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

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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 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 4^{o} 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.

Table 2. Proposed analytical budget*

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>

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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.

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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.

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APPENDIX I

GIS Maps of Chlorantraniliprole Use in Proposed Sampling Areas