APPENDIX B

Sampling Protocol for Phosphine Application Monitoring

California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for Phosphine Application Monitoring

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Prepared by:

Staff
In the
Special Purpose Monitoring Section

Signatures:

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

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

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR), (January 4, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff will monitor one application site for phosphine. This application monitoring study will be performed prior to, during and after an application of phosphine. Phosphine application monitoring is 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. Monitoring is being conducted to coincide with the use of phosphine as a selective commodity fumigant.

The draft laboratory analysis method titled “Standard Operating Procedure Sampling and Analysis of Phosphine” dated November 2008, is included as Appendix A.

2.0 Project Goals and Objectives

The goal of this monitoring project is to collect and measure phosphine concentrations in ambient air prior to, during, and after an application. In addition, air from the chamber (prior to aeration) will also be collected and measured.

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

1. Identify a suitable monitoring site that satisfies DPR’s air monitoring recommendations for phosphine.

2. Appropriate application of sampling/monitoring equipment to determine ambient phosphine concentrations.

3. Application of relevant quality assurance/quality control practices to ensure the integrity of field samples.

4. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant information and data for this project.

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4.0 Study Location and Design

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 near Ballico, CA. Monitoring will occur December, the month with the highest potential phosphine use.

Application Monitoring

Phosphine is a colorless and odorless gas, and is applied to postharvest commodities either as a gas or a metallic phosphide compound. For this study, the phosphine application will utilize a metallic phosphide (aluminum phosphide). A measured quantity (mass) of aluminum phosphide pellets will be placed inside a large chamber, and the chamber sealed. Humidity from the air inside the chamber reacts with the aluminum phosphide pellets creating phosphine gas.

The sampling/analysis method developed by the ARB Northern Laboratory Branch Special Analysis Section utilizes Silco canisters (Appendix A). During this study, a new canister sampler will be used (Tisch TE-323), enabling field staff to program equipment for unattended start and stop activation. The sampler can accommodate up to three (3) canisters for unattended sequential sampling. Canisters can be filled up to one (1) atmosphere above ambient. The target final canister pressure will be 10 psig.

Samples will be collected by pressurizing ambient air into a Silco canister. Approximately 3 lpm of air is pulled through the Tisch TE-323 inlet. By adjusting a turn style valve, a regulated portion of the 3 lpm air flow is forced into the sample canister. Except for the chamber sampler, the inlet heights will be placed at approximately 1.5 meters above the ground. The chamber sampler inlet will be placed approximately 1.0 meter above the floor.

Ten (10) Tisch TE-323 samplers were purchased for this study to reduce field staff exposure to phosphine gas during the fumigation and aeration process. Because the Tisch sampler can only be configured to sample three (3) canisters with each setup, the study will be divided into three (3) sampling episodes: Background, Fumigation & Aeration.

Background sampling: Four (4) primary samples, two (2) collocated samples and four (4) field spike samples will be deployed prior to phosphine fumigation. The four (4) primary samplers will be placed approximately 10 – 20 feet away from each side of the building. One (1) field spike sampler will be placed in parallel with each primary sampler. The collocated samplers will be placed at opposite sides of the building, one (1) of which is located at the expected downwind location. Sampling will occur concurrently. Sample duration will be configured for approximately 24 hour period. One (1) trip spike and one (1) trip blank will accompany the background samples to the field and back to the Laboratory. Please refer to Figure 5 for outside background sampling diagram.

