



Air Resources Board




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FROM: Kenneth R. Stroud, Chief 
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DATE: June 9, 2016

SUBJECT: FINAL REPORT ON PESTICIDE AIR MONITORING 2,4-DICHORPHENOXYACETIC ACID DIMETHYLAMINE SALT (2,4-D DMAS) APPLICATION STUDY STANISLAUS COUNTY NOVEMBER 2013

Attached is the pesticide report titled "Final Report on Pesticide Air Monitoring Application of 2,4-Dichorphenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) in Stanislaus County November 2013". The draft of this report was previously forwarded to your staff for review in December 2015 and their comments have been incorporated.

Thank you for your cooperation during this project. If you or your staff have any questions or need further information, please contact me at (916) 324-7630 or via email at kstroud@arb.ca.gov.

Attachment

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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>.

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**Final Report for Pesticide Air Monitoring
2,4-dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS)
Application Study Stanislaus County November 2013**

Prepared by

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Special Purpose Monitoring Section
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May 16, 2016

Monitoring Report Approval

Report Title: Final Report for Pesticide Air Monitoring 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) Application Study Stanislaus County November 2013

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
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Date

Kenneth R. Stroud, Chief
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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 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) in Stanislaus County November 2013. The 2,4-D DMAS is applied directly to fields by ground application spraying and is used as an herbicide to control a wide range of grasses and broad-leaved weeds.

Seventy one field samples, including seven (7) field spikes, one (1) trip spike, one (1) field blank and nine (9) background samples were collected from eight different locations around the perimeter of an 39 acre almond orchard located in Stanislaus County. The 2,4-D DMAS was applied by ground using a spray rig which was pulled by a small cart at a rate of 1.43 lbs. of 2,4-D DMAS per acre.

Samples were collected by passing 1.0 liter per minute (LPM) of ambient air through XAD-2 sorbent tubes positioned 1.5 meters above ground level.

There were a total of seven (7) 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 following the last post sampling period 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 target estimated quantitation limit (EQL) of 4 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) which is equal to 4000 nanograms per cubic meter (ng/m^3). The ARB's laboratory achieved an EQL of $0.027 \mu\text{g}/\text{m}^3$ ($27 \text{ng}/\text{m}^3$) based on a 12-hour sample with a flow rate of 1.0 LPM.

- There were no positive concentrations of 2,4-D DMAS above the established analytical MDL of $3.82 \text{ng}/\text{sample}$ and estimated 12-hour sampling duration MDL of $0.0053 \mu\text{g}/\text{m}^3$
- The seven (7) field spike recoveries ranged from 96 to 117% and the trip spike recovery of 106%
- The seven laboratory (7) spikes for this study reported an average recovery of 87.3% with a standard deviation of 3.46%

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APPENDIX B: Site Photographs

APPENDIX C: Sampling Protocol

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APPENDIX E: XAD2 Sample Field Log Sheet

APPENDIX F: Calibration/Certification Reports

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (2011 Memorandum, Reardon to Ayala, Appendix A), Air Resources Board (ARB) staff conducted sampling of airborne concentrations of 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) during an application in Stanislaus County.

Seventy one field samples, including seven (7) field spikes and one (1) trip spike, one (1) field blank and nine (9) background samples were collected from eight different locations around the perimeter of an 39 acre almond orchard located in Stanislaus County from November 13 through November 17, 2013.

The 2,4-D DMAS was applied by ground spraying using a spray rig which was pulled by a small cart (See Figure 1) on November 14 from approximately 08:17 to 14:18 AM PST which calculates to a 6 hours and 1 minute application period which includes an approximately one (1) hour break to reload the tank on the spray rig.

The 2,4-D DMAS application rate of 1.43 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 117.0 pints of 2,4-D DMAS was applied to a 39 acre field. Per the manufacture's listed product label specification sheet, 2,4-D DMAS Flowable Herbicide contains 3.8 lbs. of 2,4-D DMAS/gallon. The equations used to calculate the amount applied per acre is listed on page 15

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

The application sampling periods located in Table 2 have overlapping times due to the time it took to go around the field and when the samples were actually started. Each sample start/stop time is recorded on the field log sheets located in Appendix E.



Figure 1
Spray Rig with Tank

Parameter	Details
Location	Stanislaus County, CA. South of Ceres, west of Highway 99
Field Size	39 acres
Product Applied	Saber Herbicide Active Ingredients:46.6% 2,4-D DMAS (Dimethylamine salt of 2,4-Dichlorophenoxyacetic acid) Inert Ingredients: 53.4% *Contains 3.8 lbs. 2,4-Dichlorophenoxyacetic acid equivalent per U.S. gallon or 456 liter *Contains 38.7% 2,4-Dichlorophenoxyacetic acid equivalent, by weight
Application Type	Ground air-blast (cart pulled sprayer) Start = November 14, 2013, 0817 to 1418 PST
Commodity	Almond Orchard
Application Rate	0.375 gallons of 2,4-D DMAS product per acre at a calculated 1.43 lbs./acre of 2,4-D DMAS

Table 1
Application Information

Sampling Period	Sample Period Duration (Hours)	Nov-2013 (Date)	Time (Start/Stop)
Background	20.0	13-14	1212 to 0814
1 (Application)	7.0	14	0819 to 1558
2 (Nighttime)	16.8	14-15	1513 to 0800
3 (Daytime)	8.6	15	0727 to 1601
4 (Nighttime)	16.6	15-16	1526 to 0801
5 (Daytime)	8.9	16	0730 to 1625
6 (Nighttime)	16.3	16-17	1548 to 0807

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 2, 4-D DMAS Sampling Sites) presents a Google map-view of the area surrounding the application field located in Stanislaus 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.

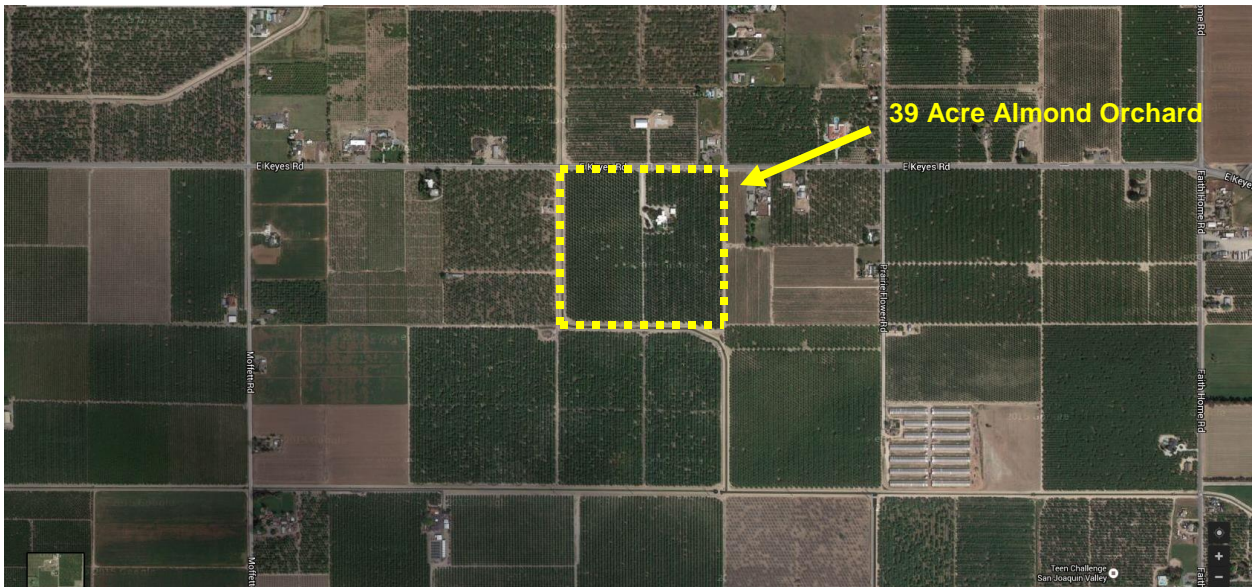


Figure 2
Satellite Map of Overview of Monitoring Area

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 39 acre almond orchard. See Appendix B for individual site photographs.

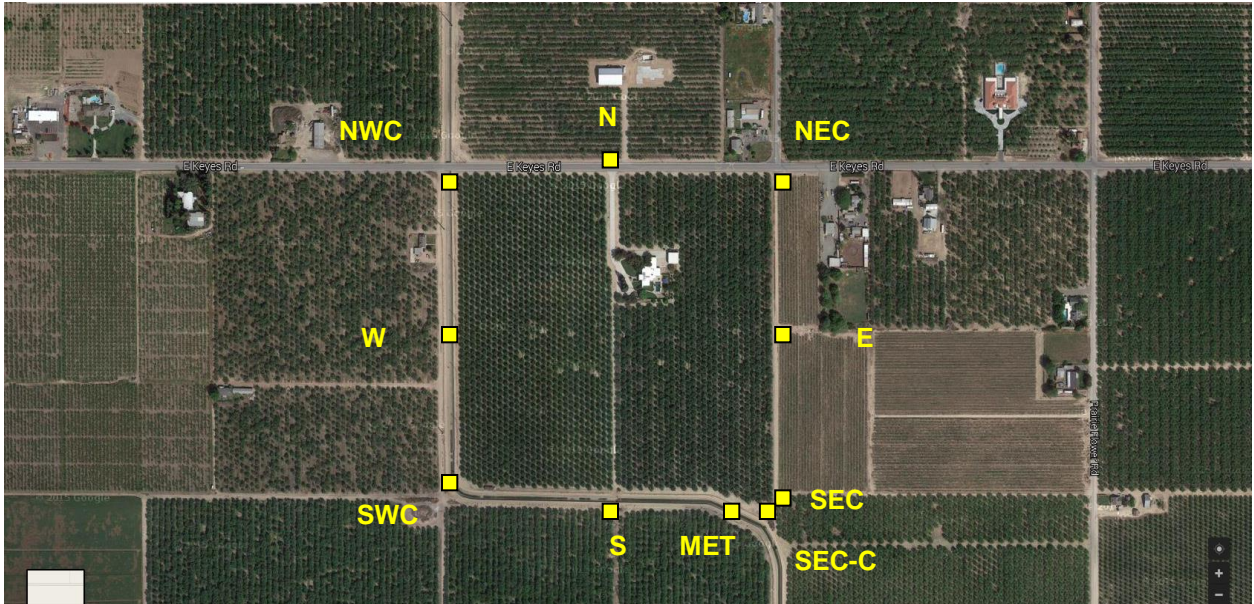


Figure 3
Satellite Map of 2, 4-D DMAS Sampling Sites

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)	53' Southeast Corner of field	Southeast Corner of Field
NEC (Northeast Corner)	60' East of the Northeast Corner of the field, Elevation = 16'	N 37°33'04.1" W 120°56'02.4"
N (North Side)	60' North of the field and 670' from the Northeast Corner, Elevation = 15'	N 37°32'51.0" W 120°56'10.9"
NWC (Northwest Corner)	60' West of the Northwest Corner of the field and 670' from North Side, Elevation = 13'	N 37°33'04.1" W 120°56'20.2"
W (West)	60' West of the field and 620' from the Northwest Corner of the field, Elevation = 13'	N 37°32'58.0" W 120°56'20.1"
SWC (Southwest Corner)	40' West of the Southwest Corner and 620' from the West of the field, Elevation = 13'	N 37°32'51.7" W 120°56'19.8"
S (South Side)	58' South of the field and 670' from the Southwest Corner of the field, Elevation = 12'	N 37°32'51.0" W 120°56'10.9"
SEC (Southeast Corner)	60' East of the Southeast Corner of the field, 670' from the South Side of the field, Elevation = 14'	N 37°32'50.4" W 120°56'03.4"
E (East)	60' East of the field and 684' from the Southeast Corner of the field, Elevation = 14'	N 37°32'57.9" W 120°56'02.6"

Table 3
Sample Waypoints

3.0 Methods

Samples were collected by passing 1.0 liter 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 seven (7) ambient sampling periods including a background as requested by DPR. Air samples were taken before, during, and after the 2, 4-D DMAS application. There were three (3) daytime and four (4) overnight sampling periods.

The background sampling started on November 13, 2013 at 12:12 (PST) and ran till the morning of November 14, 2013, 08:14 (PST).

The 2, 4-D DMAS application samples were started at 8:19 (PST) on April 14, 2013 and ended at 15:58 (PST).

Immediately after removing the application samples the post application samples were installed and ran overnight. Thereafter the post-application samples started one (1) hour before sunset and were collected one (1) hour after 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 (MFM) was used to measure and adjust sample flow rates. The flow rates were set to 1.0 LPM, as measured using a digital 0-5 LPM MFM before the start and the sample flow rate was measured at the 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, a field blank and a trip spike.

Meteorological data was collected using a Met One auto-met weather station which logged 5 minute averages for wind speed and direction along with temperature and relative humidity. See Figure 5, 6, 7, 8 for Wind Roses and APPENDIX G for meteorological data.

For details of the monitoring method, please refer to Appendix C, "Sampling Protocol for 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) Application Study" (dated November 7, 2013). The number of sampling periods were reduced from eight (8) sampling periods to seven (7) resulting in having less than the proposed number of samples reduce from (92) down to (71). There were no other 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) based on a 24 hour sampling period for this method is $0.013 \mu\text{g}/\text{m}^3$ prior to any sample dilution for sampling at one (1) LPM and a four (4) 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 (20 ng/ml), the MDL and EQL for a four-ml extract is calculated as follows:

<p><i>s = the standard deviation of the concentration calculated for the seven replicate spikes.</i> <i>For 2,4-D DMAS: $s = 0.3040$</i></p> <p>$MDL = (3.143) \times (s) = (3.143) \times (0.3040) = 0.955 \text{ ng/ml.}$ $MDL \text{ (ng/sample)} = 0.955 \text{ ng/ml} \times 4.00\text{ml} = 3.82 \text{ ng/sample}$ $EQL = (5) \times (MDL) = (5) \times (3.82) = 19.1 \text{ ng/sample}$</p>

Based on a total collection volume of 1.440 m^3 over a 24 hour sampling period the EQL would be $0.013 \mu\text{g}/\text{m}^3$. Most samples are collected during a 12 hour sampling period so to adjust for the collection volume of 0.720 m^3 the, EQL is $0.027 \mu\text{g}/\text{m}^3$ and the MDL is $0.0053 \mu\text{g}/\text{m}^3$. All laboratory results are reported in ng/sample. Results less than the calculated MDL are reported as "<3.82 ng/sample." See Appendix D

4.0 Results

The results reported indicated all levels of 2, 4-D DMAS were all less than the calculated MDL of 3.82 ng/sample.

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 m³. These values were used to calculate the reported lab results ng/sample to ng/m³ for each sampling location.

Wind roses are located in Figure 5 thru 8 showing the wind characteristics for each of the first (4) sampling periods including the background. The fourth through the sixth sampling period's meteorological data was lost due to a malfunction in the met station data logger. 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 1-6	Northeast Corner of Field
N 1-6	North Side of Field
NWC 1-6	Northwest Corner of Field
W 1-6	West Sid of Field
SWC 1-6	Southwest Corner of Field
S 1-6	South Side of Field
SEC 1-6	Southeast Corner of Field
SEC 1C-6C	Southeast Corner of Field Co-located
E 1-6	East Side of Field

