

California Environmental Protection Agency

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State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

**Final Report on Pesticide Ambient Air Monitoring  
For  
Propyzamide Application  
In Monterey County August 2009**

Prepared by

Steve Aston, Air Resources Engineer  
Special Purpose Monitoring Section  
Air Quality Surveillance Branch  
Monitoring and Laboratory Division

January 19, 2011  
Revised March 2011

This report has been reviewed by the staff of the California Air Resources Board (CARB) and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## Monitoring Report Approval

**Report Title:** Final Report on Pesticide Ambient Air Monitoring For Propyzamide Application in Monterey County August 2009

**Project Lead:** Steve Aston, Air Resource Engineer

**Approval:** The following monitoring report has been reviewed and approved by the Monitoring and Laboratory Division.

Signatures:

\_\_\_\_\_  
Mac McDougall, Manager  
Special Purpose Monitoring Section

\_\_\_\_\_  
Date

\_\_\_\_\_  
Kenneth R. Stroud, Chief  
Air Quality Surveillance Branch

\_\_\_\_\_  
Date

**Executive Summary**

**Final Report on Pesticide Ambient Air Monitoring  
For  
Propyzamide Application  
In Monterey County August 2009**

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) conducted ambient air monitoring for the pesticide propyzamide in Monterey County during August 2009. Propyzamide is applied directly to lettuce fields either by aerial application or ground spraying and is used as an herbicide to control a wide range of grasses and broad-leaved weeds.

Fifty seven field samples which includes seven (7) field spikes and two (2) laboratory spikes were collected from eight different locations around the perimeter of a 7.2 acre romaine lettuce field located in Monterey County. The propyzamide was applied by tractor at a rate of 2.0 lbs/acre and the pest target was Foxtail Barley.

The ambient air monitoring samples were collected by passing 3.0 liters per minute (LPM) of ambient air through XAD-2 sorbent tubes 1.5 meters above ground level.

There were a total of six (6) ambient sampling periods including a background as requested by DPR. At the end of each sampling period, the XAD tubes were placed in containers with an affixed identification label. At the end of each sampling period, the sample tubes were transported on dry ice to the ARB Sacramento Monitoring and Laboratory Division (MLD) laboratory for analysis. The samples were then stored in a freezer until analyzed.

The requested maximum estimated quantitation limit (EQL) of 5.0 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) requested by DPR was achieved by the ARB's lab which established an EQL of 0.35  $\mu\text{g}/\text{m}^3$  based on 24-hour collection at 3 LPM.

- Results indicated no propyzamide was detected in any of the field samples analyzed.
- The field spikes recoveries ranged from 75 to 92 % and blank results are reported at less than the method detection limit.

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## **1.0 Introduction**

At the request of the California Department of Pesticide Regulation (DPR) (2009 Memorandum, Warmerdam to Goldstene, Appendix F), the Air Resources Board (ARB) staff conducted sampling of airborne concentrations of propyzamide during an application in Monterey County.

Fifty seven field samples, including seven (7) field spikes and two (2) laboratory spikes were collected from eight different locations around the perimeter of a 7.2 acre romaine lettuce field from August 18 through August 21, 2009. The propyzamide was applied by tractor at a rate of 2.0 lbs/acre for approximately 30 minutes. The pest target was Foxtail Barley.

The monitoring was performed under the requirements of Food and Agricultural Code, Division 7, Chapter 3, Article 1.5 which requires the ARB, "...to document the level of airborne emissions...of pesticides that may be determined to pose a present or potential hazard...", when requested by the DPR.

## 2.0 Sampling Sites

Figure 1 Satellite Photo of Propyzamide Sampling Sites presents a Google map-view of the area surrounding the application field located in Monterey County and the locations of each sampler during the background, application and post-application sampling periods. See Appendix A for individual site photographs.

Eight (8) samplers were located approximately 20 meters from the treated edge of the field and were positioned down the length of the 7.2 acre romaine lettuce field.

During the background period the prevailing winds were coming out of the west, so the northeast corner of the field was chosen as the downwind site for quality control.



Figure 1  
Satellite Map of Propyzamide Sampling Sites

### 3.0 Methods

There were a total of six (6) ambient sampling periods including a background as requested by DPR. Air samples were taken before, during, and after the propyzamide application. There were three (3) daytime and two (2) overnight sampling periods. The start and end of the application occurred during early morning hours. The post-application samples were collected at early morning hours and removed one (1) hour before sunset. At the end of each sampling period, the XAD-2 sorbent tubes were placed in containers with an affixed identification label. The exposed sample XAD-sorbent tubes were transported on dry ice, as soon as possible, to the ARB Sacramento Monitoring and Laboratory Division (MLD) laboratory for analysis. The samples were then stored in a freezer until analyzed. Samples were collected by passing 3.0 liters per minute (LPM) of ambient air through XAD-2 sorbent tubes 1.5 meters above ground level as shown in (Figure 2), Ambient Air Sampler.



Figure 2  
Ambient Air Sampler

An AALBORG certified mass flow meter was used to measure and adjust sample flow rates. The flow rates were set to 3.0 lpm, as measured using a digital mass flow meter (MFM) scaled from 0-10 Lpm before the start of each sampling period.



The flow rate was checked, using the MFM, at the beginning and the end of each period. Samplers were leak checked prior to each sampling period with the sampling tubes installed. Any change in the flow rates were recorded in the field logbook. The field logbook was also used to record start and stop times, start and stop flow rates, start and stop counter readings, sample identifications and any other significant data.

In addition to ambient air samples, quality control samples consisted of collocated samples and field spikes.

For details of the monitoring method, please refer to Appendix B, "Protocol for the Ambient Air Monitoring of Propyzamide" (dated June 13, 2008). There were no significant deviations from this protocol.

Collected samples were analyzed by the Special Analysis Laboratory Section of MLD's Northern Laboratory Branch using a gas chromatography analyzer with an electron capture detector (see Appendix C).

#### **4.0 Results**

Propyzamide pesticide results indicated no propyzamide was detected in any of the field samples analyzed.

The prevailing winds were coming out of the west, so the northeast corner of the field was chosen as the downwind site for quality control.

The following abbreviation scheme is used to identify individual samples and sampling events.

#### **Site/Sample Identification**

Ambient Site Naming:

NE 1-5	Northeast Corner of Field
NE 1C-5C	Northeast Corner of Field Co-located
SE 1-5	Southeast Corner of Field
SE2 1-5	Southeast Side of Field
SW2 1-5	Southwest Side of Field
SW 1-5	Southwest Corner of Field
NW 1-5	Northwest Corner of Field
NW2 1-5	Northwest Side of Field
NE2 1-5	Northeast Side of Field

Note: See Figure 1, Satellite Map of Propyzamide Sampling Sites

**Letter Abbreviations as follows:** FS = Field Spike                      CO= Co-located

Site	No	Sample ID	Date Analyzed	ug/sample	m <sup>3</sup>	ug/m <sup>3</sup>
NE	1	BKG-NE-A	8/27/2009	< 0.057	3.05	< 0.019
	2	BKG-NE-C-B	8/27/2009	< 0.057	2.92	< 0.020
	7	NE-1	8/27/2009	< 0.057	0.20	< 0.285
	8	NE-1-C	8/27/2009	< 0.057	0.22	< 0.259
	16	NE2-1	8/28/2009	< 0.057	0.34	< 0.168
	17	NE-2	8/28/2009	< 0.057	2.39	< 0.024
	18	NE-2-C	8/28/2009	< 0.057	2.47	< 0.023
	26	NE2-2	8/28/2009	< 0.057	2.41	< 0.024
	27	NE-3	8/31/2009	< 0.057	2.27	< 0.025
	28	NE-3-C	8/31/2009	< 0.057	2.21	< 0.026
	36	NE2-3	8/31/2009	< 0.057	2.21	< 0.026
	37	NE-4	9/1/2009	< 0.057	1.81	< 0.031
	38	NE-4-C	9/1/2009	< 0.057	1.85	< 0.031
	46	NE2-4	9/1/2009	< 0.057	1.65	< 0.035
	48	NE-5	9/2/2009	< 0.057	2.57	< 0.022
	49	NE-5-C	9/2/2009	< 0.057	2.59	< 0.022
57	NE2-5	9/2/2009	< 0.057	2.44	< 0.023	

Table 1  
Result from the Northeast side of the field

Site	No	Sample ID	Date Analyzed	ug/sample	m <sup>3</sup>	ug/m <sup>3</sup>
SE	4	BKG-SE-A	8/27/2009	< 0.057	2.90	< 0.020
	10	SE-1	8/27/2009	< 0.057	0.23	< 0.248
	11	SE2-1	8/28/2009	< 0.057	0.26	< 0.219
	20	SE-2	8/28/2009	< 0.057	2.41	< 0.024
	21	SE2-2	8/28/2009	< 0.057	2.33	< 0.024
	30	SE-3	8/31/2009	< 0.057	2.20	< 0.026
	31	SE2-3	8/31/2009	< 0.057	1.67	< 0.034
	40	SE-4	9/1/2009	< 0.057	1.78	< 0.032
	41	SE2-4	9/1/2009	< 0.057	2.35	< 0.024
	51	SE-5	9/2/2009	< 0.057	2.47	< 0.023
	52	SE2-5	9/2/2009	< 0.057	2.47	< 0.023