Fumigation sampling: The fumigation process lasts between 24 hours to six (6) days, dependent on the expected phosphine concentration and ambient temperature. The duration of the fumigation process will be known prior to the application. As mentioned in the background sampling section above, one (1) trip spike and 0ne (1) trip blank will accompany the samples to and from the field.

a) Inside chamber sample: A pre-programmed sampler will be placed inside the chamber and configured to automatically sample three (3) consecutive canisters. The sampler will be programmed so the last canister will complete sampling approximately one (1) hour before aeration begins. Due to the Tisch sampler design all three canisters must have the same flow set, and therefore the same sample duration. The inside chamber sample duration will be four (4) hours each.

b) Outside fumigation sampling: Outside the chamber, samplers will be placed 10 – 20 feet away from each of the four (4) building sides and 20 – 30 feet away from each of the four (4) building corners. A collocated sampler will be placed at the estimated downwind location. The samplers will be configured to fill each canister consecutively, with a sampling duration of four (4) hours each. Samplers will be programmed to complete sampling of the last canister sample approximately four (4) hours prior to the aeration process (allowing staff time to reconfigure). Please refer to Figure 5 for outside fumigation sampling diagram.

Aeration sampling: Pending local weather conditions, there are two (2) aeration monitoring scenarios. Similar to the background and fumigation sampling section above, one (1) trip spike and 0ne (1) trip blank will accompany the aeration samples to and from the field.

a) Less than 5 knot/hour wind conditions: If local hourly averaged wind speeds are expected to be primarily less than 5 knots, then all four (4) corner samplers will be moved further outward between 40 – 60 feet away from the building, and the four (4) side samplers will be moved outward between 20 - 30 feet away from the building. Please refer to Figure 5 for this sampling scenario.

b) Greater than 5 knot/hour wind conditions: If the local hourly averaged wind speeds are expected to be primarily greater than 5 knots, all nine (9) samplers will be relocated at the expected downwind side of the building. Three (3) samplers will be located 20 – 30 feet away from the downwind corners and side of the building. Three (3) samplers will be located 60 – 70 feet away from the downwind corners and side of the building. Two (2) samplers will be located approximately 100 feet away from each downwind building corner. One (1) collocated sampler will be located next to the closest and most predominately downwind sampler. The samplers will be programmed to collect four (4) hour samples for each canister. Please refer to Figure 6 for the greater than 5 knot/hour wind speed sampling scenario.

An additional field stability spike will travel to the field along with the background canisters and return to the Laboratory with the aeration samples.

Every attempt will be made to shield all sampled canisters from direct sunlight to help reduce sampled phosphine losses. When possible, sampled canisters will be removed from the samplers and stored in a cool shaded location until they can be

transported back to the Laboratory in Sacramento. Transportation of sampled canisters to Sacramento will occur as often as feasible during regular working hours.

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

TABLE 1: Guidelines For Application Sampling Schedule

Sample period begins:	Sample duration time
Background (pre-application)	10 canisters (total) – 24 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

Background air sampling will be completed approximately four (4) hours prior to the application. Fumigation sampling will be completed approximately four (4) hours prior to the aeration process. Aeration sampling will be completed after the third four (4) hour aeration sample has ended.

Eight samplers will be positioned around the application building perimeter. One sampler will be located at approximately the midpoint of each side of the building and one at each corner. A ninth sampler will be collocated at the expected downwind side or corner. Four (4) field spike samples will be collected during background sampling using the same ambient monitoring procedures (e.g., air flow rates, sample transportation and storage), and will be located in parallel to the ambient air samplers. Three (3) trip spikes, one (1) field stability spike and three (3) trip blanks will be included. (1 trip spike and 1 trip blank for the each sampling period, 1 stability spike spanning the entire project sampling period).

5.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will transport cleaned and evacuated canisters from MLD's laboratory in Sacramento, to and from the sampling location and then return the sampled canisters back to MLD's Sacramento laboratory. These samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

Prior to removing each sampled canister, the operator will assure that the canister valve is securely closed and the corresponding sample paperwork is complete. The collected canisters will be stored in a cool shaded location until they can be transported back the Laboratory. When received by the Laboratory, the canister samples will be analyzed as soon as possible.

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

The Northern Laboratory Branch (NLB) will supply SPM with cleaned and evacuated Silco canisters. NLB will perform analyses necessary to measure for phosphine concentrations in the sampled canisters and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of Phosphine) in Appendix A.

The following Silco canister validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time**: Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established hold time will be invalidated by the Laboratory.

