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Report on Air Monitoring the Application Of Methomyl in Fresno County in October 2007

Prepared by

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Monitoring Report Approval

Report Title: Report on Air Monitoring the Application of Methomyl in Fresno County during October 2007

Project Lead: Neil Adler, Air Pollution Specialist

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

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Executive Summary

Report on Air Monitoring the Application Of Methomyl in Fresno County in October 2007

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) conducted air monitoring before, during and after an aerial application of Methomyl in Fresno County during October 2007. Methomyl is used as a pesticide to control a wide range of insects including thrips, bugs, aphids, beetles, moths, diptera and ant-hymenoptera. Monitoring was conducted to coincide with typical methomyl use.

Special Purpose Monitoring staff collected a total of 73 valid air samples from eight locations around a 149.31 acre parcel of corn designated for human consumption. Samples were collected by passing a measured volume of ambient air through XAD-2 resin tubes. The sampling flow rates were measured and set at 2.0 liters per minute (LPM) at the beginning and end of the sampling period. These values were recorded on the sample log sheet. The XAD-2 resin tubes were protected from direct sunlight and supported 1.5 meters above the ground. The sampling locations were positioned on each side and each corner of the corn field. The samplers were located 40 to 74 feet from the edge of the field. At the end of each sampling period, the XAD-2 resin tubes were capped and placed in culture tubes with an identification label affixed.

Subsequent to sampling, the sample tubes were stored and transported on dry ice to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples were stored in the freezer or extracted/analyzed immediately.

DPR requested a method estimated quantitation limit (EQL) of 10 nanograms per cubic meter (ng/m^3). Forty-one samples had values greater then the DPR requested EQL of 10 ng/m^3. The method EQL achieved during this project was 1.0 ng/m^3. Fifty-seven samples had results greater than the method EQL. Reported methomyl results indicated ambient concentrations that ranged from less than 1.7 to 564.5 ng/m^3. The Special Analysis Section, Northern Laboratory Branch, Monitoring and Laboratory Division noted in the analysis report that method development spikes ranged from 78% to 93% recovery. Breakthrough studies detected no methomyl in the secondary section of the XAD-2 cartridges.

Quality control field samples included seven collocated pairs, four field spikes, four trip spikes, one field blank and one trip blank. The collocated samples collected during this study show a high degree of variability in their relative percent difference (-51% to 51%). The field spike recoveries were poor, ranging from -305% to 192%. Lower level quality control concentrations during this study were consistent with the results reported in the "Report on Ambient Air Monitoring for Methomyl and Carbaryl in Fresno, Tulare and Kings Counties during July and August 2007", dated December 9, 2008. At higher concentrations, quality control results differ greatly. The quality control results demonstrate the overall uncertainty of the method. If methomyl remains a priority pesticide for monitoring, a redevelopment of the method is recommended.

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (January 29, 2007 Memorandum, Warmerdam to Witherspoon), the Air Resources Board (ARB) staff conducted sampling of airborne concentrations of methomyl in Fresno County. This was performed prior to, during and after an aerial application of methomyl on corn grown for human consumption.

A total of 63 air samples, seven (7) collocated and 10 quality control samples were collected at eight (8) different locations around the field on which methomyl was applied on October 10, 2007. This monitoring was performed under the requirements of AB 1807/3219 (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.

The DPR request repeats a previous study performed in 1989. In comparison, the field sampling equipment used during this study was essentially the same as the equipment used in 1989. The 1989 study included three (3) samplers at three locations (one upwind and two downwind), the 2007 study included nine (9) samplers total, one on each corner, one on each side and one collocated downwind). The sample flow rate in 1989 was 3 LPM, in 2007 it was 2 LPM. In 1989, sample analysis utilized high performance liquid chromatographic (HPLC) method. In 2007, sample analysis utilized high performance liquid chromatograph with a mass spectrometer (LC/MS) in the selected ion-monitoring mode (SIM). Reported methomyl results in 1989 were below the detection limit of the method (0.14 µg/mL or 0.28 µg/sample).

2.0 Sampling Sites

Eight (8) sampling locations were positioned around the application parameter. Samplers were located at the midpoint of each side and at each corner. An additional sampler was collocated at the predominately downwind position. Collocated samples collected during the background sampling period were positioned at the northeast corner. The remainder of the collocated samples was taken from the east side of the field. All samplers were positioned a minimum of 40 and maximum of 74 feet from the edge of the field. Field spike samples were collected at the downwind site.

The application use maps for methomyl provided by DPR in their methomyl recommendation suggested that monitoring should occur in Fresno, Kings or Tulare Counties. The maps indicated that the highest methomyl use was around the Mendota area in Fresno County. See Figure 1 “Methomyl Area Map”.

The application monitoring site was located at the SW ¼ of Section 23, Township 14S, Range 13E. See Figure 2 “Methomyl Field Map” and Figure 3 “Methomyl Sampler Locations”.

Refer to Figure 4 “Drawing of Application Area” for the location of each sampling location around the application field.

