California Department of Pesticide Regulation
Environmental Monitoring Branch

SUPPORTING INFORMATION-APPENDICES

Appendix I. Study 283 Protocol

Department of Pesticide Regulation
Environmental Monitoring Branch
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Study 283. Protocol for Field Monitoring of Chlorantraniliprole in Areas of Increased Use in California, 2013.

KayLynn Newhart and Kevin Kelley
April 24, 2013

I. INTRODUCTION

Department of Pesticide Regulation's (DPR) Environmental Monitoring Branch (EMB) began an effort to track new pesticide active ingredients (a.i.'s) during the stage of early use (Newhart, 2013). EMB's intention is to determine whether environmental fate, potential toxicity, and increases in use of newly registered a.i.'s present any risks to surrounding watersheds, and if that use warrants monitoring and closer annual scrutiny. This annual investigation and monitoring is meant as a proactive method to help improve DPR's detection of potential water quality issues and ultimately reduce possible adverse impacts to the environment.
DPR staff evaluated 118 new a.i.s registered for use from 2005-2010 and prioritized them using established criteria for monitoring (Newhart, 2013). Of the a.i.'s investigated, chlorantraniliprole became the first one that met these criteria. Those conditions include: 1) annual use that exceeded 5,000 lbs.; 2) high toxicity to aquatic organisms; 3) high probability to move off-site in water; and 4) uses that include a wide variety of pests and crops (Newhart, 2013). Moreover, chlorantraniliprole use has steadily increased in recent years. The total pounds of chlorantraniliprole active ingredient applied in California in 2009, 2010, and 2011 were 25,539, 37,757, and 42,212 lbs., respectively.

A prior study (Markle, 2011) found concentrations of chlorantraniliprole from the limit of detection of 0.03 to 1.21 parts per billion (ppb) at various locations in the Central Valley and Central Coast regions of California. The study looked at lettuce crops in the Central Coast and found that residues peaked in October/November. Chlorantraniliprole was detected in 47 of 63 samples collected in this region. In the Central Valley, there were 3 detections in the 53 samples analyzed. These detections ranged from 0.03 to 0.05 ppb. The results of this study further support that chlorantraniliprole, when utilized in flood and furrow irrigation systems with normal agricultural practices, can end up in agricultural runoff.

Site surveys of the areas proposed for sampling will be done in the spring of 2013 and sample collection location and will be identified after surveys are completed. Table 1 contains sample collection information for chlorantraniliprole monitoring. For the purpose of this study, some sampling sites may coincide with those selected by the Markle (2011) study.

II. OBJECTIVE

The objectives of this study are to:

- Determine if chlorantraniliprole is moving off-site in runoff and what concentrations are in surrounding waterways.
- Further delineate crops and uses that likely contribute to off-site runoff.
- Determine what roles weather (dry vs. rain event) and application play in off-site runoff.
- Determine if resulting concentrations exceed aquatic toxicity thresholds.

Results will also help to determine if mitigation measures are needed to help manage risks associated with potential increases in use.

III.PERSONNEL

This study will be conducted by staff from the DPR's Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Nan Singhasemanon, Senior Environmental Scientist. Other key personnel and their respective roles are listed below:

Project Leader: KayLynn Newhart
Field Coordinator: Kevin Kelley
Laboratory Liaison: Sue Peoples
Chemists: Staff Chemists from the California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry- Sacramento, California.

IV. STUDY PLAN

Database queries (CDPR, 2012) and GIS mapping of geographic regional use areas were performed (Appendix 1) to assess where chlorantraniliprole use occurs adjacent to waterways. Historical use of chlorantraniliprole is low from November through May but peaks in months from September to October. The study plan will be updated as decisions are made on additional sites.

Table 1. Sampling sites and samples proposed for collection.

