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Report on Air Monitoring of the Application of Phosphine in Merced County in December 2008

Prepared by

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Monitoring Report Approval

Report Title: Report on Air Monitoring the Application of Phosphine in Merced County during December 2008

Project Lead: Neil Adler, Air Pollution Specialist

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

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Special Purpose Monitoring Section

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Air Quality Surveillance Branch

Executive Summary

Report on Air Monitoring the Application Of Phosphine in Merced County in December 2008

At the request of the California Department of Pesticide Regulation (DPR), (January 4, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff monitored one application site for phosphine. This application monitoring study was performed prior to, during and after the use of phosphine as a post-harvest commodity fumigant. Phosphine application monitoring was requested by DPR to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions…. of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR.

Pure phosphine is a colorless, odorless gas and is used to fumigate consumable commodities such as edible nuts. Phosphine gas is created by exposing a known amount of aluminum phosphide pellets to the ambient moisture inside the fumigation chamber. At the end of the fumigation period, the remaining phosphine gas in the chamber is vented out to the ambient air.

The location chosen for this study was a commercial commodity fumigation facility located in Merced County, CA. Monitoring occurred in December which is historically the month with the highest phosphine use. Monitoring and Laboratory Division staff sampled ambient air for phosphine during three separate periods. The background sampling period began prior to the fumigation process. The second period was during fumigation and the third period was during the aeration of the fumigation chamber.

A total of 75 samples were collected and transported to the ARB Monitoring and Laboratory Division laboratory for analysis. Samples were collected from eight locations (four corners, four sides) located 15 to 40 feet from the exterior walls of the fumigation chamber. One additional sampler was located inside the chamber. Samples were collected by passing a measured volume of ambient air into six (6)-liter Silco canisters. During this study, the Tisch Environmental 3–channel canister automated sampler was used for the first time. This sampler enabled field staff to program start and stop times for up to three separate sampling periods. Canisters can be filled up to one (1) atmosphere above ambient. The sampling flow rates were set to achieve a final canister pressure near 10 psig.

All background period ambient samples were reported at less than the analytical method detection limit of 1 $\mu g/m^3$. During the fumigation period, ambient samples ranged from less than 1 to 58.33 $\mu g/m^3$ and the samples taken from inside the fumigation chamber were reported from 510,000 to 700,000 $\mu g/m^3$. Ambient samples taken during the aeration period were reported from less than 1 to 6 $\mu g/m^3$.

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (January 4, 2008 Memorandum, Warmerdam to Goldstene), the Air Resources Board (ARB) staff monitored one application site for phosphine. This application monitoring study was performed prior to, during and after the use of phosphine as a post harvest commodity fumigant. Phosphine application monitoring was requested by DPR to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions…. of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR.

Phosphine is used as a postharvest commodity fumigant in chambers or other enclosures. The location chosen for this study is a commercial commodity fumigation facility located in Merced County, CA. Monitoring occurred in December, the month with the historically highest reported phosphine use. Pure phosphine is a colorless and odorless gas, and was applied using a metallic phosphide compound (aluminum phosphide). A measured quantity (mass) of aluminum phosphide pellets was placed inside a large chamber, and the chamber was sealed. Humidity from the air inside the chamber reacted with the aluminum phosphide pellets and created phosphine gas.

The fumigation chamber measured (24'W x 48'L x 22'H) with a (4' 7"W x 3' 9.5"L x 31'H) exhaust stack located in the middle of the north side of the chamber. Access to the chamber was through a 10' x 10' door on a slide track. See Figure 1 "Phosphine Fumigation Site Drawing". A total of 75 samples (62 field and 13 field quality control) were collected. These samples were collected from eight samplers (four corners and four sides) located 15 to 40 feet from the exterior walls of the fumigation chamber. A ninth sampler was located inside the fumigation chamber and sampled during the fumigation period. Two 1.5 kg containers (3 kg total) containing approximately 2500 pellets were used. These pellets were 55% aluminum phosphide and 45% inert ingredients. The fumigation chamber was empty during the background period and was filled with almonds during the fumigation/aeration period.

This is the first time the Tisch Environmental 3 – Channel Canister Sampler was used by ARB. This sampler enabled field staff to program start and stop times for up to three separate sampling periods. Samples were collected by passing a measured volume of ambient air into 6-liter Silco canisters. Canisters can be filled up to one (1) atmosphere above ambient. The sampling flow rates of 7.5 milliliters per minute (mm/min) were measured and set during sampling of the 22.3 hour background period. The flow rate was set at 45 (mm/min) were measured and set for the three separate four (4) hour sampling periods during fumigation . The flow rate was then measured and set at 50 (mm/min) for the three separate four (4) sampling periods during aeration. The flow rate was increased to 50 milliliters per minute in an effort to achieve a final canister pressure closer to the target pressure of 10 psig.

All pertinent information (start/stop times, flow rates, canister pressures, ect.) were recorded on the log sheet. Canister tracking sheets were documented and were used to record and maintain sampling information. Subsequent to sampling, the exposed canisters were promptly transported to the ARB Monitoring and Laboratory Division laboratory for analysis. Samples were analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent 7890A gas chromatograph equipped with a flame photometric detector in the phosphorus mode.

2.0 Sampling Sites

During the background sampling period two (2) samplers were positioned at approximate midpoint of each side 15 feet from the fumigation chamber. An ambient sample and a field spike were collected from each side. The north side had an additional collocated sampler which was the predominately downwind location. Sampling took place during a 22.3 hour period prior to the fumigation period. See Figure 2 “Drawing of Background Sampling Period Locations”.

Samplers were relocated prior to the fumigation sampling period. The midpoint side samplers were positioned approximately 15 feet from the fumigation chamber. The north side included the additional collocated sampler. The corner samplers were relocated to approximately 25 feet from the corner of the fumigation chamber. The tenth sampler was placed inside the chamber prior to the start of the fumigation period. Sampling took place during three separate, four (4) hour periods near the end of the fumigation period. See Figure 3 “Drawing of Fumigation Sampling Period Locations”.