Table 2  
Results from the Southeast side of the field

Site	No	Sample ID	Date Analyzed	ug/sample	m <sup>3</sup>	ug/m <sup>3</sup>
SW	5	BKG-SW	8/27/2009	< 0.057	2.92	< 0.020
	12	SW2-1	8/28/2009	< 0.057	0.29	< 0.197
	13	SW-1	8/28/2009	< 0.057	0.31	< 0.184
	22	SW2-2	8/28/2009	< 0.057	2.33	< 0.024
	23	SW-2	8/28/2009	< 0.057	2.41	< 0.024
	32	SW2-3	8/31/2009	< 0.057	2.18	< 0.026
	33	SW-3	8/31/2009	< 0.057	2.21	< 0.026
	42	SW2-4	9/1/2009	< 0.057	1.87	< 0.030
	43	SW-4	9/1/2009	< 0.057	1.89	< 0.030
	53	SW2-5	9/2/2009	< 0.057	2.33	< 0.024
54	SW-5	9/2/2009	< 0.057	2.47	< 0.023	

Table 3  
Results from the Southwest side of the field

Site	No	Sample ID	Date Analyzed	ug/sample	m <sup>3</sup>	ug/m <sup>3</sup>
NW	6	BKG-NW	8/27/2009	< 0.057	2.92	< 0.020
	14	NW-1	8/28/2009	< 0.057	0.32	< 0.178
	15	NW2-1	8/28/2009	< 0.057	0.36	< 0.158
	24	NW-2	8/28/2009	< 0.057	2.41	< 0.024
	25	NW2-2	8/28/2009	< 0.057	2.41	< 0.024
	34	NW-3	8/31/2009	< 0.057	2.29	< 0.025
	35	NW2-3	8/31/2009	< 0.057	2.20	< 0.026
	44	NW-4	9/1/2009	< 0.057	1.84	< 0.031
	45	NW2-4	9/1/2009	< 0.057	1.78	< 0.032
	55	NW-5	9/2/2009	< 0.057	2.44	< 0.023
56	NW2-5	9/2/2009	< 0.057	2.46	< 0.023	

Table 4  
Results from the Northwest side of the field

### **The Formula below refers to Monitoring Results**

$$\text{Propyzamide } (\mu\text{g}/\text{M}^3) = \frac{\text{Propyzamide } (\mu\text{g})}{\text{Sample}} \times \frac{\text{Sample}}{\text{Total Volume } (\text{M}^3)} = (\mu\text{g}/\text{M}^3)$$

### **5.0 Quality Control Results**

The quality control results from the Special Analysis Laboratory Section of MLD's Northern Laboratory Branch are presented in Appendix C, "Propyzamide Method Development and Analytical Results for Application Air Monitoring Samples in Monterey County."

Laboratory staff analyzes a system blank with each analytical batch, before the calibration, after the control and check samples, after every tenth sample, and after samples containing high levels of propyzamide or co-extracted contaminants. Staff defines the analytical batch as all the samples extracted together, but not to exceed 20.

- Method Blanks: Laboratory staff analyzed a method blank with each analytical batch. This is an XAD tube prepared and analyzed as described for the ambient samples. All method blanks were less than the MDL. The MDL level is 0.057  $\mu\text{g}/\text{sample}$
- Laboratory Control Sample (LCS): Laboratory staff analyzed a LCS with each analytical batch. The LCS is an XAD tube spiked with 3.0  $\mu\text{g}/\text{sample}$  of propyzamide. The LCS is extracted and analyzed as described in Appendix C. The LCS recoveries averaged 81% with a standard deviation of 15.6%. One LCS recovery was, 62%, which may be due to a bad spike.
- Continuing Calibration Verification Standards (CCV): Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth sample and at the end of an analytical batch. The CCV must be within  $\pm 25\%$  of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV standard for each analytical batch is 1.0  $\mu\text{g}/\text{ml}$ .
- Field Spikes: The average propyzamide recovery was 84.5% with a standard deviation of 6.1%. Values ranged 2.25 - 2.78  $\mu\text{g}/\text{sample}$  (75 - 92.8 % recovery).
- Laboratory Spikes: The low level laboratory spike recovery was 85% (2.55  $\mu\text{g}/\text{sample}$ ). The high level spike recovery was 72%. There were no designated trip spikes. Refer to Table 5.

No	Spikes	Date	ug/ml	ug/sample	% Recovery
-	Lab Spike	8/27/2009	0.851	2.552	85.1
-	Lab Spike H	9/1/2009	3.580	10.739	71.6
	Field Spikes				
3	BKG-NE-FS-A	8/27/2009	0.877	2.631	87.7
9	NE-1-FS	8/27/2009	0.866	2.597	86.6
19	NE-2-FS	8/28/2009	0.750	2.249	75.0
29	NE-3-FS	8/31/2009	0.928	2.784	92.8
39	NE-4-FS	9/1/2009	0.842	2.527	84.2
47	NE-4-FSH	9/1/2009	3.792	11.375	75.8
50	NE-5-FS	9/2/2009	0.810	2.429	81.0

Table 5  
Quality Control Data XAD Spikes for Field and Laboratory

## 6.0 Discussion

Fifty seven field samples were collected during the background, application and post-application sampling periods from eight different locations around the perimeter of a 7.2 acre romaine lettuce field located in Monterey County. All field samples collected and analyzed reported less than the propyzamide method detection limit.

The non-detection of propyzamide may possibly be attributed to the conditions during and immediately following the application of propyzamide. First of all, the application began at 2:00 A.M. when the winds were calm. Secondly, the field was watered right after the application potentially limiting off-site movement of propyzamide in the air.