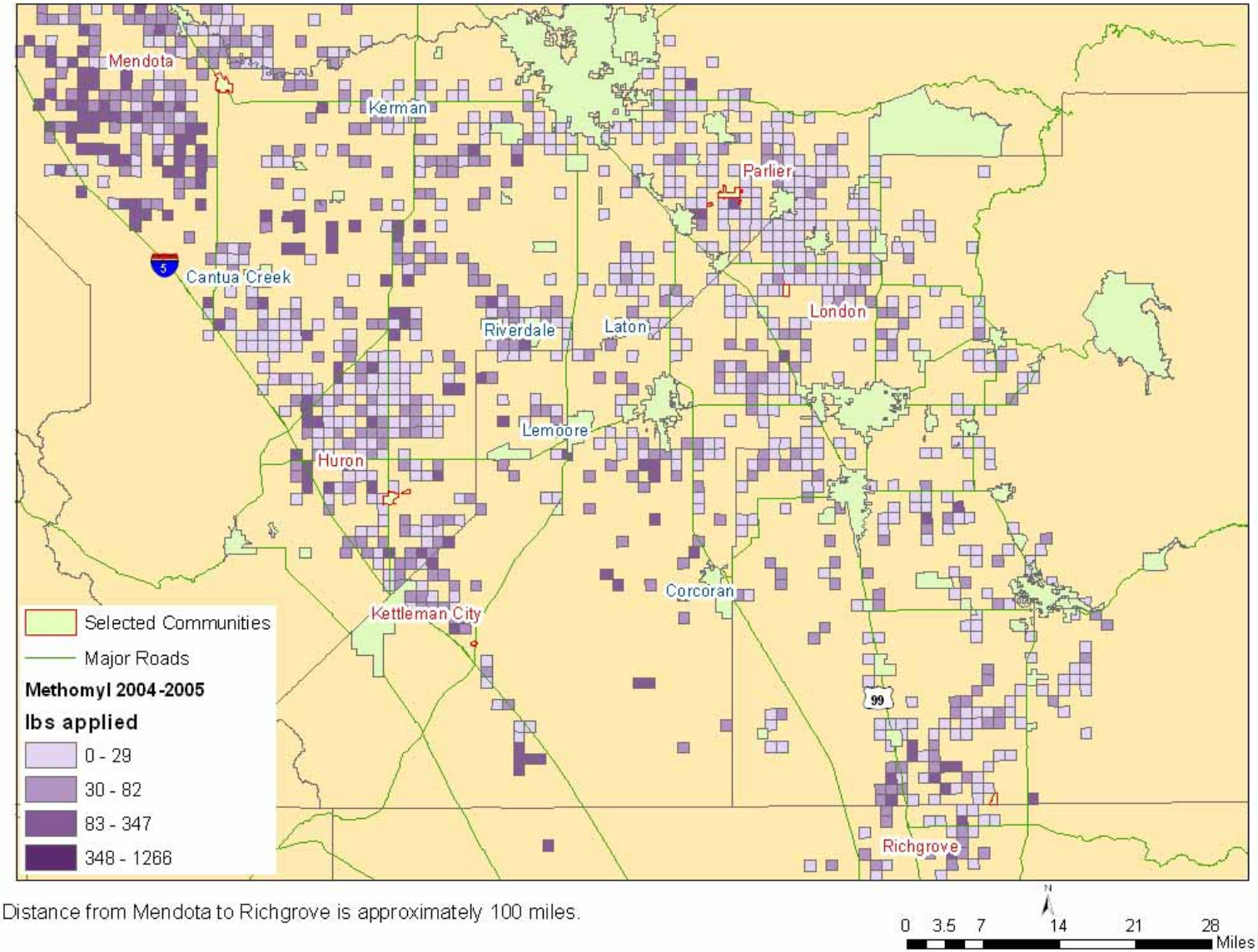
Description	Location Name	GPS Coordinates	Distance from Field
Southeast Corner	SEC	N 36º 41.455’, W 120º 31.377’	56 ft.
East Side	E	N 36º 41.677’, W 120º 31.370’	44 ft.
Northeast Corner	NEC	N 36º 41.894’, W 120º 31.382’	40 ft.
North Side	N	N 36º 41.898’, W 120º 31.645’	40 ft.
Northwest Corner	NWC	N 36º 41.902’, W 120º 31.907’	45 ft.
West Side	W	N 36º 41.684’, W 120º 31.923’	74 ft.
Southwest Corner	SWC	N 36º 41.470’, W 120º 31.924’	74 ft.
South Side	S	N 36º 41.460’, W 120º 31.651’	48 ft.

Note: The Background sites and all six (6) sampling periods were at the same locations.

Photographic images of each of the following monitoring sites are presented in Appendix A “Site Photographs”.

Staff collected a total of 73 valid air samples from eight locations around a 149.31 acre parcel of corn designated for human consumption. The application began at 1735 on 10 August, 2007 with the aircraft starting on the northeast corner going to the northwest corner. The aircraft then turned 180 degrees and made the next pass over the field. The pattern continued over the field, east to west moving north to south. Near the end of the application a pass was made around the parameter of the field. The application lasted 25 minutes and ended at 1800 on the same day.

Figure 1
Methomyl Area Map



Distance from Mendota to Richgrove is approximately 100 miles.

