72	4527	9.96	19.6	2.4
13_24	10/9/2013	Imp_Young	14:40	-	-	-	-	-
13_25	3/5/2013	Imp_Verde	10:45	7.53	2881	8.56	15.8	1.5
13_25	10/9/2013	Imp_Verde	11:44	-	-	-	-	-
13_25	3/18/2014	Imp_Verde	8:45	7.64	4621	8	18.5	2.5
13_26	3/6/2013	Imp_Clark	13:30	7.76	2244	8.27	21	1.2
13_56	3/5/2013	Imp_Rutherford	13:00	7.6	3020	8.25	16.8	1.6
13_56	10/9/2013	Imp_Rutherford	14:02	-	-	-	-	-
13_58	3/5/2013	Imp_Butte	14:35	8.08	65700	8.48	18.6	44.6
13_58	10/9/2013	Imp_Butte	16:15	-	-	-	-	-
13_69	3/5/2013	Imp_Rice3	9:45	7.45	3218	8.48	14.3	1.7
13_69	10/9/2013	Imp_Rice3	10:16	-	-	-	-	-
13_71	3/5/2013	Imp_NewRiv27	9:15	7.32	4989	6.86	16.8	2.7
13_71	10/9/2013	Imp_NewRiv27	9:45	-	-	-	-	-
13_81	3/6/2013	Imp_OFD78	14:30	7.77	2291	7.97	20.4	1.2
24_32	9/16/2013	CV_Henry	12:05	7.15	969	5.83	23.4	0.5
24_50	9/16/2013	CV_Camp	10:32	7.2	21.29	3.6	19.7	1.1
24_61	9/16/2013	CV_Lander	16:00	7.6	1058	7.63	26	0.5
24_62	9/16/2013	CV_SandDam	14:53	7.59	855	7.39	26.7	0.2
24_83	9/16/2013	CV_Belmont	13:39	8.25	421.8	9.86	29.3	0.2
24_84	9/16/2013	CV_Midway1	11:45	6.99	1946	5.32	21.8	1
24_85	9/16/2013	CV_Midway7	11:17	7.73	1415	2.93	22	0.7
24_86	9/16/2013	CV_Devon	12:22	7.88	714	7.87	25	0.3
24_88	9/16/2013	CV_SandSlough	13:16	7.33	1703	1.21	22.5	0.9
24_94	9/16/2013	CV_Wolfsen	15:30	7.56	1069	5.71	25.3	0.5
27_10	5/14/2013	Sal_Rec3	13:45	7.98	1147	-	25.4	0.6
27_10	6/11/2013	Sal_Rec3	15:45	8.8	1016	11.13	25.5	0.5
27_10	7/30/2013	Sal_Rec3	15:25	8.2	1046	6.72	28.2	0.5
27_10	8/13/2013	Sal_Rec3	14:56	8.7	1119	6.43	28.4	0.6
27_10	8/14/2013	Sal_Rec3	16:10	-	-	-	-	-

27_10	9/3/2013	Sal_Rec3	14:34	7.54	883	4.33	25	0.4
27_10	3/18/2014	Sal_Rec3	9:30	7.64	2732	3.3	14.6	1.4
27_11	6/11/2013	Sal_Potrero	8:35	8.09	3615	4.75	18.8	1.9
27_12	4/8/2013	Sal_SanJon	13:00	-	-	-	-	-
27_12	6/11/2013	Sal_SanJon	11:10	8.52	1314	4.62	19	0.7
27_13	4/9/2013	Sal_Davis	10:55	-	-	-	-	-
27_13	6/10/2013	Sal_Davis	13:20	7.93	520	7.8	22.7	0.3
27_14	5/14/2013	Sal_Monte	15:30	8.77	1160	9.2	20.6	0.6
27_14	6/10/2013	Sal_Monte	14:35	8.97	1001	-	21.2	0.5
27_50	4/9/2013	Sal_Dunes	13:15	-	-	-	-	-
27_50	6/11/2013	Sal_Dunes	9:20	8.12	1984	5.3	18.5	1
27_58	4/9/2013	Sal_Molera	8:55	-	-	-	-	-
27_58	4/9/2013	Sal_Molera	13:45	-	-	-	-	-
27_58	6/11/2013	Sal_Molera	9:45	8.29	2956	5.54	19.9	1.5
27_66	4/8/2013	Sal_Haro	14:00	-	-	-	-	-
27_66	5/14/2013	Sal_Haro	14:20	8.34	2475	10.92	19.6	1.3
27_66	6/11/2013	Sal_Haro	10:33	8.4	2794	9.16	19.3	1.5
27_66	7/30/2013	Sal_Haro	17:00	8.03	2559	11.22	-	1.3
27_66	8/13/2013	Sal_Haro	16:07	8.28	2627	8.87	24.5	1.4
27_66	9/3/2013	Sal_Haro	15:58	8.2	2695	6.08	27.2	1.4
27_7	4/8/2013	Sal_Quail	11:40	-	-	-	-	-
27_7	5/14/2013	Sal_Quail	12:15	8.3	1176	7.15	24.8	0.6
27_7	6/10/2013	Sal_Quail	11:55	7.66	1317	4.1	19.7	0.7
27_7	7/30/2013	Sal_Quail	12:45	8.07	919	0.19	19.8	0.5
27_7	8/13/2013	Sal_Quail	12:00	8.06	1141	5.99	17.5	0.6
27_7	9/3/2013	Sal_Quail	12:05	8.22	1321	4.38	23	0.7
27_70	4/8/2013	Sal_Hartnell	12:35	-	-	-	-	-
27_70	6/11/2013	Sal_Hartnell	15:10	8.29	1022	5.7	21.4	0.5
27_70	7/30/2013	Sal_Hartnell	15:00	8.17	689	5.94	19.8	0.3
27_70	8/13/2013	Sal_Hartnell	14:01	7.88	1217	2.22	18.8	0.6
27_70	9/3/2013	Sal_Hartnell	13:53	7.36	1096	3.31	20.3	0.5
27_8	4/8/2013	Sal_Chualar	12:05	-	-	-	-	-
27_8	5/14/2013	Sal_Chualar	12:45	9.39	1544	6.6	25.2	0.8
27_8	6/10/2013	Sal_Chualar	12:30	9.25	1515	15.82	26.6	0.8
27_8	7/30/2013	Sal_Chualar	14:00	8.18	1167	6.78	25.8	0.6
27_8	8/13/2013	Sal_Chualar	13:15	8.4	1928	5.89	28	0.9
27_8	9/3/2013	Sal_Chualar	13:05	8.66	1667	7.26	25.6	0.8
27_86	6/11/2013	Sal_Natividad	14:10	9.13	1529	6.45	21	0.8
27_87	6/11/2013	Sal_Gablilan	13:35	7.8	1101	3.39	22.6	0.5
27_9	4/9/2013	Sal_Blanco	11:45	-	-	-	-	-
33_11	3/6/2013	Riv_LG	12:45	7.91	2033	10.63	21.3	1