# **APPENDIX A**

## **Site Photographs**



Propyzamide being applied to lettuce



Tractor applying Propyzamide on lettuce field



Tractor finishing up application

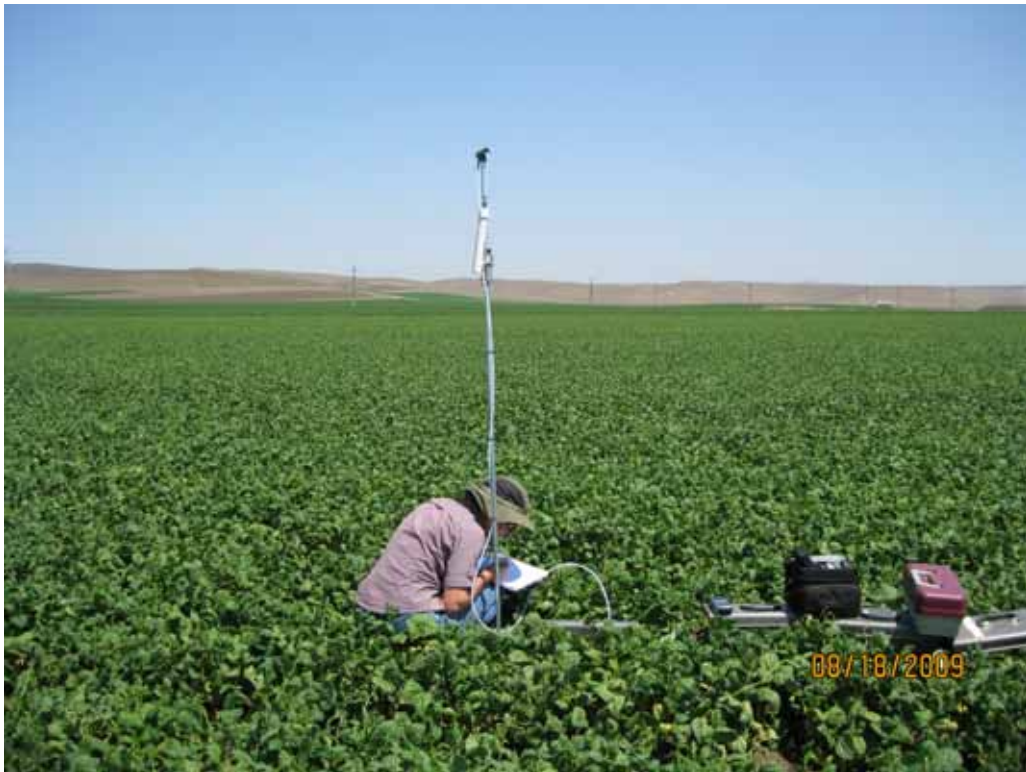


Sampling Site SW





Sampling Site NW



Sampling Site NW2



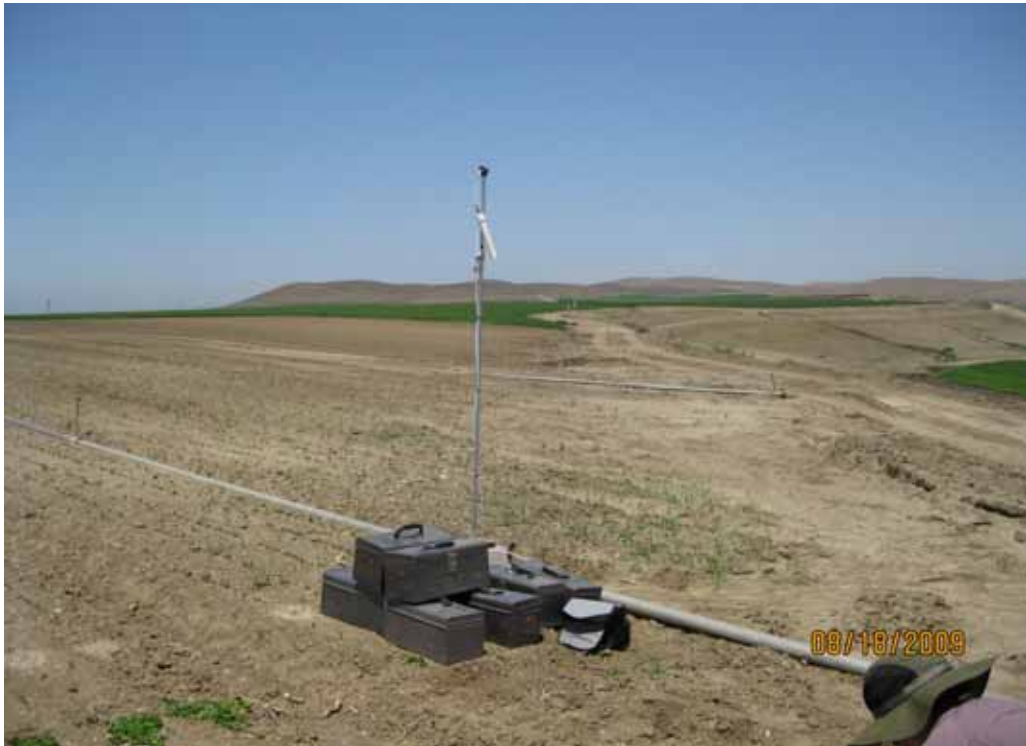
Sampling Site NW2



Sampling Site NE2



Sampling Site NE & Background



Sampling Site SE





AutoMet



Sampling Site SE2



Sampling Site SW2

# **APPENDIX B**

## **Sampling Protocol**



Monitoring and Laboratory Division  
Air Quality Surveillance Branch

**Protocol for the Application  
Air Monitoring of Propyzamide**

August 31, 2009

Prepared by:

Steve Aston  
Air Resources Engineer  
Special Purpose Monitoring Section

**Signatures:**

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Kenneth R. Stroud, Chief                      Date  
Air Quality Surveillance Branch  
Air Resources Board

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Cindy Castronovo, Chief                      Date  
Northern Laboratory Branch  
Air Resources Board

The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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APPENDIX A: STANDARD OPERATING PROCEDURE ANALYSIS FOR PROPYZAMIDE

APPENDIX B: USE RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT PROPYZAMIDE



## 1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR), (January 4, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff will determine airborne concentrations of propyzamide in Monterey County. Ambient air sampling will occur prior to, during and after an application of propyzamide. This monitoring will be performed to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of propyzamide as a selective herbicide on leaf and head lettuce for human consumption.

The study will consist of six (6) sampling periods: A background sample period, an application sampling period, a post application sampling period ending one (1) hour before sunset, two (2) overnight sampling periods and two (2) daytime sampling periods. The application sampling period will begin thirty minutes prior to the application of propyzamide. There will be a total of 58 sample XAD resin sorbent tubes (4 background, 6 field spikes, 1 trip spike, 1 trip blank, 6 collocated, 32 application and 10 spares).

Background sampling will begin one (1) to seven (7) days prior to the start of the propyzamide application and will sample for a minimum of 12 to 24 hours. Background sampling will consist of four (4) background samples, one (1) collocated sample and one (1) collocated sampler loaded with a field spike.

## 2.0 Chemical Properties of Propyzamide

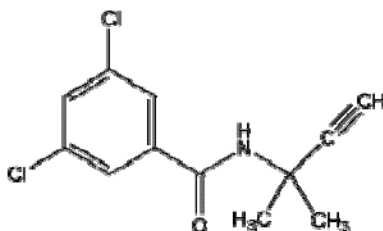


Figure 1  
Chemical structure of Propyzamide

Propyzamide is an odorless white or off-white crystalline solid (Kidd and James 1991). It is relatively stable and there should be little decomposition of this material (Berg 1986). Propyzamide is noncorrosive. It poses a fire hazard if exposed to heat or flame and explosion hazard in the presence of strong oxidizers. Thermal decomposition of propyzamide will release toxic oxides of nitrogen and carbon and toxic and corrosive fumes of chlorides (OHS 1991). It is soluble in water (15 mg/L at 25 °C), methanol (150 g/L), isopropanol (150 g/L), cyclohexanone (200 g/L), methyl ethyl ketone (200 g/L) and dimethyl sulfoxide

(330 g/L), moderately soluble in benzene, xylene and carbon tetrachloride and slightly soluble in petroleum ether (BCPC 2000). Table 1 lists some of its physical and chemical properties.

Chemical name	Propyzamide
Common name	Propyzamide, pronamide
Registered Trade names or other names <sup>†</sup>	Clanex, Kerb, Judo, Piza, RH-315 Rapier, Ronamid
CAS number	23950-58-5
CDPR Chemical Code	694
Empirical formula	C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> NO
Molecular weight	256.1
Appearance	Colorless, odorless powder
Vapor pressure	0.058 mPa (at 25 °C) 8.5 x 10 <sup>-5</sup> mmHg (at 25 °C)
Melting point	155 - 156 °C
Solubility	15 mg/L (ppm) (at 25 °C)
Henry's Law constant	9.8 x 10 <sup>-9</sup> (at 25 °C)
Octanol-water partition coefficient (log Kow)	3.1 – 3.2
Soil adsorption coefficient (Koc)	889 cm <sup>3</sup> /g
Hydrolysis half-life (20 °C)	42 days
Soil dissipation	53.3 days (17 °C) 53.7 days (23 °C)
Soil degradation half-life	392 days (aerobic conditions, 26 °C) 762 days (anaerobic conditions, 26 °C)
Stability	Decomposes above m.p., degraded photolytically on soil thin films, DT <sub>50</sub> 13-57 days in artificial sunlight. In solution for 28 days at 20 °C < 10% loss at pH 5-9
Breakdown products	3,5-dichlorobenzamide
Sources: CDPR; BCPC 2000; EXTTOXNET	
<sup>†</sup> <u>Disclaimer</u> : The mention of commercial products, their source, or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.	

Table 1  
Physical and chemical properties of Propyzamide

### **3.0 Project Goals and Objectives**

The goal of this monitoring project is monitoring to measure the concentrations of propyzamide in the ambient air prior to, during, and after a field application.

To achieve the project goal, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for application air sampling and DPR's requirements.
2. Appropriate application of sampling/monitoring equipment to determine application propyzamide concentrations.
3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
4. At the conclusion of the project, MLD will provide DPR with a final report with all relevant information and data of this project.

## 4.0 Contacts

Mac McDougall, Manager  
Special Purpose Monitoring Section  
916-327-4720  
[emcdouga@arb.ca.gov](mailto:emcdouga@arb.ca.gov)

Steve Aston, Air Resources Engineer  
Special Purpose Monitoring Section  
916-327-4724  
[saston@arb.ca.gov](mailto:saston@arb.ca.gov)

Pam Wolford, Senior Environmental Scientist  
Department of Pesticide Regulations  
Office (916) 324-4297  
[pwolford@cdpr.ca.gov](mailto:pwolford@cdpr.ca.gov)

Randy Segawa, Agriculture Program Supervisor  
Department of Pesticide Regulation  
324-4137  
[rsegawa@cdpr.ca.gov](mailto:rsegawa@cdpr.ca.gov)

Lynn Baker, Staff Air Pollution Specialist  
Special Purpose Monitoring Section  
Office 916-324-6997  
[lbaker@arb.ca.gov](mailto:lbaker@arb.ca.gov)

## 5.0 Study Location

The propyzamide application is planned for August 19, 2009 in King City, California which is located in Monterey County.

## 6.0 Study Design

The propyzamide sampling events, times and duration are listed below. For August 2009 the approximate sunrise time is 0445 PST and the approximately sunset time is 1930 PST.