Per DPR’s recommendations (Appendix B) samplers were relocated again prior to the aeration sampling period. The midpoint side samplers were repositioned approximately 25 feet from the fumigation chamber. The north side included the additional collocated sampler. The corner samplers were relocated to approximately 40 feet from the corner of the fumigation chamber. Sampling took place during three separate four (4) hour periods, starting at the beginning of the aeration period. See Figure 4 “Drawing of Aeration Sampling Period Locations”.

Figure 1

Phosphine Fumigation Site Drawing

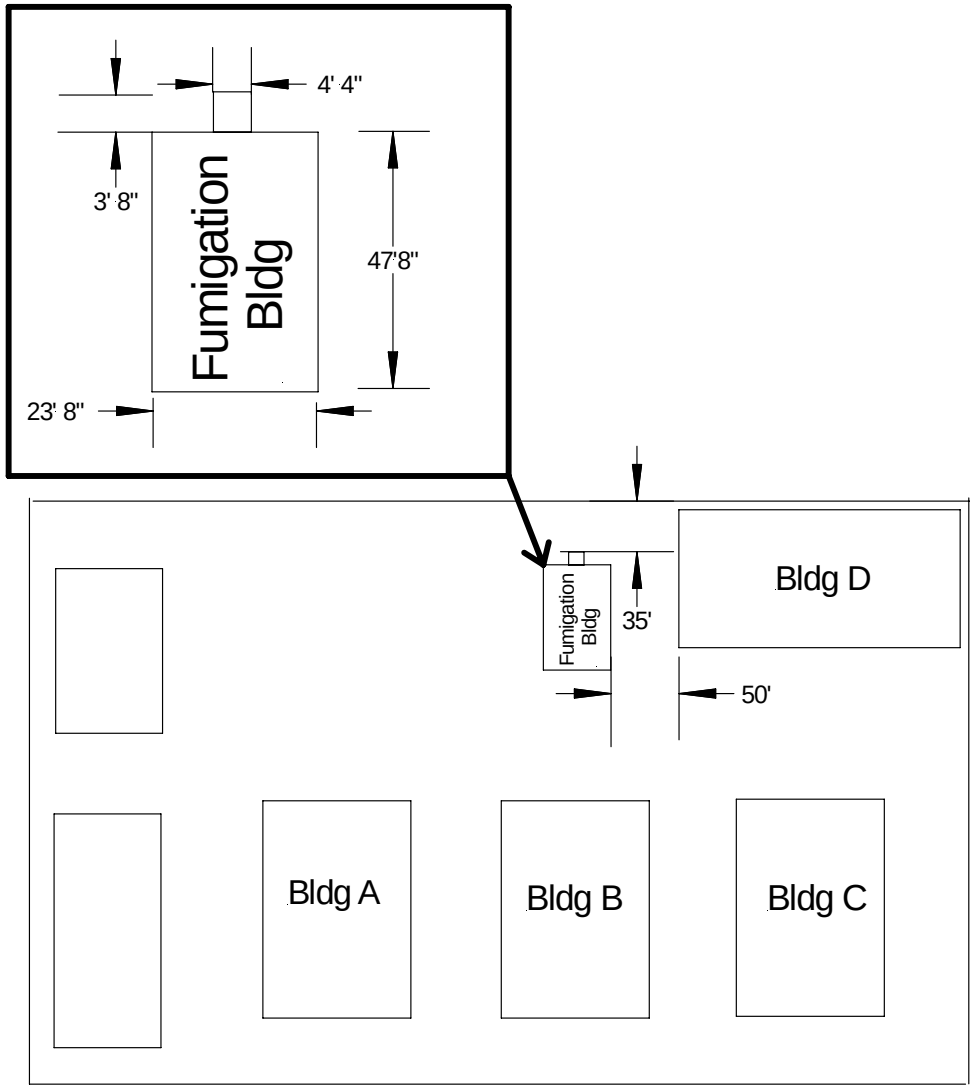


Figure 2

Drawing of Background Sampling Period Locations

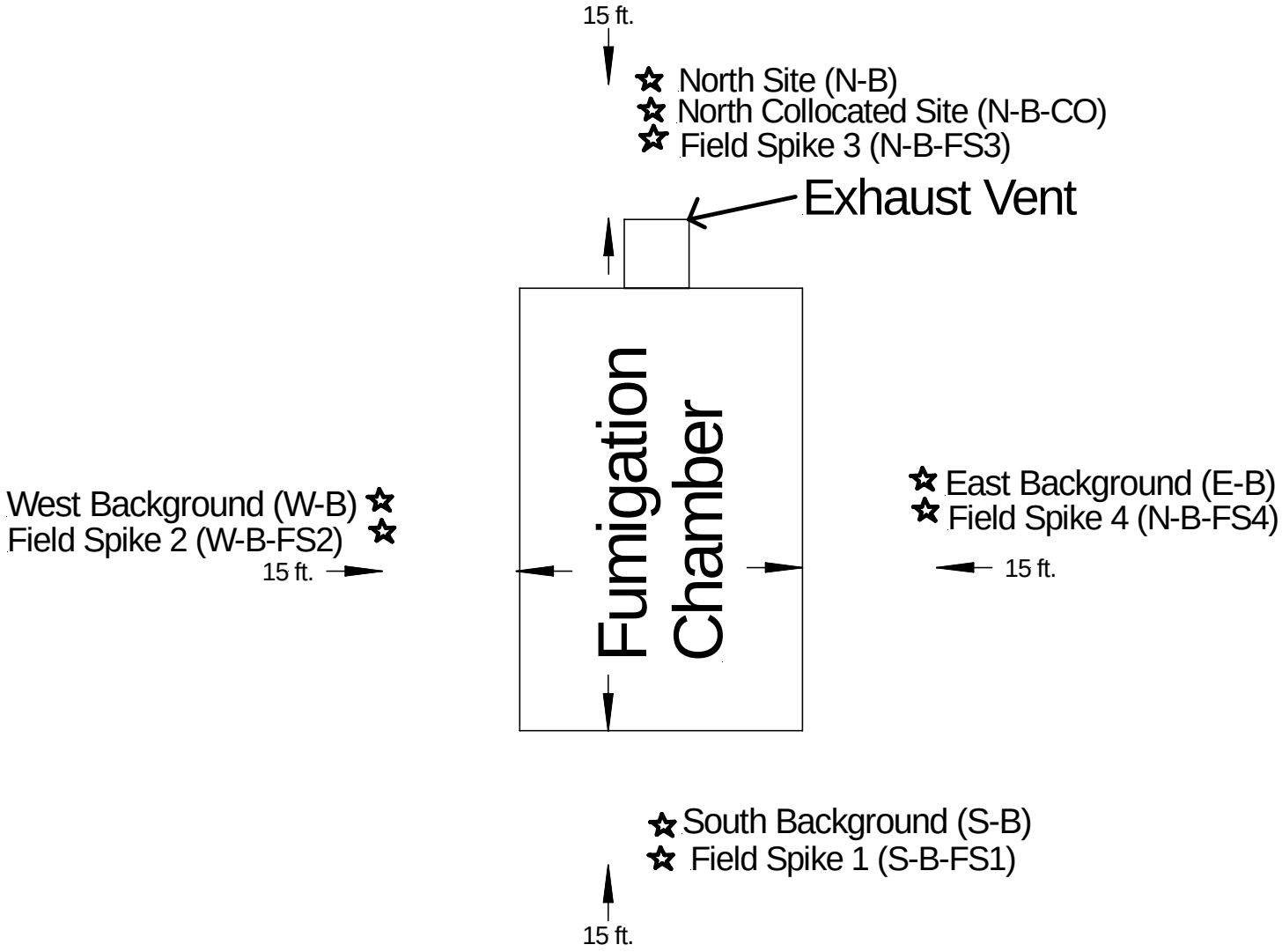
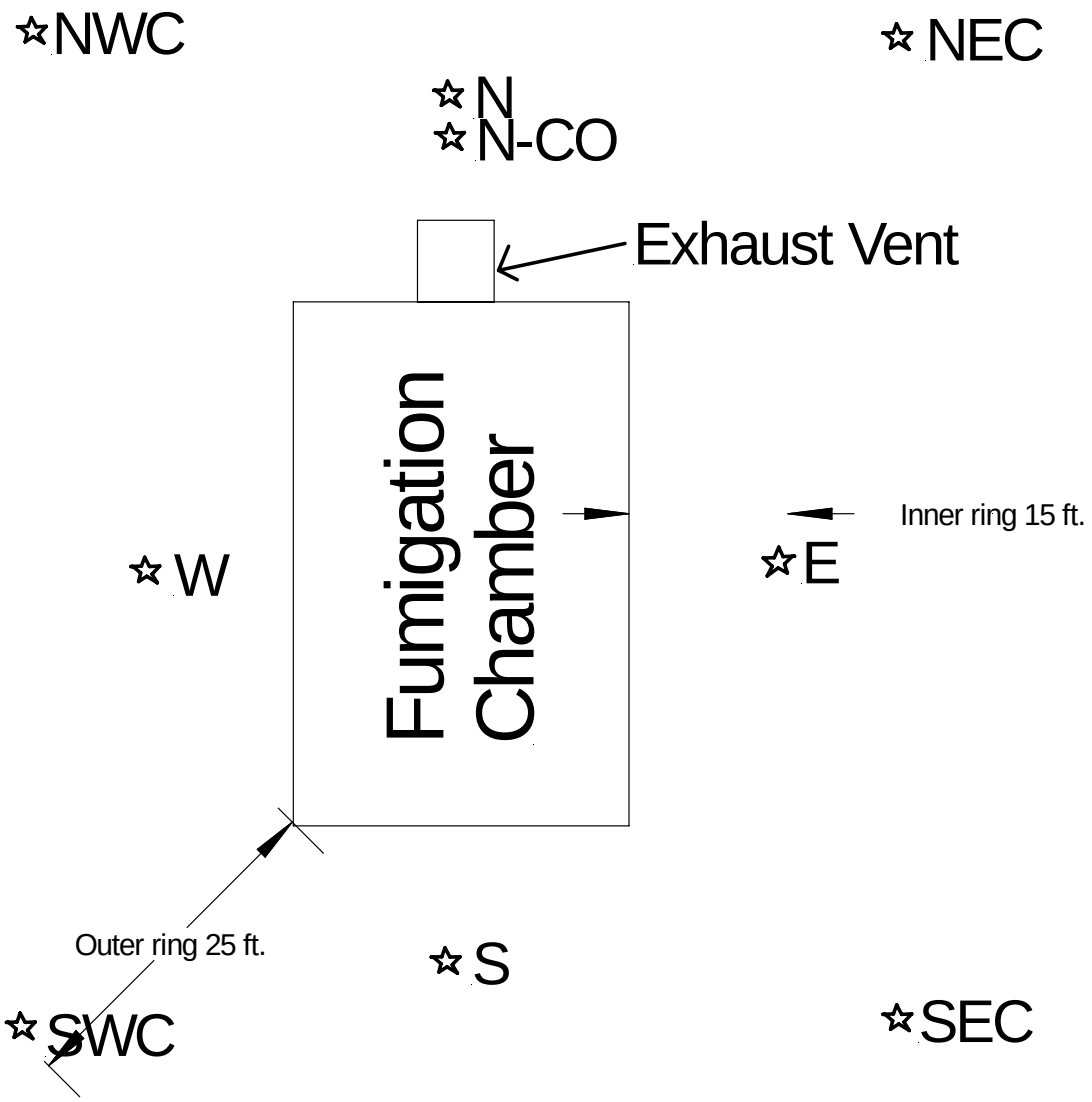