33_30	3/6/2013	Riv_PVL	11:45	7.58	2020	7.6	20.8	1
33_31	3/6/2013	Riv_South	11:30	7.49	2675	5.72	21.8	1.4
39_100	9/17/2013	CV_Grimes	15:15	-	1614	7.5	23.7	0.8
39_101	9/17/2013	CV_Inland	17:11	7.56	655	1.94	23.4	0.3
39_42	9/17/2013	CV_Wing	16:35	7.96	1111	6.58	24	0.6
39_6	9/17/2013	CV_Tracy	15:52	7.96	739	5.36	22.8	0.4
39_99	9/17/2013	CV_Canal	14:50	8.27	734	5.07	22.5	0.4
40_13	5/15/2013	SM_OFC	14:50	7.41	1359	3.82	18.8	1.2
40_13	7/31/2013	SM_OFC	14:00	7.06	2250	5.53	18.4	1.3
40_13	8/14/2013	SM_OFC	14:43	7.59	2040	3.47	23.2	1
40_13	9/4/2013	SM_OFC	13:38	7.22	1195	3.58	20.5	1.3
40_23	5/15/2013	SM_LOFC	15:30	7.67	1829	10.52	20.7	0.9
40_23	7/31/2013	SM_LOFC	15:00	7.82	1689	3.72	17.7	1
40_23	8/14/2013	SM_LOFC	15:20	7.31	1967	3.24	18.3	1
42_48	5/15/2013	SM_Solomon	11:45	7.63	3173	9.93	22.1	1.9
42_48	7/31/2013	SM_Solomon	11:30	7.18	2872	10.92	18.3	1.8
42_48	8/14/2013	SM_Solomon	12:12	8.15	2831	10.8	23.4	1.5
42_48	9/4/2013	SM_Solomon	12:19	7.11	3638	9.22	25.5	1.9
42_50	5/15/2013	SM_Orcutt	14:00	7.91	3074	7.37	23.3	1.6
42_50	7/31/2013	SM_Orcutt	12:45	7.9	2758	6.86	18	1.7
42_50	8/14/2013	SM_Orcutt	12:50	7.61	2971	3.47	20.4	1.6
42_50	9/4/2013	SM_Orcutt	11:28	7.85	2903	6.81	21.5	1.5
42_53	5/15/2013	SM_Brown	12:15	7.52	2871	7.72	19.1	1.5
42_71	9/4/2013	SM_MainDitch	14:57	8.98	1283	16.28	26.5	0.6
42_72	5/15/2013	SM_Simas	12:50	-	-	-	-	-

Appendix II. (continuing)

Table 3. US EPA Aquatic Life Benchmarks for Analytes in Study 282: Lowest Benchmark Values and Test Types

Pesticide	Lowest US EPA Benchmark (µg/L)	Test Type
Chlorpyrifos	0.04	Invertebrate chronic
Diazinon	0.105	Invertebrate chronic
Dimethoate	0.5	Invertebrate chronic
Malathion	0.035	Invertebrate chronic
Methidathion	0.66	Invertebrate chronic
Methomyl	0.7	Invertebrate chronic
Methoxyfenozide	6.3	Invertebrate chronic
Tebufenozide	4.3	Invertebrate chronic
Imidacloprid	1.05	Invertebrate chronic
Bifenthrin	0.0013	Invertebrate chronic
λ-cyhalothrin	0.002	Invertebrate chronic
Cyfluthrin	0.0074	Invertebrate chronic
Cypermethrin	0.069	Invertebrate chronic
Fenvalerate	0.0017	Invertebrate chronic
Permethrin	0.0014	Invertebrate chronic
Bensulide	290	Invertebrate chronic
Benfluralin	1.9	Fish chronic
Ethalfluralin	0.4	Fish chronic
Oryzalin	15.4	Vascular-plant acute
Pendimethalin	5.2	Nonvascular-plant acute
Prodiamine	1.5	Invertebrate chronic
Trifluralin	1.14	Fish chronic
Oxyfluorfen	0.29	Nonvascular-plant acute
Chlorothalonil	0.6	Invertebrate chronic

Appendix III. Raw Monitoring Data for Study 282

Site	Code	Sample Date	Time	Screen Group *	Analyte Name	Concentration (µg/L) **	Reporting Limit (µg/L)
CV_Belmont	24_83	16-Sep-13	13:39	CT	Chlorothalonil	ND	0.05
CV_Camp	24_50	16-Sep-13	10:32	CT	Chlorothalonil	ND	0.05
CV_Canal	39_99	17-Sep-13	14:50	CT	Chlorothalonil	ND	0.05
CV_Devon	24_86	16-Sep-13	12:22	CT	Chlorothalonil	ND	0.05
CV_Grimes	39_100	17-Sep-13	15:15	CT	Chlorothalonil	ND	0.05
CV_Henry	24_32	16-Sep-13	12:05	CT	Chlorothalonil	ND	0.05
CV_Inland	39_101	17-Sep-13	17:11	CT	Chlorothalonil	ND	0.05
CV_Lander	24_61	16-Sep-13	16:00	CT	Chlorothalonil	ND	0.05
CV_Midway1	24_84	16-Sep-13	11:45	CT	Chlorothalonil	ND	0.05
CV_Midway7	24_85	16-Sep-13	11:17	CT	Chlorothalonil	ND	0.05
CV_SandDam	24_62	16-Sep-13	14:53	CT	Chlorothalonil	ND	0.05
CV_SandSlough	24_88	16-Sep-13	13:16	CT	Chlorothalonil	ND	0.05
CV_Tracy	39_6	17-Sep-13	15:52	CT	Chlorothalonil	ND	0.05
CV_Wing	39_42	17-Sep-13	16:35	CT	Chlorothalonil	ND	0.05
CV_Wolfsen	24_94	16-Sep-13	15:30	CT	Chlorothalonil	ND	0.05
Imp_Butte	13_58	05-Mar-13	14:35	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	16:15	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.032	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Imp_Clark	13_26	06-Mar-13	13:30	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05

