

California Environmental Protection Agency

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State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

**Final Report on Pesticide Air Monitoring  
Near Application of Chlorthal-Dimethyl  
In Monterey County, April 2011**

Prepared by

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June 6, 2012

## Monitoring Report Approval

**Report Title:** Final Report on Pesticide Air Monitoring Near Application Chlorthal-Dimethyl in Monterey County, April 2011

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

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

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Date

## Executive Summary

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) conducted ambient air monitoring adjacent to an application of the pesticide chlorthal-dimethyl in Monterey County during April 2011. The chlorthal-dimethyl is applied directly to broccoli fields by ground application spraying and is used as an herbicide to control a wide range of grasses and broad-leaved weeds.

Fifty three field samples, including four (4) field spikes, four (4) trip spikes and nine (9) background samples were collected from eight different locations around the perimeter of an 8.8 acre broccoli field located in Monterey County. The chlorthal-dimethyl was applied by ground spraying using a tractor at a rate was 4.38 lbs. of chlorthal-dimethyl per acre.

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

There were a total of five (5) ambient sampling periods per DPR's request (including a background). At the end of each sampling period, the XAD tubes were placed in containers with an affixed identification label and 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. Samples were analyzed using gas chromatography with an electron capture detector.

DPR requested a maximum estimated quantitation limit (EQL) of 0.1 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). The 0.1  $\mu\text{g}/\text{m}^3$  was achieved by the ARB's laboratory based on a 24-hour collection with a sample flow rate of 3.0 LPM.

- The reported results of chlorthal-dimethyl range from  $<0.020$  to  $0.298 \mu\text{g}/\text{m}^3$ .
- The highest values reported were collected during the third and fourth post application sampling periods. The field sampling sites were downwind sites located 20 meters from the south, southeast, and east edges of the field.
- The field spike recoveries ranged from 84 to 133% and trip spikes ranged from 77 to 86%.

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APPENDIX A: Department of Pesticide Regulation Request to the Air Resource Board for Proposed Toxic Air Contaminants Monitoring for 2011

APPENDIX B: Site Photographs

APPENDIX C: Sampling Protocol

APPENDIX D: Laboratory Results Report

APPENDIX E: XAD2 Sample Field Log Sheet

APPENDIX F: Calibration/Certification Reports

APPENDIX G: Meteorological Data

## 1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (2011 Memorandum, Reardon to Goldstene, Appendix A), Air Resources Board (ARB) staff conducted sampling of airborne concentrations of chlorthal-dimethyl during an application in Monterey County.

Fifty three field samples, including four (4) field spikes and four (4) trip spikes were collected from eight (8) different locations around the perimeter of an 8.8 acre broccoli field from April 12 through April 15, 2011. The chlorthal-dimethyl (Dacthal Flowable Herbicide) was applied by ground spraying using a tractor on April 13 from approximately 09:15 to 11:21 AM PST calculating to a 126 minute application period. The pesticide application was paused for about an hour while field workers staked off a portion of the field. See figure 1

The chlorthal-dimethyl application rate of 4.38 lbs. /acre was calculated using the farmer's seed ticket and manufacture's listed product label specification sheet. The information from the seed ticket showed that 822.0 fluid ounces of chlorthal-dimethyl was applied to an 8.8 acre field. The equations used to calculate the amount applied per acre is listed on page 16.

Refer to the next page Table 1 and Table 2 for Application Information and Application Sampling periods.

The pesticide 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.



Figure 1  
Field Workers Staking Off Field

Parameter	Details
Location	Monterey County, CA. South of Salinas, west of Highway 101
Field Size	8.8 acres
Product Applied	54.9% Dacthal Flowable DCPA (dimethyl tetrachloroterephthalate) 45.1% inert ingredients (Contains 6lbs. chlorthal-dimethyl (DCPA) per gallon of Dacthal Flowable product)
Application Type	Ground air-blast (tractor pulled sprayer) Start = 0915 to 1121 PST
Commodity	Broccoli
Application Rate	0.73 gallons of Dacthal Flowable product per acre at a calculated 4.38 lbs./acre of chlorthal-dimethyl

Table 1  
Application Information

Sampling Period	Sample Period Duration (Hours)	April 2011 (Date)	Time (Start/Stop)
Background	16.6	12-13	1454 to 0838
1 (Application)	10.6	13	0851 to 1914
2 (Nighttime)	13.5	13-14	1816 to 0843
3 (Daytime)	10.7	14	0735 to 1911
4 (Nighttime)	14.0	14-15	1812 to 0905

Note: Exact duration for each sample is listed in APPENDIX D XAD2 Sample Field Log Sheets.

Table 2  
Application Sampling Periods

## 2.0 Sampling Sites

Figure 2 (Satellite Map of Overview of Monitoring Area) and Figure 3 (Satellite Photo of Chlorthal-Dimethyl 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 and the location of the Met One auto-met weather station.



Figure 2  
Satellite Map of Overview of Monitoring Area



Eight (8) samplers and one (1) co-located sampler were located approximately 20 meters from the edges of the treated field's corners and were positioned midway down the length and width of the 8.8 acre broccoli field. See Appendix B for individual site photographs.