Figure 2

Methomyl Field Map

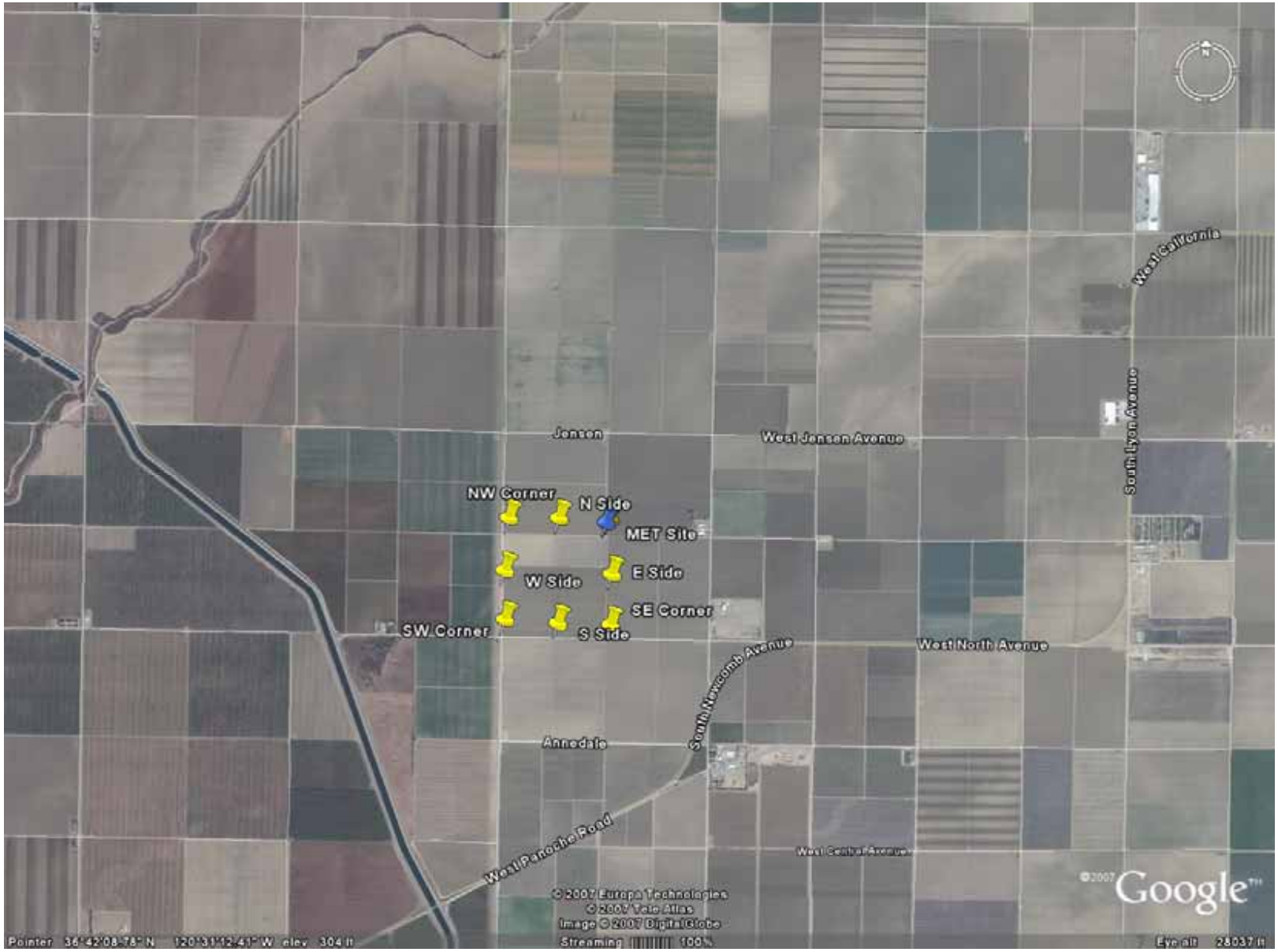
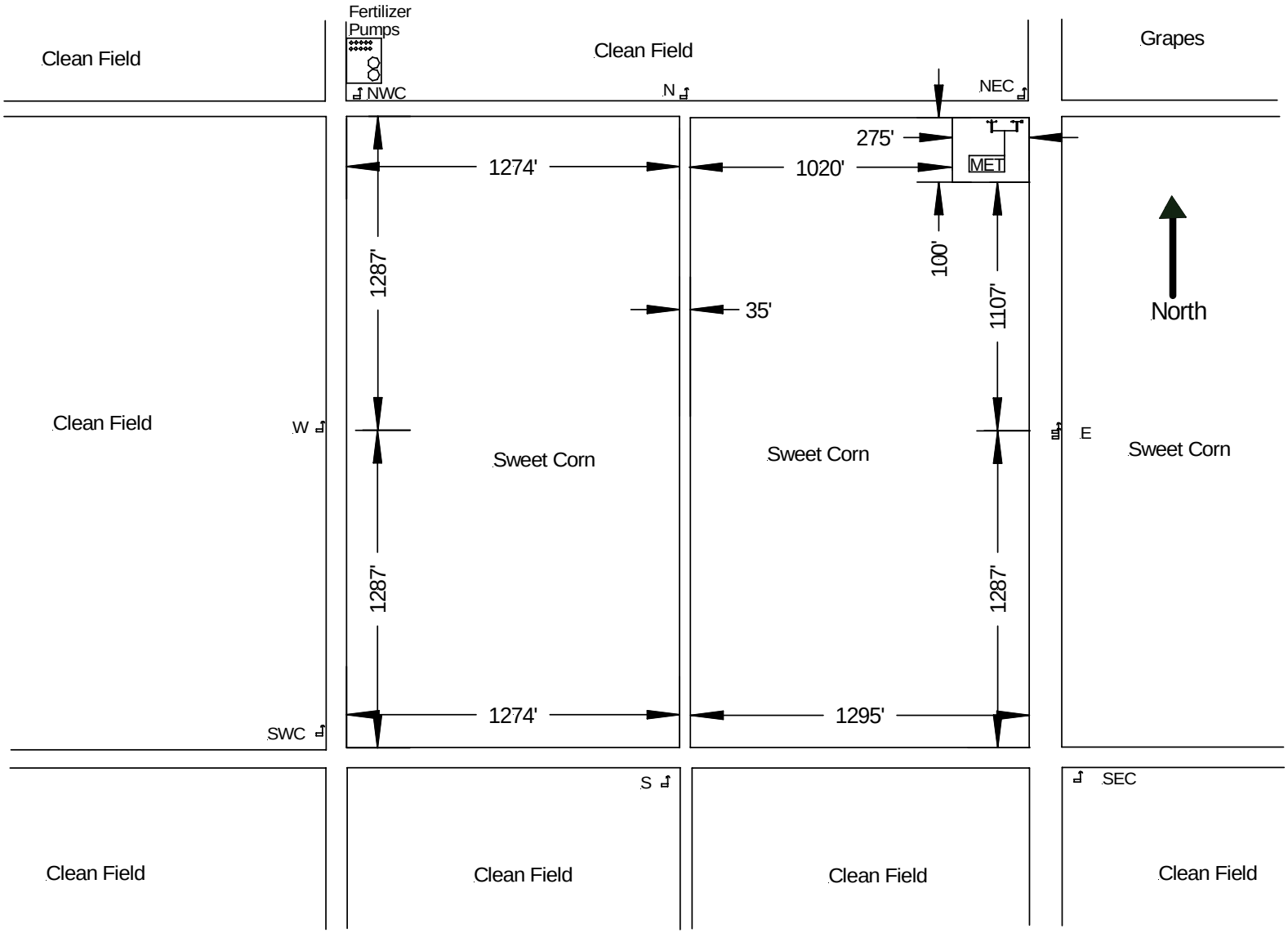


Figure 3

Methomyl Sampler Locations

Figure 4

Drawing of Application Area



3.0 Methods

Samples were collected by passing a measured flow of ambient air through XAD-2 resin tubes (SKC #226-30-06) that were mounted on a sampling tree as shown in Figure 5 "Sample Tree with Pump". The sampling flow rate of 2.0 liters per minute (LPM) was adjusted using a calibrated digital mass flow meter (MFM). The sampling system operated within a set time interval as recorded in the log sheet. The tubes were protected from direct sunlight and were supported 1.5 meters above the ground during sampling. At the end of each sampling period, the XAD-2 resin tubes were capped and placed in culture tubes with an identification label affixed and were transported on dry ice to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples were stored in a freezer or extracted/analyzed immediately

During the study a field log sheet was used to record start and stop times, start and stop flow rates, start and stop elapse time counter readings and sample identification information. A rotameter was used to control sample flow. Two rotameters were configured on a single sampling tree for collocated sampling during every sampling period at the downwind site. One rotameter controlled the primary sample flow; the second rotameter controlled the collocated sample. The rotameters are scaled from 0-5 LPM. Samplers were leak checked prior to each sampling period with the sampling XAD-2 resin tubes installed. The starting flow rates were checked and adjusted to 2.0 LPM as measured using a certified 0-5 LPM mass flow meter. The stop flow rate was checked at the end of each period using a calibrated 0-5 LPM mass flow meter.

The calibration certificates for the MFM used are presented in Appendix E "Calibration/Certification Reports".

In addition to ambient air samples, quality control samples consisted of 14 collocated samples, four field spikes, four trip spikes, one trip blanks and one field blanks were also collected.

For details of the monitoring method, please refer to Appendix B, "Protocol for the Application Air Monitoring for Methomyl" (dated October 1, 2007). There were no significant deviations from this protocol throughout the study.

Collected samples were analyzed by the Special Analysis Laboratory Section of MLD's Northern Laboratory Branch. The reported laboratory results are located in Appendix C "Standard Operating Procedure Sampling and Analysis of S-methyl-((methylcarbamoyl)oxy)thioacetamidate (Methomyl)".

Samples with concentrations above the calibration range were diluted and re-analyzed.