Location	Main Crop Use	Total Sites*	Weeks samples collected/ months	Primary Samples/week	QA/QC Samples/ week	Total Samples collected
Salinas Valley	Various row crops	10	4 (July-Oct)	8-10	4	44
Santa Maria (Santa Barbara County	Various row crops	5	4 (May-Oct)	4-6	3	23
Optional Site**				TBD***		
Totals		**15**			**7**	**67**

*****Sites selected will be determined and total sites may change due to site surveys.
******One optional site may include Napa, Fresno, or Imperial counties depending on site conditions and pesticide use.
*******To be determined

V. SAMPLING METHODS

Surface water grab samples will be collected utilizing an extendable grab-pole with 1-liter amber glass bottles affixed to the end and submersed under water 6-12 inches. Samples may also be collected using a Kemmerer sampler and parsed into 1-liter amber bottles. Following collection, samples will be stored at 4o C on wet ice, and transported to DPR's warehouse in West Sacramento, CA. Samples will then be transported to the CDFA Center for Analytical Chemistry for analysis. DPR's Standard Operating Procedures for Quality Control (QC) and Quality Assurance (QA) procedures will be followed (Segawa, 1995). Water quality parameters will be measured at the time of sample collection and will include water temperature, specific conductivity, pH, dissolved oxygen, and flow data.

VI. CHEMICAL ANALYSIS

California Department of Food and Agriculture's Center for Analytical Chemistry will analyze samples using LC/MS/MS with a method detection limit (MDL) of 0.0370 ppb and a reporting limit (RL) of 0.1 ppb (Hsu et al., 2013). Storage stability analysis showed no significant loss at less than 28 days.

VI. DATA ANALYSIS

Pesticide a.i. concentrations will be reported in micrograms per liter (µg/L) or parts per billion (ppb). Concentrations will be compared to available aquatic toxicity values and benchmarks including those from DPR pesticide evaluations from registrant studies (Bireley and Lopez,

2008; Newhart, 2008), United States Environmental Protection Agency pesticide fact sheet (USEPA, 2008), and the Footprint Pesticides Property Database (EU Footprint, 2012).

VII. TIMETABLE

Field Sampling: July/August 2013 through Oct 2013
Chemical Analysis: July/August 2013 through Oct 2013
Draft Report: March 2014

VIII. BUDGET

Table 2* shows the costs associated with the analysis of field and quality control samples.

Analysis	Cost/Sample ($)	Number of Samples	Total Cost ($) (estimated)
Primary Samples	600.00	67	39,000.00
Field Duplicates (QA/QC)	600.00	7	4,200.00
Blind Spikes (QA/QC)	600.00	4	2,400.00
Totals			**45,600.00**

*Costs reflect an average based on historic laboratory sample costs and can vary based on the complexity of analysis.

IX.REFERENCES

Bireley, R. and S. Lopez. 2008. Fish and Wildlife Registration Evaluation Report for Chlorantraniliprole (DPR #222404, 222405, 222406). California Department of Pesticide Regulation. Sacramento, CA.

California Department of Pesticide Regulation. 2012. Pesticide Use Reporting Database. Sacramento, CA. <http://www.cdpr.ca.gov/docs/pur/purmain.htm>

EU Footprint Pesticide Properties Database. 2011. Chlorantraniliprole. University of Hertfordshire. < http://sitem.herts.ac.uk/aeru/footprint/en/index.htm>

Hsu, J., J. White, S. Siegal, and E. Wong. 2013. Determination of Chlorantraniliprole in Surface Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole (EMON-SM-05-031). Department of Food and Agriculture Center for Analytical Chemistry. Sacramento, CA.

Newhart, K. 2008. Surface Water and Aquatic Toxicity Risk Review for Chlorantraniliprole (DPR# 222406). California Department of Pesticide Regulation. Sacramento, CA.

Newhart, K. 2012. Study #275: Summary of New Pesticide Active Ingredient Use Tracking for Field Monitoring in Surface Water from 2005-2010. California Department of Pesticide Regulation. Sacramento, CA.

Markle, J.C. 2011. Coalition for Urban/Rural Environmental Stewardship California (CURES) Monitoring Program for Chlorantraniliprole Report Submitted to E.I. du Pont Nemours and Company Wilmington, Delaware. CURES Study Number 09-DPT-01. Dinuba, CA.

Segawa, R. 1995. Standard Operating Procedure for Chemistry Laboratory Quality Control (QAQC001.00). California Department of Pesticide Regulation. Sacramento, CA. < http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf>

United States Environmental Protection Agency (USEPA). 2008. Fact Sheet for the Registration of Chlorantraniliprole (7505P). Office of Prevention, Pesticides, and Toxic Substances. Washington, D.C.

Maps for Appendix to Protocol available at
http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study283protocol.pdf

Appendix II: Sampling Site information for monitoring sites for Study 283 with Maps.