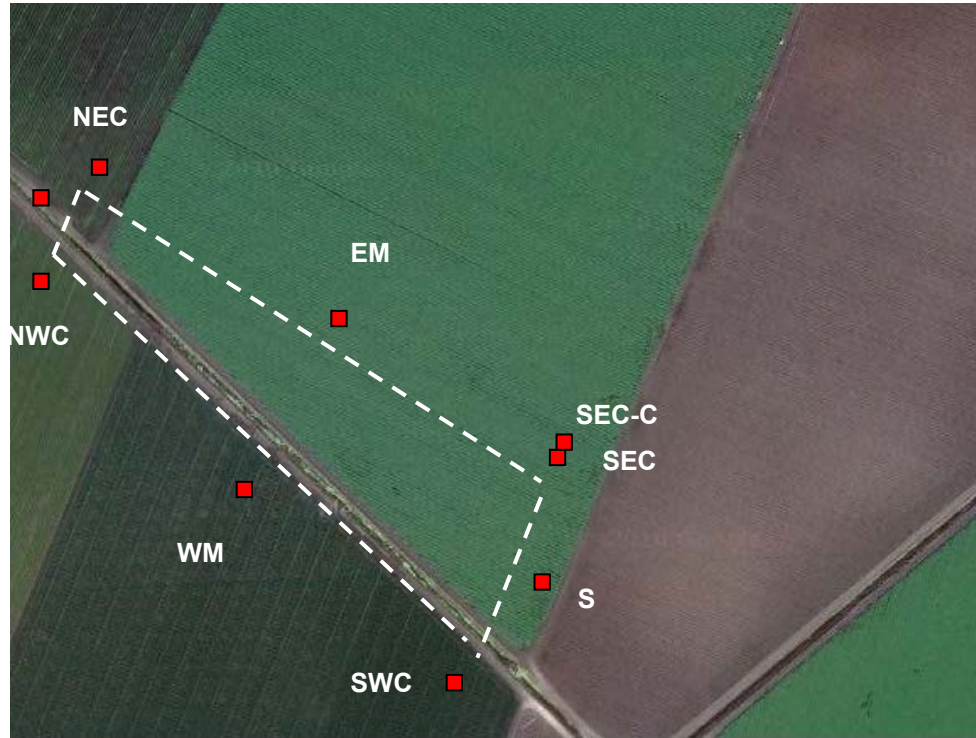


Figure 3  
Satellite Map of Chlorthal-Dimethyl Sampling Sites

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

Table 3 below lists the sampler locations and coordinates.

Sampler ID	Sample Position Related to Monitored Field	Waypoints
MET (Meteorology Station)	~1/4 mile East of field	East of Field
NEC (Northeast Corner)	66' East of the Northeast Corner of the field, Elevation = 13'	N 36°38'21.6 W 121°35'40.8
N (North Side)	66' North of the field and 100' from the Northeast Corner, Elevation = 13'	N 36°38'20.1 W 121°35'41.7
NWC (Northwest Corner)	66' West of the Northwest Corner of the field and 100' from North Side, Elevation = 14'	N 36°38'19.0 W 121°35'42.1
WM (West Middle)	66' West of the field and 543.5' from the Northwest Corner of the field, Elevation = 13'	N 36°38'15.3 W 121°35'37.3
SWC (Southwest Corner)	66' West of the Southwest Corner and 543.5' from the West Middle of the field, Elevation = 13'	N 36°38'11.7 W 121°35'32.5
S (South Side)	66' South of the field and 257' from the Southwest Corner of the field, Elevation = 13'	N 36°38'14.1 W 121°35'31.1
SEC (Southeast Corner)	66' East of the Southeast Corner of the field, 257' from the South Side of the field, Elevation = 13	N 36°38'17.0 W 121°35'29.7
EM (East Middle)	66' East of the field and 493' from the Southeast Corner of the field, Elevation = 10	N 36°38'18.5 W 121°35'35.6

Table 3  
Sample Waypoints

### 3.0 Methods

Samples were collected by passing 3.0 liters per minute (LPM) of ambient air through XAD-2 sorbent tubes, 1.5 meters above the ground level as shown in (Figure 4), Ambient Air Sampler. There were a total of five (5) ambient sampling periods including a background as requested by DPR. Air samples were taken before, during, and after the chlorthal-dimethyl application. There were three (3) daytime and two (2) overnight sampling periods.

The background sampling started on April 12, 2011 at 14:54 (PST) and ran till the morning of April 13, 2011, 08:38 (PST).

The chlorthal-dimethyl application started at 9:15 (PST) on April 13, 2011 and ended at 11:21 (PST). The post-application samples started one (1) hour before sunset and

were collected one (1) hour before sunrise and reloaded with XAD-2 sorbent tubes for the daytime sampling.

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.



Figure 4  
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 0-5 LPM before the start and end of each sampling 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 time counter readings, sample identifications and any other significant information.

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

Meteorological data was collected using a portable Met One auto-met weather station which logged 5 minute averages for wind speed and direction along with temperature

and relative humidity. See Figure 6, 7, 8, 9 for Wind Roses and APPENDIX G for meteorological data.

For details of the monitoring method, please refer to Appendix C, "Sampling Protocol for Chlorthal-Dimethyl (Dacthal) Application Study" (dated March 22, 2011). 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.