The proposed sampling events are subject to change due to state work force furloughs and overtime policies. The post application sampling may be reduced or lengthened.

Sampling Events, Times and Durations are as follows:

- **Event 1:** Background sampling minimum 12 to 24 hours prior to application (Tuesday 18th).
- **Event 2:** Application sampling start time is approximately 30 minutes prior to application. Sampling will end one (1) hour after completion of application (Wednesday 19th).
- **Event 3:** Post application sampling starts one (1) hour after application and ends one (1) hour before sunset (Wednesday 19th).
- **Event 4:** Post application sampling overnight starts one (1) hour before sunset and ends one (1) hour after sunrise (Thursday 20th).
- **Event 5:** Post application sampling starts one (1) hour after sunrise and ends one (1) before sunset (Thursday 20th).
- **Event 6:** Post application sampling overnight one (1) hour before sunset and removed one (1) hour after sunrise (Friday 21st).

ARB personnel contacts Rio Farms representative to inform them that air sampling has ended and all ARB personnel and equipment have been removed.

#### Details of Sampling Events:

- a) Background sampling will start the day before the application with minimum sample duration of twelve hours, but no more than twenty four hours. The background samples will be removed prior to the start of the application. The background samplers will be located within 20 meters from the lettuce field which is going to be treated. The field spike will be spiked with a concentration of  $3.0 \text{ ug/m}^3$  of propyzamide.
- b) The propyzamide application sampling will consist of six (6) sampling events including the background. The application sampling event will start approximately thirty minutes prior to the start of propyzamide application. Sampling will continue until one (1) hour after the application is completed. A post application sampling period will immediately start and then end one (1) hour before sunset. The rest of the study will consist of two (2) overnight sampling events and two (2) daytime sampling events. Each overnight sampling event will start one (1) hour prior to sunset and end one (1) hour after sunrise. Each daytime sampling event will start one (1) hour after sunrise and end one (1) hour before sunset.
- c) There will be eight (8) sampling sites around the lettuce field. For a square field, four (4) sites will be located at each corner and four (4) sites will be located midway on each side. The estimated downwind site will have a collocated sample on the regular sampler. All sampler intakes will be 1.7 meters ( $67 \pm 6$  inches) above the ground. Samplers will be placed within 20 meters (66 feet) from the drip line of the foliage.
- d) Each air sampler will consist of an ARB Pesticide Stick Sampler (PS sampler), a rotameter to control the flow, rubber tubing to retain the XAD resin sorbent tube in the flow path, a rain/sun screen and a DC pump box with a battery box connected. The PS sampler is powered by 12 VDC gell cell batteries. After each sampling event the used battery will be replaced with a newly charged battery. Flows will be set at 3.0 lpm and the average of the start and stop flows shall be  $3.0 \text{ lpm} \pm 20\%$  (2.4 – 3.6 lpm). Figure 1 (Pesticide Stick Sampler) demonstrates an assembled sampler.

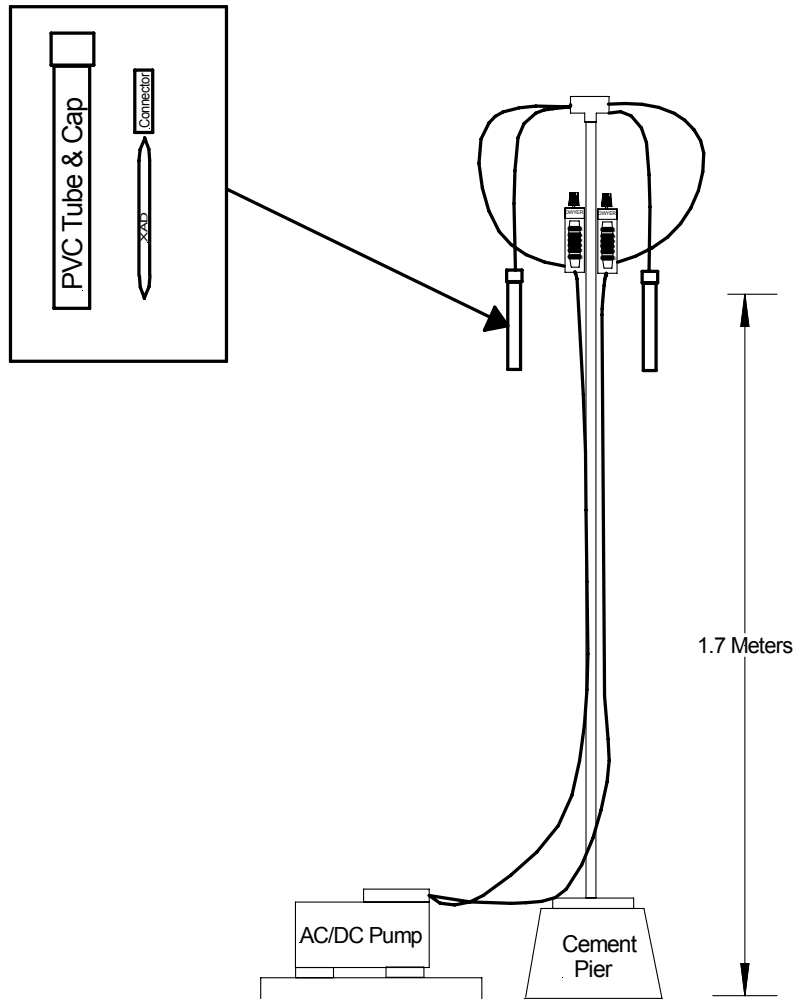


Figure 2  
Pesticide Stick Sampler

- e) In order to reduce direct pesticide exposure to ARB staff during the pesticide application event, all samplers will begin a minimum of thirty minutes prior to the start of the application. At the end of each sampling period the following general procedure will occur at each site; Flows will be verified, documentation completed, all XAD resin sorbent tubes will be removed, capped, labeled and placed in a freezer bag which will in turn be placed in a dry ice cooler, the battery replaced, a new XAD resin sorbent tube installed and flows adjusted if necessary. Field notes and observations will be recorded (such as propyzamide application flow rate and total amount of propyzamide applied).

- f) Meteorological data will be collected using a Met One Instruments' AutoMet Digital Meteorological Monitoring System located on a trailer with a crank up tower. The AutoMet will be located no closer than twenty meters from the edge of the field being monitored. The meteorological sensors will be installed between 5.9 and 6.9 meters above the ground. The AutoMet station will continuously measure and record 5 minute averages for wind speed, wind direction, ambient temperature and percent relative humidity throughout the background, application and post application sampling periods.
  
- g) The MLD will provide DPR with a final report containing all relevant information, collected data and analytical results gathered during the course of the study.



## 7.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will hand-carry samples to and from MLD's laboratory in Sacramento, and to and from the sampling location. The samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

At each sampling site, the operator will assure all required sample collection information is recorded on the affixed XAD resin sorbent tube identification labels and field log sheets. After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory. The sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. These samples will be stored in the freezer or extracted/analyzed immediately. Samples are collected in the field with a flow rate of 3.0 liters per minute (lpm).

All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with XAD resin tubes. NLB will perform analyses for propyzamide on collected application samples and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of Propyzamide). The SOP is included in this Protocol as Appendix A.

The following XAD resin tube validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time:** Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established holding time will be invalidated by the Laboratory.
2. **Duplicate Analysis:** Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Replicate analysis shall be performed on every tenth sample (10%) per analytical batch sequence (excluding standard controls and other laboratory quality control data). Replicate analysis shall be performed on every tenth (10%) per analytical batch sequence (excluding standard controls and other laboratory quality control data). Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL):** MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.
4. **Analytical Linear Range:** Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

## 8.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Auto met portable meteorology system having calibrated sensors to measuring 5 minute averages for wind speed, direction, ambient temperature, and relative humidity w/built-in data logger.
(1)	Measuring Wheel
(1)	200 ft measuring tape
(1)	Tripod and compass
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-5 Lpm.
(12)	Sampling trees/pumps
(68)	XAD resin tubes (4 background, 40 application, 6 collocated, 6 field spikes, 1 trip spike, 1 trip blank, and 10 spares).
(82)	Batteries
(4)	Power Strips
(2)	Extension cords
(1)	Miscellaneous tubing and fittings
(1)	Box of banana plug wires for pump and battery connection
(8)	Battery Chargers

## 9.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

<http://www.arb.ca.gov/aqdas/amwmn.php?c=5&t=sop>

Each XAD resin tube will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

**Field Spike (FS):** Six (6) field spikes will be prepared by the laboratory by injecting a XAD resin tube with 3 nanograms (ng) of propyzamide. The field spikes will be installed for each sampling event including the background. and will be located next to the collocated air sampler.