"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Imp_Garst	13_10	05-Mar-13	13:45	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	2.170	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	0.514	0.05
"	"	"	"	OP	Chlorpyrifos	0.329	0.01
"	"	"	"	OP	Dimethoate	1.070	0.04
"	"	"	"	OP	Malathion	0.064	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	14:50	OP	Chlorpyrifos	0.170	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.002	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Imp_Holtville	13_22	09-Oct-13	12:37	OP	Chlorpyrifos	0.019	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.021	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/Esfenva lerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	05-Mar-13	11:30	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	2.310	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	0.172	0.01

"	"	"	"	OP	Dimethoate	0.092	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Imp_Malva	13_23	05-Mar-13	12:25	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	8.350	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	0.783	0.05
"	"	"	"	OP	Chlorpyrifos	1.590	0.01
"	"	"	"	OP	Dimethoate	5.470	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	13:20	OP	Chlorpyrifos	0.039	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Imp_NewRiv27	13_71	05-Mar-13	9:15	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.322	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	0.144	0.05
"	"	"	"	OP	Chlorpyrifos	0.049	0.01
"	"	"	"	OP	Dimethoate	0.422	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	9:45	OP	Chlorpyrifos	0.064	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.023	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.005	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/Esfenva lerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.011	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002

Imp_OFD78	13_81	06-Mar-13	14:30	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Imp_Rice3	13_69	05-Mar-13	9:45	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.600	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	0.064	0.05
"	"	"	"	OP	Chlorpyrifos	0.075	0.01
"	"	"	"	OP	Dimethoate	0.047	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	10:16	OP	Chlorpyrifos	0.016	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	0.010	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.125	0.002
"	"	"	"	PY	Permethrin Total	0.004	0.002
Imp_Rutherford	13_56	05-Mar-13	13:00	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.054	0.05
"	"	"	"	DN/OX	Pendimethalin	2.420	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	0.442	0.05
"	"	"	"	OP	Chlorpyrifos	0.377	0.01
"	"	"	"	OP	Dimethoate	1.090	0.04
"	"	"	"	OP	Malathion	0.182	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	14:02	OP	Chlorpyrifos	0.225	0.01
"	"	"	"	OP	Dimethoate	0.062	0.04
"	"	"	"	OP	Malathion	ND	0.02

"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	0.006	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.003	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Imp_Verde	13_25	05-Mar-13	10:45	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.229	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	0.100	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	11:44	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.081	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.002	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Imp_Young	13_24	05-Mar-13	15:30	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.056	0.05
"	"	"	"	DN/OX	Pendimethalin	0.411	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	0.078	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.082	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	09-Oct-13	14:40	OP	Chlorpyrifos	0.038	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002

"	"	"	"	PY	Cypermethrin	0.007	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.008	0.002
"	"	"	"	PY	Permethrin Total	0.004	0.002
Riv_LG	33_11	06-Mar-13	12:45	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.051	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Riv_PVL	33_30	06-Mar-13	11:45	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.055	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Riv_South	33_31	06-Mar-13	11:30	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	0.233	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Blanco	27_9	09-Apr-13	11:45	DA	Methoxyfenozide	0.230	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005

"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Sal_Chualar	27_8	08-Apr-13	12:05	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	1.240	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	0.004	0.002
"	"	14-May-13	12:45	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	1.850	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.689	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	0.014	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	10-Jun-13	12:30	DA	Methoxyfenozide	0.253	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.680	0.04
"	"	"	"	IM	Imidacloprid	0.700	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	30-Jul-13	14:00	CB	Methomyl	2.380	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	5.210	0.04
"	"	"	"	IM	Imidacloprid	0.841	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	0.011	0.01
"	"	"	"	OP	Dimethoate	0.403	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005

"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.003	0.002
"	"	"	"	PY	Permethrin Total	0.004	0.002
"	"	13-Aug-13	13:15	CB	Methomyl	0.482	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.259	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	1.510	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.512	0.05
"	"	"	"	OP	Chlorpyrifos	0.012	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	03-Sep-13	13:05	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	2.410	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.711	0.05
"	"	"	"	OP	Chlorpyrifos	0.021	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	0.003	0.002
Sal_Davis	27_13	09-Apr-13	10:55	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	10-Jun-13	13:20	DA	Methoxyfenozide	ND	0.05

"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.115	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Dunes	27_50	09-Apr-13	13:15	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.012	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	11-Jun-13	9:20	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Gablilan	27_87	11-Jun-13	13:35	DA	Methoxyfenozide	0.134	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.353	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Haro	27_66	08-Apr-13	14:00	OP	Chlorpyrifos	0.029	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.007	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005

"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	14-May-13	14:20	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.409	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.137	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	0.108	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	11-Jun-13	10:33	DA	Methoxyfenozide	0.089	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.109	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	30-Jul-13	17:00	CB	Methomyl	0.058	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.087	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.004	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	13-Aug-13	16:07	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05

"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.143	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	0.019	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	03-Sep-13	15:58	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.110	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.009	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Sal_Hartnell	27_70	08-Apr-13	12:35	OP	Chlorpyrifos	0.012	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.024	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.006	0.002
"	"	"	"	PY	Permethrin Total	0.022	0.002
"	"	11-Jun-13	15:10	DA	Methoxyfenozide	0.061	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.548	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.499	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	0.011	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.932	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	30-Jul-13	15:00	CB	Methomyl	18.700	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	3.570	0.04
"	"	"	"	IMD/BEN	Imidacloprid	5.140	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01

"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.428	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.003	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.004	0.002
"	"	"	"	PY	Permethrin Total	0.013	0.002
"	"	13-Aug-13	14:01	CB	Methomyl	0.076	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.058	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	8.620	0.04
"	"	"	"	IMD/BEN	Imidacloprid	6.800	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	0.085	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	03-Sep-13	13:53	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	14.000	0.04
"	"	"	"	IMD/BEN	Imidacloprid	2.520	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	0.110	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.016	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Sal_Molera	27_58	09-Apr-13	8:55	DA	Methoxyfenozide	ND	0.05
"	"	"	13:45	DA	Methoxyfenozide	ND	0.05
"	"	"	8:55	DA	Tebufenozide	ND	0.05
"	"	"	13:45	DA	Tebufenozide	ND	0.05
"	"	"	8:55	OP	Chlorpyrifos	ND	0.01
"	"	"	13:45	OP	Chlorpyrifos	ND	0.01
"	"	"	8:55	OP	Dimethoate	ND	0.04