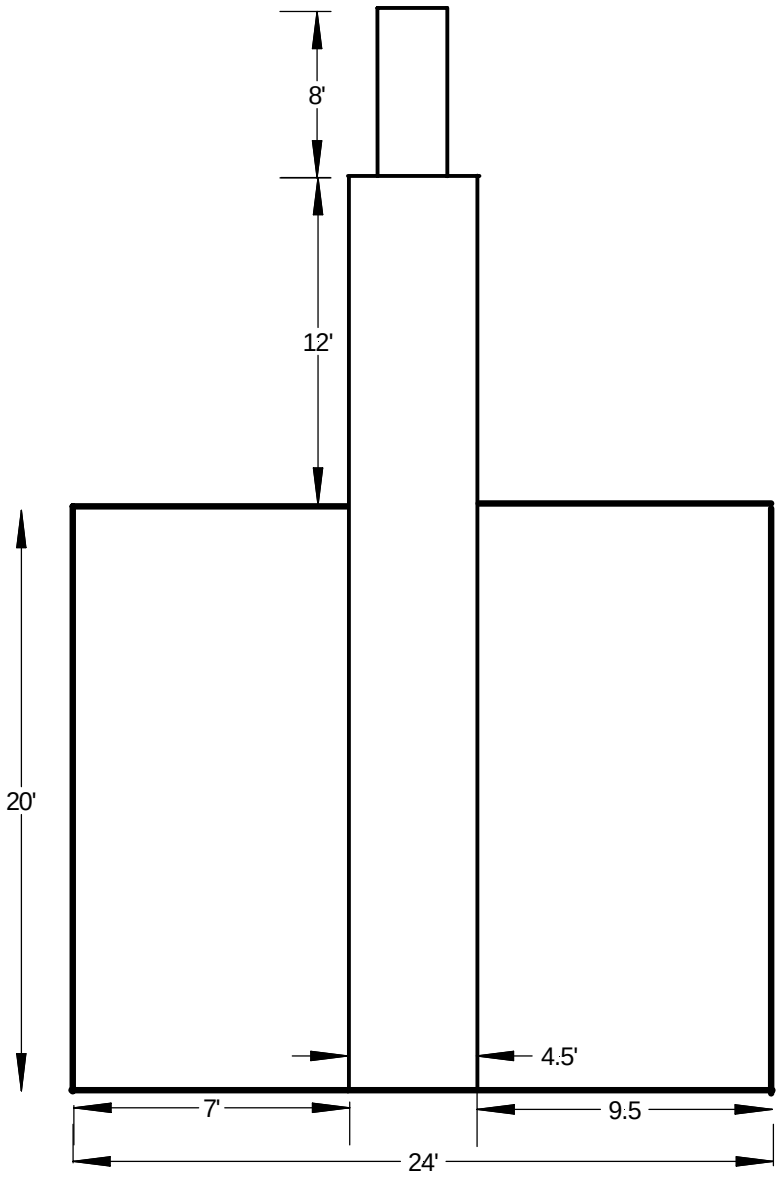
2. **Duplicate Analysis**: Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.

3. **Method Detection Limit (MDL)**: MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.