**Trip Spike (TS):** A trip spike will be prepared by the laboratory by injecting a XAD resin tube at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

**Field Blank (FB):** A field blank will be a XAD resin tube opened in the field and return but is not installed onto a sampler.

**Trip Blank (TB):** A trip blank will be an unopened XAD resin tube to the field and return but is not installed onto a sampler.

**Collocated (CO):** Collocated (side-by-side) air samplers will operate at the predominantly downwind sample site throughout all sampling events.

## Site/Sample Identification

The propyzamide application sampling sites will be named accordingly for the background, ambient, application, and post application as follows:

### Background Site Naming:

Site-1-BKGD  
Site-1CO-BKGD  
Site-1-FS

### Application Site Naming:

Site-1N      Site-2NEC  
Site-3E      Site-4SEC  
Site-5S      Site-6SWC  
Site-7W      Site-8NWC

### Letter Abbreviations as follows

N = North Side  
S = South Side  
W = West Side  
E = East Side  
BKGD = Background Sample  
FS = Field Spike  
CO= Co-located  
NEC = NE Corner Sample  
NWC = NW Corner Sample  
SEC = SE Corner Sample  
SWC = SW Corner Sample  
TS = Trip Spike  
TB = Trip Blank  
FB = Field Blank

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will ensure accurate field and lab data collection.

## 10.0 Deliverables

### 10.1 Air Quality Surveillance Branch Deliverables

Within 60 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

- 1) Sampling Protocol.
- 2) Personnel Contact List.
- 3) Site Maps.
- 4) Site Photographs.
- 5) Site Descriptions and Measurements  
Site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, and total pounds of propyzamide applied per acre.
- 6) The distance and direction of the sampler to the treated or potentially treated fields.
- 7) A map of the monitoring site locations.
- 8) Sample Summary Table.
- 9) Field Sample Log.
- 10) Laboratory Analysis Reports with calculations in electronic format.
- 11) Met Station and Sampler Calibration Reports.
- 12) Transfer Standards' Certification Reports.
- 13) Disk containing electronic files of 5-minute averaged Meteorological Data.
- 14) Disk containing electronic files of Report.

Also provided in the application monitoring report:

- 1) An accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field.
- 2) An accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, etc..
- 3) Meteorological data collected at a minimum of 1 minute intervals (averages) including wind speed, wind direction, humidity, air temperature, and comments regarding degree of cloud cover.
- 4) The elevation of each sampling station with respect to the field.
- 5) The orientation of the field with respect to North (identified as either true or magnetic north). Samples collected during fog episodes will be designated as such.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

## 10.2 Northern Laboratory Branch (NLB) Deliverables

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

- 1) Analytical result table(s) to include:
  - a. Sample identification (name).
  - b. Date sample received from field.
  - c. Date sample analyzed.
  - d. Dilution ratio (if applicable)
  - e. Analytical results.
  - f. Quality control results.
- 2) Sample equations used in calculating analytical results.
- 3) Table of duplicate/replicate results including calculated relative percent difference (RPD).
- 4) Table of analytical results from all field spikes.
- 5) Table of analytical results from all trip and laboratory spikes including percent recoveries.
- 6) Table of analytical results from all trip blanks.
- 7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.
- 8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
- 9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

## **APPENDIX A:**

### **Standard Operating Procedure Analyses for Propyzamide**

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for propyzamide collected by the XAD resin tube method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of Propyzamide.

**SEE REPORT APPENDIX C**

## **APPENDIX B:**

### **USE INFORMATION AND APPLICATION MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT PROPYZAMIDE**

[http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/air\\_rpt\\_propyzamide.pdf](http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/air_rpt_propyzamide.pdf)



# **APPENDIX C**

## **Laboratory Results Report**

California Environmental Protection Agency

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**Propyzamide Method Development and Analytical Results for Application  
Air Monitoring Samples in Monterey County**

**DATE: October 29, 2009**

**Prepared by  
T.E. Houston, PhD  
Air Pollution Specialist**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

**Reviewed and Approved by**

**Russell Grace, Manager  
Special Analysis Section**

This report has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

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## 1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) conduct application air monitoring for propyzamide. This report covers the method development, analytical and quality assurance results for propyzamide during an application in King City, Monterey County in August 2009. DPR requested a method estimated quantitation limit (EQL) of 5.0 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). The EQL achieved during this project was  $0.35 \mu\text{g}/\text{m}^3$  based on 24-hour collection at three liters per minute (LPM).

## 2.0 METHOD DEVELOPMENT

### 2.1 Overview

Application air samples are collected on XAD-2 sorbent tubes. Sampled tubes are stored at four (4) degrees centigrade ( $^{\circ}\text{C}$ ) or lower prior to extraction. Sample tubes are extracted using pesticide grade ethyl acetate. Sample analysis is performed using a gas chromatograph/electron capture detector. Analysis and quantitation uses external standard method for instrument calibration. Estimated quantitation level for this method is  $0.35 \mu\text{g}/\text{m}^3$  prior to any sample dilution for sampling at three LPM and a three-milliliter (ml) extraction volume.

### 2.2 Instrument Reproducibility

Five individual injections of 1.0 microliters ( $\mu\text{l}$ ) each were made of propyzamide at three concentrations (low, medium, and high) in order to establish the reproducibility of the instrument. Table 1 summarizes the results for the three levels with the average and standard deviation.

**Table 1: Instrument reproducibility**

	Low	Medium	High
Average	0.490	2.957	5.148
Standard Deviation	0.003	0.074	0.273
Relative Standard Deviation	0.547	2.490	5.300

### 2.3 Calibration Curve

Laboratory staff used standard concentrations of 0.5, 1.0, 2.0, 3.0 and 5.0  $\mu\text{g}/\text{ml}$  for a five-point calibration curve. All calibration curves performed have an  $r^2$  (variance) greater than or equal to 0.995. External calibration was run for each sample set and was linear in this range.

#### 2.4. Minimum Detection Limit (MDL)

The MDL calculation follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (0.5 µg/ml), the MDL and EQL for a three-ml extract is calculated as follows:

*s = the standard deviation of the concentration calculated for the seven replicate spikes.*  
*For propyzamide: s = 0.006 µg/ml*  
*MDL = (3.14) x (s) = (3.14) x (0.006) = 0.018 µg/ml.*  
*MDL for total µg/sample = 0.057 µg/sample*  
*EQL = (5) x (MDL) = (5) x (0.018) = 0.089 µg/ml*  
*EQL for total µg/sample = 0.267 µg/sample*

Based on a total collection volume of 4.32 m<sup>3</sup> the EQL would be 0.06 µg/m<sup>3</sup>. While a lower EQL is theoretically possible based on the above results, the low standard of the calibration (0.5 µg/ml) will be used corresponding to an EQL of 0.35 µg/m<sup>3</sup>. Staff report results above the EQL to two significant figures. Results below the EQL but greater than or equal to the MDL are reported to one significant figure. Results less than MDL are reported as the calculated MDL to one significant figure.

#### 2.5. Collection and Extraction Efficiency (Recovery)

Spiked XAD tubes were used to determine method field recovery. The tubes were spiked with 1.5 µg and 15 µg of propyzamide standard. A spiked tube was placed on a field sampler and sampled at approximately three LPM for 24 hours at ambient temperature. The recoveries for propyzamide were 98% at 0.5 µg and 93% at 5 µg.

#### 2.6. Storage Stability

Laboratory staff completed a storage stability study which ran for 21 days with XAD tubes being tested at 0, 7, 14, and 21 days. Table 2 summarizes the results of the storage stability test. Laboratory staff analyzed all field samples within 14 days of collection.

**Table 2: Storage stability**

Day	Average low % Recovery	Average high % Recovery
0	96.9	94.8
7	100.6	91.2
14	106.3	89.4
21	102.7	88.4

## 2.7. Breakthrough

Propyzamide spikes at 10 µg/ml were placed on a sampler. Recovery was 87% and 92%, with no detection in the back section of the tubes.

## 3.0 PROPYZAMIDE APPLICATION AIR MONITORING SAMPLE RESULTS

The laboratory received a total of 57 application samples including seven field spikes, one of which was a high level spike. The samples included background, sampling during application, and four post-application samplings. There was no propyzamide detected in any of the samples submitted. Table 3 presents the results of the analysis by site.

## 4.0 ANALYTICAL QUALITY CONTROL SAMPLES

### 4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch, before the calibration, after the control and check samples, and after every tenth sample, and after samples containing high levels of propyzamide or co-extracted contaminants. Staff defines the analytical batch as all the samples extracted together, but not to exceed 20 samples. The system blank is run to insure the solvent and instrument do not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

### 4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This is an XAD tube prepared and analyzed as described for the ambient samples. All method blanks were less than the MDL.