See Figure 3, Satellite Map of 2,4-D DMAS Sampling Sites

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

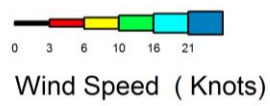
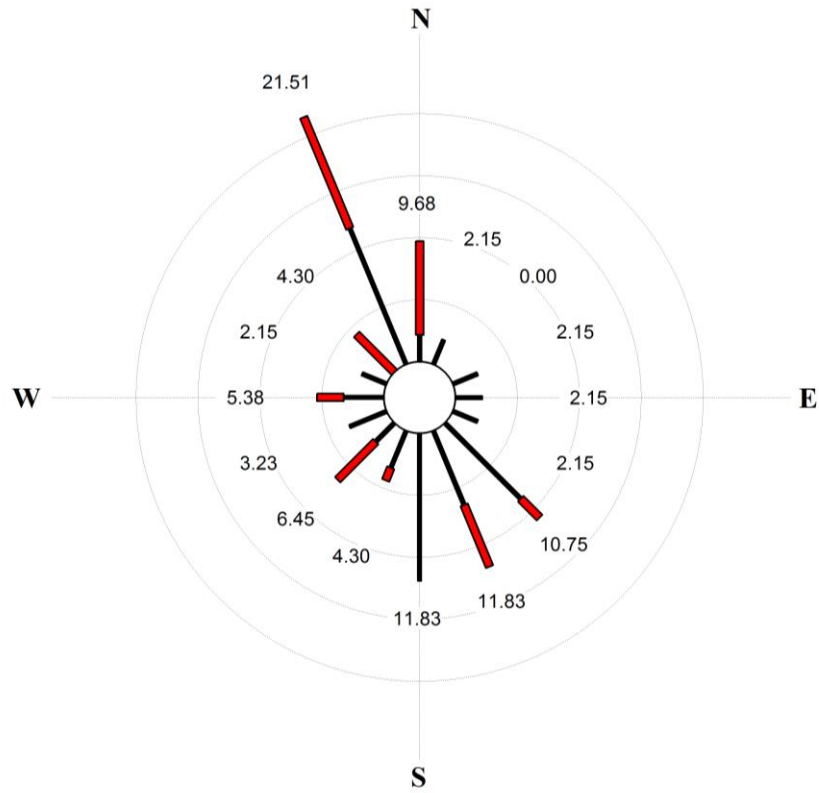
Log #	Sample Location	Elapsed Time (Minutes)	Elapsed Time (Hours)	Avg. Flow (LPM)	Total Volume (m ³)	2,4-D (ng/sample)	2,4-D (ng/m ³)
11	NWC-1	402.0	6.7	1.47	0.59	<3.82	<6.46
21	NWC-2	972.0	16.2	1.14	1.11	<3.82	<3.45
31	NWC-3	480.0	8	1.06	0.51	<3.82	<7.51
41	NWC-4	960.0	16	1.11	1.07	<3.82	<3.58
51	NWC-5	498.0	8.3	1.10	0.55	<3.82	<6.97
61	NWC-6	948.0	15.8	1.04	0.99	<3.82	<3.87
2	BKG-W	1146.0	19.1	0.80	0.92	<3.82	<4.17
12	W-1	420.0	7	1.15	0.48	<3.82	<7.91
22	W-2	972.0	16.2	1.14	1.11	<3.82	<3.45
32	W-3	480.0	8	1.08	0.52	<3.82	<7.37
42	W-4	960.0	16.0	1.10	1.06	<3.82	<3.62
52	W-5	498.0	8.3	1.08	0.54	<3.82	<7.10
62	W-6	948.0	15.8	1.05	1.00	<3.82	<3.84
3	BKG-SWC	1152.0	19.2	0.78	0.90	<3.82	<4.25
13	SWC-1	426.0	7.1	1.21	0.52	<3.82	<7.41
23	SWC-2	972.0	16.2	1.06	1.03	<3.82	<3.71
33	SWC-3	480.0	8.0	1.10	0.53	<3.82	<7.23
43	SWC-4	960.0	16.0	1.12	1.08	<3.82	<3.55
53	SWC-5	498.0	8.3	1.10	0.55	<3.82	<6.97
63	SWC-6	942.0	15.7	1.04	0.98	<3.82	<3.90
4	BKG-S	978.0	16.3	0.83	0.81	<3.82	<4.71
14	S-1	432.0	7.2	0.95	0.41	<3.82	<9.31
24	S-2	972.0	16.2	1.12	1.09	<3.82	<3.51
34	S-3	480.0	8.0	1.08	0.52	<3.82	<7.37
44	S-4	960.0	16.0	1.11	1.07	<3.82	<3.58
54	S-5	498.0	8.3	1.10	0.55	<3.82	<6.97
64	S-6	942.0	15.7	1.05	0.99	<3.82	<3.86
5	BKG-SEC	1152.0	19.2	0.86	0.99	<3.82	<3.86
15	SEC-1	438.0	7.3	1.11	0.49	<3.82	<7.86
25	SEC-2	972.0	16.2	1.18	1.15	<3.82	<3.33
35	SEC-3	480.0	8.0	1.08	0.52	<3.82	<7.37
45	SEC-4	960.0	16.0	1.13	1.08	<3.82	<3.52
55	SEC-5	498.0	8.3	1.10	0.55	<3.82	<6.97
65	SEC-6	942.0	15.7	1.08	1.02	<3.82	<3.75

Table 4
Application Results by Site

Log #	Sample Location	Elapsed Time (Minutes)	Elapsed Time (Hours)	Avg. Flow (LPM)	Total Volume (m ³)	2,4-D (ng/sample)	2,4-D (ng/m ³)
6	BKG-SEC-C	1152.0	19.2	0.81	0.93	<3.82	<4.09
16	SEC-1C	444.0	7.4	1.15	0.51	<3.82	<7.48
26	SEC-2C	966.0	16.1	1.22	1.18	<3.82	<3.24
36	SEC-3C	486.0	8.1	1.08	0.52	<3.82	<7.28
46	SEC-4C	960.0	16	1.19	1.14	<3.82	<3.34
56	SEC-5C	492.0	8.2	1.11	0.55	<3.82	<6.99
66	SEC-6C	948.0	15.8	1.05	1.00	<3.82	<3.84
7	BKG-FS-1	1152.0	19.2	0.88	1.01	<3.82	<3.77
17	SEC-1FS	438.0	7.3	1.01	0.44	<3.82	<8.64
27	SEC-2FS	972.0	16.2	1.21	1.18	<3.82	<3.25
37	SEC-3FS	480.0	8.0	1.10	0.53	<3.82	<7.23
47	SEC-4FS	960.0	16	1.12	1.08	<3.82	<3.55
57	SEC-5FS	498.0	8.3	1.08	0.54	<3.82	<7.10
67	SEC-6FS	942.0	15.7	1.05	0.99	<3.82	<3.86
8	BKG-E	1158.0	19.3	1.06	1.23	<3.82	<3.11
18	E-1	450.0	7.5	0.88	0.40	<3.82	<9.65
28	E-2	966.0	16.1	1.26	1.22	<3.82	<3.14
38	E-3	480.0	8	1.08	0.52	<3.82	<7.37
48	E-4	960.0	16	1.08	1.04	<3.82	<3.68
58	E-5	504.0	8.4	1.10	0.55	<3.82	<6.89
68	E-6	936.0	15.6	1.01	0.95	<3.82	<4.04
9	BKG-NEC	1158.0	19.3	1.05	1.22	<3.82	<3.14
19	NEC-1	414.0	6.9	0.89	0.37	<3.82	<10.37
29	NEC-2	966.0	16.1	1.25	1.21	<3.82	<3.16
39	NEC-3	480.0	8	1.13	0.54	<3.82	<7.04
49	NEC-4	960.0	16	1.10	1.06	<3.82	<3.62
59	NEC-5	504.0	8.4	1.11	0.56	<3.82	<6.83
69	NEC-6	942.0	15.7	1.05	0.99	<3.82	<3.86
10	BKG-N	1152.0	19.2	1.20	1.38	<3.82	<2.76
20	N-1	462.0	7.7	0.92	0.43	<3.82	<8.99
30	N-2	966.0	16.1	1.24	1.20	<3.82	<3.19
40	N-3	480.0	8	1.10	0.53	<3.82	<7.23
50	N-4	960.0	16	1.10	1.06	<3.82	<3.62
60	N-5	504.0	8.4	1.10	0.55	<3.82	<6.89
70	N-6	942.0	15.7	1.03	0.97	<3.82	<3.94

Table 4
Application Results by Site

Wind Rose
Stanislaus County 2,4-D DMAS Application
November 14, 2013 0820 to 1600 (5 minute averages)



Calms excluded.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

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

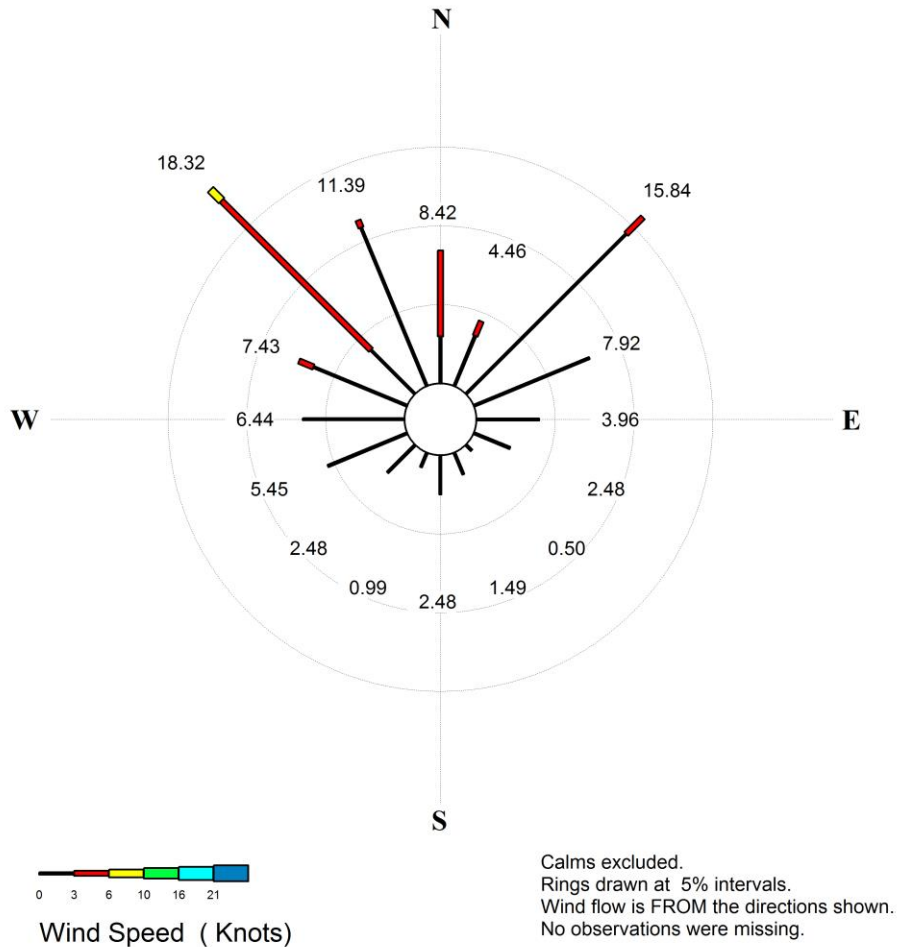
DIR	0	3	6	10	16	21
N	2.15	7.53	0.00	0.00	0.00	0.00
NNE	2.15	0.00	0.00	0.00	0.00	0.00
NE	0.00	0.00	0.00	0.00	0.00	0.00
ENE	2.15	0.00	0.00	0.00	0.00	0.00
E	2.15	0.00	0.00	0.00	0.00	0.00
ESE	2.15	0.00	0.00	0.00	0.00	0.00
SE	8.60	2.15	0.00	0.00	0.00	0.00
SSE	6.45	5.38	0.00	0.00	0.00	0.00
TOTAL OBS = 93 MISSING OBS = 0						

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

DIR	0	3	6	10	16	21
S	11.83	0.00	0.00	0.00	0.00	0.00
SSW	3.23	1.08	0.00	0.00	0.00	0.00
SW	2.15	4.30	0.00	0.00	0.00	0.00
WSW	3.23	0.00	0.00	0.00	0.00	0.00
W	3.23	2.15	0.00	0.00	0.00	0.00
WNW	2.15	0.00	0.00	0.00	0.00	0.00
NW	0.00	4.30	0.00	0.00	0.00	0.00
NNW	11.83	9.68	0.00	0.00	0.00	0.00
CALM OBS = 0						

Figure 6
Sampling Period 1 Application Wind Rose

Wind Rose
Stanislaus County 2,4-D DMAS Post Application
November 14-15, 2013 1515 to 0800 (5 minute averages)



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

DIR	0	3	6	10	16	21
N	2.97	5.45	0.00	0.00	0.00	0.00
NNE	3.47	0.99	0.00	0.00	0.00	0.00
NE	14.36	1.49	0.00	0.00	0.00	0.00
ENE	7.92	0.00	0.00	0.00	0.00	0.00
E	3.96	0.00	0.00	0.00	0.00	0.00
ESE	2.48	0.00	0.00	0.00	0.00	0.00
SE	0.50	0.00	0.00	0.00	0.00	0.00
SSE	1.49	0.00	0.00	0.00	0.00	0.00

TOTAL OBS = 202 MISSING OBS = 0

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

DIR	0	3	6	10	16	21
S	2.48	0.00	0.00	0.00	0.00	0.00
SSW	0.99	0.00	0.00	0.00	0.00	0.00
SW	2.48	0.00	0.00	0.00	0.00	0.00
WSW	5.45	0.00	0.00	0.00	0.00	0.00
W	6.44	0.00	0.00	0.00	0.00	0.00
WNW	6.44	0.99	0.00	0.00	0.00	0.00
NW	3.96	13.37	0.99	0.00	0.00	0.00
NNW	10.89	0.50	0.00	0.00	0.00	0.00

CALM OBS = 0

Figure 7
 Sampling Period 2 Overnight Wind Rose

The Formulas Used to Calculate Monitoring Results

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

$$\text{2,4-D DMAS } \frac{ng}{m^3} = \left(\frac{\text{2,4-D DMAS ng}}{\text{Sample}} \right) \times \left(\frac{\text{Sample}}{\text{Total Volume } m^3} \right)$$

$$\text{2,4-D DMAS } \frac{ng}{\text{sample}} = \left(\frac{\text{2,4-D DMAS ng}}{\text{ml}} \right) \times \left(\frac{\text{4 ml Extraction Volume}}{1 \text{ Sample}} \right)$$

$$\text{2,4-D DMAS } \frac{ng}{ml} = \left(\frac{\text{2,4-D DMAS ng}}{m^3} \right) \times \left(\frac{\text{Sample Volume } m^3}{1 \text{ Sample}} \right) \times \left(\frac{1 \text{ Sample}}{4 \text{ ml Extraction Volume}} \right)$$

Note: 4 ml sample dilution Extraction Volume per sample

Calculating Percent Recovery of Field Spikes (FS)

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

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

Note: The field spike concentrations were spiked by the laboratory at 100 ng/ml. If the field spike corresponding sample is reported less than the analytical MDL the following % recovery calculation is used.

$$\text{Percent Recovery \%} = \left(\frac{\text{Field spike Recovery } ng/ml}{100 \text{ ng/ml}} \right) \times 100$$

Calculating 2,4-D DMAS Application Rate lbs. /acre

117 pints 2,4-D DMAS Total Product Used = 1872 fluid oz 2,4-D DMAS

$\frac{1872 \text{ fluid oz.}}{128.0 \text{ oz. /gallon}} = 14.63 \text{ gallons of 2,4-D DMAS Flowable Product}$

$$\left(\frac{14.63 \text{ gallons 2,4-D DMAS Flowable product}}{39.00 \text{ acres}} \right) \times (3.8 \text{ lbs. 2,4-D DMAS/gallon}) = 1.43 \text{ lbs./acre 2,4-D DMAS}$$

Note: Per manufacture's listed product label specification sheet, 2,4-D DMAS Flowable Herbicide contains 3.8 lbs. of 2,4-D DMAS/gallon

Figure 9
Formulas Used to Calculate Application Results

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, "2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) Analytical Results for an Application Study."

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 analytical MDL (3.82 ng/sample)

- 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 analytical MDL.
- Laboratory staff analyzed a Laboratory Control Standard (LCS) with each analytical batch. The LCS is an XAD tube spiked with 100 ng/ml of 2,4-D DMAS. The LCS is extracted and analyzed as described for the samples. The acceptance criterion for LCS results is $\pm 20\%$. The LCS averaged 87.3% with a standard deviation of 3.8%.
- 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 30 ng/ml. All CCV's were in the expected range.
- Field Spikes: The seven (7) 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 100 ng/ml of 2,4-D DMAS. The average recovery for the field spikes of 2,4-D DMAS was 105% with a standard deviation of 6.06%. Refer to Table 5
- Trip Spikes: The trip spike recovery of 106%. Refer to Table 6
- Lab Spikes: The seven laboratory spikes for this study reported an average recovery of 87.3% with a standard deviation of 3.46% Refer to Table 7

Log #	Sample Location	Expected ng/ml	Measured ng/ml	Recovery %
7	BKG-FS-1	100	116.9	117
17	SEC-1FS	100	101.8	102
27	SEC-2FS	100	96.1	96
37	SEC-3FS	100	102.3	102
47	SEC-4FS	100	104.7	105
57	SEC-5FS	100	102.8	103
67	SEC-6FS	100	108.8	109

Table 5
Quality Control Data Field Spikes

Log #	Sample Location	Date Collected	Date Analyzed	Expected ng/ml	Measured ng/ml	Difference ng/ml	Recovery %
TS-1	Trip Spike 1	11/16/2013	12/17/2013	100	105.8	5.8	106

Table 6
Quality Control Data Trip Spikes

Sample Location	Date Analyzed	Expected ng/ml	Measured ng/ml	Difference ng/ml	Recovery %
Lab Spike 1	12/6/2013	100	84.1	15.9	84
Lab Spike 2	12/9/2013	100	84.6	15.4	85
Lab Spike 3	12/11/2013	100	88.1	11.9	88
Lab Spike 4	12/12/2013	100	84.3	15.7	84
Lab Spike 5	12/13/2013	100	94.6	5.4	95
Lab Spike 6	12/16/2013	100	88.8	11.2	89
Lab Spike 7	12/17/2013	100	86.2	13.8	86

Table 7
Quality Control Data Laboratory Spikes

6.0 Discussion

Seventy one field samples were collected during the background, application and post-application period (including seven field spikes, one trip spike and one field blank) from eight different locations around the perimeter of a 39 acre almond orchard located in Stanislaus County. Seven laboratory spikes were prepared and held at the laboratory at the same time the field/trip spikes were prepared. No 2,4-D DMAS was detected during the background or application sampling periods. The results reported indicated all levels of 2, 4-D DMAS were all less than the calculated analytical MDL of 3.82 ng/sample.

The non-detection of 2, 4-D DMAS may be attributed to the applicator who applied when the winds were calm. Additionally, The 2, 4-D DMAS was applied by ground using a spray rig which was low to ground and helped to contain the applied pesticide.

