Appendix A

Site Photographs

(North) East Side Sampler

Looking towards the West Sampler
All four samplers are included (ARB,DPR, and two for manufacturer).

Looking from plot towards the (North) East

Looking towards the South Sampler

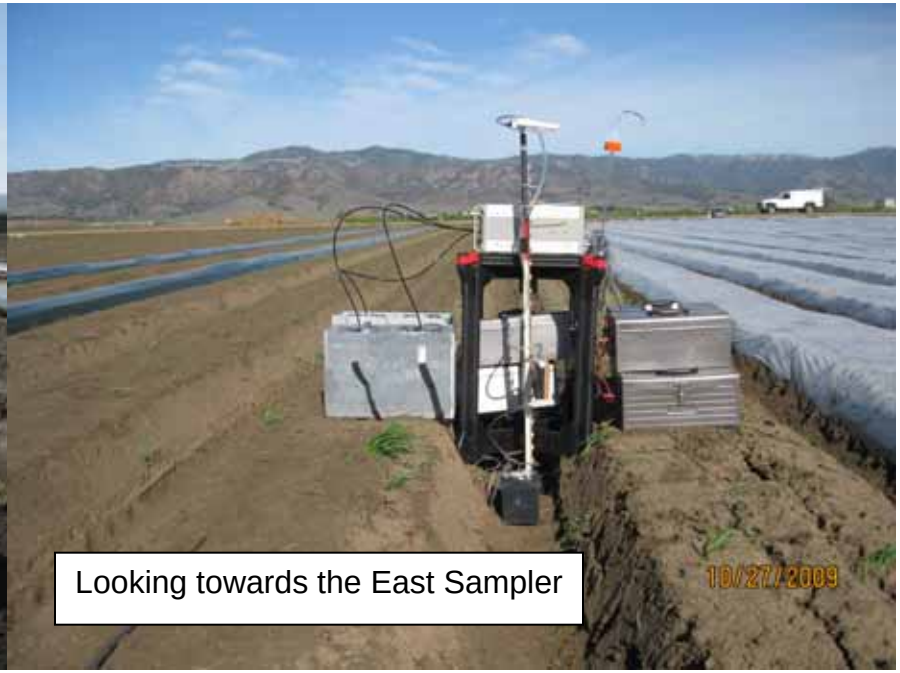
Looking towards the North Sampler

North (West) Side Sampler

Looking towards the South Sampler

Looking from plot towards the North (West)