### 4.3 Laboratory Control Sample (LCS)

Laboratory staff analyzed a LCS with each analytical batch. The LCS is an XAD tube spiked with 3.0 µg/sample of propyzamide. The LCS is extracted and analyzed as described for the samples. The LCS recoveries averaged 81% with a standard deviation of 15.6%. One of the LCS was low, 62%, which may be due to a bad spike.

### 4.4 Continuing Calibration Verification Standards (CCV)

Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth sample and at the end of an analytical batch. The CCV must be within  $\pm 25\%$  of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV standard for each analytical batch is 1.0 µg/ml.

#### 4.5 *Laboratory Duplicates*

Laboratory duplicate was a replicate of one of the extracted samples for a given analytical batch.

### 5.0 **FIELD, TRIP, AND LABORATORY SPIKES AND TRIP BLANKS**

Seven field spikes and two laboratory spikes were analyzed. There was no designated trip spike; all spikes sent to the field were placed on samplers. The field spikes were on samplers for the respective events analyzed: background, during application, and the four post-application times. Laboratory staff prepared the spikes at 3.0 µg of propyzamide per sample. One of the field spikes and one of the laboratory spikes was at a concentration of 15 µg. Table 4 presents the results for the quality control data.

#### 5.1 *Field Spikes*

The average propyzamide recovery was 84.5% with a standard deviation of 6.1%. Values ranged 2.25-2.78 µg/sample. The high spike recovery during the third post-application sampling was 76%.

#### 5.2 *Laboratory Spikes*

The laboratory spike recovery was 85% (2.55 µg/sample). The high spike recovery was 72%. There were no designated trip spikes.

#### 5.3 *Trip Blanks*

There were no designated trip blanks for this analysis.

### 6.0 **DISCUSSION**

The Laboratory received 57 field samples, including seven field spikes. Two laboratory spikes were prepared and held at the laboratory at the same time the field spikes were prepared and sent. There was no propyzamide detected in any of the field samples at an EQL over ten times lower than that requested. Recovery of the field spikes was as expected for the amounts and all the quality control samples were in established parameters.

**Table 3: Propyzamide Application Air Monitoring Results by Site for Monterey County 2009.**

Site	No	Client ID	Date Analyzed	ug/ml	ug/sample
NE	1	BKG-NE-A	8/27/2009	ND	ND
	2	BKG-NE-C-B	8/27/2009	ND	ND
	7	NE-1	8/27/2009	ND	ND
	8	NE-1-C	8/27/2009	ND	ND
	16	NE2-1	8/28/2009	ND	ND
	17	NE-2	8/28/2009	ND	ND
	18	NE-2-C	8/28/2009	ND	ND
	26	NE2-2	8/28/2009	ND	ND
	27	NE-3	8/31/2009	ND	ND
	28	NE-3-C	8/31/2009	ND	ND
	36	NE2-3	8/31/2009	ND	ND
	37	NE-4	9/1/2009	ND	ND
	38	NE-4-C	9/1/2009	ND	ND
	46	NE2-4	9/1/2009	ND	ND
	48	NE-5	9/2/2009	ND	ND
	49	NE-5-C	9/2/2009	ND	ND
	57	NE2-5	9/2/2009	ND	ND

Site	No	Client ID	Date Analyzed	ug/ml	ug/sample
SE	4	BKG-SE-A	8/27/2009	ND	ND
	10	SE-1	8/27/2009	ND	ND
	11	SE2-1	8/28/2009	ND	ND
	20	SE-2	8/28/2009	ND	ND
	21	SE2-2	8/28/2009	ND	ND
	30	SE-3	8/31/2009	ND	ND
	31	SE2-3	8/31/2009	ND	ND
	40	SE-4	9/1/2009	ND	ND
	41	SE2-4	9/1/2009	ND	ND
	51	SE-5	9/2/2009	ND	ND
	52	SE2-5	9/2/2009	ND	ND



Site	No	Client ID	Date Analyzed	ug/ml	ug/sample
SW	5	BKG-SW	8/27/2009	ND	ND
	12	SW2-1	8/28/2009	ND	ND
	13	SW-1	8/28/2009	ND	ND
	22	SW2-2	8/28/2009	ND	ND
	23	SW-2	8/28/2009	ND	ND
	32	SW2-3	8/31/2009	ND	ND
	33	SW-3	8/31/2009	ND	ND
	42	SW2-4	9/1/2009	ND	ND
	43	SW-4	9/1/2009	ND	ND
	53	SW2-5	9/2/2009	ND	ND
	54	SW-5	9/2/2009	ND	ND

Site	No	Client ID	Date Analyzed	ug/ml	ug/sample
NW	6	BKG-NW	8/27/2009	ND	ND
	14	NW-1	8/28/2009	ND	ND
	15	NW2-1	8/28/2009	ND	ND
	24	NW-2	8/28/2009	ND	ND
	25	NW2-2	8/28/2009	ND	ND
	34	NW-3	8/31/2009	ND	ND
	35	NW2-3	8/31/2009	ND	ND
	44	NW-4	9/1/2009	ND	ND
	45	NW2-4	9/1/2009	ND	ND
	55	NW-5	9/2/2009	ND	ND
	56	NW2-5	9/2/2009	ND	ND

**Table 4: Quality Control Data XAD Spikes for Field, Trip, and Laboratory.**

<b>No</b>	<b>Spikes</b>	<b>Date</b>	<b>ug/ml</b>	<b>ug/sample</b>	<b>% Recovery</b>
-	Lab Spike	8/27/2009	0.851	2.552	85.1
-	Lab Spike H	9/1/2009	3.580	10.739	71.6
	Field Spikes				
3	BKG-NE-FS-A	8/27/2009	0.877	2.631	87.7
9	NE-1-FS	8/27/2009	0.866	2.597	86.6
19	NE-2-FS	8/28/2009	0.750	2.249	75.0
29	NE-3-FS	8/31/2009	0.928	2.784	92.8
39	NE-4-FS	9/1/2009	0.842	2.527	84.2
47	NE-4-FSH	9/1/2009	3.792	11.375	75.8
50	NE-5-FS	9/2/2009	0.810	2.429	81.0

Notes:

Spikes were at 3.0 µg/sample.

High Spikes at 15 µg/sample.

**Appendix A:**  
**Standard Operating Procedure for Propyzamide**

California Environmental Protection Agency

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# Air Resources Board

**Standard Operating Procedure  
Sampling and Analysis of Propyzamide**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

**June 2009**

**Version 1**

**Approved by:**

**Russell Grace, Manager  
Special Analysis Section**

## 1. SCOPE

This is a gas chromatography/electron capture detector (GC/ECD) method for the determination of propyzamide in ambient and application air sampling.

## 2. SUMMARY OF METHOD

Ambient and application air samples are collected on XAD-2 sorbent tubes. Sampled tubes are stored at four (4) degrees centigrade (°C) or lower prior to extraction. Sample tubes are extracted using pesticide grade ethyl acetate. Sample analysis is performed using a GC/ECD. Sample analysis and quantitation uses external standard method for instrument calibration. Estimated quantitation level (EQL) for this method is approximately 5.0 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) prior to any sample dilution.

## 3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 tubes that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

## 4. EQUIPMENT AND CONDITIONS

### A. Instrumentation

- Agilent Technologies 7890 Series gas chromatograph with Agilent Model 7683B injector.
- Column: Agilent HP-5, 30 meter, 0.32mm I.D., 0.25 micron film thickness, with helium as carrier gas at constant flow and nitrogen as the makeup gas at 25 ml/min.
- GC temperature program: initial 100° C, initial time 2 minutes, to 260° C @ 12° C/min, hold 2 minutes.
- Inlet temperature 260° C; splitless.
- Detector temperature 325° C.

### B. Auxiliary Apparatus

- XAD-2 tubes (400/200 mg) (SKC cat # 226-30-6) or equivalent
- Glass amber vials, 2-ml capacity with septum caps.

## C. Reagents

- Ethyl Acetate(EtAc) (B&J brand HPLC grade or equivalent)
- Propyzamide 98.1%, Chem Services PS-349

## 5. SAMPLE COLLECTION

- a) Samples are collected in the field with a maximum flow rate of three (3) liters per minute (lpm).
- b) After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.
- c) Samples are stored at 4° C or less until ready for analysis.

## 6. SAMPLE EXTRACTON

- a) Prepare a method blank and laboratory control sample (LCS) tube with every batch of field samples not to exceed twenty (20) samples in an analytical batch. The LCS is spiked with 3 µg of propyzamide before extraction.
- b) Carefully score and break the sample XAD-2 tube just in front of the glass wool plug on the primary section.
- c) Remove the glass wool plug using forceps. Pour the XAD-2 resin from the primary section into an 8 ml glass vial.
- d) Score the tube just in front of the secondary section glass wool. Retain the secondary section for later analysis to check for breakthrough.
- e) Using three (3.0) ml of EtAc carefully rinse the inside of the primary section into the glass vial. Cap securely.
- f) The extracts are allowed to sit at room temperature for 1 hour. The extracts are ready for analysis or if not analyzed are stored in a refrigerator at 4° C.