APPENDIX A

**Department of Pesticide Regulation Request to the Air Resource
Board for Proposed Toxic Air Contaminants Monitoring for
2013**



Air Resources Board



Matthew Rodriguez
Secretary for
Environmental Protection

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Edmund G. Brown Jr.
Governor

TO: Chris Reardon, Chief Deputy Director
Department of Pesticide Regulation

FROM: Alberto Ayala, Ph.D., M.S.E.
Deputy Executive Officer

DATE: February 13, 2013

SUBJECT: PROPOSED TOXIC AIR CONTAMINANT MONITORING FOR 2013

This memorandum is in response to your January 22, 2013 request for the Air Resources Board (ARB) to monitor the following pesticides in 2013:

- 1,3-dichloropropene (1,3-D)
- Methyl Bromide (MeBr)
- Chlorpyrifos and Chlorpyrifos oxygen analog
- 2,4-D
- Mancozeb
- Carbaryl

I have directed my staff at ARB's Monitoring and Laboratory Division to include 1,3-D, MeBr, chlorpyrifos and 2,4-D in their 2013 pesticide monitoring schedule and to begin method development for mancozeb and its breakdown product ethylenthiourea (ETU) in anticipation of these compounds being included in next year's monitoring request

To the extent possible, we will include the application site study request for carbaryl. Despite extensive outreach to growers, pesticide applicators, and agriculture commissioners, ARB has been unable to secure a carbaryl monitoring application as carbaryl use has significantly declined since DPR's original request.

We look forward to receiving your agency's application monitoring date/location recommendations for chlorpyrifos and 2,4-D after reviewing the most recent pesticide use data.

I look forward to another year of productive collaboration on this important program. If you have any questions, please contact Ken Stroud, Chief of the Air Quality Surveillance Branch, at (916) 445-3745 or via email at kstroud@arb.ca.gov.

cc: See next page

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, Chief Deputy Director
February 13, 2013
Page 2

cc: George Alexeeff, Ph.D., D.A.B.T.
Director
Office of Environmental Health Hazard Assessment

Dave Duncan
Environmental Monitoring Program Manager II
Department of Pesticide Regulation

James N. Goldstene
Executive Officer

Ken Stroud, Chief
Air Quality Surveillance Branch

Chris Reardon, Chief Deputy Director
February 13, 2013
Page 2

bcc: Manjit Ahuja, MLD
Cindy Castronovo, MLD
Mac McDougall, MLD

ATS #17703

APPENDIX B

Site Photographs



Farmer using spray rig to apply 2,4-DMAS in almond orchard



Farmer going down almond rows applying 2.4-DMAS



North Sampler Looking North



North Sampler Looking South



North Sampler Looking West



North Sampler Looking East



North West Corner Sampler Looking East



North West Corner Sampler Looking North



North West Corner Sampler Looking West



North West Corner Sampler Looking South



West Sampler Looking South



West Sampler Looking North



West Sampler Looking East



South West Corner Sampler Looking South



South West Corner Sampler Looking East



South West Corner Sampler Looking North



South West Corner Sampler Looking West



South Sampler Looking East



South Sampler Looking North



South Sampler Looking West



South Sampler Looking South



South East Corner Co-located Samplers Looking South



South East Corner Co-Located Samplers Looking West



South East Corner Co-Located Samplers Looking North



South East Corner Co-Located Samplers Looking East



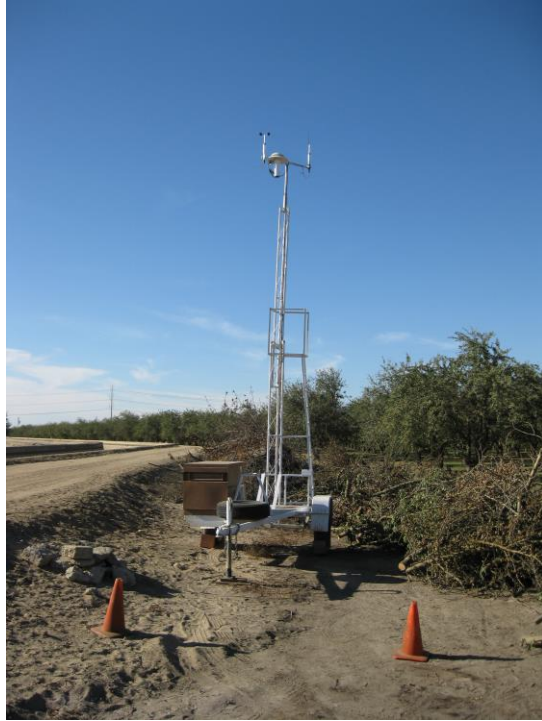
South East Corner Auto Met Station Looking North East



South East Corner Auto Met Station Looking East



South East Corner Auto Met Station Looking South



South East Corner Auto Met Station Looking West



East Sampler Looking East



East Sampler Looking North



East Sampler Looking West



East Sampler Looking South



North East Corner Sampler Looking East



North East Corner Sampler Looking West



North East Corner Sampler Looking South



North East Corner Sampler Looking North



Personal Protective Equipment Abatement Air Sampler Worn by Staff



Personal Protective Equipment Abatement Air Sampler Worn by Staff



Farmer Finishing Up Application on Almond Orchard



Spray Rig Washed Down After Application



Spray Rig Washed Down After Application

APPENDIX C
Sampling Protocol



California Environmental Protection Agency

AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) Application Study

November 7, 2013

Prepared by:

Steve Aston
Air Resources Engineer
Special Purpose Monitoring Section

Signatures:

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

Mac McDougall, Manager Date
Special Purpose Monitoring
Air Quality Surveillance Branch

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Appendix

APPENDIX A: Standard Operating Procedure Sampling and Analysis of Chlorthal-Dimethyl (DCPA).

1.0 Introduction

The California Department of Pesticide Regulation's (DPR) memorandum dated February 13, 2013, "Proposed Toxic Air Contaminant Monitoring For 2013", requests that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for the herbicide 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) during a ground application.

This study will consist of eight sampling periods.

- 1) A background sample period duration time minimum 18-24 hours (arrival Wednesday)
- 2) Application sampling period begins Thursday morning until one (1) hour after end of application
- 3) Post application sampling period begins Thursday morning one (1) hour after end of application until one (1) hour before sunset.
- 4) Post application **overnight** sampling period begins Thursday evening one (1) hour before sunset and is removed one (1) hour after sunrise Friday morning.
- 5) Post application **daytime** sampling period begins Friday morning one (1) hour after sunrise and is removed one (1) hour before sunset.
- 6) Post application **overnight** sampling period begins Friday evening one (1) hour before sunset and is removed one (1) hour after sunrise Saturday morning.
- 7) Post application **daytime** sampling period begins Saturday morning one (1) hour after sunrise and is removed one (1) hour before sunset.
- 8) Post application **overnight** sampling period begins Saturday evening one (1) hour before sunset and is removed one (1) hour after sunrise Sunday morning.

The background sampling period will be performed eighteen to twenty-four hours prior to the application of DCPA. The application sampling period will begin thirty minutes prior to the application of 2,4-D DMAS. There will be a total of 92 resin sorbent tube samples eight (8) background, eight (8) collocated, eight (8) field spikes, one (1) trip spike, one (1) trip blank, 56 application/post application and ten (10) spares.

Background sampling will be started the day before the application and end approximately one (1) hour prior to the start of the application or when the elapsed time reaches a minimum of 12 hours. Eight (8) background samplers will be placed around the perimeter of the field along with one (1) collocated sampler and one (1) field spike sampler on the downwind side.

2.0 Project Goals and Objectives

The primary goal of this monitoring project is to measure the concentrations of 2,4-D DMAS in the ambient air during and after application.

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

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.
2. Appropriate application of sampling/monitoring equipment to determine 2,4-D DMAS concentrations in the air adjacent to the application.
3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
4. A final report containing all relevant information, data and results gathered in the course of MLD's activities during the planning and execution of this project.

3.0 Contacts

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4.0 Study Location

A 2,4-D DMAS application is planned for November 14, 2013 in Stanislaus County. The field is located 2 miles south/southeast of Ceres on the west side of Highway 99.

5.0 Study Design

The 2,4-D DMAS sampling schedule is listed in Table 1 (Sampling Periods). For November 14, 2013 sunrise occurs at 0643 PST and sunset occurs at 1655 PST.

TABLE 1: SAMPLING PERIODS

Sampling Period Begins	Sampling Duration/Event Time
Background (Wednesday Arrival)	Minimum 12-24 hours (Pre-Application)
Application (8 PST Thursday Morning)	Sample is removed one (1) hour after (Application)
Post Application (Thursday Morning)	Sample is installed one (1) hour after (Application)
Post Application (Thursday Evening)	Sample is installed one (1) hour before sunset (Overnight)
Post Application (Friday Morning)	Sample is installed one (1) hour before sunrise (Morning)
Post Application (Friday Evening)	Sample is installed one (1) hour before sunset (Overnight)
Post Application (Saturday Morning)	Sample is installed one (1) hour before sunrise (Morning)
Post Application (Saturday Evening)	Sample is installed one (1) hour before sunset (Overnight)

All overnight samples must include the period from one hour before sunset to one hour after sunrise.

- a) Background sampling will start the day before the application for a minimum of twelve hours, but no more than twenty four hours. The background samples will be removed at least one (1) hour prior to the start of the application. The background samplers will be installed at all four corners and at each of the four sides of the field at quarterly lengths with one (1) field spike sampler and one (1) collocated sampler next to the downwind site for a total of ten (10) samplers. The field spike samples will be pre-spiked with a concentration of 100 nanograms (ng) per sample for 2,4-D DMAS.
- b) The application sampling period will start approximately thirty minutes prior to the ground application of 2,4-D DMAS and will continue until one (1) hour after the application. First post application sample one (1) hour after end of application until one (1) hour before sunset. Second post application **overnight** sampling period will start one (1) hour before sunset and continue until one (1) hour after sunrise. Third post application **daytime** sampling period will start one (1) hour after sunrise and will continue until one (1) hour before sunset. Fourth post

application **overnight** sampling period will start one (1) hour before sunset and will continue until one (1) hour after sunrise. Fifth post application **daytime** sampling period will start one (1) hour after sunrise and will continue until one (1) hour before sunset. Sixth post application **overnight** sampling period will start one (1) hour before sunset and will continue until one (1) hour after sunrise.

- c) There will be eight (8) sampling sites around the orchard. For a square field, four (4) sites will be located at each corner and four (4) sites will be located at quarterly lengths on each side. The projected downwind site will have two additional samplers, one (1) collocated and one (1) field spike, located within 0.6 meters of the primary sampler. All sampler intakes will be 1.7 meters (67 ± 6 inches) above the ground. Samplers will be placed 20 ± 10 meters (33 to 98 feet) from the edge of the field.
- d) Each sample will be collected by passing a measured volume of ambient air through one XAD resin sorbent tube that is mounted on a sampling tree as shown in Figure 1. Sample flow is controlled by an inline rotameter (flow range of 0-5 LPM) and the resin sorbent tube will be protected from direct sunlight or rain. Prior to each sampling period, the sampler is checked for leaks. After the sample resin sorbent tube is installed, the flow rate will be set at 1.0 lpm using a digital mass flow meter. The flow rate will be checked at the end of each sampling period and the average of the start and stop flows shall be 1.0 lpm $\pm 20\%$. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed and placed in a dry ice cooler. The field log sheet and resin sorbent tube label will contain the following information: log #, sample name, sampler ID number, start and end date/time, start/end elapsed time meter reading, start/end mass flow meter display reading, comments (if applicable), weather conditions and the start/end initials of the operator. The exposed XAD-2 resin sorbent tubes (SKC #226-30-06) with 400 and 200 mg of packing are stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory.

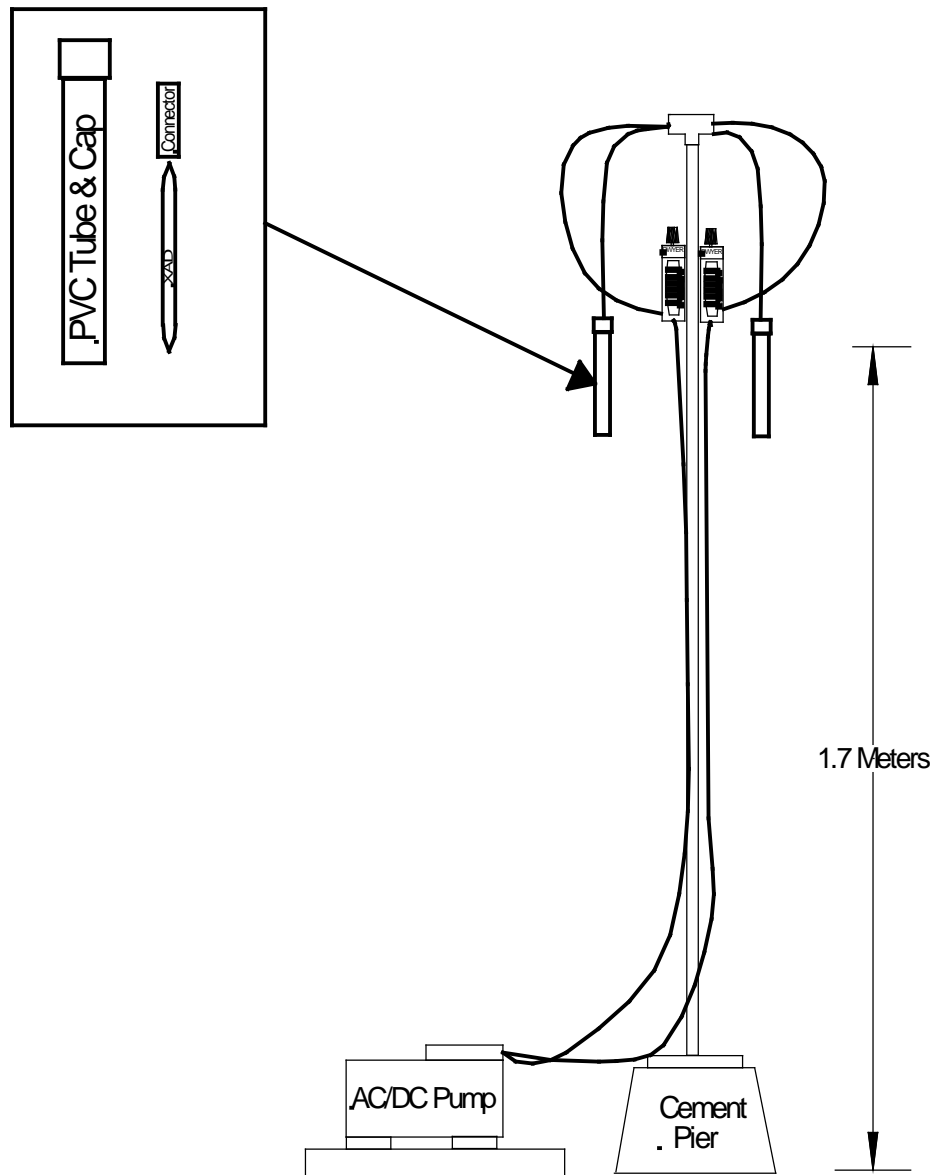


FIGURE 1: AIR SAMPLER TREE WITH PUMP

- e) In order to reduce direct exposure to ARB staff during the pesticide application period 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 resin sorbent tubes removed, the battery replaced, a new resin sorbent tube installed and flows adjusted if necessary. Field notes and observations will be recorded (such as 2,4-D DMAS application flow rate and total amount of 2,4-D DMAS applied).
- f) Meteorological data will be collected using a Met-One Automet portable meteorology system. The Automet will be located no closer than twenty meters from the edge of the field being monitored. The meteorological sensors will be installed 7.5 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 and 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.

6.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) staff will hand-carry resin sorbent tubes to and from MLD's laboratory in Sacramento, and to and from the sampling location. The resin sorbent tubes will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample. At the end of the each sampling period, all resin sorbent tubes will be removed from the sampler, placed in a culture tube, labeled, and secured in a dry ice cooler.

At each sampling site, the operator will replace the batteries for each pesticide sampler with charged batteries; install a new resin sorbent tube and install the rain/sun shield over the resin tube. The resin sorbent tube field log sheet (See Figure 2) shall be filled out a long with the resin sorbent tube label. Prior to any sampling, flows will be set to 1.0 ± 0.1 lpm. At the start of each sampling period, the pesticide samplers will be manually turned on and the start date, time, elapsed time meter reading and indicated flow rate will be recorded. At the end of each sampling period, the flow rate will be measured, the pesticide sampler manually shut off and the following recorded on the resin sorbent tube field log sheet; end date, time, elapsed time meter reading and flow.

Sampling will occur as scheduled unless ambient conditions at the start include rain or instantaneous gusts of wind over ten (10) miles per hour. All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply Special Purpose Monitoring with 92 resin sorbent tubes; eight (8) backgrounds, five (8) collocated, five (8) field spikes, one (1) trip spike, one (1) trip blank, 56 application/post application and ten (10) spares. A label will be affixed around the top section of the resin sorbent tube identifying the sample. Spikes and other QC resin sorbent tubes will be identified. The NLB will perform analyses for 2,4-D DMAS on all collected samples and report results to SPM in electronic format (Excel) and hardcopy. Laboratory analysis will be performed in accordance with the draft standard operating procedures, "Standard Operating Procedure Sampling and Analysis of 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS)." The current analytical Method Detection Limit (MDL) is 0.66 nanograms (ng) per sample for 2,4-D DMAS. The laboratory's operating procedure is included in this Protocol as Appendix A.

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

1. **Sample Hold Time:** Sample hold time criteria will be consistent with the laboratory's operation procedure stated 28 days.

2. **Duplicate Analysis:** Laboratory to provide duplicate analytical results and the corresponding relative percent difference (RPD)
3. **Method Detection Limit (MDL):** Sample analysis results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions (dilution factor will be included in the report)
4. **Analytical Linear Range:** Analytical results greater than 10% of the highest calibration standard shall be diluted and reanalyzed within the calibrated linear range.