Figure 3

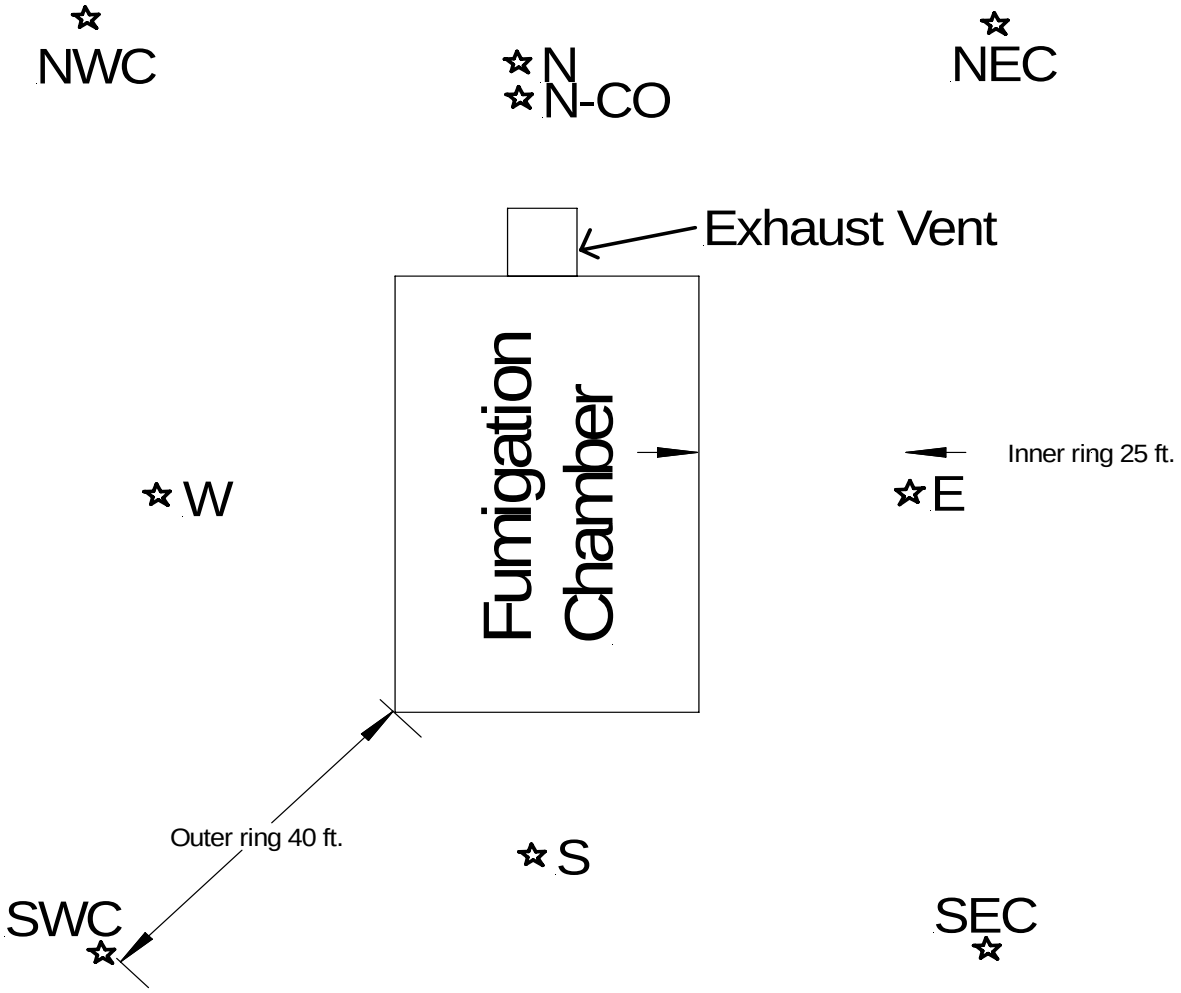
Drawing of Fumigation Sampling Period Locations



*Note: N, S, E & W designate direction, C designates corner.

Figure 4

Drawing of Aeration Sampling Period Locations



*Note: N, S, E & W designate direction, C designates corner.

3.0 Methods

The sampling method developed by the ARB Northern Laboratory Branch Special Analysis Section utilizes Silco canisters (Appendix C, Standard Operating Procedure Sampling and Analysis of Phosphine). The laboratory established a method detection limit (MDL) of 0.743 $\mu g/m^3$ and an estimated quantitation limit (EQL) of 3.715 $\mu g/m^3$. During this study, a new (Tisch TE-323) canister sampler was used. This sampler enabled field staff to program equipment for unattended start and stop activation. The sampler accommodated up to three (3) canisters for sequential sampling. Canisters were filled to a final pressure of approximately 10 psig.

Samples were collected by pressurizing ambient air into a Silco canister. Approximately three (3) lpm of air is pulled through the Tisch TE-323 inlet. By adjusting a valve, a regulated portion of the 3 lpm air flow is forced into the sample canister. Except for the chamber sampler, the inlet heights were placed at approximately 1.5 meters above the ground. The chamber sampler inlet was placed approximately 1.0 meter above the floor due to physical limitations. The application sampling periods are described below and summarized in Table 1.

Background sampling: Four (4) primary samples, one (1) collocated sample and four (4) field spike samples were deployed prior to phosphine fumigation. The four (4) primary samplers were placed approximately 15 feet away from each side of the building. One (1) field spike (40.95 to 44.29 µg/sample) sampler was placed in parallel with each primary sampler. The collocated sampler was placed at the downwind north side of the building. Background air sampling started December 4, 2008 at approximately 1400 hours and ended December 5, 2008 at approximately 1230 hours. The background sample duration was approximately a 22.3 hour period. Two (2) trip spikes and one (1) trip blank accompanied the background samples to the field and back to the Laboratory. Refer to Figure 2 “Drawing of Background Period Sampling Locations”.