A meteorological system was on the northeast corner of the application field. The meteorological data and wind roses are located in Appendix F "Meteorological Data"

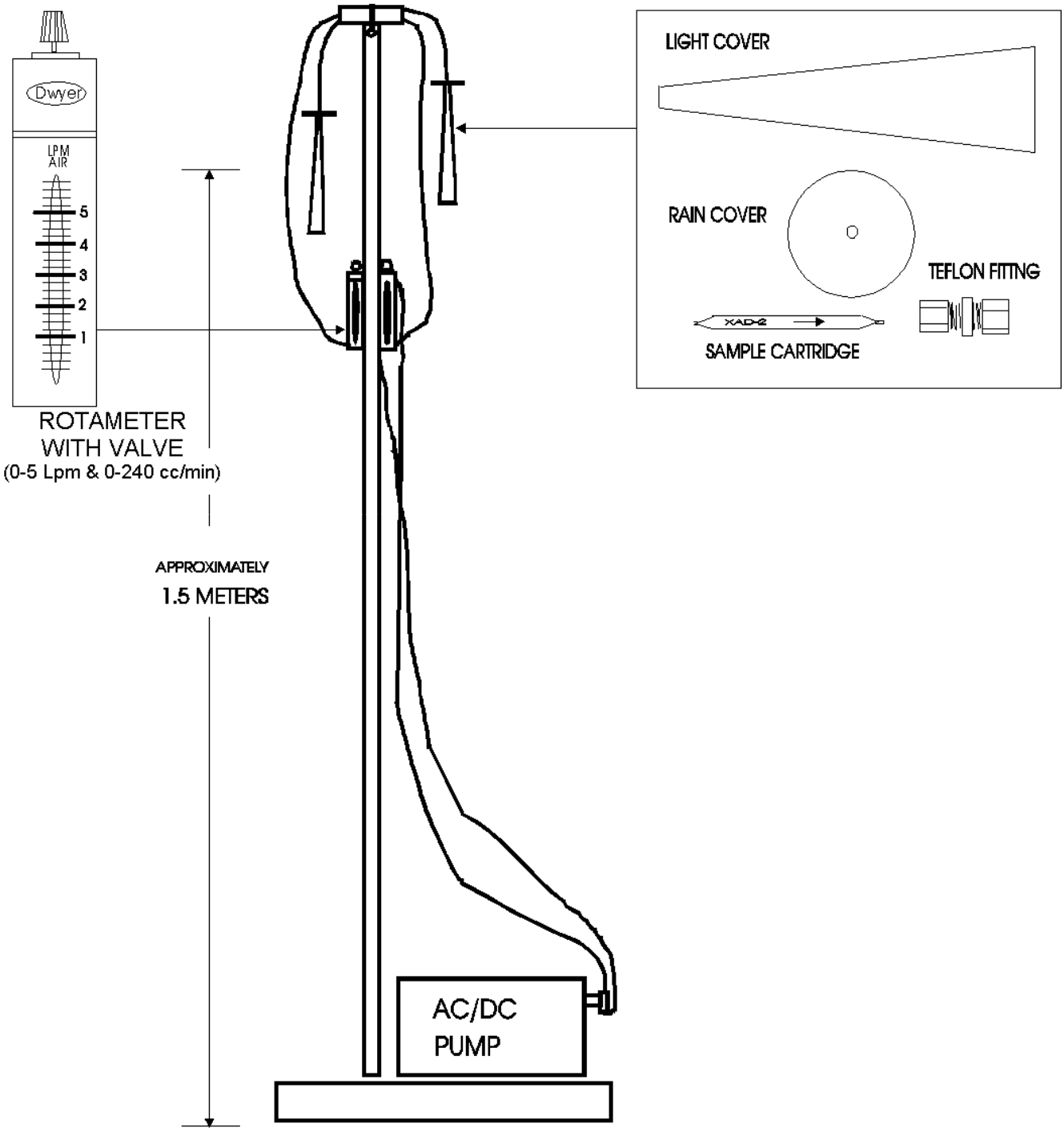


Figure 5
Air Sampler Tree with Pump

4.0 Results

The analytical results of collected samples are presented in Table 1, (Monitoring Results). These analytical results were obtained from Appendix C, (S-methyl-N((methylcarbaamoyl)oxy)thioacetimidate (Methomyl) Method Development and Analytical Results for Application Air Monitoring Samples in Fresno County). For additional information on these results, please refer to Appendix C, Laboratory Results Report.

- The reported concentrations of 57 samples are greater than the method estimated quantitation limit (EQL) of 1.0 ng/m^3. Reported methomyl results indicated ambient concentrations that ranged from less than 1.7 to 564.5 ng/m^3. A total of 41 samples have reported concentrations greater then the DPR requested EQL of 10 ng/m^3.

- A total of 11 samples required dilution. All samples requiring dilution had their secondary sections of the XAD-2 resin tubes extracted and analyzed. Of the 11 secondary sections analyzed seven (7) reported results greater than the method detection limit (MDL). Four (4) of the seven (7) reported results less than the EQL, and the remaining three (3) reported concentrations above the EQL. Log #41, Log #60, and Log #65 concentrations are greater than the EQL (1.59, 47.8, and 89.5 ng/m^3, respectively).

A sequential Log Number (#) and a Sample Identification were assigned to each sample. The methomyl sampling sites were named accordingly to locations and type of sample.

Application Site Naming (Site Identification, Background and Sampling Period 1 through 6):

Name	Location	Letter Abbreviations
SEC	Southeast Corner	FS = Field Spike
E	East Side	BG = Background
NEC	Northeast Corner	CO = Co-located
N	North Side	TB = Trip Blank
NWC	Northwest Corner	TS = Trip Spike
W	West Side	FB = Field Blank
SWC	Southwest Corner	
S	South Side	

Data capture for this study was 100% (73 total samples comprised of 63 ambient samples and 10 quality control samples). Two samples (11 and 59) were flagged due to pump failures during the sample period.