4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

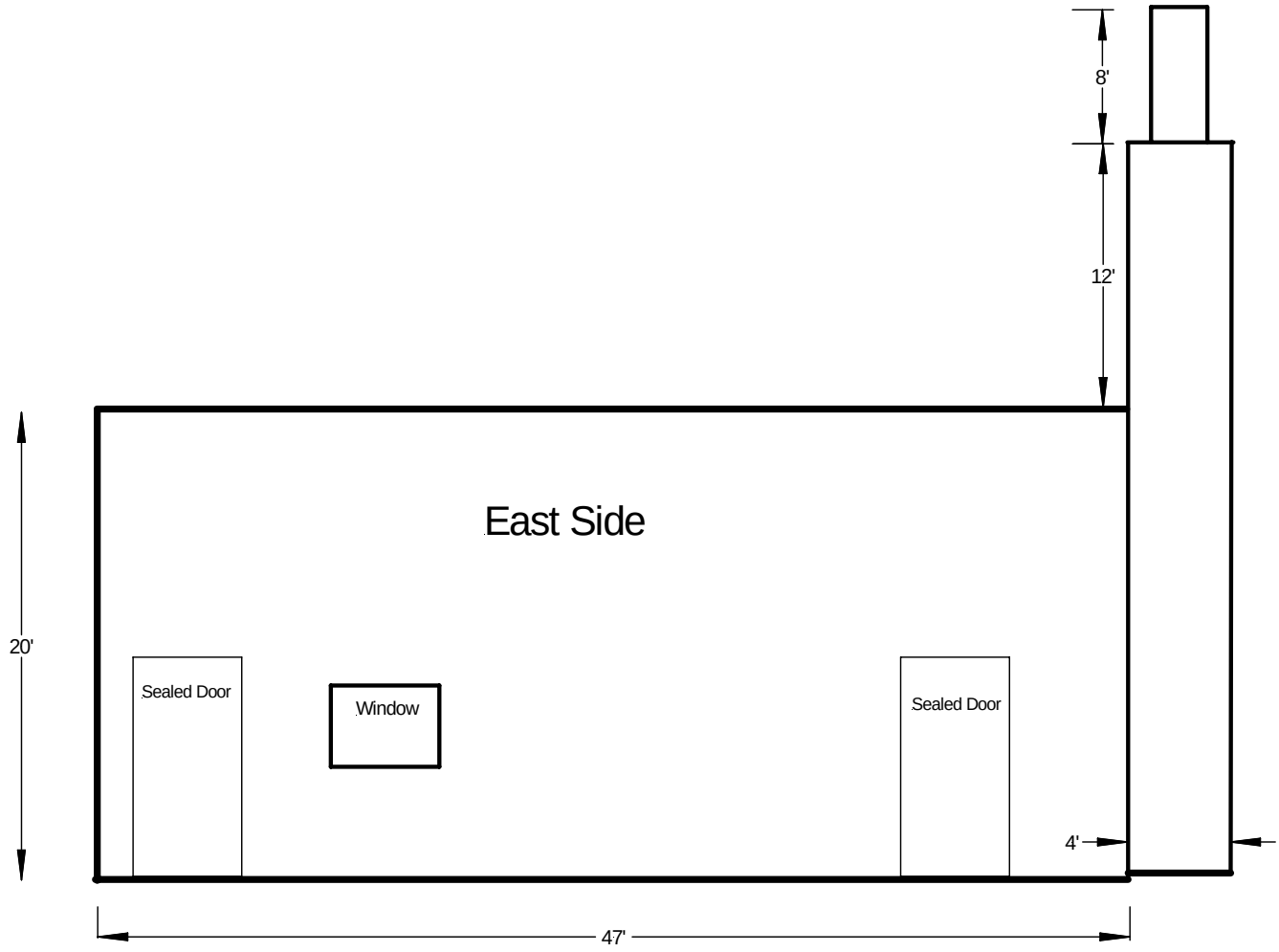
6.0 List of Field Equipment

Quantity	Item Description
(1)	Met-One Auto met portable meteorology system having calibrated sensors to measuring 1 minute averages for wind speed, direction, ambient temperature, and relative humidity w/built-in data logger.
(1)	Measuring Wheel.
(1)	A 200 ft measuring tape.
(1)	Tripod and compass.
(1)	Global Positioning System (GPS) with backup batteries and carrying case.
(1)	Digital Camera with backup batteries and carrying case.
(2)	Alborg mass flow meter 0-100 cc/min.
(10)	Tisch TE-323 canister samplers.
(79)	Silco canisters (10 background, 30 fumigation, 27 aeration, 3 field spikes, 1 stability spike, 3 trip spikes, 3 trip blanks and 2 spares).
(9)	Tripods.
(50)	Batteries.
(1)	Hard hat for each individual.
(1)	Box of laboratory quality gloves