The estimated quantitation level (EQL) for this method is 0.1 µg/m<sup>3</sup> prior to any sample dilution for sampling at three (3) LPM and a three (3) milliliter (ml) extraction.

Per the laboratory's report (APPENDIX D) the minimum detection limit (MDL) calculation follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (0.1 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 chlorthal: s = 0.006 µg/ml  
MDL = (3.14) x (s) = (3.14) x (0.006) = 0.018 µg/ml.  
MDL for total µg/sample = 0.06 µg/sample  
EQL = (5) x (MDL) = (5) x (0.018) = 0.090 µg/ml  
EQL for total µg/sample = 0.270 µg/sample*

Based on a total collection volume of 4.32 m<sup>3</sup> the EQL would be 0.1 µg/m<sup>3</sup>. Staff reported 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. See Appendix D

## 4.0 Results

The results indicated low levels of chlorthal-dimethyl ranging from <0.020 to 0.298  $\mu\text{g}/\text{m}^3$ . The highest levels were detected in the field samples during the third and fourth post application sampling periods at downwind sampling locations 20 meters from the south, southeast, and east edges of the field.

The results are located in Table 4 and are reported by sample location, elapsed time in minutes and hours, average flow in LPM, calculated total volume  $\text{m}^3$ . These values were used to calculate the reported lab results  $\mu\text{g}/\text{sample}$  to  $\mu\text{g}/\text{m}^3$  for each sampling location.

Wind roses are located in Figure 5 thru 9 showing the wind characteristics for each of the five (5) sampling periods including the background. The meteorological data was captured using five (5) minute averaging. (See APPENDIX G Meteorological Data)

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

### Site/Sample Identification

Ambient Site Naming:

NEC 1-4	Northeast Corner of Field
N 1-4	North Side of Field
NWC 1-4	Northwest Corner of Field
WM 1-4	West Middle of Field
SWC 1-4	Southwest Corner of Field
S 1-4	South Side of Field
SEC 1-4	Southeast Corner of Field
SEC 1C-4C	Southeast Corner of Field Co-located
EM 1-4	East Middle Side of Field

See Figure 2, Satellite Map of Chlorthal-Dimethyl Sampling Sites

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

Log #	Sample Location	Elapsed Time (Minutes)	Elapsed Time (Hours)	Avg. Flow (LPM)	Total Volume (m <sup>3</sup> )	Chlorthal (µg/sample)	Chlorthal (µg/m <sup>3</sup> )
P001	BKG-NEC	996.0	16.6	3.02	3.01	<0.06	<0.020
P010	NEC-1	564.0	9.4	2.99	1.69	<0.06	<0.036
P020	NEC-2	798.0	13.3	2.91	2.32	<0.06	<0.026
P030	NEC-3	636.0	10.6	3.05	1.94	<0.06	<0.031
P040	NEC-4	828.0	13.8	3.01	2.49	<0.06	<0.024
P002	BKG-N	984.0	16.4	3.04	2.99	<0.06	<0.020
P011	N-1	576.0	9.6	2.99	1.72	<0.06	<0.035
P021	N-2	798.0	13.3	2.94	2.35	<0.06	<0.026
P031	N-3	642.0	10.7	3.07	1.97	<0.06	<0.030
P041	N-4	822.0	13.7	3.00	2.47	<0.06	<0.024
P003	BKG-NWC	960.0	16.0	1.81	1.74	<0.06	<0.035
P012	NWC-1	588.0	9.8	2.98	1.75	<0.06	<0.034
P022	NWC-2	798.0	13.3	3.03	2.42	<0.06	<0.025
P032	NWC-3	636.0	10.6	2.93	1.86	<0.06	<0.032
P042	NWC-4	840.0	14.0	3.00	2.52	<0.06	<0.024
P004	BKG-WM	978.0	16.3	3.02	2.95	<0.06	<0.020
P013	WM-1	588.0	9.8	2.98	1.75	<0.06	<0.034
P023	WM-2	804.0	13.4	2.92	2.35	<0.06	<0.026
P033	WM-3	630.0	10.5	3.03	1.91	<0.06	<0.031
P043	WM-4	834.0	13.9	3.01	2.51	0.06	0.024
P005	BKG-SWC	978.0	16.3	3.00	2.93	<0.06	<0.020
P014	SWC-1	594.0	9.9	2.99	1.78	<0.06	<0.034
P024	SWC-2	804.0	13.4	2.95	2.37	<0.06	<0.025
P034	SWC-3	630.0	10.5	2.99	1.88	<0.06	<0.032
P044	SWC-4	834.0	13.9	2.99	2.49	0.07	0.028
P006	BKG-S	966.0	16.1	3.07	2.97	<0.06	<0.020
P015	S-1	624.0	10.4	3.00	1.87	<0.06	<0.032
P025	S-2	804.0	13.4	2.94	2.36	<0.06	<0.025
<b>P035</b>	<b>S-3</b>	<b>630.0</b>	<b>10.5</b>	<b>3.02</b>	<b>1.90</b>	<b>0.567</b>	<b>0.298</b>
P045	S-4	840.0	14.0	2.99	2.51	0.16	0.064