4.1 Monitoring Calculations

Table 1
Monitoring Results

Log-#	Sample ID	Start Date/Time	End Date/Time	Start Display Flow (LPM)	Corrected Start Flow (LPM)	Stop Display Flow (LPM)	Corrected Stop Flow (LPM)	ETM Start (Hours)	ETM Stop (Hours)	Calculated Total volume in cubic meters (m3)
1	BGSEC	10-9 / 1600	10-10 / 1529	2	2.118	2.07	2.188	605.1	628.8	3.061
2	BGE	10-9 / 1605	10-10 / 1548	2	2.118	2	2.118	1159.1	1182.6	2.986
3	BGNEC	10-9 / 1608	10-10 / 1537	2	2.118	2.04	2.158	156.1	179	2.937
4	BGNECCO	10-9 / 1608	10-10 / 1538	2	2.118	1.99	2.108	156.1	179	2.903
5	FSBG	10-9 / 1610	10-10 / 1540	2	2.118	1.91	2.029	517.6	540.8	2.886
6	FSBGCO	10-9 / 1610	10-10 / 1542	2	2.118	1.88	1.999	517.6	540.8	2.865
7	BGN	10-9 / 1613	10-10 / 1602	2	2.118	2.1	2.217	983.1	1001.4	2.380
8	BGNWC	10-9 / 1615	10-10 / 1606	2	2.118	1.94	2.058	632	654.1	2.769
9	BGW	10-9 / 1617	10-10 / 1608	2	2.118	2.04	2.158	563	575	2.822
10	BGSWC	10-9 / 1620	10-10 / 1614	2	2.118	2.04	2.158	214	233.2	2.463
11	BGS	10-9 / 1623	10-10 / 1619	2	2.118	2	2.118	449	457.3	1.055
12	1SEC	10-10 / 1742	10/10/1958	2	2.118	2.04	2.158	628.8	630.9	0.269
13	1E	10-10 / 1740	10/10/2003	2	2.118	2.06	2.178	179	181.4	0.309
14	1ECO	10-10 / 1740	10/10/2003	2	2.118	2	2.118	179	181.4	0.305
15	1NEC	10-10 / 1740	10/10/2009	2	2.118	2	2.118	1182.6	1185.2	0.330
16	1N	10-10 / 1739	10/10/2014	2	2.118	2	2.118	1001.4	1004	0.330
17	1NWC	10-10 / 1734	10/10/2018	2	2.118	2.02	2.138	654.1	656.9	0.357
18	1W	10-10 / 1735	10/10/2022	2	2.118	2	2.118	575	577.7	0.343
19	1SWC	10-10 / 1736	10/10/2026	2	2.118	2	2.118	233.2	236	0.356
20	1S	10-10 / 1737	10/10/2029	2	2.118	2	2.118	540.8	543.7	0.369
21	2SEC	10/10/1958	10-11 / 0701	2	2.118	1.98	2.098	630.9	641.9	1.391
22b	2E	10/10/2003	10-11 / 0704	2	2.118	1.98	2.098	181.4	192.4	1.391
22d	2E	10/10/2003	10-11 / 0704	2	2.118	1.98	2.098	181.4	192.4	1.391

4.1 Monitoring Calculations (Continued)

Table 1
Monitoring Results

Log-#	Sample ID	Start Date/Time	End Date/Time	Start Display Flow (LPM)	Corrected Start Flow (LPM)	Stop Display Flow (LPM)	Corrected Stop Flow (LPM)	ETM Start (Hours)	ETM Stop (Hours)	Calculated Total volume in cubic meters (m3)
23b	2ECO	10/10/2003	10-11 / 0704	2	2.118	1.96	2.078	181.4	192.4	1.385
23d	2ECO	10/10/2003	10-11 / 0704	2	2.118	1.96	2.078	181.4	192.4	1.385
24	2NEC	10/10/2009	10-11 / 0709	2	2.118	2	2.118	1185.2	1196.3	1.411
25	2S	10/10/2014	10-11 / 0715	2	2.118	2	2.118	1004	1015	1.398
26	2NWC	10/10/2018	10-11 / 0718	2	2.118	2	2.118	656.9	667.9	1.398
27	2W	10/10/2022	10-11 / 0722	2	2.118	2	2.118	577.7	588.7	1.398
28	2SWC	10/10/2026	10-11 / 0726	2	2.118	2	2.118	236	247	1.398
29	2S	10/10/2029	10-11 / 0729	2	2.118	2	2.118	543.7	554.6	1.385
30	3SEC	10-11 / 0701	10-11 / 1556	2	2.118	1.97	2.088	641.9	650.8	1.123
31b	3E	10-11 / 0704	10-11 / 1559	2	2.118	2	2.118	192.4	201.3	1.131
31d	3E	10-11 / 0704	10-11 / 1559	2	2.118	2	2.118	192.4	201.3	1.131
32b	3ECO	10-11 / 0704	10-11 / 1559	2	2.118	2	2.118	192.4	201.3	1.131
32d	3ECO	10-11 / 0704	10-11 / 1559	2	2.118	2	2.118	192.4	201.3	1.131
33	3NEC	10-11 / 0709	10-11 / 1608	2	2.118	2	2.118	1196.3	1205.2	1.131
34	3NEC	10-11 / 0715	10-11 / 1613	2	2.118	2	2.118	1015	1024	1.144
35	3NWC	10-11 / 0718	10-11 / 1617	2	2.118	2	2.118	667.9	676.8	1.131
36	3W	10-11 / 0722	10-11 / 1621	2	2.118	2	2.118	588.7	597.6	1.131
37	3SWC	10-11 / 0726	10-11 / 1627	2	2.118	2	2.118	247	256	1.144
38	3S	10-11 / 0729	10-11 / 1630	2	2.118	2	2.118	554.6	563.7	1.156
39b	4SEC	10-11 / 1556	10-12 / 0700	2	2.118	2	2.118	650.8	665.9	1.919
39d	4SEC	10-11 / 1556	10-12 / 0700	2	2.118	2	2.118	650.8	665.9	1.919
40b	4E	10-11 / 1559	10-12 / 0703	2	2.118	2.04	2.158	201.3	216.4	1.937
40d	4E	10-11 / 1559	10-12 / 0703	2	2.118	2.04	2.158	201.3	216.4	1.937