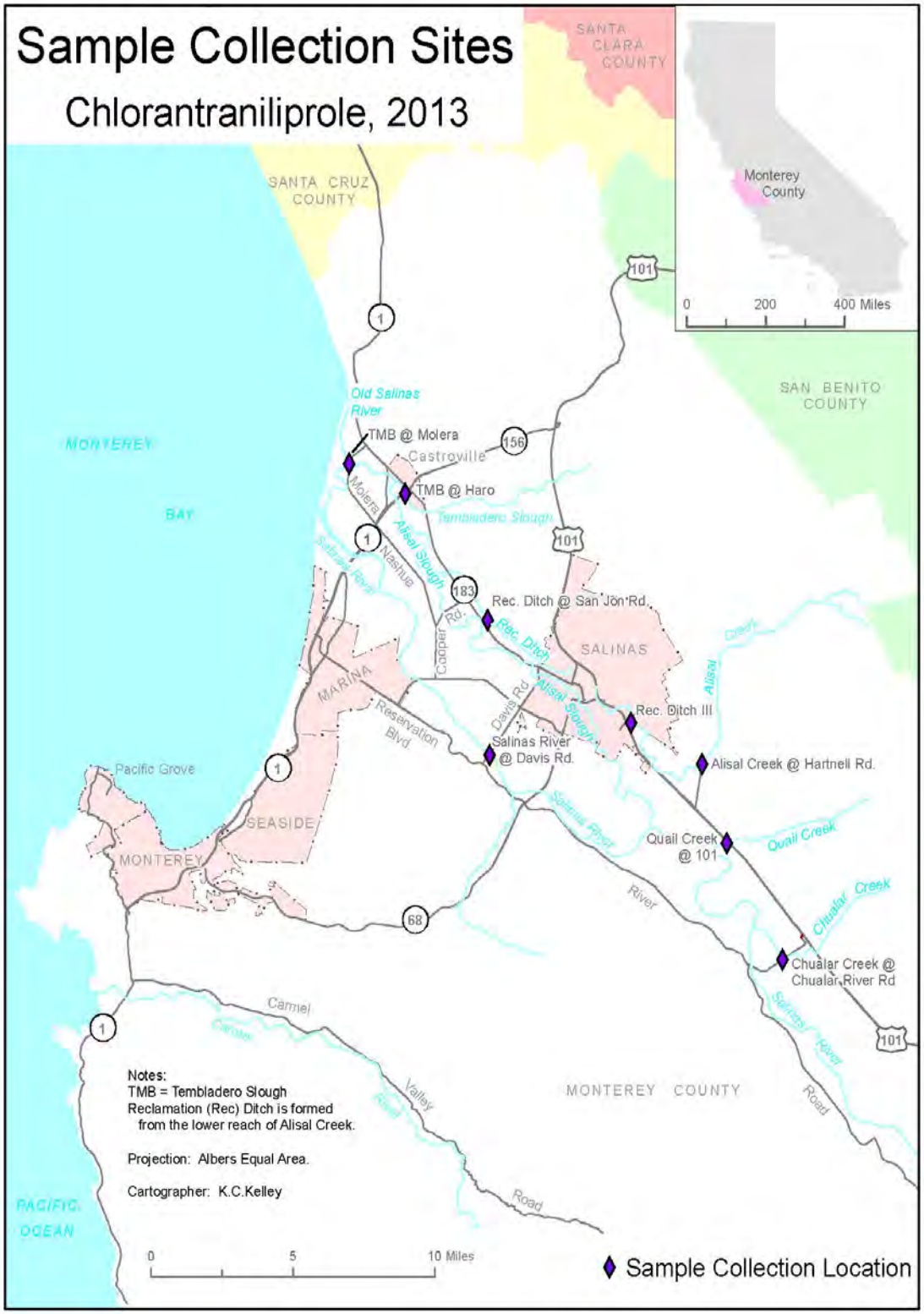
Site Name	**Latitude/Longitude**	
	Latitude (N)	Longitude (W)
Salinas Valley		
Tembladero Slough @ Molera Rd.	36.77224	-121.78653
Tembladero Slough@ Haro Rd.	36.75964	-121.75348
Reclamation Ditch @ San Jons Rd.	36.70501	-121.70408
Reclamation Ditch III	36.659	-121.61527
Salinas River @ Davis Rd.	36.64705	-121.70132
Alisal Slough @ Hartnell Rd.	36.64359	-121.57736
Quail Creek @ SR 101	36.60923	-121.56227
Chualar Creek	36.55861	-121.52886
Santa Maria Valley		
Arroyo Grande Creek@ Hwy 1	35.09743	-120.59320
Little Oso Flaco Creek	35.02275	-120.58695
Oso Flaco Creek	35.0163	-120.5875
Orcutt Creek	34.9575	-120.6325
Solomon Creek	34.9414	-120.5743