## 7. ANALYSIS OF SAMPLES

- a) Transfer approximately 0.25 ml of the sample extract into a 1.5-ml autosampler vial equipped with a 0.25 ml insert. Sample extract is now ready for analysis.
- b) A 1-µl injection volume will be used for all analyses.
- c) Perform a calibration curve using concentrations at or near the EQL to approximately 10 times higher. At least five (5) points must be analyzed to establish a calibration curve.
- d) Prepare a sample sequence for the GC/ECD. The sequence should include a system blank and a calibration control standard, for every ten (10) samples analyzed. If this batch of samples includes a method blank

and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.

- e) Because of the nature of the XAD-2 tube, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every ten (10) to twenty (20) samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.
- f) Review and edit the quantitation reports as needed.
- g) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.
- h) The final results will be adjusted by an appropriate dilution factor and reported in  $\mu\text{g/ml}$ .
- i) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc. } (\mu\text{g/m}^3) = \frac{\text{Extract Conc. } (\mu\text{g/ml}) \times 3 \text{ ml}}{\text{Air Volume Sampled } (\text{m}^3)}$$

- j) Given instrument sensitivity and a maximum sample volume of  $4.32 \text{ m}^3$  the EQL for this method will be approximately  $0.35 \mu\text{g/m}^3$ .

## 8. QUALITY ASSURANCE

- a) A system blank must be analyzed with each batch of samples. The system blank is an aliquot of the solvent used to extract the samples. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, after the calibration curve, or just prior to sample analysis.
- b) A minimum five point calibration will be run with each sample batch.
- c) A calibration control will be run after the calibration, every tenth sample and at the end of the sample batch to verify system linearity. The calibration control values must be within 25% of the actual value.
- d) A method blank will be run with each sample batch. The method blank is a blank solvent that is run through the entire method. The analyte concentration must be below the MDL established for the method.
- e) A LCS will be run with every sample batch. The LCS analyte concentration should fall within the lower half of the calibration curve. The LCS stock standard should come from a different source or lot than the daily calibration standards. If not available then this should be prepared separately from the calibration curve. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS

is outside these limits then the samples in the analytical batch must be reanalyzed.

- f) Run specific quality control samples, such as field spikes, trip spikes, and laboratory spikes prior to the field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over.

## **9. Safety**

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.



## **APPENDIX D**

### **Sample Field Log Sheets**

### FILTER FIELD LOG SHEET

Project: Propyzamide Pesticide Application Air Monitoring  
 Start Flow Set: 3.0 ±0.1 lpm End Flow Criteria: 3.0 lpm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time		Counter		TOTAL	Mass Flow Meter		Corrected Average Flow	Weather K,P,C,F&R		Initials			
			Entry Example (6/14/08 13:42)		Start	End	TIME	Display			Start	End	Start	End	Start	End
			Start	End			HOURS	Start	End							
001	BKG-NE-A	4673	8/18/09 9:53	8/19/09 2:07	1158.8	1175.2	16.4	2.83	2.99	3.1	K	F-C	SRR	SRR		
002	BKG-NE-C-B	3021	8/18/09 9:42	8/19/09 2:07	1263.2	1279.4	16.2	2.83	2.85	3.0	K	F-C	SRR	SRR		
003	BKG-NE-FS-A	4644	8/18/09 9:42	8/19/09 2:07	654.1	670.5	16.4	2.83	3.15	3.2	K	F-C	SRR	SRR		
004	BKG-SE-A	4654	8/18/09 10:13	8/19/09 2:23	610.3	626.4	16.1	2.83	2.84	3.0	K	F-C	SRR	SRR		
005	BKG-SW	4656	8/18/09 10:21	8/19/09 2:33	638.7	654.9	16.2	2.83	2.83	3.0	K	F-C	SRR	SRR		
006	BKG-NW	4645	8/18/09 10:24	8/19/09 2:41	943.2	959.4	16.2	2.83	2.87	3.0	K	F-C	SRR	SRR		
007	NE-1	4673	8/19/09 3:01	8/19/09 4:10	1175.2	1176.3	1.1	2.83	2.86	3.0	F-C	F-C	SRR	SRR		
008	NE-1C	3021	8/19/09 3:01	8/19/09 4:10	1279.4	1280.6	1.2	2.83	2.88	3.0	F-C	F-C	SRR	SRR		
009	NE-1FS	4644	8/19/09 3:01	8/19/09 4:10	670.5	671.6	1.1	2.83	2.91	3.0	F-C	F-C	SRR	SRR		
010	SE-1	4654	8/19/09 3:01	8/19/09 4:18	626.4	627.7	1.3	2.83	2.86	3.0	F-C	P	SRR	SRR		
011	SE2-1	4664	8/19/09 2:59	8/19/09 4:25	452.7	454.1	1.4	2.83	2.94	3.1	F-C	P	MM	SRR		
012	SW2-1	4651	8/19/09 2:57	8/19/09 4:30	793.5	795.1	1.6	2.83	2.84	3.0	F-C	P	MM	SRR		
013	SW-1	4656	8/19/09 2:55	8/19/09 4:37	654.9	656.6	1.7	2.83	2.86	3.0	F-C	P	SRR	SRR		
014	NW-1	4645	8/19/09 2:55	8/19/09 4:40	959.4	961.2	1.8	2.83	2.85	3.0	F-C	P	SRR	SRR		
015	NW2-1	2974	8/19/09 2:57	8/19/09 4:47	1383.8	1385.8	2.0	2.83	2.86	3.0	F-C	P	MM	SRR		
016	NE2-1	4657	8/19/09 2:59	8/19/09 4:55	715.7	717.6	1.9	2.83	2.81	3.0	F-C	P	MM	SRR		
017	NE-2	4673	8/19/09 4:14	8/19/09 17:32	1176.3	1189.6	13.3	2.83	2.89	3.0	F-C	K	SRR	SRR		
018	NE-2C	3021	8/19/09 4:14	8/19/09 17:32	1280.6	1293.9	13.3	2.83	2.92	3.1	F-C	K	SRR	SRR		
019	NE-2FS	4644	8/19/09 4:14	8/19/09 17:32	671.6	684.9	13.3	2.83	2.84	3.0	F-C	K	SRR	SRR		

MFM Used #: 2E+07 Slope: 1.104 Intercept: -0.120

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

## FILTER FIELD LOG SHEET

Project: Propyzamide Pesticide Application Air Monitoring  
 Start Flow Set: 3.0 ±0.1 lpm    End Flow Criteria: 3.0 lpm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time		Counter		TOTAL TIME HOURS	Mass Flow Meter Display		Corrected Average Flow	Weather K,P,C,F&R		Initials	
			Entry Example (6/14/08 13:42)		Start	End		Start	End		Start	End	Start	End
			Start	End										
020	SE-2	4654	8/19/09 4:19	8/19/09 17:34	627.7	641.1	13.4	2.83	2.89	3.0	F-C	K	SRR	SRR
021	SE2-2	4664	8/19/09 4:25	8/19/09 17:50	454.1	467.5	13.4	2.83	2.69	2.9	F-C	K	SRR	SRR
022	SW2-2	4651	8/19/09 4:30	8/19/09 17:56	795.1	808.5	13.4	2.83	2.73	2.9	F-C	K	SRR	SRR
023	SW-2	4656	8/19/09 4:37	8/19/09 18:02	656.6	670.0	13.4	2.83	2.74	3.0	F-C	K	SRR	SRR
024	NW-2	4645	8/19/09 4:40	8/19/09 18:08	961.2	974.6	13.4	2.83	2.81	3.0	F-C	K	SRR	SRR
025	NW2-2	2974	8/19/09 4:47	8/19/09 18:15	1385.8	1399.2	13.4	2.83	2.81	3.0	F-C	K	SRR	SRR
026	NE2-2	4657	8/19/09 4:55	8/19/09 18:21	717.6	731.0	13.4	2.83	2.81	3.0	F-C	K	SRR	SRR
027	NE-3	4673	8/19/09 17:35	8/20/09 5:49	1189.6	1201.8	12.2	2.83	2.95	3.1	K	C	SRR	SRR
028	NE-3C	3021	8/19/09 17:35	8/20/09 5:49	1293.9	1306.2	12.3	2.83	2.91	3.0	K	C	SRR	SRR
029	NE-3FS	4644	8/19/09 17:35	8/20/09 5:49	684.9	697.1	12.2	2.83	2.94	3.1	K	C	SRR	SRR
030	SE-3	4654	8/19/09 17:44	8/20/09 5:57	641.1	653.3	12.2	2.83	2.83	3.0	K	C	SRR	SRR
031	SE2-3	4664	8/19/09 17:51	8/20/09 6:05	467.5	476.8	9.3	2.83	2.83	3.0	K	C	SRR	SRR
032	SW2-3	4651	8/19/09 17:56	8/20/09 6:11	808.5	820.6	12.1	2.83	2.82	3.0	K	C	SRR	SRR
033	SW-3	4656	8/19/09 18:05	8/20/09 6:18	670.0	682.3	12.3	2.83	2.84	3.0	K	C	SRR	SRR
034	NW-3	4645	8/19/09 18:08	8/20/09 6:25	974.6	986.9	12.3	2.83	2.92	3.1	K	C	SRR	SRR
035	NW2-3	2974	8/19/09 18:15	8/20/09 6:32	1399.2	1411.4	12.2	2.83	2.74	3.0	K	C	SRR	SRR
036	NE2-3	4657	8/19/09 18:23	8/20/09 6:40	731.0	743.3	12.3	2.83	2.87	3.0	K	C	SRR	SRR
037	NE-4	4673	8/20/09 5:51	8/20/09 16:16	1201.8	1212.2	10.4	2.83	2.64	2.9	C	K	SRR	SRR
038	NE-4C	2021	8/20/09 5:51	8/20/09 16:16	1306.2	1316.5	10.3	2.83	2.74	3.0	C	K	SRR	SRR