REAR VIEW

Figure 1: Chamber/Building Rear View



EAST SIDE

Figure 2: East Side View of Building

Figure 3: Site Map

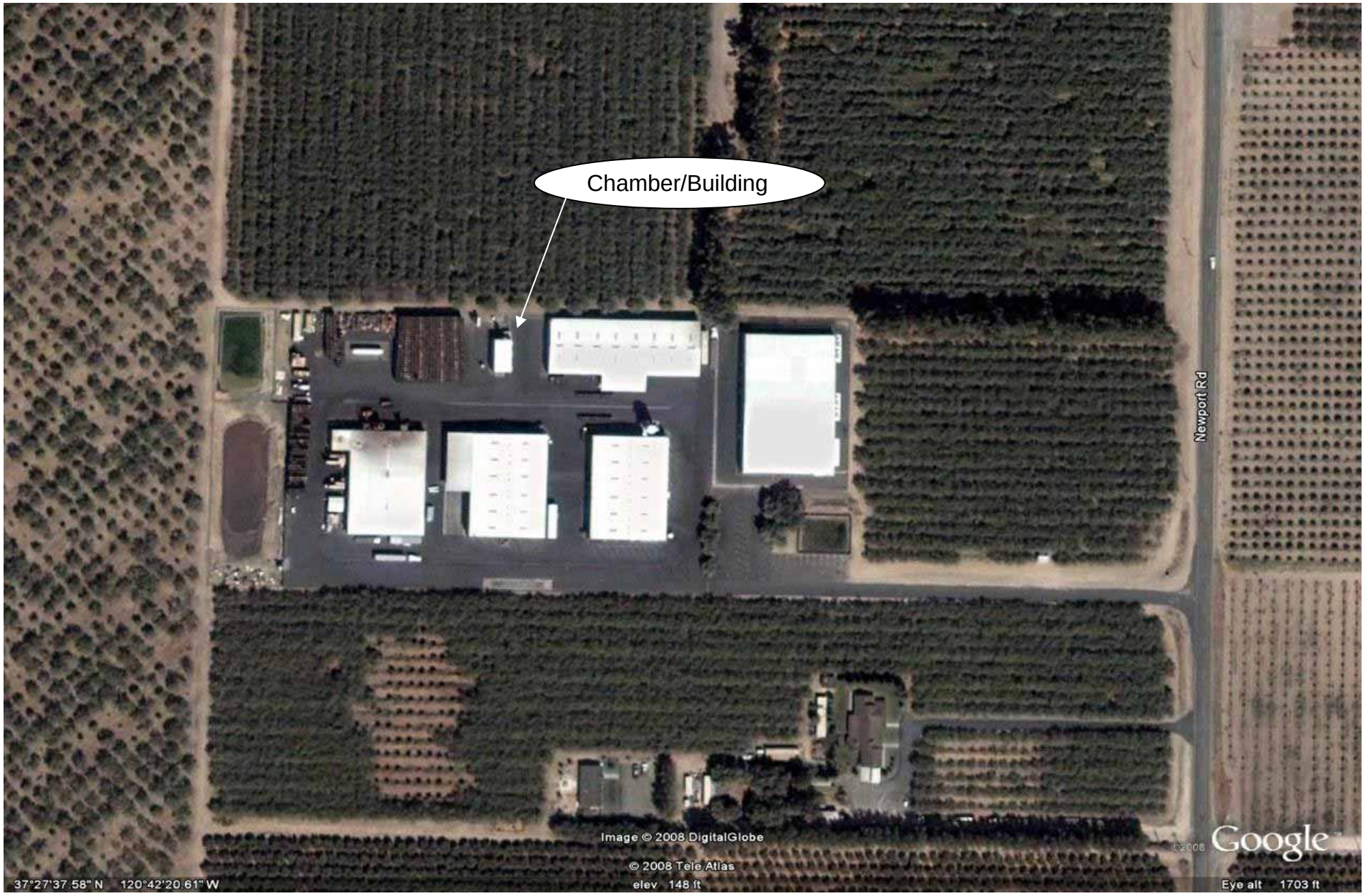


Figure 4: Site Map (zoom)