7.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Automet portable meteorology system consisting of a data logger and calibrated sensors measuring 5 minute averages for wind speed, direction, ambient temperature, and relative humidity.
(1)	Measuring Wheel
(1)	200 foot 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)	Aalborg certified mass flow meter 0-5 lpm
(92)	Resin sorbent tubes (8 backgrounds, 8 collocated, 8 field spikes, 1 trip spike, 1 trip blank, 56 application/post application and 10 spares)
(10)	Pesticide sampler each equipped with one (1) each sampling train and voloflows setup to sample one (1) resin tube.
(12)	Pump, 12 VDC.
(80)	Battery, 12 VDC 40 amps.
(6)	Chargers

8.0 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 sample flow rate of the pesticide sampler's voloflows will be measured using certified mass flow meters with a range of 0-5 liters per minute.

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://arb.ca.gov/airwebmanual/amwmn.php?c=5&t=sop>

A label will be affixed around the top section of the resin sorbent tube identifying the sample with the following information: log #, sample name, sampler ID number, start and end date and time, start and end elapsed time meter (ETM) reading, start and end mass flow meter display reading and operators initials.

Collocated (side-by-side) air samplers will operate at one site during the study period. This collocated site will be located at the projected downwind site.

Field Spike (FS): Eight (8) field spikes will be prepared by the laboratory by injecting resin sorbent tubes with a known concentration of 2,4-D DMAS. The field spike resin sorbent tubes will be coupled with a pesticide sampler and collocated next to the projected downwind sampler. One (1) each field spike will be collected during each sampling period.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a resin sorbent tube with a known concentration of 2,4-D DMAS with the same level as the field spikes. The trip spike resin sorbent tube accompanies the sample resin sorbent tubes from the lab to the field but is not sampled.

Trip Blank (TB): A trip blank will be prepared by the field staff. The trip blank resin sorbent tube accompanies the sample resin sorbent tubes from the lab to the field and returns but is not sampled.

Collocated (C): Collocated samples will be collected at the designated down wind sampling site during all sampling periods starting with the background period.

Valid samples are those that have a final corrected average flow within $\pm 20\%$ of 1.0 lpm.

Site/Sample Identification

The 2,4-D DMAS application sampling sites will be named accordingly for the background, ambient, application, and post application as follows:

Background Site Naming:

BKG-NE-1
BKG-NE-C
BKG-NE-FS-1

Letter Abbreviations as follows

N = North Side
S = South Side
W = West Side
E = East Side
BKG = Background Sample
FS = Field Spike
C = 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

Application Site Naming:

NE-1 NE-1C NE-1FS
SE1-1 SE2-1
SW1-1 SW2-1
NWC-1 NEC-1
SEC-1 SWC-1

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will insure accurate field and laboratory results.

9.0 Deliverables

9.1 Northern Laboratory Branch (NLB) Deliverables

Within 90 days after the last collected sample is received at the laboratory, the NLB will provide SPM with a report that will include the following topics:

- 1) Table(s) of sample to include:
 - a. Sample identification (name).
 - b. Date sample received from field.
 - c. Date sample analyzed.
 - d. Dilution ratio.
 - e. Analytical results.
- 2) All equations used in calculating analytical results.
- 3) Table of duplicate results including calculated relative percent difference (RPD) when applicable.
- 4) Table of collocated results.
- 5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries when applicable.
- 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 when 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.

9.2 Air Quality Surveillance Branch Deliverables

Within 90 days from receipt of the final results report from the 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, 2,4-D DMAS application rate, and total pounds or gallons of 2,4-D DMAS applied).
- 6) Sample Summary Table.
- 7) Field Log Sheets.
- 8) Laboratory Analysis Reports with calculations in electronic format.
- 9) Met Station and Sampler Calibration Reports.
- 10) Transfer Standards' Certification Reports.
- 11) Disk containing electronic files of 5-minute averaged Meteorological Data.
- 12) Disk containing electronic files of Report.

APPENDIX A: Standard Operating Procedure Sampling and Analysis of 2,4-Dichlorophenoxy Acetic Acid Dimethylamine Salt (2,4-D DMAS).

The Special Analysis Section of MLD's Northern Laboratory Branch will perform the analyses for 2,4-D DMAS collected by the resin sorbent tube method. This analytical procedure is entitled, "Standard Operating Procedure Sampling and Analysis of 2,4-Dichlorophenoxy Acetic Acid Dimethylamine Salt (2,4-D DMAS)" and can be located starting on the next page.

APPENDIX D

Laboratory Results Report



Air Resources Board



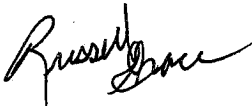
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Secretary for
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Edmund G. Brown Jr.
Governor

TO: Mac McDougall, Manager
Special Purpose Monitoring Section
Air Quality Surveillance Branch

FROM: Michael Werst, Chief 
Northern Laboratory Branch

Russell Grace, Manager 
Special Analysis Section
Northern Laboratory Branch

DATE: April 24, 2015

SUBJECT: APPLICATION AIR MONITORING OF 2,4-DICHLOROPHENOXYACETIC
ACID DIMETHYLAMINE SALT (2,4-D DMAS) IN STANISLUAS COUNTY
IN NOVEMBER 2013

The Special Analysis Section (SAS) provided laboratory support for the 2,4-dichlorophenoxyacetic acid dimethylamine salt (2,4-D DMAS) application air monitoring conducted in Stanislaus County in November 2013. The SAS laboratory received 71 samples including 7 field spikes, 1 trip spike, and 1 trip blank. The samples were collected on XAD-2 sorbent tubes.

The data are presented in the attached report, titled "2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS) Analytical Results for an Application Study" which includes the standard operating procedure for 2,4-D DMAS. Also included in the report is the document titled "Method Development for the Sampling and Analysis of 2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS)."

If you have any questions or comments, please contact Glenn Peoples at 322-8972 or me at 322-2496.

Attachment

cc: Ken Stroud
Glenn Peoples
Lynn Baker, SSD

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

California Environmental Protection Agency



Air Resources Board

**2,4-Dichlorophenoxyacetic Acid Dimethylamine Salt (2,4-D DMAS)
Analytical Results for an Application Study**

DATE: 04/22/15

**Prepared by
Glenn Peoples
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 California Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct an air monitoring study for the herbicide 2,4-dichlorophenoxyacetic acid dimethylamine salt (2,4-D DMAS) during an application in Stanislaus County in November 2013. DPR requested a method estimated quantitation limit (EQL) of 4 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). Based on 24 hour sample collection at 1 liter per minute (LPM), the EQL achieved during this project was $0.013 \mu\text{g}/\text{m}^3$.

2.0 METHOD DEVELOPMENT

2.1 Overview

Application air samples are collected on XAD-2 sorbent tubes. Sampled tubes are stored at 4 degrees centigrade ($^{\circ}\text{C}$) or lower prior to extraction. Sample tubes are extracted using 4 milliliters (ml) of pesticide grade 25 percent methanol in ethyl acetate. Appendix A contains the 2,4-D DMAS standard operating procedure (SOP) and Appendix B the method development report for 2,4-D DMAS.

2.2 Calibration Curve

Standard concentrations of 5.0, 10, 50, 100, 250, 500, 1,000, and 2,000 nanograms per milliliter (ng/ml) of 2,4-D DMAS are used to produce an 8-point calibration curve. All calibration curves performed have an r^2 (variance) greater than or equal to 0.995. Calibrations are performed at the beginning of the monitoring program, after instrument maintenance, after remaking of calibration curve standards, and whenever the continuing calibration verification standard (CCV) does not fall within ± 25 percent of expected value.

2.3 Minimum Detection Limit (MDL)

The MDL calculation follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDLs. Using the analysis of 7 low-level matrix spikes at 20 ng/ml, the MDL and EQL for a 4-ml extract are calculated as follows:

<p>$s = \text{the standard deviation of the concentration calculated for the seven replicate spikes.}$ For 2,4-D DMAS: $s = 0.3040$ $\text{MDL} = (3.143) \times (s) = (3.143) \times (0.3040) = 0.955 \text{ ng/ml}$ $\text{MDL (ng/sample)} = 0.955 \text{ ng/ml} \times 4.00 \text{ ml} = 3.82 \text{ ng/sample}$ $\text{EQL} = (5) \times (\text{MDL}) = (5) \times (3.82) = 19.1 \text{ ng/sample}$</p>

Based on a total collection volume of 1.440 m^3 the EQL for this method would be $0.013 \mu\text{g}/\text{m}^3$. All results are reported in ng/sample. Results less than the calculated MDL are reported as "<3.82 ng/sample."

3.0 2,4-D DMAS APPLICATION AIR MONITORING SAMPLE RESULTS

The laboratory received a total of 62 application air samples plus 7 field spikes, 1 trip blank and 1 trip spike on November 18, 2013. There were no detected levels present. Table 1 presents the results of the analysis of the 2,4-D DMAS application air samples by field location.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch, one before each calibration standard, one before each CCV, and one after every tenth sample. Staff defines the analytical batch as all the samples analyzed together, but not to exceed 20 samples. A system blank is analyzed to insure the instrument does not contribute interferences to the analysis and to minimize carryover from high-level samples. All system blanks were less than the MDL (3.82 ng/sample).

4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This is an XAD-2 sorbent tube prepared and analyzed as described for the application samples. All method blank results were less than the MDL (3.82 ng/sample).

4.3 Laboratory Control Samples (LCS)

Laboratory staff analyzed a LCS with each analytical batch. The LCS is an XAD-2 sorbent tube spiked with 100 ng/ml of 2,4-D DMAS. The LCS is then extracted and analyzed with that day's analytical batch. The acceptance criterion for LCS results is ± 20 percent. The LCS average was 87.3 percent with a standard deviation of 3.8 percent. All LCS met the acceptance criteria.

4.4 Continuing Calibration Verification Standards (CCV)

Following standard laboratory 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 ± 25 percent of the expected value. If any of the CCV's are outside this limit, the affected samples are re-analyzed. The CCV standard concentration was 30 ng/ml. All the CCV's were within the ± 25 percent acceptance range.

4.5 Laboratory Duplicates

Seven pairs of laboratory duplicates were analyzed with this project. The duplicate analyses are analyzed from two aliquots of a single sorbent tube extract. Since there were no positive concentrations detected, there were no relative percent difference calculations. Table 2 presents the duplicate results.

4.6 *Co-located Samples*

Seven pairs of co-located samples were analyzed during this study. There was no 2,4-D DMAS detected in any of the co-located samples. Table 3 presents the results of the co-located samples.

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

For the Stanislaus County 2013 project, 7 field spikes, 1 trip spike, 7 laboratory spikes and 1 trip blank were analyzed. Laboratory staff prepared the spikes with a target value of 100 ng/sample.

5.1 *Field Spikes*

Table 4 presents the results of the field spikes. Seven field spikes were analyzed during this study. Field and trip spikes were fortified with 2,4-D. The average recovery for the field spikes of 2,4-D was 104.8 percent with a standard deviation of 6.56 percent.

5.2 *Trip Spike*

One 2,4-D trip spike was analyzed and had a recovery of 105.8 percent. The acceptance criterion for trip spikes is ± 20 percent.

5.3 *Laboratory Spikes*

Table 4 presents the laboratory spikes. Seven laboratory spikes were analyzed during this study. Laboratory spikes were fortified with 2,4-D DMAS. The acceptance criterion for laboratory spikes is ± 20 percent. The average recovery of 2,4-D DMAS laboratory spikes was 87.3 percent with a standard deviation of 3.77 percent.

5.4 *Trip Blanks*

One trip blank was received during this project and the result was less than the MDL (3.82 ng/sample).

6.0 **DISCUSSION**

The Laboratory received 62 field samples, 7 field spike, 1 trip spike and 1 trip blank for a total of 71 samples. There were no positive concentrations (above MDL) found during this study. Results of the 2,4-D DMAS method development are shown in Appendix B.

**Table 1: Application Air Monitoring Results
Stanislaus County
2013**

Field Location	Log #	Sample ID	Date Received	Date Analyzed	ng/sample
North West Corner	11	NWC-1	11/18/13	12/09/13	<3.82
	21	NWC-2	11/18/13	12/11/13	<3.82
	31	NWC-3	11/18/13	12/12/13	<3.82
	41	NWC-4	11/18/13	12/13/13	<3.82
	51	NWC-5	11/18/13	12/16/13	<3.82
	61	NWC-6	11/18/13	12/17/13	<3.82
West Side	2	BKG-W	11/18/13	12/06/13	<3.82
	12	W-1	11/18/13	12/09/13	<3.82
	22	W-2	11/18/13	12/11/13	<3.82
	32	W-3	11/18/13	12/12/13	<3.82
	42	W-4	11/18/13	12/13/13	<3.82
	52	W-5	11/18/13	12/16/13	<3.82
Southwest Corner	3	BKG-SWC	11/18/13	12/06/13	<3.82
	13	SWC-1	11/18/13	12/09/13	<3.82
	23	SWC-2	11/18/13	12/11/13	<3.82
	33	SWC-3	11/18/13	12/12/13	<3.82
	43	SWC-4	11/18/13	12/13/13	<3.82
	53	SWC-5	11/18/13	12/16/13	<3.82
South Side	63	SW-6	11/18/13	12/17/13	<3.82
	4	BKG-S	11/18/13	12/06/13	<3.82
	14	S-1	11/18/13	12/09/13	<3.82
	24	S-2	11/18/13	12/11/13	<3.82
	34	S-3	11/18/13	12/12/13	<3.82
	44	S-4	11/18/13	12/13/13	<3.82
South East Corner	54	S-5	11/18/13	12/16/13	<3.82
	64	S-6	11/18/13	12/17/13	<3.82
	5	BKG-SEC	11/18/13	12/06/13	<3.82
	15	SEC-1	11/18/13	12/09/13	<3.82
	25	SEC-2	11/18/13	12/11/13	<3.82
	35	SEC-3	11/18/13	12/12/13	<3.82
South East Corner Collocated	45	SEC-4	11/18/13	12/13/13	<3.82
	55	SEC-5	11/18/13	12/16/13	<3.82
	65	SEC-6	11/18/13	12/17/13	<3.82
	6	BKG-SEC-C	11/18/13	12/06/13	<3.82
	16	SEC-1C	11/18/13	12/09/13	<3.82
	26	SEC-2C	11/18/13	12/11/13	<3.82
South East Corner Collocated	36	SEC-3C	11/18/13	12/12/13	<3.82
	46	SEC-4C	11/18/13	12/13/13	<3.82
	56	SEC-5C	11/18/13	12/16/13	<3.82
	66	SEC-6C	11/18/13	12/17/13	<3.82

Field Location	Log #	Sample ID	Date Received	Date Analyzed	ng/sample
South East Corner Collocated Field Spike	7	BKG-FS-1	11/18/13	12/06/13	117
	17	SEC-1FS	11/18/13	12/09/13	85
	27	SEC-2FS	11/18/13	12/11/13	96
	37	SEC-3FS	11/18/13	12/12/13	84
	47	SEC-4FS	11/18/13	12/13/13	105
	57	SEC-5FS	11/18/13	12/16/13	103
	67	SEC-6FS	11/18/13	12/17/13	109
East Side	8	BKG-E	11/18/13	12/06/13	<3.82
	18	E-1	11/18/13	12/09/13	<3.82
	28	E-2	11/18/13	12/11/13	<3.82
	38	E-3	11/18/13	12/12/13	<3.82
	48	E-4	11/18/13	12/13/13	<3.82
	58	E-5	11/18/13	12/16/13	<3.82
	68	E-6	11/18/13	12/17/13	<3.82
Northeast Corner	9	BKG-NEC	11/18/13	12/06/13	<3.82
	19	NEC-1	11/18/13	12/09/13	<3.82
	29	NEC-2	11/18/13	12/11/13	<3.82
	39	NEC-3	11/18/13	12/12/13	<3.82
	49	NEC-4	11/18/13	12/13/13	<3.82
	59	NEC-5	11/18/13	12/16/13	<3.82
	69	NEC-6	11/18/13	12/17/13	<3.82
North Side	10	BKG-N	11/18/13	12/06/13	<3.82
	20	N-1	11/18/13	12/09/13	<3.82
	30	N-2	11/18/13	12/11/13	<3.82
	40	N-3	11/18/13	12/12/13	<3.82
	50	N-4	11/18/13	12/13/13	<3.82
	60	N-5	11/18/13	12/16/13	<3.82
	70	N-6	11/18/13	12/17/13	<3.82

Table 1 Notes

If the analytical result is <MDL it is reported as less than the established method detection limit multiplied by the dilution factor.

ng/sample = nanograms per sample

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

Field location identification:

E: East Side
 NEC: North East Corner
 N: North Side
 NWC: North West Corner
 SEC: South East Corner
 SEC-C: South East Corner Collocated
 S: South Side
 SWC: South West Corner
 W: West Side

**Table 2: Application Air Monitoring Duplicate Results
Stanislaus
2013**

Sample Log Number	Sample ID	Date Received	Date Analyzed	ng/sample
8	BKG-E	11/18/13	12/06/13	<3.82
8D	BKG-E Dup	11/18/13	12/06/13	<3.82
16	SEC-1C	11/18/13	12/09/13	<3.82
16D	SEC-1C Dup	11/18/13	12/09/13	<3.82
25	SEC-2	11/18/13	12/11/13	<3.82
25D	SEC-2 Dup	11/18/13	12/11/13	<3.82
36	SEC-3C	11/18/13	12/12/13	<3.82
36D	SEC-3C Dup	11/18/13	12/12/13	<3.82
45	SEC-4	11/18/13	12/13/13	<3.82
45D	SEC-4 Dup	11/18/13	12/13/13	<3.82
55	SEC-5	11/18/13	12/16/13	<3.82
55D	SEC-5 Dup	11/18/13	12/16/13	<3.82
65	SEC-6	11/18/13	12/17/13	<3.82
65D	SEC-6 Dup	11/18/13	12/17/13	<3.82