MFM Used #: 2E+07      Slope: 1.104      Intercept: -0.120

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

## FILTER FIELD LOG SHEET

Project: Propyzamide Pesticide Application Air Monitoring  
 Start Flow Set: 3.0 ±0.1 lpm    End Flow Criteria: 3.0 lpm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time		Counter		TOTAL TIME HOURS	Mass Flow Meter Display		Corrected Average Flow	Weather K,P,C,F&R		Initials			
			Entry Example (6/14/08 13:42)		Start	End		Start	End		Start	End	Start	End	Start	End
			Start	End												
039	NE-4FS	4644	8/20/09 5:51	8/20/09 16:16	697.1	707.5	10.4	2.83	2.6	2.9	C	K	SRR	SRR		
040	SE-4	4654	8/20/09 5:57	8/20/09 16:21	653.3	663.9	10.6	2.83	2.49	2.8	C	K	SRR	SRR		
041	SE2-4	4664	8/20/09 6:06	8/20/09 16:38	476.8	490.3	13.5	2.83	2.7	2.9	C	K	SRR	SRR		
042	SW2-4	4651	8/20/09 6:12	8/20/09 16:44	820.6	831.0	10.4	2.83	2.74	3.0	C	K	SRR	SRR		
043	SW-4	4656	8/20/09 6:19	8/20/09 16:54	682.3	692.8	10.5	2.83	2.76	3.0	C	K	SRR	SRR		
044	NW-4	4645	8/20/09 6:25	8/20/09 17:02	986.9	997.5	10.6	2.83	2.73	2.9	C	K	SRR	SRR		
045	NW2-4	2974	8/20/09 6:32	8/20/09 17:08	1411.4	1422.0	10.6	2.83	2.53	2.8	C	K	SRR	SRR		
046	NE2-4	4657	8/20/09 6:42	8/20/09 17:15	743.3	753.9	10.6	2.83	2.08	2.6	C	K	SRR	SRR		
047	NE-4HS	4666	8/20/09 5:51	8/20/09 16:16	453.3	463.7	10.4	2.83	2.65	2.9	C	K	SRR	SRR		
048	NE-5	4673	8/20/09 16:20	8/21/09 5:45	1212.2	1225.6	13.4	2.83	3.22	3.2	K	C	SRR	SRR		
049	NE-SC	3021	8/20/09 16:20	8/21/09 5:45	1316.5	1330.0	13.5	2.83	3.1	3.2	K	C	SRR	SRR		
050	NE-5FS	4644	8/20/09 16:28	8/21/09 5:45	707.5	720.9	13.4	2.83	2.92	3.1	K	C	SRR	SRR		
051	SE-5	4654	8/20/09 16:31	8/21/09 5:51	663.9	677.2	13.3	2.83	2.96	3.1	K	C	SRR	SRR		
052	SE2-5	4664	8/20/09 16:38	8/21/09 5:57	490.3	503.6	13.3	2.83	2.94	3.1	K	C	SRR	SRR		
053	SW2-5	4651	8/20/09 16:45	8/21/09 6:02	790.4	802.9	12.5	2.83	2.99	3.1	K	C	SRR	SRR		
054	SW-5	4656	8/20/09 16:59	8/21/09 6:08	692.9	706.2	13.3	2.83	3.08	3.1	K	C	SRR	SRR		
055	NW-5	4645	8/20/09 17:03	8/21/09 6:11	997.5	1010.6	13.1	2.83	2.97	3.1	K	C	SRR	SRR		
056	NW2-5	2974	8/20/09 17:09	8/21/09 6:18	1422.0	1435.2	13.2	2.83	3.08	3.1	K	C	SRR	SRR		
057	NE2-5	4657	8/20/09 17:17	8/21/09 6:25	753.9	767.0	13.1	2.83	2.98	3.1	K	C	SRR	SRR		

MFM Used #: 2E+07      Slope: 1.104      Intercept: -0.120

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

## **APPENDIX E**

**Department of Pesticide Regulation Request to the Air Resource Board for Proposed Toxic Air Contaminants Monitoring for 2009**



# Department of Pesticide Regulation



Mary-Ann Warmerdam  
Director

## MEMORANDUM

Arnold Schwarzenegger  
Governor

TO: James Goldstene  
Executive Officer  
Air Resources Board  
1001 I Street  
Sacramento, California 95814

FROM: Mary-Ann Warmerdam  
Director  
(916) 445-4000

DATE:

SUBJECT: PROPOSED TOXIC AIR CONTAMINANT MONITORING FOR 2009

Pursuant to Food and Agricultural Code section 14022(c), the Department of Pesticide Regulation (DPR) requests that the Air Resources Board (ARB) monitor for the following pesticides in 2009:

- Diazinon
- Iodomethane
- Propyzamide

DPR requests that ARB monitor two application sites for diazinon. This organophosphate insecticide is used primarily on orchards and vegetable crops, and is high priority for risk assessment. High use occurs during summer and winter. DPR requests that ARB monitor the same application site during summer and winter to determine which season has higher concentrations. DPR will provide recommendations for dates and locations of monitoring after evaluating recent pesticide use data. ARB should investigate the possibility of including the oxygen analog breakdown product in the monitoring.

DPR requests that ARB develop a method to monitor iodomethane using canisters. This is a fumigant pesticide and may be used as a replacement for methyl bromide. This pesticide is not yet registered for use in California. However, DPR recently approved several field research studies. In the event DPR registers this pesticide, we anticipate high use and extensive monitoring may be needed. DPR requests limited monitoring of an application site as part of the process to validate the sampling and analytical methods. No iodomethane breakdown products need to be monitored. DPR plans to collect and analyze collocated samples using sorbent media and compare to ARB's canister results.

DPR requests that ARB monitor one application site and conduct ambient monitoring for propyzamide. This herbicide is used primarily on lettuce and is high priority for risk assessment. DPR will provide recommendations for dates and locations of monitoring after evaluating recent



James Goldstene

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pesticide use data. In addition, ARB should investigate the possibility of including the breakdown product 3,5-dichlorobenzamide in the monitoring.

Based on a preliminary assessment of the toxicology data, DPR requests the following target quantitation limits:

- Diazinon and breakdown product      0.013  $\mu\text{g}/\text{m}^3$
- Iodomethane      0.1 ppb
- Propyzamide and breakdown product      5  $\mu\text{g}/\text{m}^3$

Thank you for your consideration of this request. If you have any questions, please feel free to contact me, or Dr. John S. Sanders, of my staff, at (916) 324-4155, or <jsanders@cdpr.ca.gov>.

cc: Dr. John S. Sanders, DPR Environmental Program Manager II  
Dr. Joan E. Denton, Office of Environmental Health Hazard Assessment Director  
Bill Loscutoff, ARB Division Chief

bcc: Kenneth Stroud, ARB Branch Chief  
Eric McDougall, ARB Monitoring and Lab Division  
James Behrmann, ARB Research Division  
Lynton Baker, ARB Stationary Source Division  
George Alexeeff, Office of Environmental Health Hazard Assessment Deputy Director  
Melanie Marty, Office of Environmental Health Hazard Assessment Supervising Toxicologist  
Anna Fan-Cheuk, Office of Environmental Health Hazard Assessment Supervising Toxicologist  
Marylou Verder-Carlos, DPR Assistant Director  
Susan Edmiston, DPR Branch Chief  
Gary Patterson, DPR Supervising Toxicologist

Randy Segawa, Environmental Program Manager I (Supervisor )  
Pamela Wofford, Senior Environmental Scientist (Supervisor)  
Shifang Fan, Environmental Scientist (1807 files)  
Segawa Surname File