Fumigation sampling: The fumigation process started December 5, 2008 at 14:00 and ended at December 10, 2008 at 08:00. The fumigation lasted almost six days due to low ambient temperature. One (1) trip spike and one (1) trip blank accompanied the samples to and from the field.

a) Inside chamber sample: A pre-programmed sampler was placed inside the chamber and configured to automatically sample three (3) consecutive canisters. The sampler was programmed so the last canister finished sampling on December 10, 2008 at 06:00. This was two (2) hours before aeration began. Due to the Tisch sampler design all three canisters were set at the same flow rate (45 ml/minute) and the same sample duration of four (4) hours each.

b) Outside fumigation sampling: Outside the chamber, samplers were placed 15 feet away from each of the four (4) building sides and 25 feet away from each of the four (4) building corners. A collocated sampler was placed at the downwind north location. The samplers were configured to fill each canister consecutively, with a sampling duration of four (4) hours each. Samplers were programmed to complete sampling of the last canister sample two (2) hours prior to the aeration process. This allowed ARB staff time to reconfigure the samplers. Please refer to Figure 3, “Drawing of Fumigation Period Sampling Locations”.

Aeration sampling: The local wind conditions were less than 5 knots/hour. All four (4) outer ring corner samplers were 40 feet away from the building, and the four (4) inner ring side samplers were 25 feet away from the building. A collocated sampler was placed at the downwind location. Please refer to Figure 4 "Drawing of Aeration Sampling Period Locations". The samplers were configured to fill each canister consecutively, with a sampling duration of four (4) hours each. Covered commodity containers were located along the east and west side of the chamber. ARB staff believe these boxes did not significantly influence sample collection during the aeration sampling period.

Two additional field stability spikes traveled to the field along with the background canisters and returned to the Laboratory at the end of sampling with the aeration samples. These spiked canisters were at the site for the whole sampling period.

Every attempt was made to shield all sampled canisters from direct sunlight to help reduce sampled phosphine losses. Samples were transported to Sacramento upon completion of the last sampling cycle.

DPR's "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Phosphine", dated September 2008 is included as Appendix B.

Table 1
Application Sampling Schedule

Sample period:	Sample duration time
Background (pre-application)	9 canisters (total) – 22.3 hours each
Fumigation (inside building)	3 canisters (total) – 4 hours each.
Fumigation (outside building)	27 canisters (total) – 4 hours each
Aeration	27 canisters (total) – 4 hours each

The calibration certificate for the mass flow meter (MFM) used is presented in Appendix E "Calibration/Certification Reports".

For details of the monitoring method, please refer to Appendix B, "Sampling Protocol for Phosphine Application Monitoring" (dated December 3, 2008). There were no significant deviations from this protocol during the actual monitoring.

Collected samples were analyzed by the Special Analysis Laboratory Section of MLD's Northern Laboratory Branch. The reported laboratory results are located in Appendix C "Phosphine Analytical Results for Application Air Monitoring Samples (October 2009)".

A meteorological system was approximately 200 yards southwest of the fumigation chamber. The meteorological data and wind roses are located in Appendix F "Meteorological Data".

4.0 Results

Sampling period information used to determine the total volume of ambient air collected into the canisters is located in Table 2 “Background Sampling Period Information”, Table 3 “Fumigation Sampling Period Information” and Table 4 “Aeration Sampling Period Information”.

All background period ambient samples were reported at less than the analytical method detection limit of 1 µg/m^3. See Table 5, “Background Sampling Period Results”. The fumigation period ambient samples reported values that ranged from less than 1 to 58.33 µg/m^3 and the samples taken from inside the fumigation chamber were reported from 510,000 to 700,000 µg/m^3. See Table 6, “Fumigation Sampling Period Results”. The aeration period ambient samples reported values that ranged from less than 1 to 6 µg/m^3. See Table 7, “Aeration Sampling Period Results”.

All quality control information is located in Section 5 “Quality Control”.

For additional information on these results, please refer to APPENDIX C: “Phosphine Analytical Results for Application Air Monitoring Samples (October 2009)”.

Site/Sample Identification

The phosphine application sampling sites were named accordingly for the background, fumigation and aeration as follows:

Site Naming Examples:

N-BK = North side background
W-BK-CO = Collocated west side Background
E-F-1 = East side fumigation Period 1
S-A-3 = South side aeration Period 3

Letter Abbreviations as follows:

N = North Side
NWC = NW Corner Sample
W = West Side
SWC = SW Corner Sample
S = South Side
SEC = SE Corner Sample
E = East Side
NEC = NE Corner Sample
CO= Collocated
B= Background Sample
F = Fumigation
A = Aeration
FS = Field Spike
F = Fumigation
STAB = Stability Spike
TS = Trip Spike
TB = Trip Blank
IN = Inside