**Table 3: Application Air Monitoring Co-Located Results
Stanislaus County
2013**

Sample Log Number	Sample ID	Date Received	Date Analyzed	ng/sample
5	BKG-SEC	11/18/13	12/06/13	<3.82
6	BKG-SEC-C	11/18/13	12/06/13	<3.82
15	SEC-1	11/18/13	12/09/13	<3.82
16	SEC-1C	11/18/13	12/09/13	<3.82
25	SEC-2	11/18/13	12/11/13	<3.82
26	SEC-2C	11/18/13	12/11/13	<3.82
35	SEC-3	11/18/13	12/12/13	<3.82
36	SEC-3C	11/18/13	12/12/13	<3.82
45	SEC-4	11/18/13	12/13/13	<3.82
46	SEC-4C	11/18/13	12/13/13	<3.82
55	SEC-5	11/18/13	12/16/13	<3.82
56	SEC-5C	11/18/13	12/16/13	<3.82
65	SEC-6	11/18/13	12/17/13	<3.82
66	SEC-6C	11/18/13	12/17/13	<3.82

Table 2 and 3 Notes:

- ID = Identification
- ng = nanograms
- na = not applicable
- C = Co-located sample
- Dup = Duplicate Analysis

**Table 4: Field and Laboratory QC Sample Results
Stanislaus County
2013**

QC Type	Lab ID	Date Analyzed	Amount recovered ng/sample
Lab Spike	LCS120613	12/06/13	84.1
	LCS120913	12/09/13	84.6
	LCS121113	12/11/13	88.1
	LCS121213	12/12/13	84.3
	LCS121312	12/13/13	94.6
	LCS121613	12/16/13	88.8
	LCS121713	12/17/13	86.2
Trip Spike	TS-1	12/17/13	105.8
Field Spike	BKG-SEC-FS-1	12/06/13	116.9
	SEC 1FS	12/09/13	101.8
	SEC 2FS	12/11/13	96.1
	SEC 3FS	12/12/13	102.3
	SEC 4FS	12/13/13	104.7
	SEC 5FS	12/16/13	102.8
	SEC 6FS	12/17/13	108.8
Trip Blank	FB-1	12/17/13	<1.1

Notes:

Lab and field spikes were at 100 ng/ml

ID= Identification

ng= nanograms

Appendix A: 2,4-D

Standard Operating Procedure for 2,4-D DMAS

Equipment	Material	Time	Notes
1. 2,4-D	1. 2,4-D	1. 2,4-D	1. 2,4-D
2. 2,4-D	2. 2,4-D	2. 2,4-D	2. 2,4-D
3. 2,4-D	3. 2,4-D	3. 2,4-D	3. 2,4-D
4. 2,4-D	4. 2,4-D	4. 2,4-D	4. 2,4-D
5. 2,4-D	5. 2,4-D	5. 2,4-D	5. 2,4-D
6. 2,4-D	6. 2,4-D	6. 2,4-D	6. 2,4-D
7. 2,4-D	7. 2,4-D	7. 2,4-D	7. 2,4-D
8. 2,4-D	8. 2,4-D	8. 2,4-D	8. 2,4-D
9. 2,4-D	9. 2,4-D	9. 2,4-D	9. 2,4-D
10. 2,4-D	10. 2,4-D	10. 2,4-D	10. 2,4-D

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure

Title: Air Sampling and Analysis of 2,4-Dichlorophenoxyacetic Acid
Dimethylamine Salt (2,4-D DMAS)

SOP: NLB SOP SAS13-01, Revision 1

Section: Special Analysis Section

Branch: Northern Laboratory Branch

Division: Monitoring and Laboratory Division

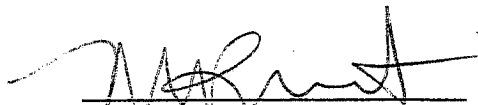
Approval: This SOP has been reviewed and approved by:



Russell Grace, Manager
Special Analysis Section
Northern Laboratory Branch

12-01-13

Date



Michael Werst, Chief
Northern Laboratory Branch

4.28.15

Date

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used. This method is restricted to use by or under direct supervision of analysts experienced in the use of air sampling methods and analysis by gas chromatography with electron capture detector (GC/ECD).

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(2,4-D DMAS)

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1. SCOPE

This is a gas chromatography/electron capture detector (GC/ECD) method for the determination of 2,4-dichlorophenoxyacetic acid dimethylamine salt (2,4-D DMAS). Department of Pesticide Regulation (DPR) requested Air Resource Board (ARB) to conduct monitoring for 2,4-D DMAS with an estimated quantitation limit (EQL) of 4 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

2. SUMMARY OF METHOD

Ambient and application air samples are collected on XAD-2 sorbent tubes at a collection flow rate of 1 liter per minute (lpm). Sampled tubes are stored at 4 degrees Celsius ($^{\circ}\text{C}$) or lower prior to extraction. Sample sorbent tubes are extracted using 25 percent pesticide grade methanol in ethyl acetate (EtAc). Sample extracts are sonicated for 15 minutes then 100 microliters (μl) of 2.0 molar (M) (trimethylsilyl)diazomethane is added to create a derivative. Analysis and quantitation is performed using a GC/ECD and uses an 8-point 2,4-D DMAS standard calibration curve of a derivatized standard. With a sample dilution of 4.0 milliliters (ml) the EQL for this method was $0.013 \mu\text{g}/\text{m}^3$.

3. DEFINITIONS OF TERMS/ACRONYMS

BATCH – an analytical batch is a set of prepared samples (i.e. extracts) analyzed together as a group in an uninterrupted sequence. A preparation (extraction) batch is a set of samples which is processed all in one group using the same equipment, reagents and staff within a single work shift.

BLANK - a sample that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value.

CARTRIDGE BLANK – a new, unused XAD-2-cartridge from the same lot as those used for samples that is not exposed to the target analyte or sample matrix but is carried through all extraction and analytical steps to determine any possible background contribution from the cartridge. The cartridge blank is used to represent the cleanliness of all samples in a single manufacturing lot.

METHOD BLANK (Extraction Blank) – a new, unused XAD-2-cartridge free of analyte and matrix to which all reagents are added in the same volumes or proportions as used in sample processing, and which is taken through the entire sample preparation process. It is used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment.

SOLVENT BLANK – a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

CALIBRATION - Calibration refers to the act of evaluating and adjusting the precision and accuracy of measurement equipment using known values (standards).

CO-LOCATED SAMPLE - – a sample used to assess total precision (sampling and analysis) which is located within a specified radius of the primary sampler. The collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.

CONTINUING CALIBRATION VERIFICATION SAMPLE (CCV) – a sample containing analyte at a known concentration obtained from a source other than that of the calibration standards.

DUPLICATE - two aliquots taken from and representative of the same sample or product and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis.

ESTIMATED QUANTITATION LIMIT (EQL) – defined as five times the method detection limit (MDL) and used as the lower limit for reporting data.

INTERFERENCE – discrete artifacts or elevated baselines from solvents, reagents, glassware, and other sample processing hardware that may cause misinterpretation of the chromatographic data.

METHOD DETECTION LIMIT (MDL) – the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and statistically different from a blank. It is determined from replicate analyses of a sample in a given matrix containing the analyte.

REPLICATE – a separate analysis of the same sample. The sample extract used for replicate analyses must be chosen at random. Relative percent difference between the sample and its replicate is calculated and must meet specified quality control criteria or be reanalyzed. Replicate analytical results are used to evaluate analytical precision but not the precision of sampling, preservation, or storage internal to the laboratory.

4. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware, and the XAD-2 sorbent 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 solvent blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

5. PERSONNEL QUALIFICATIONS

All analysts performing analyses pursuant to this SOP will be experienced and adequately trained in the use of air sampling methods and analysis by GC/ECD, handling all pertinent solvents and sampling media, and have an understanding of the chemistry involved in the chemical analyses of the target analytes. All analysts will also be trained in proper safety procedures adopted by the laboratory.

6. HEALTH, SAFETY, AND CAUTIONS

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 safety data sheets (SDS) of any chemicals used in this procedure.

7. EQUIPMENT, SUPPLIES, AND CONDITIONS

A. Instrumentation

Agilent Technologies 7890 Series gas chromatograph with Agilent Model G4513A injector.

Column: Agilent HP-5, 30 meter, 0.32 millimeter (mm) inner diameter (I.D.), 0.25 micron (μm) film thickness, with helium (He) as carrier gas at a constant flow rate of 1.095 milliliters per minutes (ml/min) and nitrogen as the makeup gas at 25 ml/min.

GC temperature program:

Ramp 1: initial 150° C, initial time 6 minutes, to 200° C @ 10° C/min.

Ramp 2: 25° C/min to 310° C holds 3 min.

Total run time 25 minutes.

Inlet temperature: 250° C.

Split ratio: 1:1.

Detector temperature: 325° C.

Injection Volume: 1 microliter (μl).

B. Auxiliary Apparatus

- XAD-2 Cartridges (400/200 milligrams (mg)) SKC cat # 226-30-6 or equivalent.
- Glass amber vials, 2-ml capacity with septum caps.
- 250 µl flat bottom inserts.

C. Reagents

- Ethyl Acetate (EtAc) (B&J brand pesticide grade or equivalent).
- Methanol (BDH brand residue grade or equivalent).
- Prepared 25 percent Methanol in ETAc.
- 2,4-D DMAS (AccuStandard S-25374) 100 µg/ml CAS# 2008-39-1.

D. Gases

- Compressed Helium grade 5.
- Compressed Nitrogen grade 5.

8. SAMPLE COLLECTION

- A. Samples are collected in the field with a maximum flow rate of one 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.

9. SAMPLE EXTRACTON

- A. Prepare a method blank and laboratory control sample (LCS) tube with every batch of field samples not to exceed 20 samples in an analytical batch.
- B. Spike the LCS with 100 nanograms (ng) 2,4-D DMAS.
- C. Carefully score and break the sample XAD-2 sorbent tubes just above the glass wool plug on the front section.
- D. Remove the cap from the XAD-2 resin tube. Remove the glass wool plug using tweezers. Pour the XAD-2 resin from the front section into an 8-ml glass vial. Gently tap glass tube containing the XAD-2 resin removing as much of the XAD-2 as possible.
- E. Retain the back section for later analysis to check for sample breakthrough. Recap the front section of XAD-2 resin.
- F. Using 3.9 ml of 25 percent methanol in EtAc, carefully rinse the inside of the front section of the XAD into the glass vial and vortex for 10 seconds.
- G. Place the 8-ml glass vial in a sonication bath for 15 minutes.

- H. Following sonication add 100 μ l of a 2.0 M (trimethylsilyl)diazomethane to the glass vial.
- I. Allow to sit for approximately one hour, checking after 30 minutes to ensure the yellow color from the (trimethylsilyl)diazomethane is present. The disappearance of the yellow color indicates there is a very high concentration of 2,4-D DMAS present and that all of the (trimethylsilyl)diazomethane has been consumed during the derivatization process. If the yellow color disappears after 30 minutes, add an additional 30 μ l of 2.0 M (trimethylsilyl)diazomethane and let sit an additional 30 minutes, making sure the yellow color is present.
- J. After extraction the samples are ready for analysis. If analysis is not started immediately the samples should be stored in a refrigerator at 4°C until analysis.

10. 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 one- μ l injection volume will be used for all analyses.
- C. Perform an initial calibration curve using concentrations at or near the EQL to at least 100 times higher. At least a five-point calibration curve must be established (eight points were used for this study) with a calibration curve acceptance r^2 criteria of at least 0.995. Appendix 1 lists the standard concentrations used when the EQL is approximately 0.013 μ g/m³.
- D. Prepare a sample sequence for the GC/ECD. The sequence should include a solvent blank and a continuing calibration verification (CCV) standard for every ten samples analyzed.
- E. If a batch of samples includes a method blank and/or LCS, those method blanks and/or LCS should be analyzed prior to field samples to verify that quality control (QC) criteria have been met.
- F. Because of the nature of the XAD-2 sorbent tube, extraneous components will be extracted along with the analytes of interest. To minimize carryover of these contaminants from one analysis to the next, a solvent blank should be analyzed after every 10 to 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 solvent blank analysis.
- G. Review and edit the quantitation reports as needed.
- H. The samples must be diluted if the analytical results are not within the range of the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.
- I. The final results will be adjusted by an appropriate dilution factor and reported in ng/sample.

J. The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc. (ng/m}^3\text{)} = \frac{\text{Extract Conc. (ng/ml)} \times 4 \text{ ml}}{\text{Air Volume Sampled (m}^3\text{)}}$$

K. Given instrument sensitivity and a maximum sample volume of 1.44 m³ the EQL for this method will be approximately 0.013µg/m³.

11. DATA MANAGEMENT AND REPORTING

Data generated from the analysis of samples, solvents, standards, and blanks will be entered into a spreadsheet, where calculations are performed. All data will be reviewed by the analyst prior to the generation of a summary report. The summary report will be reviewed and approved by the laboratory supervisor.

12. QUALITY ASSURANCE

- A. A solvent blank must be analyzed with each batch of samples. The solvent 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 solvent blank is analyzed at the beginning of the analytical batch and after the calibration curve or CCV just prior to sample analysis.
- B. A minimum five-point calibration curve is established at the beginning of each project, immediately after major instrument maintenance or repair, and whenever the CCV exceeds the acceptance criteria.
- C. A CCV is analyzed at the start of each analytical batch and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25 percent of the actual value.
- D. A method blank will be analyzed with each batch of samples. The method blank is a blank XAD-2 sorbent tube that is analyzed through the entire method. The analyte concentration must be below the MDL established for the method.
- E. A LCS is analyzed with every batch of samples. The LCS analyte concentrations should fall within the lower half of the calibration curve. The LCS stock standard should come from a different source or lot than the standard used to make the calibration curve. If a differing lot number is not available, the LCS should be made up independently from the calibration curve standard. 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. Other project specific quality control samples, such as lab spikes, trip spikes, and field spikes, are analyzed prior to field samples. A solvent blank should be analyzed after the spiked samples to ensure that the spiked analyte does not carry over into the field samples.

Appendix 1

Calibration Standard Preparation for 2,4-D DMAS

The certified standard of 2,4-D DMAS salt was purchased from AccuStandard, Inc., New Haven, Connecticut and has the following specification:

Lot No:	213031379
Expiration date:	March 21, 2014
2,4-D DMAS:	100 µg/ml

2,4-D DMAS was diluted from the AccuStandard Solution of 100 µg/ml. Using a serial dilution technique the following 2,4-D DMAS standard concentrations were prepared in 25 percent methanol in ethyl acetate: 5, 10, 50, 100, 250, 500, 1,000, and 2,000 ng/ml.

Eight standard concentrations were used to generate the calibration curve with 5.0 ng/ml the low point. The low point equates to approximately 13.8 ng/m³ (0.013 µg/ m³).

All standard and sample injections used a volume of 1.0 µl.

Initial calibration curve acceptance requires an r^2 of at least 0.995.

Appendix B:

Method Development for 2,4-D DMAS

California Environmental Protection Agency



**Method Development for the Sampling and Analysis of
2, 4-Dichlorophenoxyacetic Acid Dimethylamine Salt
(2,4-D DMAS)**

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

September 2013

Version 1

Approved
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.

1. SCOPE

This method was developed for the air sampling and analysis of 2, 4-dichlorophenoxyacetic acid dimethylamine salt (2,4-D DMAS) using gas chromatography/electron capture detector (GC/ECD). The 2,4-D DMAS method development establishes the 2,4-D DMAS extraction efficiency, storage stability, breakthrough, reproducibility, and minimum detection limit (MDL). The requested estimated quantitation limit (EQL) was four micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

2. SUMMARY OF METHOD

Ambient and/or application air samples are to be collected on XAD-2 sorbent tubes. Sampled tubes are stored at four degrees centigrade ($^{\circ}\text{C}$) or lower prior to extraction. Samples are extracted using pesticide grade 25 percent methanol in ethyl acetate. Sample extracts are sonicated for 15 minutes then 100 microliters (μl) of 2.0 molar (M) (trimethylsilyl)diazomethane is added to create a derivative. Analysis and quantitation is performed using a GC/ECD and uses an 8-point 2,4-D DMAS standard calibration curve of a derivatized standard. EQL for this method, sampling at one liter per minute (LPM) and using a four milliliter (ml) volume to extract the XAD-2 tubes, is $0.013 \mu\text{g}/\text{m}^3$.

3. INTERFERENCES / LIMITATIONS

Method interference possibility caused by contaminants in solvents, reagents, glassware and the XAD-2 tubes can lead to discrete artifacts or elevated baselines. During method development there were no interferences eluting at the retention time of 2,4-D DMAS. 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 G4513A injector.

Column: Agilent HP-5, 30 meter, 0.32 millimeter (mm) inner diameter (I.D.), 0.25 micron (μm) film thickness, with helium (He) as carrier gas at a constant flow rate of 1.095 ml/min and nitrogen as the makeup gas at 25 ml/min.

GC temperature program:

Ramp 1: initial 150°C , initial time 6 minutes, to 200°C @ $10^{\circ}\text{C}/\text{min}$.