"	"	"	13:45	OP	Dimethoate	ND	0.04
"	"	"	8:55	OP	Malathion	ND	0.04
"	"	"	13:45	OP	Malathion	ND	0.04
"	"	"	8:55	OP	Methidathion	ND	0.05
"	"	"	13:45	OP	Methidathion	ND	0.05
"	"	"	8:55	PY	Bifenthrin	0.014	0.001
"	"	"	13:45	PY	Bifenthrin	ND	0.001
"	"	"	8:55	PY	Cyfluthrin	ND	0.002
"	"	"	13:45	PY	Cyfluthrin	ND	0.002
"	"	"	8:55	PY	Cypermethrin	ND	0.005
"	"	"	13:45	PY	Cypermethrin	ND	0.005
"	"	"	8:55	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	13:45	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	8:55	PY	λ-cyhalothrin	ND	0.002
"	"	"	13:45	PY	λ-cyhalothrin	ND	0.002
"	"	"	8:55	PY	Permethrin Total	0.003	0.002
"	"	"	13:45	PY	Permethrin Total	ND	0.002
"	"	11-Jun-13	9:45	DA	Methoxyfenozide	0.118	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.107	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Monte	27_14	14-May-13	15:30	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	10-Jun-13	14:35	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04

"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Natividad	27_86	11-Jun-13	14:10	DA	Methoxyfenozide	0.172	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.595	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.156	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Potrero	27_11	11-Jun-13	8:35	DA	Methoxyfenozide	0.078	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
Sal_Quail	27_7	08-Apr-13	11:40	OP	Chlorpyrifos	0.013	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.002	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.002	0.002
"	"	"	"	PY	Permethrin Total	0.004	0.002
"	"	14-May-13	12:15	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.424	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	10-Jun-13	11:55	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	1.440	0.04

"	"	"	"	IMD/BEN	Imidacloprid	0.714	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	0.395	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	30-Jul-13	12:45	CB	Methomyl	1.770	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	4.100	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.528	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	0.063	0.04
"	"	"	"	OP	Malathion	0.027	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.001	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.005	0.002
"	"	"	"	PY	Permethrin Total	0.027	0.002
"	"	13-Aug-13	12:00	CB	Methomyl	0.224	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	1.120	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.698	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	03-Sep-13	12:05	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.315	0.04
"	"	"	"	IMD/BEN	Imidacloprid	1.360	0.05
"	"	"	"	OP	Chlorpyrifos	0.021	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	2.650	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005

"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	0.042	0.002
Sal_Rec3	27_10	14-May-13	13:45	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.065	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.351	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	11-Jun-13	15:45	DA	Methoxyfenozide	ND	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.345	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.330	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	30-Jul-13	15:25	CB	Methomyl	1.600	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.254	0.04
"	"	"	"	IMD/BEN	Imidacloprid	1.220	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.002	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.004	0.002
"	"	"	"	PY	Permethrin Total	0.002	0.002
"	"	13-Aug-13	14:56	CB	Methomyl	0.461	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.059	0.05

"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.278	0.04
"	"	"	"	IMD/BEN	Imidacloprid	2.420	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	03-Sep-13	14:34	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.043	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.188	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.056	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	0.007	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	0.023	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	0.004	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
Sal_SanJon	27_12	08-Apr-13	13:00	OP	Chlorpyrifos	0.191	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	11-Jun-13	11:10	DA	Methoxyfenozide	0.111	0.05
"	"	"	"	DA	Tebufenozide	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.591	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
SM_Brown	42_53	15-May-13	12:15	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	2.280	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.469	0.04
"	"	"	"	OP	Methidathion	ND	0.05
SM_LOFC	40_23	15-May-13	15:30	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04

"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	31-Jul-13	15:00	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	14-Aug-13	15:20	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	ND	0.05
"	"	"	"	DN/OX	Pendimethalin	0.070	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	ND	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
SM_MainDitch	42_71	04-Sep-13	14:57	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.126	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002

SM_OFC	40_13	15-May-13	14:50	IMD/BEN	Bensulide	1.330	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.439	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.251	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	31-Jul-13	14:00	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.530	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.495	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	14-Aug-13	14:43	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	9.230	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.964	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.343	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.175	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	04-Sep-13	13:38	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	5.060	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.298	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005

"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
SM_Orcutt	42_50	15-May-13	14:00	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.447	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	31-Jul-13	12:45	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.833	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	14-Aug-13	12:50	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.063	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.069	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.756	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	04-Sep-13	11:28	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	1.030	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.112	0.02

"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	0.004	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	0.003	0.002
SM_Simas	42_72	15-May-13	12:50	IMD/BEN	Bensulide	0.424	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.573	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
SM_Solomon	42_48	15-May-13	11:45	IMD/BEN	Bensulide	ND	0.04
"	"	"	"	IMD/BEN	Imidacloprid	0.750	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.04
"	"	"	"	OP	Methidathion	ND	0.05
"	"	31-Jul-13	11:30	CB	Methomyl	0.104	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.296	0.04
"	"	"	"	IMD/BEN	Imidacloprid	1.010	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002
"	"	14-Aug-13	12:12	CB	Methomyl	ND	0.05
"	"	"	"	CT	Chlorothalonil	ND	0.05
"	"	"	"	DN/OX	Benfluralin	ND	0.05
"	"	"	"	DN/OX	Ethalfluralin	ND	0.05
"	"	"	"	DN/OX	Oryzalin	ND	0.05
"	"	"	"	DN/OX	Oxyfluorfen	0.195	0.05
"	"	"	"	DN/OX	Pendimethalin	ND	0.05
"	"	"	"	DN/OX	Prodiamine	ND	0.05
"	"	"	"	DN/OX	Trifluralin	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.162	0.04
"	"	"	"	IMD/BEN	Imidacloprid	1.250	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01