Table 2
Background Sampling
Period Information

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42) Start	Date & Time Entry Example (6/14/08 13:42) End	Elapsed Time In Hours:Mins	Elapse Time Counter Start	Elapse Time Counter End	Elapsed Time In Minutes	Mass Flow Meter Display (ml/min) Start	Mass Flow Meter Display (ml/min) End	Corrected Average Flow (ml/min)	Total Volume ml
001	S-B	122	12/4/08 14:00	12/5/08 12:24	22:24:00	0.0	1344.00	1344.0	7.00	7.00	7.535	10127
002	S-B-FS1	114	12/4/08 14:00	12/5/08 12:24	22:24:00	0.0	1346.00	1346.0	7.00	7.00	7.535	10142
003	W-B	116	12/4/08 14:00	12/5/08 12:28	22:28:00	0.0	1348.00	1348.0	7.00	7.00	7.535	10157
004	W-B-FS2	115	12/4/08 14:00	12/5/08 12:28	22:28:00	0.0	1350.00	1350.0	7.00	7.00	7.535	10172
005	N-B	113	12/4/08 14:05	12/5/08 12:31	22:26:00	0.0	1346.00	1346.0	7.00	7.00	7.535	10142
006	N-B-C	118	12/4/08 14:00	12/5/08 12:32	22:32:00	0.0	1353.00	1353.0	7.00	7.00	7.535	10195
007	N-B-FS3	121	12/4/08 14:05	12/5/08 12:34	22:29:00	0.0	1348.00	1348.0	7.00	7.00	7.535	10157
008	E-B	117	12/4/08 14:15	12/5/08 12:35	22:20:00	0.0	1340.00	1340.0	7.00	7.00	7.535	10097
009	E-B-FS4	119	12/4/08 14:15	12/5/08 12:35	22:20:00	0.0	1340.00	1340.0	7.00	7.00	7.535	10097
010	TB	N/A	12/4/08 14:20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
011	TS1	N/A	12/4/08 12:11	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
012	TS2	N/A	12/4/08 12:13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
013	IN-F1	120	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
014	IN-F2	120	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
015	IN-F3	120	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787

MFM Used #: 5345 **Slope:** 1.003 **Intercept:** 0.514

Table 3
Fumigation Sampling
Period Information (Part 1 of 2)

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42)		Elapsed Time In	Elapse Time Counter		Elapsed Time In	Mass Flow Meter Display (ml/min)		Corrected Average Flow	Total Volume
			Start	End	Hours:Mins	Start	End	Minutes	Start	End	(ml/min)	ml
016	SEC-F-1	117	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
017	SEC-F-2	117	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
018	SEC-F-3	117	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
019	S-F-1	114	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
020	S-F-2	114	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
021	S-F-3	114	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
022	SWC-F-1	122	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
023	SWC-F-2	122	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
024	SWC-F-3	122	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
025	W-F-1	115	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
026	W-F-2	115	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
027	W-F-3	115	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
028	NWC-F-1	116	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
029	NWC-F-2	116	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
030	NWC-F-3	116	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
031	N-F-1	113	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
032	N-F-2	113	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
033	N-F-3	113	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
034	N-F-1-CO	118	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
035	N-F-2-CO	118	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
036	N-F-3-CO	118	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787

MFM Used #: 5345 **Slope:** 1.003 **Intercept:** 0.514

Table 3
Fumigation Sampling
Period Information (Part 2 of 2)

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42)		Elapsed Time In Hours:Mins	Elapse Time Counter		Elapsed Time In Minutes	Mass Flow Meter Display (ml/min)		Corrected Average Flow (ml/min)	Total Volume ml
			Start	End		Start	End		Start	End		
037	NEC-F-1	121	12/9/08 18:00	NO RUN	0:00:00	0.0	0.0	0.0	44.30	0.00	0.00	0
038	NEC-F-2	121	12/9/08 22:00	NO RUN	0:00:00	0.0	0.0	0.0	44.30	0.00	0.00	0
039	NEC-F-3	121	12/10/08 2:00	NO RUN	0:00:00	0.0	0.0	0.0	44.30	0.00	0.00	0
040	E-F-1	119	12/9/08 18:00	12/9/08 22:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
041	E-F-2	119	12/9/08 22:00	12/10/08 2:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
042	E-F-3	119	12/10/08 2:00	12/10/08 6:00	4:00:00	0.0	240.0	240.0	44.30	44.30	44.947	10787
043	TS	N/A	12/10/08 7:12	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
044	TB	N/A	12/10/08 7:13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

MFM Used #: 5345 **Slope:** 1.003 **Intercept:** 0.514

Table 4
Aeration Sampling
Period Information (Part 1 of 2)

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42) Start	Date & Time Entry Example (6/14/08 13:42) End	Elapsed Time In Hours:Mins	Elapse Time Counter Start	Elapse Time Counter End	Elapsed Time In Minutes	Mass Flow Meter Display (ml/min) Start	Mass Flow Meter Display (ml/min) End	Corrected Average Flow (ml/min)	Total Volume ml
045	SEC-A-1	117	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
046	SEC-A-2	117	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
047	SEC-A-3	117	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
048	S-A-1	114	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
049	S-A-2	114	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
050	S-A-3	114	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
051	SWC-A-1	122	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
052	SWC-A-2	122	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
053	SWC-A-3	122	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
054	W-A-1	115	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
055	W-A-2	115	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
056	W-A-3	115	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
057	NWC-A-1	116	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
058	NWC-A-2	116	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
059	NWC-A-3	116	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
060	N-A-1	113	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
061	N-A-2	113	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
062	N-A-3	113	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
063	N-A-1-CO	118	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
064	N-A-2-CO	118	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
065	N-A-3-CO	118	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159

MFM Used #: 5345 **Slope:** 1.003 **Intercept:** 0.514

Table 4
Aeration Sampling
Period Information (Part 2 of 2)

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42) Start	Date & Time Entry Example (6/14/08 13:42) End	Elapsed Time In Hours:Mins	Elapse Time Counter Start	Elapse Time Counter End	Elapsed Time In Hours	Mass Flow Meter Display (ml/min) Start	Mass Flow Meter Display (ml/min) End	Corrected Average Flow (ml/min)	Total Volume ml
066	NEC-A-1	121	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
067	NEC-A-2	121	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
068	NEC-A-3	121	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
069	E-A-1	119	12/10/08 8:00	12/10/08 12:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
070	E-A-2	119	12/10/08 12:00	12/10/08 16:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
071	E-A-3	119	12/10/08 16:00	12/10/08 20:00	4:00:00	0.0	240.0	240.0	50.00	50.00	50.7	12159
072	TS	N/A	12/10/08 7:12	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
073	TB	N/A	12/10/08 7:13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
74	STAB-1	N/A	12/10/08 7:13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
75	STAB-2	N/A	12/10/08 7:13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