Ramp 2: $25^{\circ}\text{C}/\text{min}$ to 310°C holds 3 min.

Inlet temperature: 250°C.
Split ratio: 1:1.
Detector temperature: 325°C.
Injection Volume: 1µl.

B. Auxiliary Apparatus

XAD-2 cartridges (400/200 milligram (mg)) SKC cat # 226-30-6 or equivalent.
Glass amber vials, two-ml capacity with septum caps.
250 µl flat bottom inserts.

C. Solvents

Methanol (BDH brand residue grade or equivalent).
Ethyl Acetate (EtAc) (EMD brand or equivalent).

D. Derivatization reagent

(Trimethylsilyl)diazomethane 2.0 M in hexanes (yellow in color).

5. Method Development

A. Instrument Reproducibility

The reproducibility of the instrument was established by 5 separate injections of 100 nanograms (ng)/ml 2,4-D DMAS standard. Table 1 lists the results for the 2,4-D DMAS reproducibility study.

Table 1: 2,4-D DMAS Instrument Reproducibility

Injection	Results (ng/ml)
1	88.965
2	93.303
3	92.259
4	92.675
5	90.578
Average	91.555
Standard Deviation	1.765
Relative Standard Deviation	1.930

Target: 100 ng/ml

B. Linearity

An eight-point calibration is performed. Calibration standards ranging from near the EQL to 400 times higher are used. For this analysis, concentrations of 5.0, 10.0, 50, 100, 250, 500, 1,000, and 2,000 ng/ml of 2,4-D DMAS is used. A linear

regression with an r^2 value 0.995 or higher is required for the calibration to be acceptable.

C. Method Detection Limit

MDL and EQL are based on the United States Environmental Protection Agency (US EPA) MDL calculation. The analyses of seven replicates of a low-level standard are used to calculate the MDL and EQL for 2,4-D DMAS. Those results are presented in Table 2.

Table 2: 2,4-D DMAS MDL and EQL Determination

Replicate Analyses	Results (ng/ml)
1	10.235
2	10.752
3	10.668
4	10.695
5	9.912
6	10.605
7	10.443
Average	10.473
Standard Deviation (STD)	0.3040
MDL= 3.143*STD	0.9554
EQL=5*MDL	4.777

Target: 10.0 ng/ml

The calculated MDL for 2,4-D DMAS is 0.9554 ng/ml. The EQL for 2,4-D DMAS is 4.777 ng/ml. Using a 4-ml extraction volume and a sample collection volume of 1 LPM for 24 hours, the 4.777 ng/ml EQL equates to $0.013 \mu\text{g}/\text{m}^3$. The analytical method meets the requested EQL of $4.0 \mu\text{g}/\text{m}^3$.

D. Collection and Extraction Efficiency (Recovery)

Collection and efficiency (recovery) data for 2,4-D DMAS is established using two concentration levels (100 ng and 1000 ng). XAD-2 cartridges are spiked and the 2,4-D DMAS is extracted and derivatized before analysis by GC/ECD. The recovery of 2,4-D DMAS is listed in Table 3.

Table 3: Extraction Efficiency 2,4 D DMAS

Spike level	Sample 1 (% Recovery)	Sample 2 (% Recovery)	Sample 3 (% Recovery)	Average % Recovery	Standard Deviation
100 ng	122.84	125.96	134.87	127.89	6.24
1000 ng	84.77	90.64	77.76	84.39	6.45

E. Storage Stability

Storage stability studies were performed using 100 ng of 2,4-D DMAS spiked on the primary section of XAD-2 tubes. The study was conducted for 28 days, in triplicate, with spikes analyzed at days 7, 14, 21 and day 28. Table 4 lists the results for the storage stability study.

Table 4: Storage Stability Study 2,4- D DMAS

Day	1st replicate (% Recovery)	2nd replicate (% Recovery)	3rd replicate (% Recovery)	Average % Recovery	Standard Deviation
7	125.57	129.71	123.61	126.29	3.11
14	99.86	115.66	109.52	108.35	7.97
21	134.16	154.16	135.94	141.42	11.07
28	102.62	103.62	104.89	103.71	1.138

F. Breakthrough

This study consisted of three XAD-2 tubes spiked with 2,4-D DMAS at 6000 ng in the front section. Air was drawn through the spiked XAD-2 tube at approximately 1 LPM for 24 hours. Both the front and back sections of the spiked XAD-2 tubes were extracted and derivatized prior to analysis by GC/ECD. Table 5 presents the results of the breakthrough study.

Table 5: Breakthrough Study 2,4-D DMAS

Spike amount (ng)	Amount recovered in front section (ng)	% Recovery	Rear Analyzed?	Amount Break-through
6000	6988.321	116.47	Yes	0
6000	7456.545	124.28	Yes	0
6000	6826.741	113.78	Yes	0

The results indicate there was no breakthrough of 2,4-D DMAS at 6000 ng. The average recovery at the 6000 ng spike level is 118.18 percent with a standard deviation of 5.452 percent.

APPENDIX E

XAD2 Sample Field Log Sheets

FILTER FIELD LOG SHEET

Project: 2, 4-DMAS Pesticide Application Air Monitoring
 Start Flow Set: 1.0 ±0.1 lpm End Flow Criteria: 1.0 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 (11/14/13 13:42)		Start	End	TIME	Display			Start	End	Start	End	Start	End
			Start	End			HOURS	Start	End							
001	BKG-NWC	2957	11/13/13 12:12	11/14/09 0:00	475.1	0.0	-475.1	0.95	0	0.5	K	PC	SA	SA		
002	BKG-W	4665	11/13/13 12:17	11/14/13 7:25	506.2	525.3	19.1	0.95	0.53	0.8	K	PC	SA	SA		
003	BKG-SWC	4675	11/13/13 12:22	11/14/13 7:37	557.7	576.9	19.2	0.95	0.5	0.8	K	PC	SA	SA		
004	BKG-S	4644	11/13/13 12:26	11/14/13 7:42	726.2	745.4	19.2	0.95	0.59	0.8	K	PC	SA	SA		
005	BKG-SEC	4661	11/13/13 12:37	11/14/13 7:50	326.0	345.2	19.2	0.95	0.66	0.9	K	PC	SA	SA		
006	BKG-SEC-C	4677	11/13/13 12:39	11/14/13 7:53	872.9	892.1	19.2	0.95	0.55	0.8	K	PC	SA	SA		
007	BKG-SEC-FS-1	4663	11/13/13 12:42	11/14/13 7:54	884.6	903.8	19.2	0.95	0.69	0.9	K	PC	SA	SA		
008	BKG-E	4673	11/13/13 12:48	11/14/13 8:08	1252.1	1271.4	19.3	0.95	1.05	1.1	K	PC	SA	SA		
009	BKG-NEC	4664	11/13/13 12:56	11/14/13 8:10	508.9	528.2	19.3	0.95	1.04	1.1	K	PC	SA	SA		
010	BKG-N	4676	11/13/13 13:00	11/14/13 8:14	529.6	548.8	19.2	0.95	1.34	1.2	K	PC	SA	SA		
011	NWC-1	4654	11/14/13 8:19	11/14/13 15:13	747.3	754.0	6.7	0.95	1.87	1.5	PC	PC	SSR	SRR		
012	W-1	4665	11/14/13 8:20	11/14/13 15:19	525.4	532.4	7.0	0.95	1.23	1.1	PC	PC	SSR	SRR		
013	SWC-1	4675	11/14/13 8:20	11/14/13 15:23	576.9	584.0	7.1	0.95	1.35	1.2	PC	PC	SRR	SRR		
014	S-1	4644	11/14/13 8:21	11/14/13 15:28	745.4	752.6	7.2	0.95	0.84	1.0	PC	PC	SRR	SRR		
015	SEC-1	4661	11/14/13 8:23	11/14/13 15:35	345.2	352.5	7.3	0.95	1.15	1.1	PC	PC	SRR	SRR		
016	SEC-1C	4677	11/14/13 8:23	11/14/13 15:39	892.1	899.5	7.4	0.95	1.23	1.1	PC	PC	SRR	SRR		
017	SEC-1FS	4663	11/14/14 8:23	11/14/13 15:40	903.9	911.2	7.3	0.95	0.95	1.0	PC	PC	SRR	SRR		
018	E-1	4673	11/14/13 8:20	11/14/13 15:48	1271.4	1278.9	7.5	0.95	0.69	0.9	PC	PC	SRR	SRR		
019	NEC-1	4664	11/14/13 8:18	11/14/13 15:52	528.2	535.7	7.5	0.95	0.71	0.9	PC	PC	SRR	SRR		
020	N-1	4676	11/14/13 8:17	11/14/13 15:58	548.8	556.5	7.7	0.95	0.78	0.9	PC	PC	SRR	SRR		
021	NWC-2	4654	11/14/13 15:13	11/15/13 7:27	754.0	770.2	16.2	1.05	1.12	1.1	K	K	JP	JP		
022	W-2	4665	11/14/13 15:19	11/15/13 7:31	532.4	548.6	16.2	1.05	1.11	1.1	K	K	JP	JP		

MFM Used #: 2E+07 Slope: 1.004 Intercept: 0.052

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

FILTER FIELD LOG SHEET

Project: 2, 4-DMAS Pesticide Application Air Monitoring
 Start Flow Set: 1.0 ±0.1 lpm End Flow Criteria: 1.0 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 (11/14/13 13:42)		Start	End		Start	End		Start	End	Start	End
			Start	End	Start	End		Start	End		Start	End	Start	End
023	SWC-2	4675	11/14/13 15:23	11/15/13 7:35	584.0	600.2	16.2	1.05	0.96	1.1	K	K	JP	JP
024	S-2	4644	11/14/13 15:28	11/15/13 7:39	752.6	768.8	16.2	1.05	1.08	1.1	K	K	JP	JP
025	SEC-2	4661	11/14/13 15:35	11/15/13 7:45	352.5	368.7	16.2	1.05	1.2	1.2	K	K	JP	JP
026	SEC-2C	4677	11/14/13 15:39	11/15/13 7:46	899.5	915.6	16.1	1.05	1.28	1.2	K	K	JP	JP
027	SEC-2FS	4663	11/14/13 15:40	11/15/13 7:48	911.2	927.4	16.2	1.05	1.25	1.2	K	K	JP	JP
028	E-2	4673	11/14/13 15:48	11/15/13 7:52	1278.9	1295.0	16.1	1.05	1.36	1.3	K	K	JP	JP
029	NEC-2	4664	11/14/13 15:52	11/15/13 7:55	535.7	551.8	16.1	1.05	1.34	1.3	K	K	JP	JP
030	N-2	4676	11/14/13 15:58	11/15/13 8:00	556.5	572.6	16.1	1.05	1.32	1.2	K	K	JP	JP
031	NWC-3	4654	11/15/13 7:27	11/15/13 15:26	770.2	778.2	8.0	1.05	0.96	1.1	K	K	JP	JP
032	W-3	4665	11/15/13 7:31	11/15/13 15:30	548.6	556.6	8.0	1.05	1	1.1	K	K	JP	JP
033	SWC-3	4675	11/15/13 7:35	11/15/13 15:34	600.2	608.2	8.0	1.05	1.03	1.1	K	K	JP	JP
034	S-3	4644	11/15/13 7:39	11/15/13 15:38	768.8	776.8	8.0	1.05	1	1.1	K	K	JP	JP
035	SEC-3	4661	11/15/13 7:45	11/15/13 15:45	368.7	376.7	8.0	1.05	1	1.1	K	K	JP	JP
036	SEC-3C	4677	11/15/13 7:46	11/15/13 15:47	915.6	923.7	8.1	1.05	1	1.1	K	K	JP	JP
037	SEC-3FS	4663	11/15/13 7:48	11/15/13 15:49	927.4	935.4	8.0	1.05	1.04	1.1	K	K	JP	JP
038	E-3	4673	11/15/13 7:52	11/15/13 15:53	1295.0	1303.0	8.0	1.05	1	1.1	K	K	JP	JP
039	NEC-3	4664	11/15/13 7:55	11/15/13 15:59	551.8	559.8	8.0	1.05	1.09	1.1	K	K	JP	JP
040	N-3	4676	11/15/13 8:00	11/15/13 16:01	572.6	580.6	8.0	1.05	1.03	1.1	K	K	JP	JP
041	NWC-4	4654	11/15/13 15:26	11/16/13 7:30	778.2	794.2	16.0	1.05	1.06	1.1	K	K	JP	JP
042	W-4	4665	11/15/13 15:30	11/16/13 7:33	556.6	572.6	16.0	1.05	1.04	1.1	K	K	JP	JP
043	SWC-4	4675	11/15/13 15:34	11/16/13 7:37	608.2	624.2	16.0	1.05	1.08	1.1	K	K	JP	JP
044	S-4	4644	11/15/13 15:38	11/16/13 7:40	776.8	792.8	16.0	1.05	1.05	1.1	K	K	JP	JP

MFM Used #: 2E+07 Slope: 1.004 Intercept: 0.052

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

FILTER FIELD LOG SHEET

Project: 2, 4-DMAS Pesticide Application Air Monitoring
 Start Flow Set: 1.0 ±0.1 lpm End Flow Criteria: 1.0 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 (11/14/13 13:42)	Start	End	Start		End	Start		End	Start	End	Start	End
045	SEC-4	4661	11/15/13 15:45	11/16/13 7:45	376.7	392.7	16.0	1.05	1.09	1.1	K	K	JP	JP	
046	SEC-4C	4677	11/15/13 15:47	11/16/13 7:48	923.7	939.7	16.0	1.05	1.22	1.2	K	K	JP	JP	
047	SEC-4FS	4663	11/15/13 15:49	11/16/13 7:50	935.4	951.4	16.0	1.05	1.08	1.1	K	K	JP	JP	
048	E-4	4673	11/15/13 15:53	11/16/13 7:54	1303.0	1319.0	16.0	1.05	1	1.1	K	K	JP	JP	
049	NEC-4	4664	11/15/13 15:57	11/16/13 7:57	559.8	575.8	16.0	1.05	1.04	1.1	K	K	JP	JP	
050	N-4	4676	11/15/13 16:01	11/16/13 8:01	580.6	596.6	16.0	1.05	1.04	1.1	K	K	JP	JP	
051	NWC-5	4654	11/16/13 7:30	11/16/13 15:48	794.2	802.5	8.3	1.05	1.03	1.1	K	K	JP	JP	
052	W-5	4665	11/16/13 7:33	11/16/13 15:51	572.6	580.9	8.3	1.05	1	1.1	K	K	JP	JP	
053	SWC-5	4675	11/16/13 7:37	11/16/13 15:54	624.2	632.5	8.3	1.05	1.03	1.1	K	K	JP	JP	
054	S-5	4644	11/16/13 7:40	11/16/13 15:58	792.8	801.1	8.3	1.05	1.03	1.1	K	K	JP	JP	
055	SEC-5	4661	11/16/13 7:45	11/16/13 16:04	392.7	401.0	8.3	1.05	1.03	1.1	K	K	JP	JP	
056	SEC-5C	4677	11/16/13 7:48	11/16/13 16:06	939.7	947.9	8.2	1.05	1.06	1.1	K	K	JP	JP	
057	SEC-5FS	4663	11/16/13 7:50	11/16/13 16:09	951.4	959.7	8.3	1.05	1	1.1	K	K	JP	JP	
058	E-5	4673	11/16/13 7:54	11/16/13 16:17	1319.0	1327.4	8.4	1.05	1.03	1.1	K	K	JP	JP	
059	NEC-5	4664	11/16/13 7:57	11/16/13 16:21	575.8	584.2	8.4	1.05	1.05	1.1	K	K	JP	JP	
060	N-5	4676	11/16/13 8:01	11/16/13 16:25	596.6	605.0	8.4	1.05	1.03	1.1	K	K	JP	JP	
061	NWC-6	4654	11/16/13 15:48	11/17/13 7:34	802.5	818.3	15.8	1.05	0.92	1.0	K	K	JP	JP	
062	W-6	4665	11/16/13 15:51	11/17/13 7:36	580.9	596.7	15.8	1.05	0.93	1.0	K	K	JP	JP	
063	SWC-6	4675	11/16/13 15:54	11/17/13 7:39	632.5	648.2	15.7	1.05	0.92	1.0	K	K	JP	JP	
064	S-6	4644	11/16/13 15:58	11/17/13 7:42	801.1	816.8	15.7	1.05	0.94	1.1	K	K	JP	JP	
065	SEC-6	4661	11/16/13 16:04	11/17/13 7:47	401.0	416.7	15.7	1.05	1	1.1	K	K	JP	JP	
066	SEC-6C	4677	11/16/13 16:06	11/17/13 7:49	947.9	963.7	15.8	1.05	0.94	1.1	K	K	JP	JP	

MFM Used #: 2E+07 Slope: 1.004 Intercept: 0.052

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

APPENDIX F

Calibration/Certification Report

CALIFORNIA AIR RESOURCES BOARD

FLOW CALIBRATION REPORT

Log Number: 2012322

To: STEVE RIDER
SPECIAL PURPOSE MONITORING

From: ROBERT RUSSELL
OPERATIONS PLANNING & ASSESSMENT

Calibration Date: 12/6/2012
Report Date: 12/7/2012

IDENTIFICATION

Instrument:	AALBORG MFM GFM17		
Property No.:	20005063		
Serial No.:	G15285		
Previous Log No.:	0		
Bar Code No.:	20005063		
Elevation:	25.00'		
Property of:	SPECIAL PURPOSE MONITORING		

Site Name:	MLD Standards Lab
Site Number:	34-299
Location:	1927 13th Street Sacramento, CA 95811

CALIBRATION STANDARDS	ID Number
MOLBOX FLOW STANDARD	20021121
MOLBOXn FLOW STANDARD	20021493

CALIBRATION RESULTS

MFM / MFC Position	POS	1
Instrument Range	5 lpm	
Maxium Display	5	
Best Fit Linear Regression	Slope:	0.9961
	Intercept:	-0.0521
Change From Previous Calibration (%)	0.07%	
Previous Calibration Date	12/20/2011	

Certification Equation:

Certification Expires: 12/6/2013

5 lpm Corrected Air Flow = 1.0039 * (Instrument Display) - 0.0523
+ 0.1%

Comments:

The Calibration Results Table explains the linear relationship between the guest transfer and the Standards Laboratory references standard. It is for informational use only. DO NOT USE THES VALUES TO CORRECT THE INSTRUMENTS DISPLAY. The Calibration Equation should be used to adjust the instrument display. If this is a Verification report, the Verification Equation is for information use only.