**Note:** Bold µg/m<sup>3</sup> values are greater than EQL 0.1 µg/m<sup>3</sup>

Table 4  
Application Results by Site

Log #	Sample Location	Elapsed Time (Minutes)	Elapsed Time (Hours)	Avg. Flow (LPM)	Total Volume (m <sup>3</sup> )	Chlorthal (µg/sample)	Chlorthal (µg/m <sup>3</sup> )
P007	BKG-SEC	960.0	16.0	3.04	2.92	<0.06	<0.021
P008	BKG-C-SEC	972.0	16.2	3.11	3.02	<0.06	<0.020
P016	SEC-1	624.0	10.4	2.98	1.86	<0.06	<0.032
P017	SEC-C-1	624.0	10.4	3.00	1.87	<0.06	<0.032
P026	SEC-2	810.0	13.5	2.92	2.37	<0.06	<0.025
P027	SEC-C-2	810.0	13.5	2.88	2.33	<0.06	<0.026
<b>P036</b>	<b>SEC-3</b>	<b>624.0</b>	<b>10.4</b>	<b>2.81</b>	<b>1.75</b>	<b>0.444</b>	<b>0.253</b>
<b>P037</b>	<b>SEC-C-3</b>	<b>630.0</b>	<b>10.5</b>	<b>3.09</b>	<b>1.95</b>	<b>0.543</b>	<b>0.279</b>
P046	SEC-4	840.0	14.0	2.95	2.48	<0.13	<0.052
P047	SEC-C-4	834.0	13.9	2.99	2.49	<0.12	<0.048
P009	BKG-EM	960.0	16.0	3.07	2.95	<0.06	<0.020
P019	EM-1	636.0	10.6	2.89	1.84	<0.06	<0.033
P029	EM-2	810.0	13.5	2.89	2.34	<0.06	<0.026
<b>P039</b>	<b>EM-3</b>	<b>630.0</b>	<b>10.5</b>	<b>2.97</b>	<b>1.87</b>	<b>0.42</b>	<b>0.224</b>
P049	EM-4	828.0	13.8	2.93	2.43	0.12	0.049

**Note:** Bold µg/m<sup>3</sup> values are greater than EQL 0.1 µg/m<sup>3</sup>

Table 4  
Application Results by Site

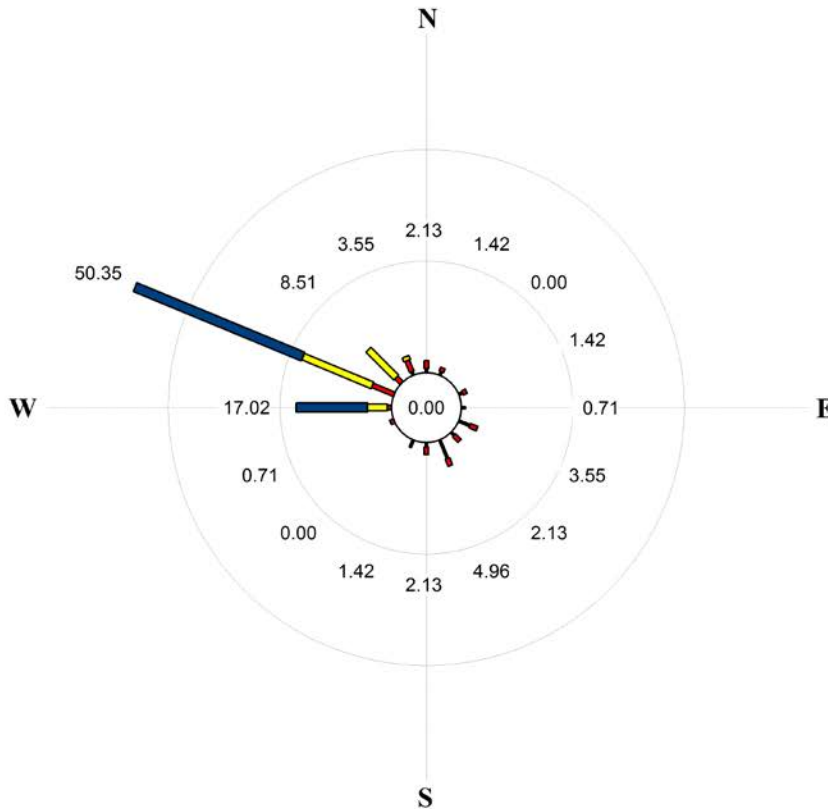








**Wind Rose**  
**Monterey County Chlorthal Dimethyl Sampling Period 3 Daytime**  
**April 14 from 0735 to 1915 (5 minute averaging)**



Wind Speed (Knots)