4.1 Monitoring Calculations (Continued)

Table 1
Monitoring Results

Log-#	Sample ID	Start Date/Time	End Date/Time	Start Display Flow (LPM)	Corrected Start Flow (LPM)	Stop Display Flow (LPM)	Corrected Stop Flow (LPM)	ETM Start (Hours)	ETM Stop (Hours)	Calculated Total volume in cubic meters (m3)
41b	4ECO	10-11 / 1559	10-12 / 0703	2	2.118	2	2.118	201.3	216.4	1.919
41d	4ECO	10-11 / 1559	10-12 / 0703	2	2.118	2	2.118	201.3	216.4	1.919
42	FS 2	10-11 / 1601	10-12 / 0705	2.00	2.118	2.06	2.178	419.5	434.5	1.933
43	FS 2 CO	10-11 / 1601	10-12 / 0705	2.00	2.118	2.00	2.118	419.5	434.5	1.906
44	4NEC	10-11 / 1608	10-12 / 0708	2.00	2.118	2.00	2.118	1205.2	1220.2	1.906
45	4N	10-11 / 1613	10-12 / 0712	2.00	2.118	2.04	2.158	1024.0	1038.9	1.911
46	4NWC	10-11 / 1618	10-12 / 0716	2.00	2.118	2.04	2.158	676.8	691.8	1.924
47	4W	10-11 / 1621	10-12 / 0719	2.00	2.118	2.00	2.118	597.6	612.6	1.906
48	4SWC	10-11 / 1627	10-12 / 0722	2.00	2.118	2.10	2.217	256.0	271.0	1.951
49b	4S	10-11 / 1630	10-12 / 0725	2.00	2.118	2.04	2.158	563.7	578.6	1.911
49d	4S	10-11 / 1630	10-12 / 0725	2.00	2.118	2.04	2.158	563.7	578.6	1.911
50	TS-1	10-11 / 1609	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
51	TS-1A	10-11 / 1609	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
52	5SEC	10-12 / 0700	10-12 / 1558	2.00	2.118	1.98	2.098	665.9	674.9	1.138
53	5E	10-12 / 0703	10-12 / 1601	2.00	2.118	2.11	2.227	216.4	225.3	1.160
54b	5ECO	10-12 / 0703	10-12 / 1601	2.00	2.118	2.08	2.197	216.4	225.3	1.152
54d	5ECO	10-12 / 0703	10-12 / 1601	2.00	2.118	2.08	2.197	216.4	225.3	1.152
55	5NEC	10-12 / 0708	10-12 / 1607	2.00	2.118	2.08	2.197	1220.2	1229.2	1.165
56	5N	10-12 / 0712	10-12 / 1611	2.00	2.118	2.06	2.178	1038.9	1047.9	1.160
57	5NWC	10-12 / 0716	10-12 / 1614	2.00	2.118	2.08	2.197	691.8	700.7	1.152
58	5W	10-12 / 0719	10-12 / 1617	2.00	2.118	2.08	2.197	612.6	621.6	1.165
59	5SWC	10-12 / 0722	10-12 / 1621	2.00	2.118	2.00	2.118	271.0	275.1	0.521
60b	5S	10-12 / 0725	10-12 / 1627	2.00	2.118	2.08	2.197	578.6	587.6	1.165
60d	5S	10-12 / 0725	10-12 / 1627	2.00	2.118	2.08	2.197	578.6	587.6	1.165

4.1 Monitoring Calculations (Continued)

Table 1
Monitoring Results

Log-#	Sample ID	Start Date/Time	End Date/Time	Start Display Flow (LPM)	Corrected Start Flow (LPM)	Stop Display Flow (LPM)	Corrected Stop Flow (LPM)	ETM Start (Hours)	ETM Stop (Hours)	Calculated Total volume in cubic meters (m3)
61	TS-2	10-12 / 0640	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
62	TS-2A	10-12 / 0640	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
63	TB	10-12 / 0645	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
64	FB	10-12 / 0645	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
65b	6SEC	10-12 / 1558	10-13 / 0659	2.00	2.118	1.96	2.078	674.9	689.9	1.888
65d	6SEC	10-12 / 1558	10-13 / 0659	2.00	2.118	1.96	2.078	674.9	689.9	1.888
66	6E	10-12 / 1601	10-13 / 0701	2.00	2.118	2.00	2.118	225.3	240.3	1.906
66b	6E	10-12 / 1601	10-13 / 0701	2.00	2.118	2.00	2.118	225.3	240.3	1.906
67	6ECO	10-12 / 1601	10-13 / 0701	2.00	2.118	2.00	2.118	225.3	240.3	1.906
68	6NEC	10-12 / 1607	10-13 / 0704	2.00	2.118	2.00	2.118	1229.2	1244.1	1.893
69	6NEC	10-12 / 1611	10-13 / 0706	2.00	2.118	1.96	2.078	1047.9	1062.8	1.876
70	6NWC	10-12 / 1614	10-13 / 0708	2.00	2.118	1.93	2.048	700.7	715.6	1.862
71	6W	10-12 / 1617	10-13 / 0711	2.00	2.118	1.94	2.058	621.6	636.4	1.854
72	6SWC	10-12 / 1621	10-13 / 0713	2.00	2.118	1.96	2.078	786.2	800.9	1.851
73	6S	10-12 / 1627	10-13 / 0715	2.00	2.118	2.00	2.118	587.6	602.4	1.881

Notes:

ID	**Identification**
ng	**Nanograms**
d	**Result used is from a diluted extract**
b	**Secondary section results**
N/A	**Not Applicable**
ETM	**Elapse Time Meter**

4.1 Monitoring Calculations (Continued)

The formula below refers to Table 1, Monitoring Calculations:
Total in cubic meters (m_3) of ambient air =

((((Sample Flow Start + Sample Flow Stop)/2)*Slope of 0.993) + Offset of 0.132)*((ETM Stop - ETM Start)*60 minutes)= Liters of ambient air / 1000 = Corrected Total Volume in cubic meters (m_3)

or

$$\left[\frac{(\text{Start Flow + Stop Flow})}{2}(m)\right]+b = \text{Corrected Average Ambient Air Flow Per Minute}$$

[(ETM Stop Hours- ETM Start Hours)*60 Minutes] = Total Elapse Time in Minutes

Corrected Average Ambient Air Flow Per Minute Multiplied by the Total Elapse Time in Minutes = Total Liters of Ambient Air Collected Divided by 1000 = Corrected Total Volume in cubic meters (m_3)

If the analytical result is <MDL it is reported as less than the established method detection limit. If the analytical result is $\geq$ MDL and < EQL, it is reported in the table as the measured value to one significant figure. Levels at or above the EQL are reported as the actual measured value and are reported to three significant figures.

Sample ID (Sample identification) numbers followed by the letters CO are collocated samples for the samples with the corresponding number.

Sample ID numbers followed by the letter b are samples results from the secondary section of the sample cartridge.

Sample ID numbers followed by the letter d are samples results from a diluted sample.

Log Numbers 11 and 59 were flagged due to pump shut-off early.

4.2 Laboratory Results

Table 2
Laboratory Results

Log- #	Sample ID	Total Volume m^3	Methomyl ng/sample	Methomyl ng/m^3
1	BGSEC	3.061	1.08 E+01	3.53
2	BGE	2.986	1.94 E+02	64.96
3	BGNEC	2.937	4.75 E+01	16.17
4	BGNECCO	2.903	5.06 E+01	17.43
5	FSBG	2.886	1.47 E+02	Field Spike
6	FSBGCO	2.865	8.05 E+01	Field Spike
7	BGN	2.380	3.42 E+01	14.37
8	BGNWC	2.769	1.14 E+01	4.12
9	BGW	2.822	8.44 E+00	2.99
10	BGSWC	2.463	2.94 E+01	11.94
11	BGS	1.055	2.66 E+01	25.22
12	1SEC	0.269	5.80 E+01	215.32
13	1E	0.309	7.09 E+01	229.24
14	1ECO	0.305	5.76 E+01	188.86
15	1NEC	0.330	4.36 E+00	13.20
16	1N	0.330	2.00 E+00	6.05
17	1NWC	0.357	<6 E-01	<1.68
18	1W	0.343	<6 E-01	<1.75
19	1SWC	0.356	<6 E-01	<1.69
20	1S	0.369	1.41E+02	382.60
21	2SEC	1.391	8.90 E+01	63.97
22b	2E	1.391	1.00 E+00	0.72
22d	2E	1.391	2.68 E+02	192.62
23b	2ECO	1.385	1.00 E+00	0.72
23d	2ECO	1.385	4.00 E+02	288.86
24	2NEC	1.411	1.04 E+02	73.73
25	2N	1.398	1.04 E+02	74.40
26	2NWC	1.398	2.00 E+00	1.43
27	2W	1.398	1.81 E+01	12.95
28	2SWC	1.398	<6 E-01	<0.43
29	2S	1.385	9.76 E+01	70.46
30	3SEC	1.123	4.13 E+01	36.77
31b	3E	1.131	<6 E-01	<0.53
31d	3E	1.131	5.15 E+02	455.34