MFM Used #: 5345 **Slope:** 1.003 **Intercept:** 0.514

Table 5
Background Sampling
Period Results

Log Number	Sample ID	Sample Dilution	Phosphine concentration (ug/m^3)
1	S-B	1	<1
2	S-B-FS		35.71
3	W-B	1	<1
4	W-B-FS2		41.85
5	N-B	1	<1
6	N-B-CO	1	<1
7	N-B-FS3		33.08
8	E-B	1	<1
9	E-B-FS4		37.68
10	TB		<1.47
11	TS1		28.28
12	TS2		26.26

Quality Control Samples (Spikes and Blanks)

Table 6
Fumigation Sampling
Period Results

Log Number	Sample ID	Sample Dilution	Phosphine concentration (ug/m^3)
13dl	In-F1	42987	610000
14dl	In-F2	45405	510000
15dl	In-F3	41222	700000
16	SEC-F-1	1.28	<2
17	SEC-F-2	No Sample	na
18	SEC-F-3	No Sample	na
19	S-F-1	1.26 Note: 1	12
20	S-F-2	1	7
21	S-F-3	1	<2
22	SWC-F-1	1	3
23	SWC-F-2	1	4
24	SWC-F-3	1	<2
25	W-F-1	1	<2
26	W-F-2	1	<2
27	W-F-3	1	58.33
28	NWC-F-1	1	41.69
29	NWC-F-2	1	<2
30	NWC-F-3	1	<2
31	N-F-1	1	<1
32	N-F-2	1	<1
33	N-F-3	1	<1
34	N-F-1CO	1	<1
35	N-F-2CO	1	3
36	N-F-3CO	1	<1
37	NEC-F-1	No Sample	na
38	NEC-F-2	No Sample	na
39	NEC-F-3	No Sample	na
40	E-F-1	1	<1
41	E-F-2	1	<1
42	E-F-3	1	<2
43	TS(10th)		21.43
44	TB(10th)		<1.51

Quality Control Samples (Spikes and Blanks)
Invalid Sample

Note: 1 Sample 19, SF-1, was diluted by a factor of 1.26 by the automated Wasson sampler. This resulted in a value of 12 µg/m^3. No other samples were diluted based on initial sample concentration being out of calibration range.

Table 7
Aeration Sampling
Period Results

Log Number	Sample ID	Sample Dilution	Phosphine concentration (ug/m^3)
45	SEC-A-1	1	5
46	SEC-A-2	1	<1
47	SEC-A-3	1	<1
48	S-A-1	1	<1
49	S-A-2	1	<1
50	S-A-3	1	<1
51	SWC-A-1	1	<1
52	SWC-A-2	1	<1
53	SWC-A-3	1	<1
54	W-A-1	1	<1
55	W-A-2	1	<1
56	W-A-3	1	<1
57	NWC-A-1	1	<2
58	NWC-A-2	1	<2
59	NWC-A-3	1	<2
60	N-A-1	1	<1
61	N-A-2	1	<1
62	N-A-3	1	<1
63	N-A-1CO	1	<1
64	N-A-2CO	1	<1
65	N-A-3CO	1	<1
66	NEC-A-1	1	6
67	NEC-A-2	1	<1
68	NEC-A-3	1	<1
69	E-A-1	1	6
70	E-A-2	1	<1
71	E-A-3	1	<1
72	TB-A		<1.43
73	TS-A		22.5
74	STAB-1		26.29
75	STAB-2		5.52

Quality Control Samples (Spikes and Blanks)

Note: Two stability spike samples (STAB 1 and STAB 2) were on site the entire time of the monitoring period.

5.0 Quality Control

Quality Control samples collected from the field consisted of:

6 total collocated samples (3 collocated pairs)
8 Spikes (4 Field Spikes, 4 Trip Spikes)
3 Trip Blanks
2 (stability) Spikes
These (stability) spikes were on site during the entire monitoring period and used to determine the amount of degradation of the spikes over the entire monitoring period. These stability spikes were requested by the laboratory.

The background period field spike recoveries (4 each) reported values from 33.08 µg/m^3 to 41.85 µg/m^3, resulting in 83.2% to 94.5% recoveries. The background period trip spike recoveries (2 each) reported values from 26.26 µg/m^3 to 28.28 µg/m^3, resulting in 84.6% to 91.3% recoveries. The background period collocated ambient samples were less than the method detection limit (MDL). The background period trip blank was less than the MDL.

The fumigation period collocated ambient samples reported values from less than the MDL to 3 µg/m^3. The fumigation period trip spike reported a value of 21.43 µg/m^3, resulting in 66.6% recovery. The fumigation period trip blank reported values less than the MDL.

The aeration period collocated ambient samples reported values from less than 1 to 6 µg/m^3. The aeration period trip spike reported a value of 22.5 µg/m^3, resulting in 72.1% recovery. The aeration period trip blank reported values than the MDL.

Two stability spike samples were on site the entire time of the monitoring period. Log number 74 reported a value of 26.29 µg/m^3, resulting in 81.9% recovery. Log number 75, reported a value of 5.52 µg/m^3, resulting in 17.2% recovery.

There is a noticeable difference in values reported on the two stability spike samples. The Phosphine Analytical Results for Application Air Monitoring dated October 2009 (Appendix C) states that: "*The two stability spike samples had very different recoveries. This variation may be due to the condition of the canister lining. Over the course of this study it was noted that some calibrations lasted longer than others. The only difference was the canister they were made up in. During the last 10 years these canisters have been used many times for a variety of analyte studies. During this time the state of the silco lining may have changed and possibly degraded to the point that a very reactive analyte like phosphine would react with the metal surface resulting in lower than expected values. This may be the case with the stability samples. Since the sample canisters were only used once each during this study, a specific canister trend could not be evaluated.".*

The analysis report (Appendix C) also states that "*Another factor that may have an effect on the phosphine results is the high level of water present in the samples. During the course of this study the relative humidity ranged from 60% to over 100%. The presence of high levels of water had an effect on the GC system's chromatography. The GC system's Nafion™*

dryer was not always able to remove all the water vapor present during sample concentration resulting in peak splitting and a retention time shift. But if the sample was diluted with nitrogen the phosphine peak shape and retention time returned to normal. Since most samples had no phosphine detected or were at a level far below the MDL, no samples were diluted with nitrogen to improve the peak chromatography.".