Figure 5: Sample Data Sheet

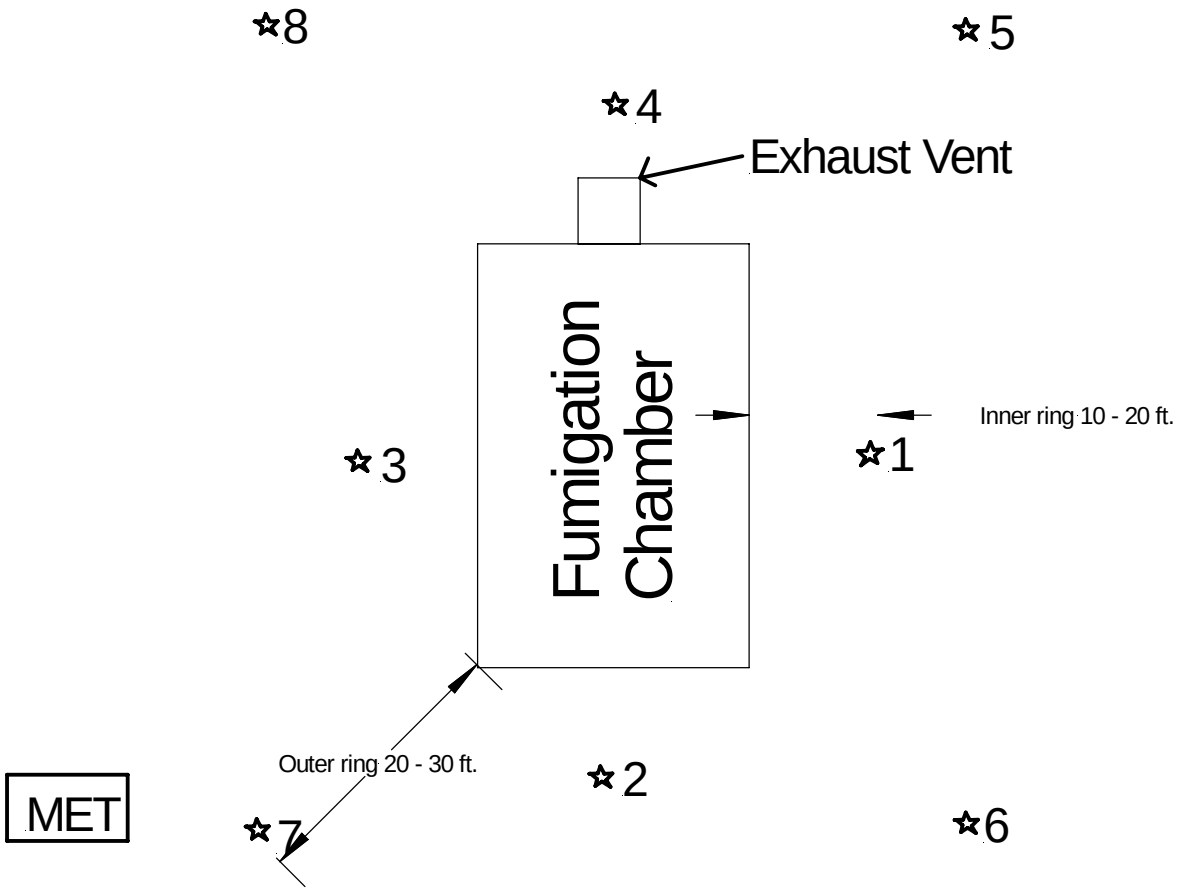


Figure 5: Fumigation Monitoring (2X distance for aeration monitoring if WS < 5 knots)