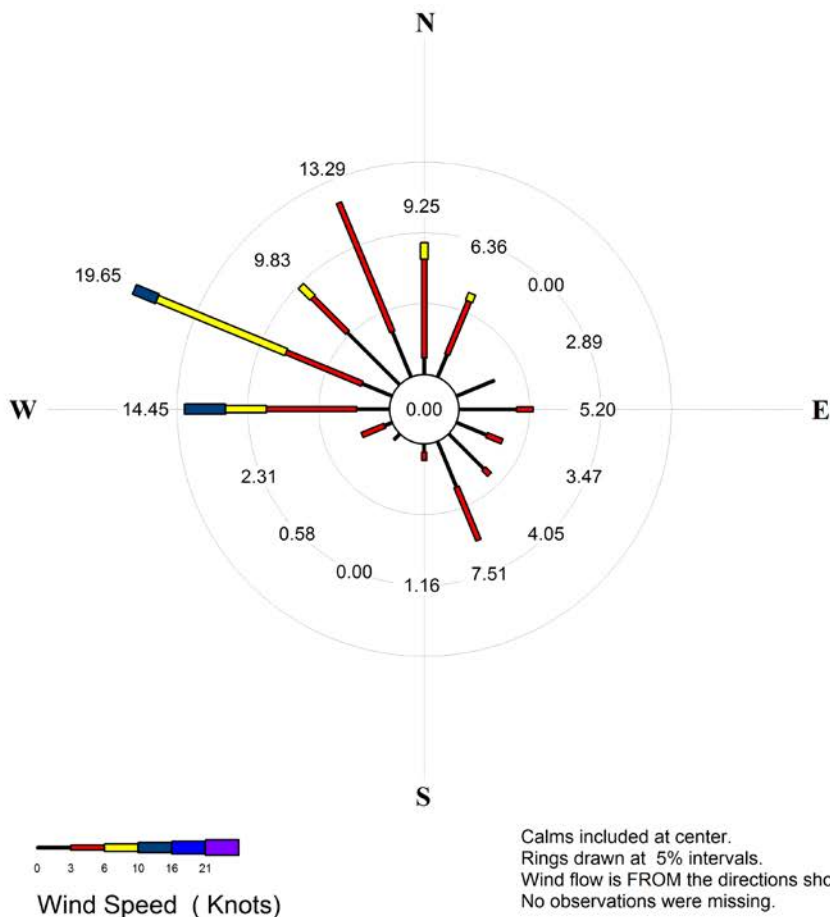
Calms included at center.  
 Rings drawn at 20% intervals.  
 Wind flow is FROM the directions shown.  
 No observations were missing.

PERCENT OCCURRENCE: Wind Speed (Knots)						
LOWER BOUND OF CATEGORY						
DIR	0	3	6	10	16	21
N	0.71	1.42	0.00	0.00	0.00	0.00
NNE	0.71	0.71	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	0.71	0.71	0.00	0.00	0.00	0.00
E	0.71	0.00	0.00	0.00	0.00	0.00
ESE	2.13	1.42	0.00	0.00	0.00	0.00
SE	0.71	1.42	0.00	0.00	0.00	0.00
SSE	3.55	1.42	0.00	0.00	0.00	0.00
TOTAL OBS = 141 MISSING OBS = 0						

PERCENT OCCURRENCE: Wind Speed (Knots)						
LOWER BOUND OF CATEGORY						
DIR	0	3	6	10	16	21
S	0.71	1.42	0.00	0.00	0.00	0.00
SSW	1.42	0.00	0.00	0.00	0.00	0.00
SW	0.00	0.00	0.00	0.00	0.00	0.00
WSW	0.00	0.71	0.00	0.00	0.00	0.00
W	0.00	0.71	3.55	12.77	0.00	0.00
WNW	0.00	4.26	13.48	32.62	0.00	0.00
NW	0.00	1.42	7.09	0.00	0.00	0.00
NNW	0.71	2.13	0.71	0.00	0.00	0.00
CALM OBS = 0 PERCENT CALM = 0.00						

Figure 8  
 Sampling Period 3 Daytime Wind Rose

**Wind Rose**  
**Monterey County Chlorthal Dimethyl Sampling Period 4 Overnight**  
**April 14 to 15 from 1815 to 0835 (5 minute averaging)**



PERCENT OCCURRENCE: Wind Speed ( Knots)  
LOWER BOUND OF CATEGORY

DIR	0	3	6	10	16	21
N	1.16	6.94	1.16	0.00	0.00	0.00
NNE	1.73	4.05	0.58	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	2.89	0.00	0.00	0.00	0.00	0.00
E	4.05	1.16	0.00	0.00	0.00	0.00
ESE	2.31	1.16	0.00	0.00	0.00	0.00
SE	3.47	0.58	0.00	0.00	0.00	0.00
SSE	3.47	4.05	0.00	0.00	0.00	0.00

TOTAL OBS = 173 MISSING OBS = 0

PERCENT OCCURRENCE: Wind Speed ( Knots)  
LOWER BOUND OF CATEGORY

DIR	0	3	6	10	16	21
S	0.58	0.58	0.00	0.00	0.00	0.00
SSW	0.00	0.00	0.00	0.00	0.00	0.00
SW	0.58	0.00	0.00	0.00	0.00	0.00
WSW	0.58	1.73	0.00	0.00	0.00	0.00
W	2.31	6.36	2.89	2.89	0.00	0.00
WNW	2.31	5.78	9.83	1.73	0.00	0.00
NW	5.20	3.47	1.16	0.00	0.00	0.00
NNW	3.47	9.83	0.00	0.00	0.00	0.00