No other anomalous events occurred.

For additional information see **Table 6**: "Collocated Samples", **Table 7**: "Canister Field and Trip Spikes, Field and Trip Blanks", **Table 8**: "Duplicate Results "and The Phosphine Analytical Results for Application Air Monitoring dated October 2009 (Appendix C).

Table 8
Collocated Sampling Results

Log Number	Sample ID	Phosphine concentration (ug/m^3)
5	N-B	<1
6	N-B-CO	<1
31	N-F-1	<1
32	N-F-2	<1
33	N-F-3	<1
34	N-F-1CO	<1
35	N-F-2CO	3
36	N-F-3CO	<1
60	N-A-1	<1
61	N-A-2	<1
62	N-A-3	<1
63	N-A-1CO	<1
64	N-A-2CO	<1
65	N-A-3CO	<1

Table 9
Canister Spike and Blank Results

Quality Control Type	Log Number	Sample ID	Starting Phosphine Spike Concentration (µg/sample)	Ending Phosphine Spike Concentration (µg/sample)	Percent Recovery
Lab Spike	N/A	N/A	31.17	33.11	106.22%
	N/A	N/A	32.37	33.4	103.18%
	N/A	N/A	32.53	32.51	99.94%
	N/A	N/A	29	32.96	113.66%
	N/A	N/A	32.44	30.29	93.37%
Trip Spike	11	TS1	30.96	28.28	91.34%
	12	TS2	31.05	26.26	84.57%
	43	TS(10th)	32.18	21.43	66.59%
	43d	TS(10th)	32.49	22.09	67.99%
	73	TS-A	31.19	22.5	72.14%
	73d	TS-A	31.49	22.48	71.39%
Field Spike	2	S-B-FS	42.90	35.71	83.24%
	2d	S-B-FS	42.90	35.73	83.29%
	4	W-B-FS2	44.29	41.85	94.49%
	7	N-B-FS3	40.95	33.08	80.78%
	9	E-B-FS4	41.85	37.68	90.03%
Stability Spike	74	STAB-1	32.10	26.29	81.90%
	74d	STAB-1	31.78	27.78	87.41%
	75	STAB-2	32.14	5.52	17.17%
	75d	STAB-2	31.82	5.46	17.16%

Blanks	Log Number	Sample ID	Phosphine Concentration (µg/sample)
Trip Blank	10	TB	<1.47
	44	TB (10TH)	<1.51
	72	TB-A	<1.43

Notes:

Field Spike levels not background subtracted.

ID Identification
µg Micrograms
d Result is from duplicate analysis
na not applicable

Table 10
Duplicate Analysis Results

Log Number	Sample ID	Phosphine concentration (ug/m3)	Relative Percent Difference
2	S-B-FS	35.71	
2d	S-B-FS	35.73	-0.06
8	E-B	<1	
8d	E-B	<1	na
16	SEC-F-1	<2	
16d	SEC-F-1	<2	na
21	S-F-3	<2	
21d	S-F-3	<2	na
27	W-F-3	58.33	
27d	W-F-3	49.68	16.02
28	NWC-F-1	41.69	
28d	NWC-F-1	39.16	6.26
36	N-F-3CO	<1	
36d	N-F-3COd	<1	na
43	TS(10th)	21.43	
43d	TS(10th)	22.09	-3.03
56	W-A-3	<1	
56d	W-A-3	<1	na
57	NWC-A-1	<2	
57d	NWC-A-1	<2	na
64	N-A-2CO	<1	
64d	N-A-2CO	<1	na
65	N-A-3CO	<1	
65d	N-A-3CO	<1	na
73	TS-A	22.5	
73d	TS-A	22.48	0.09
74	STAB-1	26.29	
74d	STAB-1	27.78	-5.51
75	STAB-2	5.52	
75d	STAB-2	5.46	1.09

Notes:
ID Identification
µg Micrograms
d Result is from duplicate analysis
na not applicable

6.0 Discussion

Monitoring and Laboratory Division staff collected a total of 62 application samples plus 13 field quality control samples. These quality control samples consisted of four field spikes, three trip blanks, four trip spikes, and two stability spikes. Five (5) of the 62 canisters did not collect a sample due to equipment failure.

Results for phosphine ranged from less than the MDL to 700 mg/m^3 (44 samples were less than the MDL). The slight variation of the reported MDL was dependant on the laboratory's lowest calibration standard which ranged from 1 to 2 µg/m^3. Seven (7) samples were reported less than the EQL ranging from 3 µg/m^3 to 7 µg/m^3. Three (3) outdoor samples reported results above the EQL ranging from 12 µg/m^3 to 58 µg/m^3. As expected, the reported concentrations from the three (3) samples collected inside the fumigation chamber were significantly higher (510,000 µg/m^3 to 700,000 µg/m^3).

The percent recoveries of the two trip spikes (stability spikes) varied greatly. This variation may be due to the condition of the canister lining. Over the course of this study it was noted that some ending spike concentrations were higher than others. It is believed that the condition of each canister's interior lining may have impacted these results. Since the sample canisters were only used once each during this study, a specific canister trend could not be evaluated. We recommend a thorough canister reactivity evaluation be conducted prior to future use of these canisters.

The processing facility that performed the fumigation was very cooperative and their assistance is appreciated.