California Department of Pesticide Regulation
Environmental Monitoring Branch

Surface Water Sample Sites

Chlorantraniliprole, 2013

California Department of Pesticide Regulation
Environmental Monitoring Branch



Appendix III. Water quality measurements for chlorantraniliprole

Sample #	Site Name & Description	Date Collected	pH	Conductivity	Dissolved Oxygen	Temp (^{o}F)	Salinity
1001	Quail Creek	7/10	8.37	1143	6.03	26	0.6
1003	Chualar Creek	7/10	8.13	1648	12.98	23.2	0.9
1005	Alisal Creek@ Hartnell	7/10	7.99	928	0.27	23	0.5
1007	Reclamtion Ditch #3	7/10	7.68	734	7.16	24.1	0.4
1009	Reclamation Ditch @ San Jons Rd.	7/10	8.22	89.9	8.98	22.7	0.7
1011	Tembladero Slough @ Haro Rd.	7/10	7.95	2515	6.39	24	1.3
1013	Tembladero Slough@ Molera Rd.	7/10	8.3	1778	10.68	22	0.9
1015	Salinas River @ Davis Rd.	7/10	8.55	421.2	4.39	24.9	0.2
1017	Solomon-Orcutt Creek@ SR1	7/11	8.04	3097	10.26	23.1	1.6
1019	Orcutt Creek	7/11	7.96	2645	6.23	22.2	1.5
1021	Oso-Flako Creek	7/11	7.74	2107	4.82	21	1.2
1023	Little Oso-Flako Creek	7/11	7.93	1670	4.89	19.5	1.0
1027	Quail Creek @ Hwy101	7/30	8.07	919	0.19	19.8	0.5
1028	Chualar Creek Chualar River Rd.	7/30	8.18	1167	6.78	25.8	0.6
1029	Alisal Creek Hartnell Rd.	7/30	8.17	689	5.94	19.8	0.3
1030	Reclamation Ditch #3	7/30	8.2	1046	6.72	28.2	0.5
1031	Reclamation Ditch	7/30	8.21	1526	14.06	22.2	0.8
1033	Tembladero Slough	7/30	8.03	2559	11.22	23.3	1.3

Appendix III. Water quality measurements (continued)

Sample #	Site Name & Description	Date Collected	pH	Conductivity	Dissolved Oxygen	Temp (°F)	Salinity
1034	Tembladero Slough (Molera Rd.)	7/30	8.39	2017	6.85	21.5	1.1
1036	Salinas River Davis Rd.	7/30	8.4	0.5	6.23	25.3	0.2
1038	Solomon Creek	7/31	7.18	2872	10.92	18.3	1.8
1039	Orcutt Creek @ Main	7/31	7.9	2758	6.86	18.0	1.7
1041	Oso Flaco Creek Flaco Rd.	7/31	7.06	2250	5.53	18.4	1.3
1042	Oso Flaco Creek #2	7/31	7.82	1689	3.72	17.7	1.0
5001	Quail Creek @ Hwy 101	8/13	8.06	1141	5.99	17.5	0.6
5002	Chualar Creek @Chualar River Rd.	8/13	8.4	1829	5.89	28	0.9
5003	Alisal Creek @ Harnell Rd.	8/13	7.88	1217	2.22	18.8	0.6
5004	Reclamation Ditch Site #3	8/13	8.7	1119	6.43	28.4	0.6
5005	Reclamation Ditch	8/13	8.54	1402	6.33	22.5	0.7
5007	Tembladero Slough Haro St.	8/13	8.28	2627	8.87	24.5	1.4
5008	Tembladero Slough Molera Rd.	8/13	8.96	2555	10.73	21.4	1.3
5010	Salinas River @Davis Rd.	8/13	8.54	440.2	4.56	24.6	0.2
5012	Solomon Creek @Hwy 1	8/14	8.15	2831	10.8	23.4	1.5
5013	Orcutt Creek @ Main	8/14	7.61	2971	3.47	20.4	1.6