"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	0.272	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	04-Sep-13	12:19	CT	Chlorothalonil	ND	0.05
"	"	"	"	IMD/BEN	Bensulide	0.099	0.04
"	"	"	"	IMD/BEN	Imidacloprid	2.160	0.05
"	"	"	"	OP	Chlorpyrifos	ND	0.01
"	"	"	"	OP	Diazinon	ND	0.01
"	"	"	"	OP	Dimethoate	ND	0.04
"	"	"	"	OP	Malathion	ND	0.02
"	"	"	"	OP	Methidathion	ND	0.05
"	"	"	"	PY	Bifenthrin	ND	0.001
"	"	"	"	PY	Cyfluthrin	ND	0.002
"	"	"	"	PY	Cypermethrin	ND	0.005
"	"	"	"	PY	Fenvalerate/ Esfenvalerate	ND	0.005
"	"	"	"	PY	λ-cyhalothrin	ND	0.002
"	"	"	"	PY	Permethrin Total	ND	0.002

Note: * Screen Group: OP = Organophosphates; DN/OX = Dinitroanilines & Oxyfluorfen; CT = Chlorothalonil; DA = Diacylhydrazines; PY = Pyrethroids; IMD/BEN = Imidacloprid & Bensulide; CB = Carbamates
** ND = No Detection

Appendix IV. Analytical Laboratory QA/QC Data

Table 1. Reporting Limit and Method Detection Limit for Study 282

Pesticide	Screen Group*	Reporting limit ($\mu g/L$)	Method Detection Limit ($\mu g/L$)
Chlorpyrifos	OP	0.01	0.01024
Diazinon	OP	0.01	0.01093
Dimethoate	OP	0.04	0.01202
Malathion	OP	0.02	0.00935
Methidathion	OP	0.05	0.01136
Methomyl	CB	0.05	0.011
Methoxyfenozide	DA	0.05	0.00641
Tebufenozide	DA	0.05	0.00573
Imidacloprid	IMD/BEN	0.05	0.0394
Bifenthrin	PY	0.001	0.00091
λ-cyhalothrin	PY	0.002	0.00174
Cyfluthrin	PY	0.002	0.00146
Cypermethrin	PY	0.005	0.00154
Fenvalerate	PY	0.005	0.00166
Permethrin	PY	0.002	0.00105
Bensulide	IMD/BEN	0.04	0.0198
Benfluralin	DN/OX	0.05	0.015
Ethalfluralin	DN/OX	0.05	0.017
Oryzalin	DN/OX	0.05	0.021
Pendimethalin	DN/OX	0.05	0.19
Prodiamine	DN/OX	0.05	0.02
Trifluralin	DN/OX	0.05	0.015
Oxyfluorfen	DN/OX	0.05	0.023
Chlorothalonil	CT	0.05	0.0348

Note: * Screen Group: OP = Organophosphates; DN/OX = Dinitroanilines & Oxyfluorfen; CT = Chlorothalonil; DA = Diacylhydrazines; PY = Pyrethroids; IMD/BEN = Imidacloprid & Bensulide; CB = Carbamates

Appendix IV. Analytical Laboratory QA/QC Data

Table 2. Blind Spikes for Study 282

Extraction Date	Sample Number	Screen Group	Pesticide	Spike Level (µg/L)	Result (µg/L)	% Recovery	Exceed CLs
3/12/2013	2822070	DN	Oryzalin	0.2	0.191	96	no
3/12/2013	2822070	DN	Trifluralin	0.15	0.149	99	no
3/13/2013	2822069	CT	Chlorothalonil	0.15	0.117	78	no
4/12/2013	2821051	DA	Methoxyfenozide	0.15	0.138	92	no
4/12/2013	2821052	PY	Permethrin Cis	0.1	0.0742	74	no
4/12/2013	2821052	PY	Permethrin Total	0.35	0.288	82	no
4/12/2013	2821052	PY	Permethrin Trans	0.25	0.214	86	no
5/21/2013	2821107	DN	Oryzalin	0.1	0.092	92	no
5/21/2013	2821107	DN	Trifluralin	0.2	0.165	83	no
6/13/2013	2821174	OP	Chlorpyrifos	0.1	0.079	79	no
6/13/2013	2821175	OP	Diazinon	0.05	0.035	70	no
6/13/2013	2821174	OP	Malathion	0.2	0.16	80	no
6/14/2013	2821176	IMD/BEN	Bensulide	0.2	0.125	63	no
6/14/2013	2821176	IMD/BEN	Imidacloprid	0.15	0.142	95	no
8/19/2013	2821096	CB	Methomyl	0.15	0.112	75	no
8/22/2013	2821095	CT	Chlorothalonil	0.1	0.11	110	no
9/6/2013	2821388	OP	Diazinon	0.05	0.043	86	no
9/10/2013	2821389	IMD/BEN	Bensulide	0.1	0.081	81	no
9/10/2013	2821389	IMD/BEN	Imidacloprid	0.2	0.212	106	no
10/11/2013	2822133	OP	Dimethoate	0.1	0.082	82	no
10/14/2013	2822134	PY	Permethrin Cis	0.05	0.0343	69	no
10/14/2013	2822134	PY	Permethrin Trans	0.1	0.0699	70	no

Appendix IV. (continuing)

Table 3. Matrix Spikes - Organophosphate Screen for Study 282

Extraction Date	Sample Numbers	% Recovery			
		Chlorpyrifos	Malathion	Methidathion	Dimethoate
3/11/2013	2001, 2007, 2012, 2017, 2024, 2029, 2034, 2039, 2044, 2049, 2053, 2057, 2061, 2065	69.2	81.7	75.6	77.7
4/11/2013	1001, 1006, 1011, 1016, 1021, 1026, 1031, 1036, 1041, 1046	97.6	84.4	84.4	109.0
5/17/2013	1053, 1059, 1065, 1071, 1077, 1083, 1087, 1091, 1095, 1099, 1103	96.8	108.0	73.6	73.6
6/13/2013	1109, 1114, 1119, 1124, 1129, 1134, 1139, 1144, 1149, 1154, 1159, 1164, 1169, (1174)	72.0	101.0	96	90
8/2/2013	1181, 1189, 1197, 1205, 1213, 1221, 1229, 1237, 1245	99.2	71.7	67.8	76
8/16/2013	1257, 1267, 1277, 1287, 1297, 1307, 1317, 1327, 1337	74.4	81.4	83.5	79.6
9/6/2013	1395, 1405, 1415, 1425, 1435, 1445, 1455, 1465, 1475	107	76.8	70.7	95.5
10/11/2013	2073, 2079, 2085, 2091, 2097, 2103, 2109, 2115, 2121, (2133)	108	87.7	88.1	81.0
Average Recovery		90.5	86.6	80.0	85.3
Standard Deviation		16.0	12.2	9.6	12.1
CV		17.7	14.1	12.0	14.2
Upper Control Limit		119	126	128	117
Upper Warning Limit		111	116	117	108
Lower Warning Limit		77.2	75.7	74.6	73.2
Lower Control Limit		68.8	65.7	63.9	64.5