4.2 Laboratory Results (Continued)

Table 2
Laboratory Results

Log- #	Sample ID	Total Volume m^3	Methomyl ng/sample	Methomyl ng/m^3
32b	3ECO	1.131	<6 E-01	<0.53
32d	3ECO	1.131	4.87 E+02	430.59
33	3NEC	1.131	4.95 E+00	4.38
34	3N	1.144	7.00 E+00	6.12
35	3NWC	1.131	1.84 E+01	16.27
36	3W	1.131	3.20 E+01	28.29
37	3SWC	1.144	2.35 E+01	20.55
38	3S	1.156	1.88 E+02	162.57
39b	4SEC	3.050	<6 E-01	<0.2
39d	4SEC	3.050	2.23 E+02	73.12
40b	4E	1.937	<6 E-01	<0.31
40d	4E	1.937	7.33 E+02	378.44
41b	4ECO	1.919	3.06 E+00	1.59
41d	4ECO	1.919	4.36 E+02	227.21
42	FS 2	1.933	6.08 E+02	Field Spike
43	FS 2 CO	1.906	4.28 E+02	Field Spike
44	4NEC	1.906	7.68 E+01	40.29
45	4N	1.911	8.80 E+01	46.04
46	4NWC	1.924	4.56 E+01	23.70
47	4W	1.906	7.52 E+01	39.45
48	4SWC	1.951	6.32 E+01	32.40
49b	4S	1.911	1.00 E+00	0.52
49d	4S	1.911	2.53 E+02	132.37
50	TS-1	N/A	4.08 E+01	Trip Spike
51	TS-1A	N/A	4.13 E+01	Trip Spike
52	5SEC	1.138	3.81E+01	33.47
53	5E	1.160	1.70 E+02	146.53
54b	5ECO	1.152	<6 E-01	<0.52
54d	5ECO	1.152	2.85 E+02	247.35
55	5NEC	1.165	5.79 E+01	49.69
56	5N	1.160	7.33 E+01	63.20
57	5NWC	1.152	4.34 E+01	37.67
58	5W	1.165	9.56 E+01	82.05
59	5SWC	0.521	3.03 E+01	58.15

4.2 Laboratory Results (Continued)

Table 2
Laboratory Results

Log- #	Sample ID	Total Volume m^3	Methomyl ng/sample	Methomyl ng/m^3
60b	5S	1.165	5.57 E+01	47.80
60d	5S	1.165	4.01 E+02	344.16
61	TS-2	N/A	4.26 E+01	Trip Spike
62	TS-2A	N/A	4.37 E+01	Trip Spike
63	TB	N/A	<6-E01	Trip Blank
64	FB	N/A	<6-E01	Field Blank
65b	6SEC	1.888	1.69 E+02	89.50
65d	6SEC	1.888	8.97 E+02	475.02
66b	6E	1.906	2.00 E+00	1.05
66	6E	1.906	6.18 E+01	32.42
67	6ECO	1.906	4.78 E+01	25.08
68	6NEC	1.893	2.77 E+01	14.63
69	6N	1.876	2.87 E+01	15.30
70	6NWC	1.862	1.45 E+01	7.79
71	6W	1.854	2.28 E+01	12.30
72	6SWC	1.851	5.42 E+00	2.93
73	6S	1.881	8.41 E+01	44.72

Notes:

d = Result used is from a diluted extract
b = Secondary section results

The formulas below refer to Table 2 Laboratory Results:

Total in Liters / 1000 = Cubic Meters (m^3)
Methomyl ng/m^3 = Methomyl ng/sample divided by Total Volume (m^3)

4.2 Laboratory Results (Continued)

Table 3
Laboratory Results
Diluted and Secondary Section

Log- #	Sample ID	Total Volume m3	Methomyl ng/Sample	Methomyl ng/m3	Total ng/Sample	Total ng/m3
22b	2E	1.39	1.00 E+00	0.72		
22d	2E	1.39	2.68 E+02	192.62	**269.00**	**193.34**
23b	2ECO	1.38	1.00 E+00	0.72		
23d	2ECO	1.38	4.00 E+02	288.86	**401.00**	**289.58**
31b	3E	1.13	<6 E-01	<0.53		
31d	3E	1.13	5.15 E+02	455.34	**515.60**	**455.87**
32b	3ECO	1.131	<0.6 E-01	<0.53		
32d	3ECO	1.131	4.87 E+02	430.59	**487.60**	**431.12**
39b	4SWC	3.05	<6 E-01	<0.2		
39d	4SWC	3.05	2.23 E+02	73.12	**223.60**	**73.22**
40b	4E	1.94	<6 E-01	<0.31		
40d	4E	1.94	7.33 E+02	378.44	**733.6**	**378.75**
41b	4ECO	1.92	3.06 E+00	1.59		
41d	4ECO	1.92	4.36 E+02	227.21	**439.06**	**228.81**
49b	4S	1.91	1.00 E+00	0.52		
49d	4S	1.91	2.53 E+02	132.37	**254.00**	**132.90**
54b	5ECO	1.15	<6 E-01	<0.52		
54d	5ECO	1.15	2.85 E+02	247.35	**285.60**	**247.87**
60b	5S	1.17	5.57 E+01	47.80		
60d	5S	1.17	4.01 E+02	344.16	**456.70**	**391.96**
65b	6SEC	1.89	1.69 E+02	89.50		
65d	6SEC	1.89	8.97 E+02	475.02	**1066.00**	**564.52**
66b	6E	1.91	2.00 E+00	1.05		
66	6E	1.91	6.18 E+01	32.42	**63.80**	**33.47**

Total ng/Sample results are the diluted and secondary sections which consist of the sum of the two sections of the XAD-2 resin tubes.

Total ng/m3 results are the diluted and secondary sections which consist of the sum of the two sections of the XAD-2 resin tubes divided by Total Volume m^3.

4.3 Discussion of Results

The current usage of methomyl has dropped from the amount reported in DPR's "Use Information and Application Monitoring Recommendations for the Pesticide Active Ingredient Methomyl and the Ambient Air Monitoring Recommendations for methomyl, dated March 2007.