CALM OBS = 0 PERCENT CALM = 0.00

Figure 9  
Sampling Period 4 Overnight Wind Rose

### **The Formulas Used to Calculate Monitoring Results**

$$\text{Sample Volume } m^3 = \left( \frac{\text{Sample Flow liters}}{\text{minute}} \right) \times (\text{Sample Time minute}) \times \left( \frac{1 m^3}{1000 \text{ liters}} \right)$$

$$\text{Chlorthal-Dimethyl } \frac{\mu g}{m^3} = \left( \frac{\text{Chlorthal } \mu g}{\text{Sample}} \right) \times \left( \frac{\text{Sample}}{\text{Total Volume } m^3} \right)$$

$$\text{Chlorthal-Dimethyl } \frac{\mu g}{\text{sample}} = \left( \frac{\text{Chlorthal } \mu g}{\text{ml}} \right) \times \left( \frac{3 \text{ ml Extraction Volume}}{1 \text{ Sample}} \right)$$

$$\text{Chlorthal-Dimethyl } \frac{\mu g}{\text{ml}} = \left( \frac{\text{Chlorthal } \mu g}{m^3} \right) \times \left( \frac{\text{Sample Volume } m^3}{1 \text{ Sample}} \right) \times \left( \frac{1 \text{ Sample}}{3 \text{ ml Extraction Volume}} \right)$$

**Note:** 3 ml sample dilution Extraction Volume per sample

### **Calculating Percent Recovery of Field Spikes (FS)**

$$\text{Difference } \frac{\mu g}{m^3} = \text{FS } \frac{\mu g}{m^3} - \text{Primary Sample } \frac{\mu g}{m^3}$$

$$\text{Percent Recovery } \% = \left( \frac{\text{Difference } \mu g}{m^3} \right) \times \left( \frac{\text{FS Volume } m^3}{\text{FS Concentration } \frac{\mu g}{ml}} \right) \times 100$$

**Note:** The Laboratory Field Spike Concentrations were 0.150  $\frac{\mu g}{ml}$

### **Calculating Chlorthal-Dimethyl Application Rate lbs. /acre**

$$\frac{822.0 \text{ fluid oz.}}{128.0 \text{ oz. /gallon}} = 6.42 \text{ gallons of Dacthal Flowable product}$$

$$\frac{(6.42 \text{ gallons Dacthal Flowable product}) \times (6.00 \text{ lbs. chlorthal-dimethyl/gallon})}{8.8 \text{ acres}} = 4.38 \text{ lbs. chlorthal-dimethyl}$$

**Note:** Per manufacture's listed product label specification sheet Dacthal Flowable Herbicide contains 6.00 lbs. of chlorthal-dimethyl/gallon

## 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 D, "Chlorthal 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, and after every tenth sample, and after samples containing high levels of chlorthal-dimethyl or co-extracted contaminants. The staff defines an analytical batch as all the samples extracted together, but not to exceed 20 samples. The system blank is analyzed to ensure the solvent and instrument does not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

- 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 was 0.06 µg/sample
- Laboratory staff analyzed a Laboratory Control Standard (LCS) with each analytical batch. The LCS is an XAD tube spiked with 0.150 µg/ml of chlorthal-dimethyl. The LCS is extracted and analyzed as described for the samples. The LCS averaged 89.2% with a standard deviation of 1.6%.
- Following standard lab procedures, laboratory staff analyzed a Continuing Calibration Verification (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 was 0.250 µg/ml. All CCV's were in the expected range.
- Field Spikes: The four field spikes were collected in the SEC quadrant. Samples were collected during the application and the three post-application periods. All field spikes were prepared with 0.150 µg/ml of chlorthal-dimethyl. The recoveries were 108% (during application) and 85%, 133% and 84% (during post application). Refer to Table 5
- Trip Spikes: The trip spike recoveries ranged from 77% to 86%. Refer to Table 6
- Lab Spikes: The two laboratory spikes for this study reported a recovery of 84% and 89%. Refer to Table 7

Log	Sample Location	Expected µg/ml	Measured µg/ml	Measured µg/m <sup>3</sup>	Primary Sample µg/m <sup>3</sup>	Difference Spike-Primary	Recovery %
P018	SEC-FS-1	0.150	0.162	0.258	0.000 <LOD	0.258	108
P028	SEC-FS-2	0.150	0.127	0.162	0.000 <LOD	0.162	85
P038	SEC-FS-3	0.150	0.371	0.547	0.253	0.294	133
P048	SEC-FS-4	0.150	0.170	0.202	0.052	0.150	84

Table 5  
Quality Control Data Field Spikes

Log #	Sample Location	Date Collected	Date Analyzed	Expected µg/ml	Measured µg/ml	Difference µg/ml	Recovery %
P050	Trip Spike 1	4/15/2011	4/20/2011	0.150	0.121	0.029	81
P051	Trip Spike 2	4/15/2011	4/21/2011	0.150	0.115	0.035	77
P052	Trip Spike 3	4/15/2011	4/22/2011	0.150	0.129	0.021	86
P053	Trip Spike 4	4/15/2011	4/25/2011	0.150	0.123	0.027	82

Table 6  
Quality Control Data Trip Spikes

Sample Location	Date Analyzed	Expected µg/ml	Measured µg/ml	Difference µg/ml	Recovery %
Lab Spike 1	4/18/2011	0.150	0.126	0.024	84
Lab Spike 2	4/22/2011	0.150	0.133	0.017	89