Appendix IV. (continuing)

Table 4. Matrix Spikes - Diazinon Screen for Study 282

Extraction Date	Sample Numbers	% Recovery
		Diazinon
4/11/2013	1002, 1007, 1012, 1017, 1022	90.4
5/17/2013	1054, 1060, 1066, 1072, 1078	94.0
6/13/2013	1110, 1115, 1120, 1125, 1130, 1135, 1140, 1145, 1150, 1155, 1160, 1165, 1170, (1175)	76.8
8/2/2013	1178, 1186, 1194, 1202, 1210, 1218, 1226, 1234, 1242	85.2
8/16/2013	1254, 1264, 1274, 1284, 1294, 1304, 1314, 1324, 1334	78.8
9/6/2013	1393, 1403, 1413, 1423, 1433, 1443, 1453, 1463, 1473, (1388)	83.8
10/11/2013	2074, 2080, 2086, 2092, 2098, 2104, 2110, 2116, 2122	89.6
Average Recovery		85.5
Standard Deviation		6.28
CV		7.34
Upper Control Limit		117
Upper Warning Limit		109
Lower Warning Limit		77.2
Lower Control Limit		69.2

Appendix IV. (continuing)

Table 5. Matrix Spikes - Methomyl Screen for Study 282

Extraction Date	Sample Numbers	% Recovery
		Methomyl
8/5/2013	1180, 1188, 1196, 1204, 1212, 1220, 1228, 1236, 1244	78.9
8/19/2013	1256, 1266, 1276, 1286, 1296, 1306, 1316, 1326, 1336, (1096)	89.1
Average Recovery		84
Standard Deviation		7.2
CV		8.6
Upper Control Limit		107.0
Upper Warning Limit		101.0
Lower Warning Limit		78.2
Lower Control Limit		72.3

Appendix IV. (continuing)

Table 6. Matrix Spikes - Imidacloprid Screen for Study 282

Extraction Date	Sample Numbers	% Recovery
		Imidacloprid
5/20/2013	1055, 1061, 1067, 1073, 1079, 1084	97.0
6/14/2013	1111, 1116, 1121, 1126, 1131, 1136, 1141, 1146, 1151, 1156, 1161, 1166, 1171, (1176)	96.0
8/6/2013	1179, 1187, 1195, 1203, 1211, 1219, 1227, 1235, 1243	90.0
8/19/2013	1255, 1265, 1275, 1285, 1295, 1305, 1315, 1325, 1335	83.9
9/10/2013	1394, 1404, 1414, 1424, 1434, 1444, 1454, 1464, 1474, (1389)	89.0
Average Recovery		91.2
Standard Deviation		5.4
CV		5.9
Upper Control Limit		124.0
Upper Warning Limit		115.6
Lower Warning Limit		81.2
Lower Control Limit		72.6

Appendix IV. (continuing)

Table 7. Matrix Spikes - Bensulide Screen for Study 282

Extraction Date	Sample Numbers	% Recovery
		Bensulide
5/20/2013	1055, 1061, 1067, 1073, 1079, 1084	97.0
6/14/2013	1111, 1116, 1121, 1126, 1131, 1136, 1141, 1146, 1151, 1156, 1161, 1166, 1171, (1176)	90.0
8/6/2013	1179, 1187, 1195, 1203, 1211, 1219, 1227, 1235, 1243	86.0
8/19/2013	1255, 1265, 1275, 1285, 1295, 1305, 1315, 1325, 1335	88.4
9/10/2013	1394, 1404, 1414, 1424, 1434, 1444, 1454, 1464, 1474, (1389)	83.0
Average Recovery		88.9
Standard Deviation		5.25
CV		5.91
Upper Control Limit		130.7
Upper Warning Limit		118.3
Lower Warning Limit		68.7
Lower Control Limit		56.3

Appendix IV. (continuing)

Table 8. Matrix Spikes - Chlorothalonil Screen for Study 282

Extraction Date	Sample Numbers	% Recovery
		Chlorothalonil
3/13/2013	2002, 2008, 2013, 2018, 2025, 2030, 2035, 2040, 2045, (2069)	95.0
8/13/2013	1177, 1185, 1193, 1201, 1209, 1217, 1225, 1233, 1241	83.0
8/22/2013	1252, 1262, 1272, 1282, 1292, 1302, 1312, 1322, 1332, (1095)	78.0
9/13/2013	1392, 1402, 1412, 1422, 1432, 1442, 1452, 1462, 1472	64.0
9/19/2013	3015, 3017, 3019, 3021, 3023, 3025, 3027, 3029	89.5
Average Recovery		82
Standard Deviation		11.9
CV		14.5
Upper Control Limit		123
Upper Warning Limit		113
Lower Warning Limit		73.4
Lower Control Limit		63.5

Appendix IV. (continuing)

Table 9. Matrix Spikes - Diacylhydrazines Screen for Study 282

Extraction Date	Sample Numbers	% Recovery	
		Methoxyfenozide	Tebufenozide
4/12/2013	1027, 1032, 1037, 1042, 1047, (1051)	89.0	93.0
6/17/2013	1112, 1117, 1122, 1127, 1132, 1137, 1142, 1147, 1152, 1157, 1162, 1167, 1172	98.0	99.0
Average Recovery		93.5	96.0
Standard Deviation		6.4	4.2
CV		6.8	4.4
Upper Control Limit		113.0	111.0
Upper Warning Limit		106.0	105.0
Lower Warning Limit		80.3	80.8
Lower Control Limit		73.8	74.7

Appendix IV. (continuing)