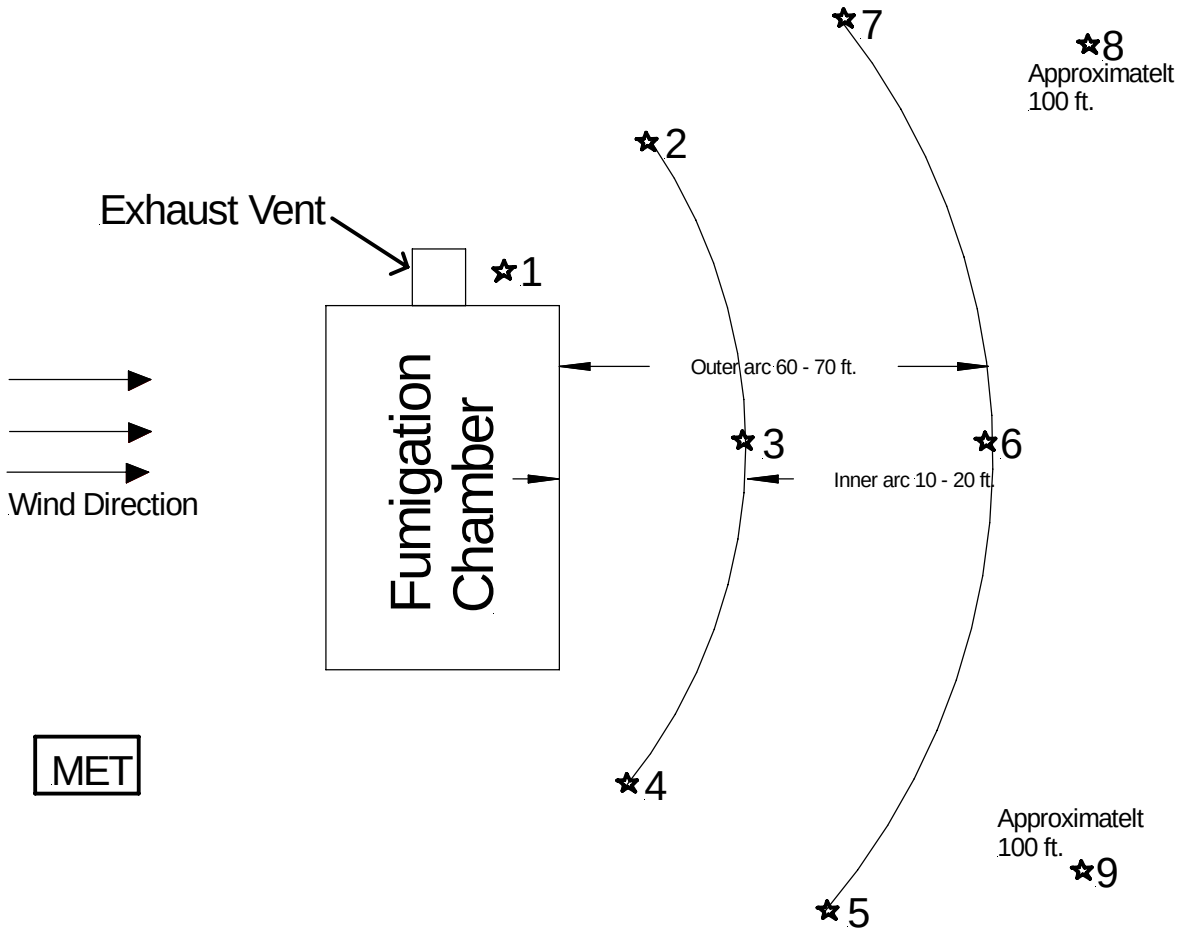


Figure 6: Aeration Monitoring (if wind speeds > 5 knots)

[Place data sheet inside plastic pouch]

CALIFORNIA AIR RESOURCES BOARD
SILCO Canister Pesticide Data/Sample Tracking Sheet