Table 7  
Quality Control Data Laboratory Spikes

## 6.0 Discussion

Fifty-three field samples were collected during the background, application and post-application period (including four field spikes and four trip spikes) from eight different locations around the perimeter of an 8.8 acre broccoli field located in Monterey County. Two laboratory spikes were prepared and held at the laboratory at the same time the field/trip spikes were prepared. No chlorthal-dimethyl was detected during the background or application sampling periods, but the third sampling period had four measured concentrations that were greater than the EQL of  $0.1 \mu\text{g}/\text{m}^3$ . During the third sampling period, chlorthal-dimethyl was detected in the SEC, S, and EM quadrants with concentrations ranging from 0.224 to  $0.298 \mu\text{g}/\text{m}^3$ . These four measured concentrations coincide with the wind direction during the third sampling period (See Figure 8 Sampling Period 3 Daytime Wind Rose). The wind was coming out of the northwest and west 50.35% and 17.02% of the time ranging from 6 to 10 knots. The last sampling time shows that these same quadrants (SEC, S, EM) had dropped below the EQL of  $0.1 \mu\text{g}/\text{m}^3$ . Refer to Figure 9 Sampling Period 4 Overnight Wind Rose Samples. The wind was still coming out of the northwest and west ranging from 9.83% to 19.65%, but the winds calmed down to 3 to 6 knots.

SEC-3 and SEC-C-3 were combined, concentrated and reanalyzed to confirm the presence of chlorthal-dimethyl. There were no other peaks in the GC/ECD analysis to indicate the presence of a metabolite.

The low frequency of chlorthal-dimethyl detections may be attributed to the applicator who applied when the winds were calm. Additionally, the field was watered right after the application which limited off-site movement of chlorthal-dimethyl in the air, resulting in low levels of chlorthal-dimethyl in the air at the field samplers which were located 20 meters away from the treated field edges.



## **APPENDIX A**

**Department of Pesticide Regulation Request to the Air Resource  
Board for Proposed Toxic Air Contaminants Monitoring for  
2011**



# 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: Chris Reardon  
Chief Deputy Director  
916-445-4000

DATE: DRAFT 10-25-10

SUBJECT: PROPOSED TOXIC AIR CONTAMINANT MONITORING FOR 2011

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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 2011:

- 1,3-dichloropropene
- Carbaryl
- Chlorthal-dimethyl
- Methyl bromide
- Methyl iodide

DPR's requests that ARB continue the simultaneous ambient air monitoring for three fumigants: 1,3-dichloropropene, methyl bromide, and methyl iodide. Last year, DPR requested monitoring for these fumigants for a 15-month period. Consistent with the original request, this monitoring should continue at both the Camarillo site and Santa Maria site through October 2011. DPR has not made a final decision regarding the registration of products containing methyl iodide. However, ARB's monitoring should continue to include this pesticide, pending a final decision.

DPR also requested that ARB conduct an application-site study for chlorthal-dimethyl (dacthal, DCPA) last year, including the monomethyl tetrachloroterephthalate (MTP) and tetrachloroterephthalic acid (TPA) breakdown products. ARB staff were unable to conduct this monitoring due to travel and overtime constraints beyond their control. Therefore, DPR requests that ARB conduct this monitoring in 2011.

DPR requests that ARB conduct an application-site study for carbaryl. Carbaryl is a hazardous air pollutant, and was administratively listed as a toxic air contaminant. DPR's risk assessment for this pesticide is currently in progress, and air monitoring will provide data needed for a complete evaluation of the exposure. ARB previously conducted ambient air monitoring for carbaryl in 2007. Additional ambient monitoring is not needed at this time.



James Goldstene

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DPR requests the following target quantitation limits:

- 1,3-dichloropropene: 0.1 ppb for each isomer (current ARB quantitation limit)
- Carbaryl: 0.04  $\mu\text{g}/\text{m}^3$
- Chlorthal-dimethyl and breakdown products: 0.1  $\mu\text{g}/\text{m}^3$
- Methyl bromide: 0.03 ppb (current ARB quantitation limit)
- Methyl iodide: 0.1 ppb (current ARB quantitation limit)

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

cc: John S. Sanders, Ph.D., DPR Environmental Program Manager  
Joan E. Denton, Ph.D., Office of Environmental Health Hazard Assessment Director  
Kenneth Stroud, ARB Branch Chief



**Linda S. Adams**  
Acting Secretary for  
Environmental Protection

# Air Resources Board

**Mary D. Nichols, Chairman**  
1001 I Street • P.O. Box 2815  
Sacramento, California 95812 • [www.arb.ca.gov](http://www.arb.ca.gov)



**Edmund G. Brown Jr.**  
Governor

TO: Chris Reardon  
Chief Deputy Director  
Department of Pesticide Regulation

FROM: James N. Goldstene  
Executive Officer

DATE: March 29, 2011

SUBJECT: PROPOSED TOXIC AIR CONTAMINANT MONITORING FOR 2011

---

This is in response to your memorandum requesting the Air Resources Board (ARB) monitor the following pesticides in 2011:

- 1,3-dichloropropene
- Carbaryl
- Chloropicrin
- Chlorthal-dimethyl
- Methyl bromide
- Methyl iodide

Specifically, the Department of Pesticide Regulation (DPR) requests ARB to continue the 15 month simultaneous ambient air monitoring for four fumigants: 1,3-dichloropropene (1,3-D), methyl bromide, methyl iodide and chloropicrin. Monitoring for these four fumigants is currently underway at two sites (Camarillo and Santa Maria). Monitoring will end October 2011.