Appendix III. Water quality measurements (continued)

Sample #	Site Name & Description	Date Collected	pH	Conductivity	Dissolved Oxygen	Temp (°F)	Salinity
5014	Oso Flaco Creek @Oso Flaco Rd.	8/14	7.59	2040	3.47	23.2	1.0
5015	Little Oso Fl Flaco Creek	8/14	7.31	1967	3.24	18.3	1.0
5016	Arroyo Grande Creek	8/14	7.78	1305	5.02	18.6	0.7
5073	Quail Creek Hwy 101	9/24	7.77	12.78	4.86	21.9	0.6
5075	Chualar Creek	9/24	7.95	1599	7.78	24.3	0.8
5077	Alisal Creek @Hartnell Rd.	9/24	7.79	513	4.36	19	0.2
5079	Reclamation Ditch #3	9/24	8.23	929	18.53	29.3	0.5
5081	Reclamation Ditch #3 @San Jons Rd.	9/24	7.83	103	6.5	20.4	0.5
5083	Tembladero Slough @Haro	9/24	8.22	2101	11.41	21.4	1.1
5085	Tembladero Slough Molera Rd.	9/24	9.12	1365	11.14	21.4	1.1
5087	Salinas River @Davis Rd.	9/24	8.8	426.3	6.96	21.7	0.2
5089	Solomon Creek Creek CreeCreek	9/25	7.02	143.2	12.68	19.8	2.0
5091	Orcutt Creek	9/25	7.45	85.8	8.08	18.2	1.7
5093	Oso Flaco Creek @Oso Flaco Lake	9/25	7.31	25.2	3.49	17.4	0.2

Appendix III. Water quality measurements (continued)

Sample #	Site Name & Description	Date Collected	pH	Conductivity	Dissolved Oxygen	Temp (^{o}F)	Salinity
5101	Quail Creek @ Salinas River	10/15	8.5	566	11.18	12.5	0.3
5103	Chualar Creek @ Chualar River Road HWY 101	10/15	8.61	2005	8.56	20.9	0.6
5105	Reclamation Ditch Site #3 (near Airport Blvd)	10/15	8.26	1364	4.29	20.3	0.7
5107	Reclamation Ditch (San Jons Road)	10/15	8.78	1378	5.91	17.0	0.7
5109	Tembladero Slough (Haro Rd.)	10/15	7.53	2424	5.55	15.7	1.3
5111	Tembladero Slough (Molera Rd.)	10/15	8.48	2470	7.62	18.1	1.3
5113	Salinas River (Davis Rd.)	10/15	8.42	529	11.25	17.5	0.3
5115	Chualar Creek		7.92	1211	10.49	8.4	0.6
5117	Arroyo Grande Creek	10/16	7.98	1046	9.46	14	0.5
5119	Solomon-Orcutt Creek (@ Hwy 1)	10/16	7.92	3676	16.5	20.5	1.9
5121	Orcutt Creek @ W. Main St.	10/16	7.87	3135	9.38	17.8	1.6
5123	Oso Flaco Creek	10/16	7.7	1932	5.45	20.1	7.7

Appendix IV. Chlorantraniliprole sampling results

Sampling Location	Date Sample Collected	Sample Number	Concentrations Detected (ppb)
Quail Creek	7/10	1001	0.544
	7/30	1027	0.148
	8/13	5001	0.383
	9/24	5073	0.139
	10/15	5101	9.37
	10/15	5102 (dup)	9.71
Chualar Creek	7/10	1003	0.244
	7/30	1028	0.579
	8/13	5002	0.540
	9/24	5075	1.57
	10/15	5103	2.79
	10/16	5115	2.90
Alisal Slough @ Hartnell	7/10	1005	0.132
	7/30	1029	0.147
	8/13	5003	0.534
	9/24	5077	1.68
	10/15	No water/no sample	no results
Rec. Ditch III	7/10	1007	ND
	7/30	1030	0.755
	8/13	5004	0.363
	9/24	5079	0.264
	10/15	5105	0.655
Rec. Ditch @ San Jons Rd.	7/10	1009	trace
	7/30	1031	trace
	8/13	5005	0.271
	9/24	5081	trace
	10/15	5107	0.290
Tembladero Slough @ Haro	7/10	1011	trace
	7/30	1033	ND
	8/13	5007	trace
	9/24	5083	Trace