Pesticides
Tisch
Sampler

Project Name: _____

Site/Sample Name: _____

Lab I.D.: | Operator & Agency: _____

			CANISTER		LABORATORY	SAMPLER			
	Date	Time (PST)	Vacuum ("Hg)		Pressure or Vacuum	MFC Reading		Vacuum	
			LAB	FIELD					
Set-Up									
Start									
Stop					LAB**				

Type of Sample: [ ] Regular [ ] Collocated [ ] Spike [ ] Blank [ ] Other

Field Log Number: _____ Canister ID Number: _____ Sampler ID Number: _____

Observed Unusual Sampling Condition: [ ] Wind-Blown Sand/Dust [ ] Rain /Fog/Elevated Humidity [ ] Farming Nearby [ ] Construction Nearby [ ] Fire Nearby [ ] Other _____

[ ] INVALID SAMPLE INFORMATION

Reason for Sample Invalidation

[ ] Vacuum lower than 5 psig
[ ] Vacuum higher than 20 psig
[ ] Sampling period out of range (<___ or >___ hours)
[ ] Other reasons: _____
[ ] Sampling equipment inoperative

Field Comments: _____

Sample Tracking

Action	Transfer Method (Check one)		Name & Initials	Date/Time
	Carrier	Person		
Released by Lab				
Received by Field				
Released by Field				
Received by Lab				

===FOR LABORATORY USE ONLY====

Lab Comments: _____

** = Calibrated Guage Pressure or Vacuum

07/13/07

Figure 7: Sample Data Sheet

7.0 Quality Control

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

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

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

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

Field Spike (FS): A field spike will be prepared by the laboratory by injecting a known concentration of phosphine gas into a cleaned and evacuated Silco canister. The background field spikes (4 total) will be positioned in parallel with the primary background samples. The field spikes will be removed and handled identically to the other samples.

Field Stability Spike (SS): A field stability spike will be prepared by the laboratory by injecting a known concentration of phosphine gas into a cleaned and evacuated Silco canister. Similar to the Field Spike mentioned above, this spike will be created prior to background sampling and will remain in the field until it is brought in along with the last batch of samples. There will be only one (1) field stability spike during the monitoring portion of this study. The field stability spike will be removed and handled identically to the other samples.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a known concentration of phosphine gas into a cleaned and evacuated Silco canister at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler and not sampled.

Trip Blank (TB): A trip blank will be a cleaned and evacuated Silco canister transported to the field and returned to the Laboratory unopened.

Collocated (CO): A collocated (side-by-side) air sampler will operated exactly the same as the primary sampler and will be installed alongside the predominantly downwind sample site.

Site/Sample Identification

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

Site Naming Examples:

N-BK = Northside 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
BK= Background Sample
F = Fumigation
A = Aeration
FS = Field Spike
SS = Field Stability Spike
TS = Trip Spike
TB = Trip Blank
IN = Inside

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

8.0 Deliverables

8.1 Air Quality Surveillance Branch Deliverables

Within 90 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

1) Sampling Protocol.
2) Personnel Contact List.
3) Site Maps.
4) Site Photographs.
5) Site Descriptions and Measurements: Site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, and amount of aluminum phosphide used.
6) The distance and direction of the sampler to the building.
7) A map of the monitoring site locations.
8) Sample Summary Table.
9) Field Sample Log.
10) Laboratory Analysis Reports with calculations in electronic format.
11) Meteorological data and supporting documentation.
12) Transfer Standards' Certification Reports.
13) Disk containing 1-minute averaged Meteorological Data.
14) Disk containing electronic files of Report.

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

8.2 Northern Laboratory Branch (NLB) Deliverables

Within 90 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

1) Table(s) of sample results 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).

4) Table of collocated results.

5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.

6) Table of analytical results from all trip blanks.

7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.

8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.

9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

APPENDIX A:
Standard Operating Procedure and Analyses for Phosphine

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for phosphine collected by Silco canister method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of Phosphine. (See Appendix C of Report)

APPENDIX B:

USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT PHOSPHINE

http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/air_rpt_phosphine.pdf