Table 10. Matrix Spikes - Dinitroanilines + Oxyfluorfen Screen for Study 282

Extraction Date	Sample Numbers	% Recovery						
		Oryzalin	Ethalfuralin	Trifluralin	Benfluralin	Prodiamine	Pendimethalin	Oxyfluorfen
3/12/2013	2003, 2009, 2014, 2019, 2026, 2031, 2036, 2041, 2046, 2050, 2054, 2058, 2062, 2066, (2070)	76.7	94.7	97.3	98.0	110.0	107.0	111.0
5/21/2013	1056, 1062, 1068, 1074, 1080, 1107	86.7	96.7	88.0	100.0	80.7	88.0	98.7
8/20/2013	1253, 1263, 1273, 1283, 1293, 1303, 1313, 1323, 1333	68.0	91.3	91.3	90.0	87.3	90.7	92.0
Average Recovery		77.4	94.0	89.7	95.0	84.0	89.4	95.4
Standard Deviation		13.22	3.82	2.33	7.07	4.67	1.91	4.74
CV		17.09	4.06	2.60	7.44	5.56	2.14	4.97
Upper Control Limit		112	119	117	120	134	127	142
Upper Warning Limit		103.2	112	111	112.7	123	118	127
Lower Warning Limit		66.1	84.8	84.2	82.3	77.0	79.8	65.8
Lower Control Limit		56.9	77.9	77.5	74.7	65.6	70.4	50.6

Appendix IV. (continuing)

Table 11. Matrix Spikes - Pyrethroids Screen for Study 282

Extraction Date	Sample Numbers	% Recovery						
		Bifenthrin	λ-cyhalothrin	Permethrin cis	Permethrin trans	Cyfluthrin	Cypermethrin	Fenvalerate/ Esfenvalerate
4/12/2013	1003, 1008, 1013, 1018, 1023, 1028, 1033, 1038, 1043, 1048, (1052)	79.7	91.3	76.3	70.0	83	84.7	82.7
8/5/2013	1182, 1190, 1198, 1206, 1214, 1222, 1230, 1238,1246	64.3	65.7	69.0	57.3	70.0	70.7	64.7
9/9/2013	1396, 1406, 1416, 1426, 1436, 1446, 1456, 1466, 1476	70.0	78.3	84.7	81.3	77.7	75.3	74
10/14/2013	2075, 2081, 2087, 2093, 2099, 2105, 2111, 2117, 2123, (2134)	72.0	74.7	68.3	70.0	73.7	78	74
Average Recovery		71.5	77.5	74.6	69.7	76.1	77.2	73.9
Standard Deviation		6.37	10.6	7.7	9.8	5.6	5.9	7.4
CV		8.90	13.7	10.3	14.1	7.3	7.6	10.0
Upper Control Limit		98.6	99.8	98.9	101	110	93.3	98.9
Upper Warning Limit		91.8	92.8	92.0	92.4	100	86.0	91.4
Lower Warning Limit		64.5	64.8	64.3	56.4	61.1	56.9	61.5
Lower Control Limit		57.6	57.9	57.4	47.4	51.3	49.6	54.0

*Highlighted cells are percent recoveries exceeding control limits

( ) Sample numbers are blind spikes

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 Date
Environmental Scientist

Written By:

Original signed by: 1/11/2011

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Jane White Date
Environmental Scientist

Approved By:

Original signed by: 1/10/2011

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Elaine Wong Date
Environmental Program Manager I

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?

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
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Date

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Elaine Wong
Environmental Program Manager I

Date

Revision Log:

Date	What was revised? Why?

Title: Determination of Methoxyfenozide and Tebufenozide in Surface Water by Ultra Performance Liquid Chromatography Coupled to Tandem Mass Spectrometry

1. Scope:

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

2. Principle:

The methoxyfenozide and tebufenozide are extracted from the surface water sample 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 an autosampler vial for analysis on Ultra Performance Liquid Chromatography (UPLC) coupled to a positive electrospray ionization triple quadrupole mass spectrometry (ES-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 methoxyfenozide and tebufenozide 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 ES ion source.

6. Reagents and Supplies:

6.1 Methoxyfenozide CAS#161050-58-4
6.2 Tebufenozide CAS#112410-23-8
6.3 Methylene Chloride, nanograde or equivalent pesticide grade
6.4 Water, MS grade, Burdick & Jackson or equivalent
6.5 Methanol, MS grade, Burdick & Jackson or equivalent
6.6 Formic Acid, HPLC grade
6.7 Ammonium formate, reagent grade or equivalent
6.8 Separatory funnel, 2 L
6.9 Boiling flask, 500 mL
6.10 Sodium Sulfate, ACS grade
6.11 Funnels, long stem, 60°, 100 mm I.D.
6.12 Volumetric Pipette, 0.5 mL
6.13 Graduated conical tubes with glass stopper, 15 mL
6.14 Glass wool, Pyrex® fiber glass slivers 8 microns
6.15 Disposable Pasteur pipettes, and other laboratory ware as needed
6.16 Recommended analytical column:
Waters Acquity BEH C18 1.7µm, 2.1 x 100 mm
6:17 Aqueous Solution: For 500 mL, mix 470 ± 2mL water, 25 ± 0.5 mL methanol, 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.
6.18 Organic Solution: For 500mL, mix 450 ± 2mL methanol and 45 ± 0.5 mL water with 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.

7. Standards Preparation:

7.1 The individual stock standards of 1.0 mg/mL were obtained from the CDFA/CAC Standards Repository. The standards were diluted to10 µg/mL with methanol for identification purposes.

A combination standard of 1 µg/mL was prepared from the individual 10 µg/mL standards with methanol. The standard was also used to dilute the following concentrations: 0.025, 0.05, 0.1, 0.25 and 0.5 µg/mL in methanol for 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 Regulations (DPR) provides the background water for matrix blank and spikes.

9.2 Preparation of blank and spike

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

Matrix spike: Weigh out 500 g of background water. Spike a client requested amount of insecticides into the background water, mix well and let it stand for one minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Remove samples from the refrigerator and allow them to reach ambient temperature.

9.3.2 Mix sample well before weighting aliquot. Weight 500 ± 0.1 g of water samples by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.3.3 Shake with 80 ± 5 mL of methylene chloride for 1 minute. 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 60 ± 5 mL of methylene chloride and shake 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. Transfer the extract to a calibrated 15 mL graduated test tube.

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

9.3.9 Evaporate the sample extract to dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 0.5 mL with methanol, mix well and transfer to an autosampler vial. Submit extract for LC-MS analysis.

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 limit. The current working standard levels are 0.025, 0.05, 0.1, 0.25, and 0.5 µg/mL.

10.2 Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995, with all levels weighted 1/x.

11. Analysis**:**

11.1 Injection Scheme

The LC-MS needs to be conditioned with standard or a sample extract 2 to 5 runs before running the following sequence: A set of calibration standards, a matrix blank, a matrix spike, a set of up to 12 test samples, then a set of standards, etc.