DPR also requests ARB to conduct an application site study for chlorthal-dimethyl, and if possible, the monomethyl tetrachloroterephthalate and tetrachloroterephthalic acid breakdown products. DPR has already provided monitoring recommendations which include high use dates and locations.

Lastly, DPR also requests ARB to conduct an application site study for carbaryl. DPR has already provided monitoring recommendations which include high use dates and locations.

I have directed my staff at ARB's Monitoring and Laboratory Division to include 1,3-D, chloropicrin, methyl bromide, and methyl iodide in their 2011 air monitoring test schedule. To the extent possible, we will include the application site study requests for

*The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.*

California Environmental Protection Agency

Chris Reardon

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chlorthal-dimethyl and carbaryl. As these studies are dependant on the cooperation of growers and their pesticide application schedules, weekend and extended hours are often necessary. Furlough and overtime restrictions could impair our ability to complete these studies.

If you have any questions, please contact Ken Stroud at (916) 445-3745 or via email at [kstroud@arb.ca.gov](mailto:kstroud@arb.ca.gov).

cc: George Alexeeff, Ph.D.  
Acting Director  
Office of Environmental Health Hazard Assessment

John S. Sanders, Ph.D.  
Environmental Program Manager II  
Department of Pesticide Regulation

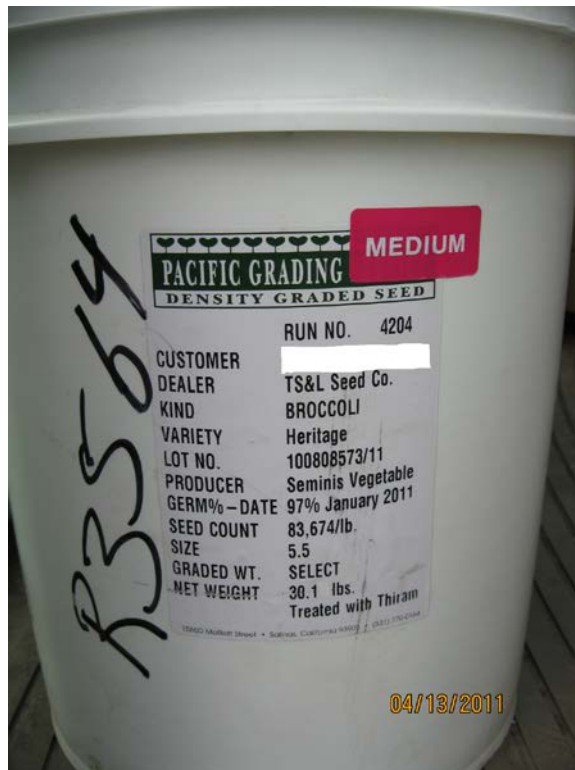
Ken Stroud, Chief  
Air Quality Surveillance Branch

## **APPENDIX B**

### **Site Photographs**



Chlorthal in tanks and broccoli seeds being loaded before application



Broccoli seeds which were loaded prior to Chlorthal



Watering after Chlorthal application and seeding



Sampling Site NEC





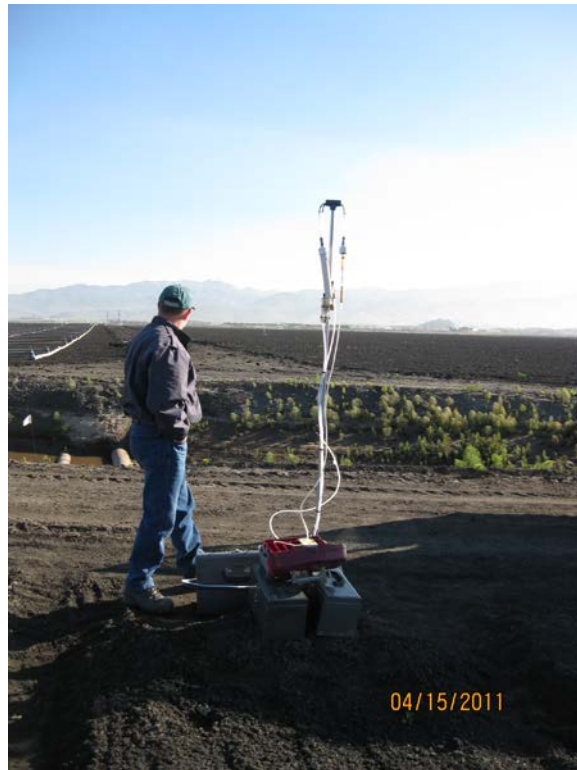
Sampling Site N



Sampling Site NWC



Sampling Site WM



Sampling Site SWC





Sampling Site S



Sampling Site SEC and Co-Located



Sampling Site EM



Difficult driving conditions





Sampler Site EM



Swapping out batteries at SEC