Calibrated by: Staff

Checked by: RR

APPENDIX G

Meteorological Data

ARB Calibration Report - Outside Temperature

Calibration Summary:

ID Information:

Station Name:	Automet 5304
Site #:	Pre-2,4-D Application
Station Address:	Sacto. 5th St. Warehouse
Agency:	ARB

Calibration Info.:

Manufacturer:	Met One	AS-IS:	
Model #:	060A-2	FINAL:	X
Serial #:	A6801	Calibration Date:	03/13/13
Translator #:	466A	Report Date:	03/15/13
Serial #:	X1042	Previous Cal. Date:	09/06/11

Calibration Results:

Component:	Outside Temp.
Instrument Range (degrees centigrade):	-50 to 50
AS-LEFT Average Ice Bath Difference (°C):	0.34
AS-LEFT Average Ambient Bath Difference (°C):	0.22
AS-LEFT Average Hot Bath Difference (°C):	0.25
Slope:	1.002
Intercept:	-0.318
Correlation:	1.00000
AS-LEFT Meets PSD °C Difference Requirement:	YES

Meteorology:

Temperature (°C):	20.0
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	20.5
Feet Above Roof:	N.A.

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Slope:	Intercept:
Digi-Sense 93410-50 Digital Thermometer	196743	01/22/13	0.9990	-0.3300
Cole Parmer Thermister Probe	N.A.	N.A.	N.A.	N.A.

Calibration Data:

If Average Difference of any bath is >0.50°C, correct.

Translator:

Reference Bath	DAS Degree C (x)	Digital Degree C	True Degree C (y)	Difference DAS - True	Zero Scale:	
ICE	0.16	0.17	-0.16	0.32	N.A.	N.A.
	0.21	0.17	-0.16	0.37	DMM Volts	Degrees C
	0.16	0.17	-0.16	0.32	N.A.	N.A.
	Average	0.18		-0.16	0.34	Full Scale:
AMBIENT	27.53	27.61	27.25	0.28	Regression & Graph Data:	
	27.42	27.60	27.24	0.18	x	y
	27.42	27.57	27.21	0.21	0.18	-0.16
	Average	27.46		27.24	0.22	27.46
HOT	48.44	48.55	48.17	0.27	48.42	48.17
	48.39	48.53	48.15	0.24	PSD Data:	0.34
	48.44	48.58	48.20	0.24		0.22
	Average	48.42		48.17		0.25

Outside Temperature Regression Data

Regression Results:

x Coefficient (Slope):	1.0019
y Constant (Intercept):	-0.3182
Number of Observations:	3
Correlation:	0.999999

Corrected OTEMP:

(DAS * x) + y
-0.14
27.19
48.20

Comments:	Initial around +0.5 diff. Changed AutoMet intercept from -72.89 to -79.09.		
Calibrated by:	Steve Rider		Checked by:

ARB Calibration Report - Resultant Wind Speed

Calibration Summary:

ID Information:

Station Name:	Automet 5304
Site #:	Post-2,4-D Application
Station Address:	Sacto. 5th St. Warehouse
Agency:	ARB

Calibration Info.:

Manufacturer:	Met One	AS-IS:	
Model #:	010C	FINAL:	X
Serial #:	A6703	Calibration Date:	01/23/14
Translator #:	466A	Report Date:	01/23/14
Serial #:	X1042	Previous Cal. Date:	03/13/13

Calibration Results:

Component:	Wind Speed	
Instrument Range (knots per hour):	0 to 86.84	
AS-LEFT Starting Torque (gm-cm):	0.27	
AS-LEFT Absolute Avg Speed Difference (knots):	0.02	
Wind Speed Best Fit Line	Slope:	0.999
	Intercept:	0.020
	Correlation:	1.00000
AS-LEFT Meets Both PSD Requirements:	YES	

Meteorology:

Temperature (°C):	23.2
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	22.5
Roof height in feet.:	0.0
Calculated data to meet EPA height:	10.3
To meet EPA height:	-22.5
	10.3

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
R.M. Young 18310 Torque Disc (0 to 15 gm-cm):		Factory	N.A.
R.M. Young 18810 Selectable Drive (10-1,000 rpm):	10329	01/18/13	RPM=(Meter*10)+0

Calibration Data:

Translator:

Zero Scale:		Full Scale:	
DMM Voltage:	Knots:	DMM Voltage:	Knots:
N.A.	N.A.	N.A.	N.A.

Starting Torque:

In gm-cms:	0.1	Starting speed in meters/sec:	0.27
K Factor:	1.4	Meets PSD torque standard:	YES

Speed Accuracy (@ 0 <0.54 & Difference DAS - True <±5% of True)

RPM:	True (y): Knots per Hour	DAS (x): Knots	Difference DAS - True	PSD Differ- ence Data	Meets PSD Difference Standard:
0	0.52	0.50	-0.02	1	YES
50	3.11	3.10	-0.01	0.3%	
110	6.22	6.21	-0.01	0.1%	Absolute Avg. Diff.: 0.02
220	11.92	11.88	-0.04	0.3%	
450	23.83	23.84	0.01	0.1%	
920	48.17	48.18	0.01	0.0%	

Wind Speed Regression Data

Regression Results:

x Coefficient (Slope):	0.9993
y Constant (Intercept):	0.0203
Number of Observations:	6
Correlation:	1.00000

Corrected RWS:

(DAS * x) + y
0.52
3.12
6.23
11.89
23.84
48.17

Comments:	Post-2,4-D Cal. Performed in Sacto.		
Calibrated by:	Steve Aston		Checked by:

ARB Calibration Report - Resultant Wind Speed

Calibration Summary:

ID Information:

Station Name:	Automet 5304
Site #:	Pre-2,4-D Application
Station Address:	Sacto. 5th St. Warehouse
Agency:	ARB

Calibration Info.:

Manufacturer:	Met One	AS-IS:	
Model #:	010C	FINAL:	X
Serial #:	A6703	Calibration Date:	03/13/13
Translator #:	466A	Report Date:	03/15/13
Serial #:	X1042	Previous Cal. Date:	09/06/11

Calibration Results:

Component:	Wind Speed	
Instrument Range (knots per hour):	0 to 86.84	
AS-LEFT Starting Torque (gm-cm):	0.38	
AS-LEFT Absolute Avg Speed Difference (knots):	0.02	
Wind Speed Best Fit Line	Slope:	1.000
	Intercept:	0.018
	Correlation:	1.00000
AS-LEFT Meets Both PSD Requirements:	YES	

Meteorology:

Temperature (°C):	20.0
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	22.5
Roof height in feet.:	0.0
Calculated data to meet EPA height:	10.3
To meet EPA height:	-22.5
	10.3

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
R.M. Young 18310 Torque Disc (0 to 15 gm-cm):		Factory	N.A.
R.M. Young 18810 Selectable Drive (10-1,000 rpm):	10329	01/18/13	RPM=(Meter*10)+0

Calibration Data:

Translator:

Zero Scale:		Full Scale:	
DMM Voltage:	Knots:	DMM Voltage:	Knots:
N.A.	N.A.	N.A.	N.A.

Starting Torque:

In gm-cms:	0.2	Starting speed in meters/sec:	0.38
K Factor:	1.4	Meets PSD torque standard:	YES

Speed Accuracy (@ 0 <0.54 & Difference DAS - True <±5% of True)

RPM:	True (y): Knots per Hour	DAS (x): Knots	Difference DAS - True	PSD Differ- ence Data	Meets PSD Difference Standard:
0	0.52	0.50	-0.02	1	YES
50	3.11	3.10	-0.01	0.3%	
110	6.22	6.21	-0.01	0.1%	Absolute Avg. Diff.: 0.02
220	11.92	11.88	-0.04	0.3%	
450	23.83	23.80	-0.03	0.1%	
920	48.17	48.14	-0.03	0.1%	

Wind Speed Regression Data

Regression Results:

x Coefficient (Slope):	1.0003
y Constant (Intercept):	0.0179
Number of Observations:	6
Correlation:	1.000000

Corrected RWS:

(DAS * x) + y
0.52
3.12
6.23
11.90
23.83
48.17

Comments:	Pre-2,4-D Cal. Performed in Sacto.		
Calibrated by:	Steve Rider		Checked by:

ARB Calibration Report - Resultant Wind Direction

Calibration Summary:

ID Information:
Calibration Info.:

Station Name:	Automet 5304	Manufacturer:	Met One	AS-IS:	
Site #:	Pre-2,4-D Application	Model #:	020C-1	FINAL:	X
Station Address:	Sacto. 5th St. Warehouse	Serial #:	A6978	Calibration Date:	01/23/14
Agency:	ARB	Translator #:	466A	Report Date:	01/23/14
		Serial #:	X1042	Installation Date:	03/13/13

Calibration Results:

Component:	Wind Direction	
Instrument Range (degrees):	0 to 360	
AS-LEFT Azimuth in relation to True North (deg):	2.1	
AS-LEFT Starting Torque (gm-cms):	2.4	
AS-LEFT Absolute Average Difference (degrees):	2.1	
Wind Direction Best Fit Line	Slope:	1.021
	Intercept:	-3.631
	Correlation:	1.00000
AS-LEFT Meets Both PSD Requirements:		NO

Meteorology:

Temperature (°C):	23.2
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	22.5
Roof height in feet.:	0.0
Calculated data to meet EPA height:	10.3
To meet EPA height:	-22.5
	10.3

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
Brunton 5008 Pocket Transit	5081192140	Factory	WYSIWYG
R.M. Young 18310 Torque Disk	N.A.	Factory	N.A.
Met One 040 Degree Fixture	N.A.	Factory	WYSIWYG

Calibration Data:

Direction Accuracy:

True Degrees (y):	DAS Degrees (x):	Difference DAS - True	Calculated Data to Meet PSD Direction	Translator:	DMM Voltage:	Degrees:
				Zero Scale:	N.A.	N.A.
10	13.3	3.3	1	Half Scale:	N.A.	N.A.
90	91.5	1.5	1	Starting Torque:	gram-centimeters:	2.4
180	180.1	0.1	0		K Factor:	38
270	268.4	-1.6	1		Speed in m/sec.:	0.25
350	346.0	-4.0	1		Meets torque std.:	YES
Absolute Avg. Diff.:		2.1			PSD Correction:	2.1

Wind Direction Regression Data

Regression Results:

x Coefficient (Slope):	1.0210
y Constant (Intercept):	-3.6309
Number of Observations:	5
Correlation:	0.999997

Corrected RWD:

(DAS * x) + y
9.9
89.8
180.2
270.4
349.6

AS-LEFT Condition (0 to 360° only):

Declination of Site (Degrees East):			Calculated Data to Meet PSD Direction
Calculated True North Heading:	360.0		
Crossarm Orientation Uncorrected Transit Reading:		Meets Direction Standard	1
Crossarm Degrees in Relation to True North:	0.0		0
DAS Output with Vane Parallel to Crossarm:	2.1		1
DAS Output Degrees off from True North:	-357.9		NO
Azimuth computed from above measurements:	2.1		1

Comments:	Cal in Sac. Crossarm Orientation Uncorrected Transit Reading at site.		
Calibrated by:	Steve Rider		Checked by:

ARB Calibration Report - Resultant Wind Direction

Calibration Summary:

ID Information:
Calibration Info.:

Station Name:	Automet 5304	Manufacturer:	Met One	AS-IS:	
Site #:	Pre-2,4-D Application	Model #:	020C-1	FINAL:	X
Station Address:	Sacto. 5th St. Warehouse	Serial #:	A6978	Calibration Date:	01/23/14
Agency:	ARB	Translator #:	466A	Report Date:	01/23/14
		Serial #:	X1042	Installation Date:	11/13/13

Calibration Results:

Component:	Wind Direction	
Instrument Range (degrees):	0 to 360	
AS-LEFT Azimuth in relation to True North (deg):	2.1	
AS-LEFT Starting Torque (gm-cms):	3.7	
AS-LEFT Absolute Average Difference (degrees):	2.2	
Wind Direction Best Fit Line	Slope:	1.021
	Intercept:	-2.866
	Correlation:	0.99999
AS-LEFT Meets Both PSD Requirements:		YES

Meteorology:

Temperature (°C):	20.0
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	22.5
Roof height in feet.:	0.0
Calculated data to meet EPA height:	10.3
To meet EPA height:	-22.5
	10.3

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
Brunton 5008 Pocket Transit	5081192140	Factory	WYSIWYG
R.M. Young 18310 Torque Disk	N.A.	Factory	N.A.
Met One 040 Degree Fixture	N.A.	Factory	WYSIWYG

Calibration Data:

Direction Accuracy:

True Degrees (y):	DAS Degrees (x):	Difference DAS - True	Calculated Data to Meet PSD Direction	Translator:	DMM Voltage:	Degrees:
				Zero Scale:	N.A.	N.A.
10	11.9	1.9	1	Half Scale:	N.A.	N.A.
90	91.6	1.6	1	Starting Torque:	gram-centimeters:	3.7
180	179.8	-0.2	1		K Factor:	38
270	267.1	-2.9	1		Speed in m/sec.:	0.31
350	345.5	-4.5	1		Meets torque std.:	YES
Absolute Avg. Diff.:		2.2		PSD Correction:	2.1	

Wind Direction Regression Data

Regression Results:

x Coefficient (Slope):	1.0206
y Constant (Intercept):	-2.8659
Number of Observations:	5
Correlation:	0.999990

Corrected RWD:

(DAS * x) + y
9.3
90.6
180.6
269.7
349.7

AS-LEFT Condition (0 to 360° only):

Declination of Site (Degrees East):			Calculated Data to Meet PSD Direction
Calculated True North Heading:	360.0		
Crossarm Orientation Uncorrected Transit Reading:		Meets Direction Standard	1
Crossarm Degrees in Relation to True North:	0.0		
DAS Output with Vane Parallel to Crossarm:	2.1		
DAS Output Degrees off from True North:	-357.9		
Azimuth computed from above measurements:	2.1		

Comments:	Cal in Sac. Crossarm Orientation Uncorrected Transit Reading at site.		
Calibrated by:	Steve Rider		Checked by:

ARB Calibration Report - Relative Humidity

Calibration Summary:

ID Information:

Station Name:	Automet 5304	Manufacturer:	Vaisala	AS-IS:	
Site #:	Post-2,4-D Application	Model #:	HMP45D	FINAL:	X
Station Address:	5th St. Warehouse in Sacto.	Serial #:	W4410024	Calibration Date:	03/13/13
Agency:	ARB	Translator #:	466A	Report Date:	03/15/13
		Serial #:	X1042	Previous Cal. Date:	09/06/11

Calibration Info.:
Calibration Results:

	Component:	Relative Humidity
Instrument Range (Percent Relative Humidity):		0 to 100
	Slope:	1.065
Relative Humidity Best Fit Line	Intercept:	-0.502
	Correlation:	0.99914
Absolute Average Percent Difference (%RH):		2.7
AS-LEFT Meets PSD Requirements:		YES

Meteorology:

Temperature (°C):	23.2
Elevation (Ft.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	20.5
Feet Above Roof:	N.A.

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
Rotronic ER25 Calibration Device:	None	Factory	N.A.
Rotronic EA10 Salt Standard:	101201	01/25/12	(10 x 1)+0
Rotronic EA35 Salt Standard:	351103	11/21/11	(35 x 1)+0
Rotronic EA50 Salt Standard:	501103	11/16/11	(50 x 1)+0
Rotronic EA80 Salt Standard:	801201	02/24/12	(80 x 1)+0

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Calibration Data:
Translator:

Zero Scale:		Full Scale:	
DMM Voltage:	%RH:	DMM Voltage:	%RH:
N.A.	N.A.	N.A.	N.A.