11.2 UPLC-MS/MS

11.2.1 UPLC Instrument: Waters Acquity Ultra Performance LC
Column: Waters Acquity BEH C18 1.7µm, 2.1 x 100 mm
Column Temperature: 60 °C
Mobile Phase: Gradient

Solvent 1: Aqueous Solution
Solvent 2: Organic Solution
Gradient:

Time(min)	Flow rate (mL/min)	Solvent 1	Solvent 2
0	0.60	90.0	10.0
0.5	0.60	90.0	10.0
7.00	0.60	10.0	90.0
7.80	0.60	10.0	90.0
8.00	0.60	90.0	10.0
8.50	0.60	90.0	10.0

Injection Volume: 1.0 µL

11.2.2 Mass Spectrometry and Operating Parameters

Model: Waters Xevo Triple Quadrupole
Ion ProbeType: Electrospray Ionization (ESI)
Ion Mode: Positive
Source Temp: 150 °C

Compound	Retention Time (min)	Precursor ion	Product Ion	Dwell (s)	Cone(V)	Collision Energy/-ev
Methoxyfenozide	5.80	369.24 369.24	**149.05** 313.13	0.128 0.128	12.0 12.0	16.0 6.00
Tebufenozide	6.33	353.25 353.25	**133.05** 297.15	0.128 0.128	14.0 14.0	16.0 6.00

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 0.1ppb 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 methoxyfenozide and tebufenozide 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 for each analyte. The upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the percent 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 percent 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 triple quadrupole LCMS software used a linear curve fit, with all levels weighted 1/x. 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 A storage stability study was done with this project. The storage stability study consisted of a 1.0 ppb spike level and 3 replicates over a 28 day period. Twelve liters of background well water were spiked and then transferred to twelve one liter amber bottles. These spiked samples were stored in the refrigerator until analyzed on 0, 2, 4, 7, 15, 21 and 28 days. Along with the storage spikes, a blank and method control spike were also extracted. This storage study showed no significant degradation for these compounds within 28 days. Results for the storage study are shown in Appendix 3.

15.2 Solid phase extraction using an Oasis HLB 500mg cartridge was also tried. A 500 mL surface water sample was filtered through a glass fiber filter.
The filtered sample was passed through a solid phase extraction HLB cartridge and methoxyfenozide and tebufenozide were eluted from the solid phase cartridge with acetonitrile. The extract was concentrated to just dryness with nitrogen in a heated water bath, and then adjusted to a 0.5 mL volume with methanol. Recoveries were good and in the 80-90% range. There were some concerns about filtering away the sediment that could be in more turbid samples and the possible loss of methoxyfenozide and tebufenozide that might occur during that process. It was decided to retain liquid /liquid extraction as the primary extraction process.

16. References:

16.1 Hall,Gregory; Engebretson, Jo; Hengel, Mathew J. and Shibamoto, Takayuki "Analysis of Methoxyfenozide Residues in Fruits, Vegetables, and Mint by Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS), J. Agric. Food Chem. 2004, 52, 672-676

16.2 "Crop Protection Handbook, 2010", MeisterPro Executive Office 27722 Euclid Ave., Willoughby, OH

Appendix 1

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

Lab #	**Spk\Analyte**	Methoxyfenozide	Tebufenozide
2011-1806	blk	nd	nd
2011-1807	0.1ppb spk 1	0.086	0.088
2011-1808	0.1ppb spk 2	0.087	0.087
2011-1809	0.1ppb spk 3	0.086	0.087
2011-1810	0.1ppb spk 4	0.089	0.089
2011-1811	0.1ppb spk 5	0.089	0.088
2011-1812	0.1ppb spk 6	0.092	0.092
2011-1813	0.1ppb spk 7	0.088	0.0088
	SD	0.00204	0.001822
Reported	**MDL**	**0.00641**	**0.00573**
	RL	**0.05**	**0.05**

All concentrations are expressed in ppb.

Appendix 2

Method Validation Data:

Analyte	Spike ppb	Recovery (%) Set1	Set2	Set3	Set4	Set5		%
Methoxyfenozide	0.1	93.0	97.0	114	87.0	91.0	Mean:	93.3
	0.25	94.0	93.6	96.4	87.2	92.8	SD:	6.49
	0.5	94.8	96.2	95.6	100	90.6	UCL:	113
	1	90.2	86.6	91.8	90.4	83.7	UWL:	106
	5	94.6	94.6	99.4	98.0	79.6	LWL:	80.3
							LCL:	73.8
Tebufenozide	0.1	92.0	97.0	112	87.0	91.0	Mean:	93.0
	0.25	93.6	94.0	95.6	87.2	93.2	SD:	6.07
	0.5	94.9	96.2	94.6	99.8	90.8	UCL:	111
	1	90.5	86.6	91.1	90.6	84.7	UWL:	105
	5	93.4	92.4	98.6	97.6	79.6	LWL:	80.8
							LCL:	74.7

Appendix 3

Storage study Summary for Methoxyfenozide & Tebufenozide in Surface Water

Analyte \ Recovery %		Day 0	Day 2	Day 4	Day 7	Day 14	Day 21	Day 28
Methoxyfenozide	blank	ND	ND	ND	ND	ND	ND	ND
	QC spike		81.5%	85.9%	82.4%	84.7%	87.5%	84.7%
	Spike 1	85.5%	81.5%	81.3%	91.4%	87.2%	91.9%	86.7%
	Spike 2	91.5%	87.7%	88.3%	85.2%	82.5%	89.6%	87.8%
	Spike 3	86.6%	82.9%	87.8%	86.2%	82.5%	88.0%	83.4%
Tebufenozide	blank	ND	ND	ND	ND	ND	ND	ND
	QC spike		80.5%	85.2%	81.6%	84.2%	88.6%	84.2%
	Spike 1	86.1%	81.8%	81.5%	90.0%	87.1%	91.1%	87.7%
	Spike 2	90.5%	88.4%	85.8%	86.4%	82.6%	87.4%	85.3%
	Spike 3	85.7%	82.5%	87.9%	86.0%	81.3%	87.7%	79.4%

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Revision Log:

Date	What was revised? Why?

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 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

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Steve Siegel Date
Sr. Environmental Scientist

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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.

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 Date
Chemist

Written By:

Original signed by : 3/17/2009

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Jane White Date
Chemist

Approved By:

Original signed by : 3/17/2009

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Steve Siegel Date
Section Supervisor

Approved By:

Original signed by : 3/19/2009

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Elaine Wong Date
Program Supervisor

Revision Log:

Date	What was revised? Why?