Appendix IV. Chlorantraniliprole sampling results (continued)

Sampling Location	Date Sample Collected	Sample Number	Concentrations Detected (ppb)
	10/15	5109	0.135
Tembladero Slough @ Molera	7/10	1013	ND
	7/30	1034	ND
	8/13	5008	ND
	9/24	5085	ND
	10/15	5111	0.169
Salinas River @ Davis Rd.	7/10	1015	ND
	7/30	1036	ND
	8/13	5010	ND
	9/24	5087	ND
	10/15	5113	ND
Solomon Creek @ SR1	7/11	1017	0.479
	7/31	1038	0.102
	8/14	5012	0.453
	9/25	5089	0.213
	10/16	5119	0.351
Orcutt Creek	7/10	1019	trace
	7/10	1020 (dup)	trace
	7/31	1039	0.103
	8/14	5013	trace
	9/25	5091	0.138
	10/16	5121	0.172
	10/16	5122(dup)	0.175
Oso Flaco Creek	7/11	1021	0.7
	7/31	1041	0.261
	8/14	5014	0.585
	9/25	5093	1.64
	10/16	5123	1.25

Appendix IV. Chlorantraniliprole sampling results (continued)

Sampling Location	Date Sample Collected	Sample Number	Concentrations Detected (ppb)
Little Oso Flaco Creek	7/11	1023	ND
	7/31	1042	ND
	7/31	2043 (dup)	ND
	8/14	5015	ND
Arroyo Grande	7/11	1025	ND
	8/14	5016	trace
	10/16	5117	ND

Appendix IV. Summary of chlorantraniliprole detections in water. Lowest USEPA Benchmark for chlorantraniliprole is 4.5 ppb. Overall detection frequency is 75%. Reporting Limit (RL) is 0.1 ppb.

Site	Number of samples	Number of detections	Concentration range (ppb)	Detection frequency (%)(per site)	USEPA Benchmark exceeded
Quail Creek	6	6	0.139-9.71	100	1
Chualar Creek	6	6	0.244-2.90	100	0
Alisal Slough @Hartnell	4	4	0.534-1.68	100	0
Reclamation Ditch III	5	4	0.264-0.755	80	0
Reclamation Ditch @ San Jons Road	5	5	0.271-0.290	100	0
Tembladero Slough @ Haro Road	5	4	0.135	80	0
Tembladero Slough @ Molera Road	5	1	0.169	25	0
Salinas River @ Davis Road	5	0	0	0	0
Solomon Creek @ SR1	5	5	0.102-0.479	100	0
Orcutt Creek	6	6	0.103-0.175	100	0
Oso Flaco Creek	5	5	0.261-1.64	100	0
Little Oso Flaco Creek	4	0	0	0	0
Arroyo Grande Creek	3	1	trace	25	0

Appendix V: Analytical Method

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Environmental Analysis Section
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Title: Determination of Chlorantraniliprole in Surface Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole

1. Scope:

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

2. Principle:

The chlorantraniliprole is 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 to just dryness on a nitrogen evaporator and diluted to a final volume of 2 mL in methanol/ water (1:1). The extract is then transfer into an autosampler vial and analyzed by Liquid Chromatography coupled to a Linear Ion Trap Quadrupole 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.

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

4. Interferences:

There were no matrix interferences for chlorantraniliprole 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 HPLC coupled to a linear ion trap quadrupole mass spectrometry.