The only known methomyl application in California is around the Mendota area. The Agricultural Commission personnel, Pesticide Control Advisors and applicators all stated that alternative pesticides are being used in lieu of methomyl. The usage rates (pounds per acre) were a half pound or less when used. The higher rates indicated by DPR's recommendation may be due to multiple applications to a field during the same growing period.

The reported quality control results raise questions regarding the overall interpretation of the data. During the development of the analytical method, the Northern Laboratory Branch's Special Analysis Section noted laboratory spike recoveries ranging from 43.38 ng/sample (85% recovery) to 46.12 ng/sample (90% recovery). The field study trip spikes reported recoveries ranging from 40.76 ng/sample (80% recovery) to 43.70 ng/sample (86% recovery). Breakthrough studies showed no detectable methomyl concentrations in the secondary section of the XAD-2 cartridge.

Although the field spikes were prepared similarly to the laboratory and trip spikes, the field spike recoveries were very poor, ranging from -305% to 192%. Field spike results ranged from 80 to 600 ng/sample. The best field spike result was 80.52 ng/sample (62% recovery). The poorest recovery was over 400 ng/sample (-305% recovery). The other two field spike levels were at 147 & 607 ng/sample (38% and 192% recovery, respectively). These spikes were exposed to ambient air with reportable ambient methomyl concentrations. In addition, the collocated samples collected during the field study reported a high degree of variability in their relative percent difference (RPD). While two collocated pairs reported RPD's of less then 10%, five other collocated pairs reported RPD's ranging from -51% to +51%.

At concentrations lower than the spike level (51 ng/sample), the field spike and collocated results were consistent to the results as reported in the "Report on Ambient Air Monitoring for Methomyl and Carbaryl in Fresno, Tulare and Kings Counties during July and August 2007", dated December 9, 2008. The best collocated data set was sampled during the background period with reported analytical results of 47.5 and 50.6 ng/sample (16 and 17 ng/m3). The second best collocated data set was collected during the last sampling period at 61.8 and 47.8 ng/sample (32 and 25 ng/m3). These analytical levels are near the 51 ng/sample spike, and sampled when ambient methomyl levels were at their lowest. At higher concentrations, field spike recoveries and collocated data differ greatly.

We cannot determine or explain why the field QC results at higher concentrations are so poor, and therefore, we cannot state with confidence that the field data are 'good' or 'usable'. Each analytical result could have been influenced by ambient methomyl concentration levels, humidity, temperature, winds, sampler location, general field conditions, the sample matrix, sample flow rate, pesticide application technique and/or the

analytical method. In summary, we recommend redevelopment of the method if methomyl risk exposure remains a priority with DPR and/or the Scientific Review Panel, and the data reported for this application study should not be used for decision making purposes.

5.0 Quality Assurance

Quality Control samples collected from the field consisted of:

14 total collocated samples (7 collocated pairs)

8 Spikes (4 Field Spikes, 4 Trip Spikes)

Blanks (1 Trip Blank and 1 Field Blank)

The following bullets summarize the Quality Control results of these samples. For more detailed information. See **Table 2,** "XAD-2 Cartridge Spikes, Field and Trip Blanks Methomyl Application 2007" and **Appendix C** of the Laboratory Results Report.

- Collocated sample results are located in **Table 1**, "Monitoring Results" of this report.

- A review of the collocated unspiked samples show a high degree of variability. Two (2) pairs report RPDs of less than 10%, while five (5) other pairs report RPD's that ranged from -51% to +51%.

- Four (4) field spikes were analyzed during this study. Two (2) field spikes were collected prior to the methomyl application during background sampling and two (2) were collected during the forth sampling period. The first set of spikes was collected at the northeast corner (NEC) while the second set was collected on the East side (E) of the field. Examination of the results shows a high degree of variability between the collocated spiked samples. The methomyl spikes (51 ng) reported the following results:

  Log #5 reported a 192 percent of recovery.
  Log #6 reported a 62 percent of recovery.
  Log #42 reported a 38 percent of recovery.
  Log #43 reported a -305 percent of recovery.

  Both Log #42b and Log #43b had a low level of breakthrough above the method detection limit.

- During this study one (1) field blank and one (1) trip blank were analyzed. Methomyl was not detected in either blank.

- Four (4) trip and four (4) laboratory spikes were analyzed during this study. The average recovery for the trip spikes was 83% $\pm$ 2.57%. The laboratory spikes reported an average recovery of 87% $\pm$ 2.76%. No anomalous events occurred with these samples.

5.0 Quality Assurance (Continued)

Table 4: XAD-2 Cartridge Spikes, Field and Trip Blanks for the Methomyl Application 2007

Quality Control Type	Log Number	Laboratory ID	Date Analyzed	Methomyl amount[1] (ng/sample)	Percent Recovery
Laboratory Spike (51 ng/sample)	na	LS101607a	10/20/07	45.48	89.18
	na	LS101707b	10/22/07	46.12	90.43
	na	LS101707ac	10/23/07	43.38	85.06
	na	LS101807d	10/23/07	43.43	85.16
Trip Spike (51 ng/sample)	50	TS-1	10/23/07	40.76	79.92
	51	TS-1A	10/23/07	41.34	81.06
	61	TS-2	10/23/07	42.58	83.49
	62	TS-2A	10/23/07	43.70	85.69
Trip Blank	63	MA063	10/23/07	<0.6	
Field Blank	64	MA064	10/23/07	<0.6	

6.0 Quality Assurance (Continued)

Table 4: XAD-2 Cartridge Spikes, Field and Trip Blanks for the Methomyl Application 2007 (Continued)

Field Spikes

Log #	Sample ID	Field spike Sample **(ng/sample)**	Total Volume Sampled Ambient Air **($m^{3)}$**	Field spike Sample **(ng/m^3)**	Average Collocated Sample **(ng/m^3)**	net spike **(ng/m^3)**	net spike **(ng/Sample)**	Percent Recovery of 51 ng Spike
5	FSBG	147.34	2.937	50.17	Avg. Log # 3&4	33.37	98.00	192%
6	FSBGCO	80.52	2.903	27.74	16.8	10.94	31.75	62%
42	FS 2	607.68	1.937	313.72	Avg. Log # 40&41	9.94	19.26	38%
43	FS 2 CO	427.56	1.919	222.80	303.78	-80.98	-155.39	-305%

Field spike percent recoveries of 51 ng field spikes are calculated as follows:

Field spike sample (**ng/sample**) *****Total Volume Sampled Ambient Air **($m^{3)}$** = Field spike sample (**ng/m^3**) Avg.
Field spike sample (**ng/m^3**) Avg – Average collocated sample **(ng/m^3)** = Net Spike (**ng/m^3**)
Net Spike (**ng/m^3**) ***** Total Volume Sampled Ambient Air **(m^3) =** Net spike ng/sample
Net spike (**ng/sample**) / spike 51 (**ng/sample**) ***** (100%) = percent recovery of 51 ng