% Relative Humidity Accuracy (If Any Difference > 5.0%RH, adjust so Avg. Diff. Is <2.0%RH Difference)

TRUE %RH (y)	DAS %RH (x)	DAS Voltage	Difference DAS - True	Meets PSD Criteria
0	0.5	N.A.	N.A.	YES
10.0	11.0	N/A	1.0	1
35.0	32.2	N/A	-2.8	1
50.0	46.6	N/A	-3.4	1
80.0	76.4	N/A	-3.6	1
ABS Avg. Diff.:			2.7	

Relative Humidity Regression Data

Regression Results:

X Coefficient (Slope):	1.0650
Y Constant (Intercept):	-0.5017
Number of Observations:	4
Correlation:	0.999135

Corrected %RH:

(DAS * x) + y
0.0
11.2
33.8
49.1
80.9
100.0

Comments:	Pre-2,4-D cal. Performed in Sacto. Initial was 78.4 @ 79.9. Adjusted Wet Pot.
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ARB Calibration Report - Relative Humidity

Calibration Summary:

ID Information:
Calibration Info.:

Station Name:	Automet 5304	Manufacturer:	Vaisala	AS-IS:	
Site #:	Pre-2,4-D Application	Model #:	HMP45D	FINAL:	X
Station Address:	5th St. Warehouse in Sacto.	Serial #:	W4410024	Calibration Date:	03/13/13
Agency:	ARB	Translator #:	466A	Report Date:	03/15/13
		Serial #:	X1042	Previous Cal. Date:	09/06/11

Calibration Results:

	Component:	Relative Humidity
Instrument Range (Percent Relative Humidity):		0 to 100
	Slope:	1.010
Relative Humidity Best Fit Line	Intercept:	-0.270
	Correlation:	0.99988
Absolute Average Percent Difference (%RH):		0.5
AS-LEFT Meets PSD Requirements:		YES

Meteorology:

Temperature (°C):	20.0
Elevation (Ft.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	20.5
Feet Above Roof:	N.A.

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Cert. Factor:
Rotronic ER25 Calibration Device:	None	Factory	N.A.
Rotronic EA10 Salt Standard:	100701	04/12/07	(10 x 1)+0
Rotronic EA35 Salt Standard:	350704	01/09/08	(35 x 1)+0
Rotronic EA50 Salt Standard:	500604	08/17/06	(50 x 1)+0
Rotronic EA80 Salt Standard:	800706	12/12/07	(80 x 1)+0

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Calibration Data:
Translator:

Zero Scale:		Full Scale:	
DMM Voltage:	%RH:	DMM Voltage:	%RH:
N.A.	N.A.	N.A.	N.A.

% Relative Humidity Accuracy (If Any Difference > 5.0%RH, adjust so Avg. Diff. Is <2.0%RH Difference)

TRUE %RH (y)	DAS %RH (x)	DAS Voltage	Difference DAS - True	Meets PSD Criteria
0	0.3	N.A.	N.A.	YES
9.7	10.3	N/A	0.6	1
34.6	33.9	N/A	-0.7	1
50.2	49.9	N/A	-0.3	1
79.9	79.6	N/A	-0.3	1
ABS Avg. Diff.:			0.5	

Relative Humidity Regression Data

Regression Results:

X Coefficient (Slope):	1.0102
Y Constant (Intercept):	-0.2698
Number of Observations:	4
Correlation:	0.999876

Corrected %RH:

(DAS * x) + y
0.0
10.1
34.0
50.1
80.1
100.0

Comments:	Pre-2,4-D cal. Performed in Sacto. Initial was 78.4 @ 79.9. Adjusted Wet Pot.
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ARB Calibration Report - Outside Temperature

Calibration Summary:

ID Information:

Station Name:	Automet 5304
Site #:	Post-2,4-D Application
Station Address:	Sacto. 5th St. Warehouse
Agency:	ARB

Calibration Info.:

Manufacturer:	Met One	AS-IS:	
Model #:	060A-2	FINAL:	X
Serial #:	A6801	Calibration Date:	01/23/14
Translator #:	466A	Report Date:	01/23/14
Serial #:	X1042	Previous Cal. Date:	03/13/13

Calibration Results:

Component:	Outside Temp.
Instrument Range (degrees centigrade):	-50 to 50
AS-LEFT Average Ice Bath Difference (°C):	0.39
AS-LEFT Average Ambient Bath Difference (°C):	0.30
AS-LEFT Average Hot Bath Difference (°C):	0.46
Slope:	0.999
Intercept:	-0.348
Correlation:	1.00000
AS-LEFT Meets PSD °C Difference Requirement:	YES

Meteorology:

Temperature (°C):	23.0
Elevation (Feet.):	25
Pressure (mmHg):	760.0

Sensor Height:

Feet Above Ground:	20.5
Feet Above Roof:	N.A.

Calibration Standards:

Standard:	I.D. #:	Cert. Date:	Slope:	Intercept:
Digi-Sense 93410-50 Digital Thermometer	196743	01/22/13	0.9990	-0.3300
Cole Parmer Thermister Probe	N.A.	N.A.	N.A.	N.A.

Calibration Data:

If Average Difference of any bath is >0.50°C, correct.

Translator:

Reference Bath	DAS Degree C (x)	Digital Degree C	True Degree C (y)	Difference DAS - True	Zero Scale:	
ICE	0.98	0.92	0.59	0.39	N.A.	N.A.
	0.98	0.92	0.59	0.39	DMM Volts	Degrees C
	0.98	0.92	0.59	0.39	N.A.	N.A.
Average	0.98		0.59	0.39	Full Scale:	
AMBIENT	23.59	23.66	23.31	0.28	Regression & Graph Data:	
	23.59	23.66	23.31	0.28	x	y
	23.64	23.65	23.30	0.34	0.98	0.59
Average	23.61		23.30	0.30	23.61	23.30
HOT	48.00	47.92	47.54	0.46	48.00	47.54
	48.00	47.92	47.54	0.46	PSD Data:	0.39
	48.00	47.92	47.54	0.46		0.30
Average	48.00		47.54	0.46		0.46

Outside Temperature Regression Data

Regression Results:

x Coefficient (Slope):	0.9985
y Constant (Intercept):	-0.3481
Number of Observations:	3
Correlation:	0.999996

Corrected OTEMP:

(DAS * x) + y	
	0.63
	23.22
	47.58

Comments:	Initial around +0.5 diff. Changed AutoMet intercept from -72.89 to -79.09.		
Calibrated by:	Steve Aston		Checked by:

Channel	1	2	
Sensor	RWS	RWD	
Units	KNT	DEG	sampling period #1
8:20	1.58	97.3	
8:25	1.48	99	
8:30	2	132.3	
8:35	2.49	122.4	
8:40	3.23	151.2	
8:45	3.17	133.5	
8:50	2.39	137.3	
8:55	2.64	143.2	
9:00	3.13	155.7	
9:05	2.98	170.5	
9:10	3	159.9	
9:15	2.58	174.4	
9:20	3.47	149.8	
9:25	2.98	171	
9:30	1.75	173.3	
9:35	2.47	190.8	
9:40	2.47	180.8	
9:45	1.77	60.2	
9:50	2.28	140.2	
9:55	2	155.8	
10:00	3.11	157.9	
10:05	2.58	118.4	
10:10	2.85	126.4	
10:15	3.62	142	
10:20	3.13	164.1	
10:25	2.6	188.6	
10:30	2.81	170.1	
10:35	2.43	180.9	
10:40	2.73	215.3	
10:45	3.36	217.8	
10:50	3.21	206.4	
10:55	2.43	213.7	
11:00	3.57	217.5	
11:05	1.79	212.1	
11:10	3.23	218.9	
11:15	3.02	227.3	
11:20	2.87	157.8	
11:25	3	163.6	
11:30	2.56	179	
11:35	2.62	167.2	
11:40	1.67	198.1	
11:45	2.49	246.8	
11:50	2.43	135.3	

11:55	2.6	276.9
12:00	2.81	282.8
12:05	2.66	255.5
12:10	2.56	146.1
12:15	1.84	70.7
12:20	2.92	259.5
12:25	2.45	237.6
12:30	2.47	222.4
12:35	1.67	169.4
12:40	1.64	137.4
12:45	1.81	33.4
12:50	2.75	334.6
12:55	2.7	278.9
13:00	1.43	151.5
13:05	1.62	12.9
13:10	3.28	280
13:15	3.59	269.9
13:20	2.98	294.8
13:25	2.62	335.2
13:30	3.76	327.2
13:35	2.07	335.6
13:40	3.11	350.5
13:45	3.11	323.6
13:50	2.77	344.1
13:55	2.51	336.7
14:00	3.32	345.4
14:05	2.85	353.2
14:10	3.38	346.3
14:15	2.68	327.8
14:20	2.77	337.6
14:25	3.91	3
14:30	3.21	337.4
14:35	3.81	305.4
14:40	4.17	322.8
14:45	4.44	319.3
14:50	3.66	336
14:55	3.02	348.1
15:00	3.72	4
15:05	3.76	334.8
15:10	3.59	335.5
15:15	3.49	350.5
15:20	2.56	342.4
15:25	3.06	346.3
15:30	2.77	353.3
15:35	2.79	343.7
15:40	2.64	345.3
15:45	2.77	339.9

15:50	3.02	349.8
15:55	3.23	350.2
16:00	3.93	352.9

Channel	1	2	
Sensor	RWS	RWD	
Units	KNT	DEG	sampling period #2
15:15	3.49	350.5	
15:20	2.56	342.4	
15:25	3.06	346.3	
15:30	2.77	353.3	
15:35	2.79	343.7	
15:40	2.64	345.3	
15:45	2.77	339.9	
15:50	3.02	349.8	
15:55	3.23	350.2	
16:00	3.93	352.9	
16:05	2.64	341	
16:10	3.04	352.9	
16:15	3.76	359.3	
16:20	3.62	356.1	
16:25	3.68	358.5	
16:30	3.55	2.1	
16:35	3.45	2.8	
16:40	3.17	351.8	
16:45	2.09	346.7	
16:50	1.79	337.3	
16:55	1.48	330.9	
17:00	1.6	335.5	
17:05	2.03	353	
17:10	2.03	337.8	
17:15	1.94	324.5	
17:20	1.71	335.6	
17:25	1.84	326.5	
17:30	2.3	339.9	
17:35	2.28	340.7	
17:40	2.49	343	
17:45	2.45	350	
17:50	1.88	343.2	
17:55	1.35	321.8	
18:00	1.37	304.7	
18:05	1.37	237.2	
18:10	1.58	246.9	
18:15	2.07	281.5	
18:20	2.13	290.2	
18:25	1.6	277.7	
18:30	1.54	264.5	
18:35	1.79	263.5	
18:40	2.07	293.6	
18:45	2.39	300.8	

18:50	2.2	289.8
18:55	2.34	280.6
19:00	2.41	282.8
19:05	2.43	277.6
19:10	2.2	268.2
19:15	1.58	259.1
19:20	1.24	274
19:25	0.97	266.2
19:30	0.84	262.7
19:35	1.75	281.4
19:40	1.26	302
19:45	0.63	291.7
19:50	0.73	298.7
19:55	0.8	316.3
20:00	0.71	225.2
20:05	0.61	257.5
20:10	1.35	322.4
20:15	1.64	325.7
20:20	0.65	313
20:25	0.84	314.1
20:30	0.5	330.6
20:35	0.71	328.8
20:40	1.39	27.4
20:45	1.33	36.1
20:50	1.07	2.9
20:55	0.99	23.9
21:00	1.43	33.8
21:05	0.86	65.3
21:10	0.69	80.6
21:15	0.5	110.6
21:20	0.65	97.6
21:25	1.24	51.7
21:30	1.54	41.5
21:35	1.64	60.9
21:40	1.96	37.3
21:45	1.9	37.8
21:50	1.64	80.2
21:55	2.47	66.7
22:00	2.73	62
22:05	2.81	58.3
22:10	1.84	41.7
22:15	2.3	51.5
22:20	1.9	42.8
22:25	2.45	45.9
22:30	2.15	43.5
22:35	2.81	45.6
22:40	1.94	39.7

22:45	2.66	35.5
22:50	3.32	37.8
22:55	3.36	38.5
23:00	3.26	35.7
23:05	3.34	32.1
23:10	3.23	29
23:15	2.81	20.8
23:20	2.41	26.9
23:25	2.62	35.7
23:30	2.87	38.7
23:35	2.81	43.9
23:40	2.66	45.5
23:45	2.92	47.2
23:50	2.15	47.7
23:55	1.28	40.3
0:00	1.31	45
0:05	2.26	39.4
0:10	2.32	41.7
0:15	1.45	40.4
0:20	1.22	19.7
0:25	1.28	28.2
0:30	1.35	52.3
0:35	1.52	68.1
0:40	1.18	118.1
0:45	1.56	64.3
0:50	1.39	111.2
0:55	1.52	100.9
1:00	1.11	156
1:05	1.28	182.2
1:10	1.64	194.6
1:15	1.41	186.1
1:20	1.14	169.3
1:25	1.5	179
1:30	1.75	179.1
1:35	0.95	166
1:40	0.75	250.4
1:45	1.01	251.8
1:50	1.24	281.7
1:55	1.67	277.4
2:00	1.05	278
2:05	0.9	237.9
2:10	0.8	273
2:15	1.41	61.7
2:20	1.5	50.7
2:25	0.65	59.6
2:30	0.58	140.3
2:35	0.73	108.5

2:40	1.16	62.8
2:45	0.58	81.8
2:50	0.5	83.3
2:55	0.63	44.8
3:00	1.2	248
3:05	1.05	250.1
3:10	0.73	226.8
3:15	0.97	235.1
3:20	0.67	244.6
3:25	0.8	220.6
3:30	0.71	211.9
3:35	0.97	88.1
3:40	2	48.6
3:45	1.11	61.7
3:50	0.5	66.6
3:55	1.2	74.5
4:00	1.24	77
4:05	0.56	66.1
4:10	0.69	146.7
4:15	0.69	226.8
4:20	0.95	20.2
4:25	0.92	1.2
4:30	1.07	287.1
4:35	0.5	247.7
4:40	0.5	93.8
4:45	0.82	65.9
4:50	0.56	107.5
4:55	0.73	252.4
5:00	0.92	299.4
5:05	1.33	339.2
5:10	1.86	349.1
5:15	2.37	336.6
5:20	2.73	326.3
5:25	2.66	335
5:30	3.32	325.6
5:35	4.12	318.5
5:40	4.04	325.8
5:45	3.85	316.4
5:50	4.53	322.6
5:55	4.36	317.9
6:00	4.57	309.9
6:05	3.87	313.3
6:10	4.46	314.1
6:15	4.19	321
6:20	4.21	323.6
6:25	5.01	325.2
6:30	5.35	317

6:35	4.48	316.3
6:40	4.15	313.2
6:45	3.76	309.1
6:50	4.06	303.9
6:55	4.4	305.1
7:00	4.93	301
7:05	4.32	307.7
7:10	5.08	302.2
7:15	5.69	304.9
7:20	5.82	306.4
7:25	5.63	307.8
7:30	5.76	311.7
7:35	5.82	314.5
7:40	5.8	320.2
7:45	5.29	315.1
7:50	6.27	322.6
7:55	6.03	313.2
8:00	5.69	317

Channel	1	2	
Sensor	RWS	RWD	
Units	KNT	DEG	sampling period #3
7:30	5.76	311.7	
7:35	5.82	314.5	
7:40	5.8	320.2	
7:45	5.29	315.1	
7:50	6.27	322.6	
7:55	6.03	313.2	
8:00	5.69	317	
8:05	6.44	313.4	
8:10	5.42	316.3	
8:15	5.61	321.7	
8:20	5.44	328	
8:25	6.54	318.2	
8:30	5.95	326.8	
8:35	5.54	332.4	
8:40	7.81	320.1	
8:45	9.17	319	
8:50	7.58	319.4	
8:55	7.37	324.7	
9:00	7.81	323.5	
9:05	6.46	320.7	
9:10	6.41	309.6	
9:15	7.39	320.5	
9:20	7.62	316.6	
9:25	9.68	318.5	
9:30	7.69	317.3	
9:35	6.44	327.9	
9:40	8.66	322.8	
9:45	9.08	314.4	
9:50	8.19	332.7	
9:55	9.28	330.3	
10:00	8.02	328.9	
10:05	7.88	331.5	
10:10	8.19	318.3	
10:15	7.54	299	
10:20	7.62	319.7	
10:25	8.6	310.2	
10:30	8.07	315.4	
10:35	8.28	307.2	
10:40	6.56	321.1	
10:45	7.18	311.2	
10:50	11.12	290.1	
10:55	10.04	293.6	
11:00	8	300.7	

11:05	8.55	300.9
11:10	8.15	295.5
11:15	8.24	292.1
11:20	8.81	283.6
11:25	9.95	298.4
11:30	9.08	299.9
11:35	8.49	295.2
11:40	6.77	322.8
11:45	7.11	322
11:50	7.13	322.9
11:55	5.46	320.2
12:00	8.11	296.3
12:05	8.75	286.9
12:10	6.77	287.4
12:15	6.94	308.7
12:20	6.99	301.3
12:25	7.47	292.1
12:30	8.26	304
12:35	9.61	292.1
12:40	8.32	289.2
12:45	8.51	294.6
12:50	7.13	309.1
12:55	7.49	302.2
13:00	7.43	304.2
13:05	7.26	319.1
13:10	7.73	303.9
13:15	8.28	289
13:20	8.49	291.2
13:25	6.99	297.1
13:30	6.58	300.3
13:35	8.34	301
13:40	8.62	292.9
13:45	7.62	307.5
13:50	8.24	319.3
13:55	7.35	309.9
14:00	7.66	304.6
14:05	7.96	298.8
14:10	7.41	307.5
14:15	7.45	295.9
14:20	6.8	304.2
14:25	6.29	300.7
14:30	6.03	313.5
14:35	8.36	300.6
14:40	7.54	297.8
14:45	6.01	302.3
14:50	6.03	326.3
14:55	7.35	306.4

15:00	7.94	315.7
15:05	5.12	321.4
15:10	5.69	306.8
15:15	5.74	327.7
15:20	5.29	329
15:25	5.63	314.3
15:30	3.89	314.1
15:35	5.46	321.4
15:40	4.63	304.7
15:45	4.21	311.9
15:50	5.06	302.5
15:55	4.8	300
16:00	4.44	298.5
16:05	4.53	301.7
16:10	3.4	307.4