6. Reagents and Supplies:

6.1 Chlorantraniliprole CAS#500008-45-7
6.2 Methylene Chloride, nanograde or equivalent pesticide grade
6.3 Water, MS grade, Burdick & Jackson or equivalent
6.4 Methanol, MS grade, Burdick & Jackson or equivalent
6.5 Formic Acid, HPLC grade
6.6 Ammonium formate, reagent grade or equivalent
6.7 Separatory funnel, 1 L
6.8 Boiling flask, 500 mL
6.9 Sodium Sulfate, ACS grade
6.10 Funnels, long stem, 60, 100 mm I.D.
6.11 Graduated conical tubes with glass stopper, 15 mL
6.12 Glass wool, Pyrex® fiber glass slivers 8 microns
6.13 Disposable Pasteur pipettes, and other laboratory ware as needed
6.14 Recommended analytical column:
Waters SymmetryShieldRP$_{18}$ 5 µm, 3.9 x 150 mm column or equivalent
6:15 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.
6.16 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 An individual stock standard of 1.0 mg/mL was obtained from the CDFA/CAC Standards Repository. The standard was diluted to10 µg/mL with methanol. A working standard of 1 µg/mL was prepared from the 10 µg/mL standard with methanol. The standard was also used to dilute the following concentrations: 0.01, 0.025, 0.05, 0.1, 0.25 and 0.5 µg/mL in methanol. These standards were then diluted in half with water to make the following concentrations: 0.005, 0.0125, 0.025, 0.05, 0.125, 0.25 ug/mL 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 f or 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 insecticide 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 weighing 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 just dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then bring to a volume of 1.0 mL with methanol, mix well and add 1.0 mL of water, mix well. Transfer the final extract into 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 0.005, 0.0125, 0.025, 0.05, 0.125 and 0.25µg/mL.

10.2 Calibration is obtained using a quadratic regression with the correlation coefficient (r) equal to or greater than 0.995, with all levels weighted none.

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 Linear Ion Trap Quadrupole LC/MS/MS Mass Spectrometer

11.2.1 LC Instrument: Shimadzu LC30
Column: Waters SymmetryShieldRP_{18} 5 µm, 3.9 x 150 mm column
Column Temperature: 40 °C
Mobile Phase: Gradient
Solvent 1: Aqueous Solution

Solvent 2: Organic Solution
Gradient:

Time(min)	Flow rate (mL/min)	Solvent 1	Solvent 2
0.1	0.8	90.0	10.0
5.00	0.8	10.0	90.0
10.0	0.8	10.0	90.0
10.1	0.8	90.0	10.0
13.0	0.8	90.0	10.0

Injection Volume: 4.0 µL

11.2.2 Mass Spectrometry and Operating Parameters

Model:	ABSciex QTRAP 5500
Ion ProbeType:	Electrospray Ionization (ESI)
Ion Mode:	Positive
Curtain Gas:	40.00
Ion Spray Voltage:	5500.0
Temp: 500.0	
Ion Source Gas 1	40.0
Ion Source Gas 2	40.0
Collision:	Medium
Declustering Potential:	46.0
Entrance Potential:	10.0
Electron Multipler:	2400.0

Compound	Retention Time (min)	Precursor ion	Product Ion	Dwell (msec)	Collision Energy	Exit Potential
Chlorantraniliprole	6.84	484.000	**453.000**	150.00	21.00	36.00
		484.000	**286.000**	150.00	19.00	20.00
		484.000	**112.000**	150.00	81.00	8.00

Quantition ion is in bold.

12. Quality Control:

12.1 Method Detection Limits (MDL)

APPENDIX 2

Method Validation Data:

Analyte	Spike ppb	Recovery % set 1 set 1	set 2	set 3	set 4	set 5	%
Chlorantraniliprole	0.1	94.5	93.3	97.2	96.3	95.2	mean: 97.2
	0.25	100	102	100	102	107	SD: 4.26
	0.5	92.4	89.6	95.0	104	90.8	UCL: 110
	1.0	99.6	95.0	101	99.6	99.6	UWL: 106
	5.0	97.4	91.6	93.8	95.0	97.8	LWL: 88.7
							LCL: 84.4

APPENDIX 3

Storage Study Summary of Chlorantraniliprole in Surface Water

Analyte/Recovery %		day 0	day 2	day 4	day 7	day 15	day 21	day 28
Chlorantraniliprole	blank	ND	ND	ND	ND	ND	ND	ND
	QC Spike		91.2%	85.0%	90.9%	92.7%	87.4%	91.5%
	Spike 1	96.0%	90.1%	90.8%	87.3%	91.5%	89.5%	99.6%
	Spike 2	88.3%	89.8%	84.6%	95.9%9	90.7%	95.0%	82.7%
	Spike 3	84.8%	94.0%	93.7%	1.9%	93.4%	90.0%	93.7%
								5
								82.7%9
								3.7%

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Revision Log:

Date	What was revised? Why?