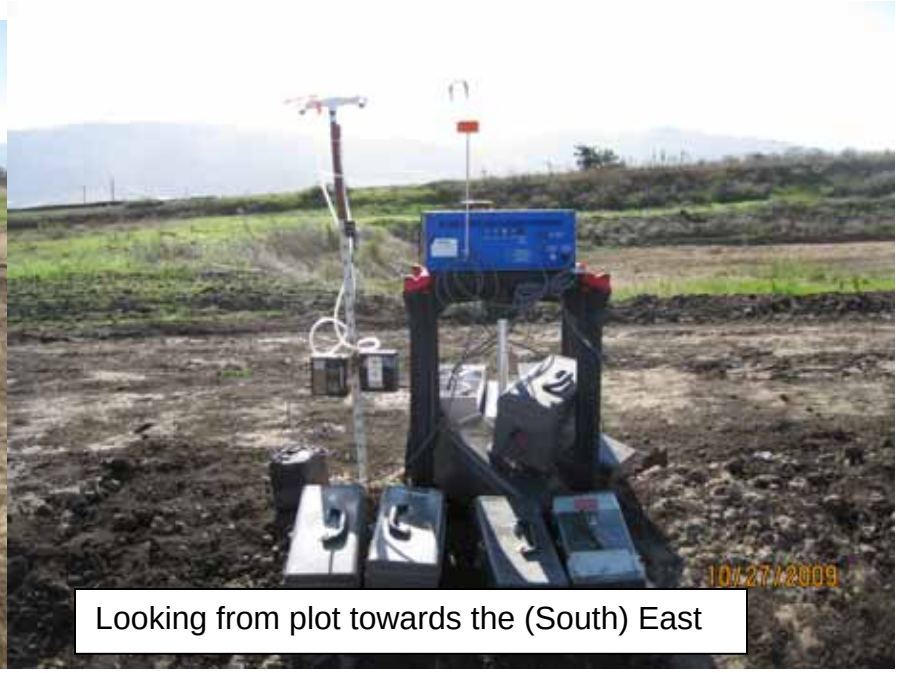
Looking towards the West Sampler



Looking towards the East Sampler

(South) West Side Sampler

Looking towards the South Sampler

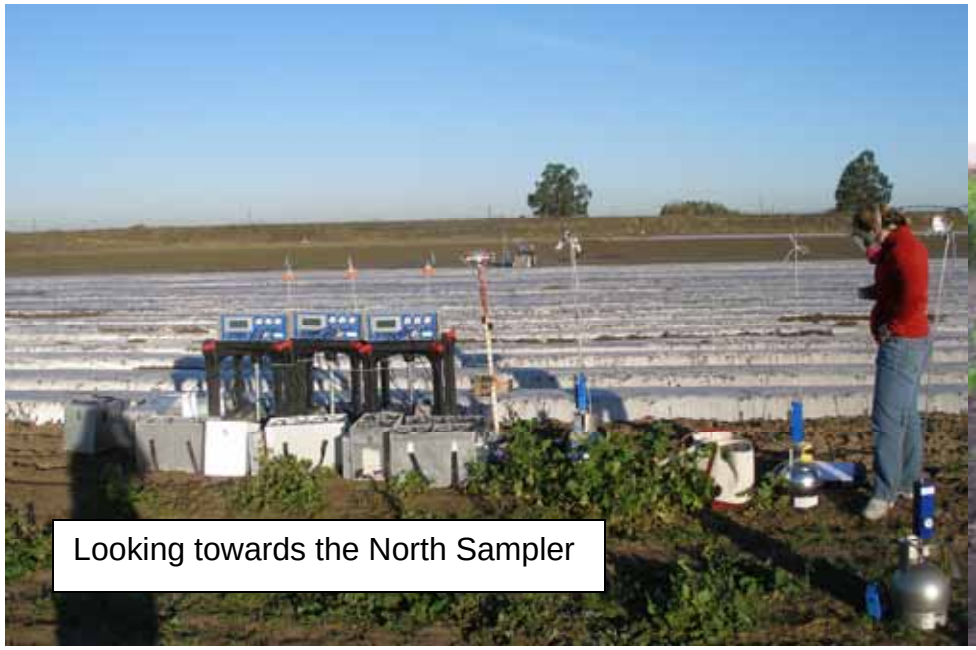


Looking from plot towards the (South) East

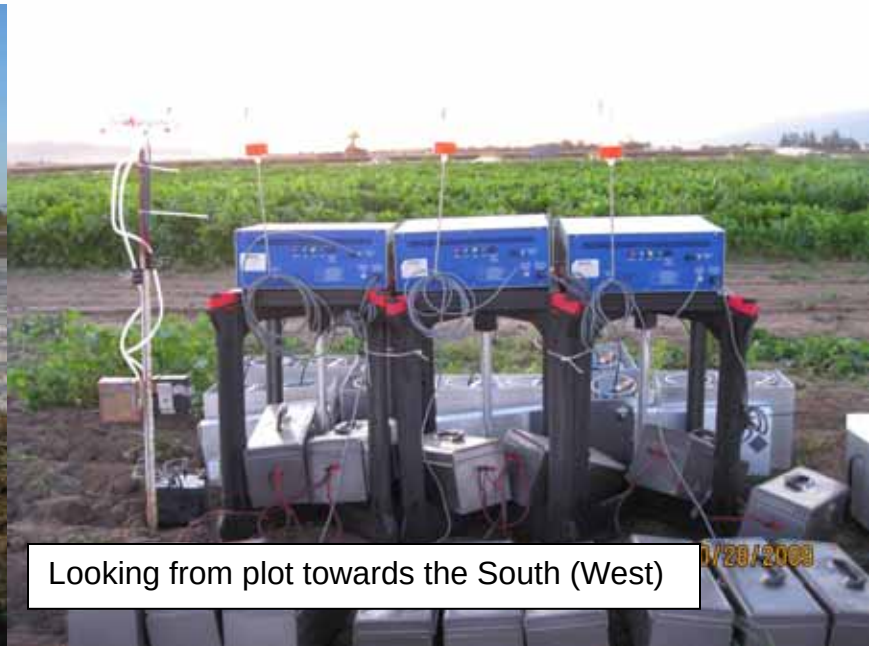
Looking towards the East Sampler

Looking towards the North Sampler

South (East) Side Sampler

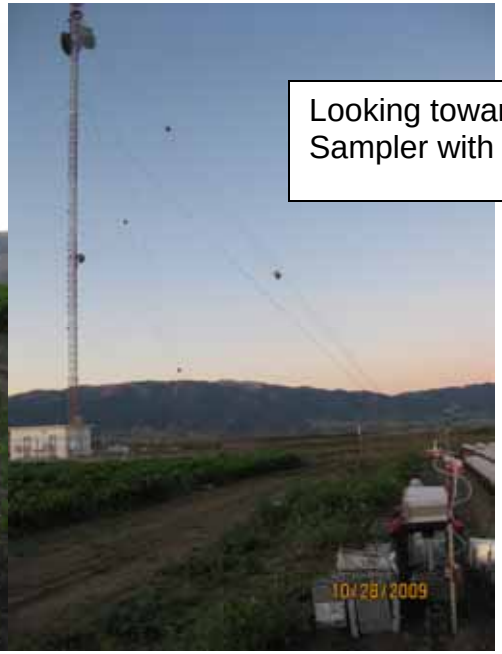


Looking towards the North Sampler



Looking from plot towards the South (West)

Looking towards the East Sampler



Looking towards the West Sampler with view of the tower.

Appendix B

Sampling Protocol for Methyl Iodide Application Monitoring

California Environmental Protection Agency

Air Resources Board

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for Methyl Iodide Application Monitoring

October 22, 2009

Prepared by:

Megan McKay
Special Purpose Monitoring Section

Signatures:

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.

Table of Contents

1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR), (December 15, 2008 Memorandum, Warmerdam to Goldstene) the Air Resources Board (ARB) staff will monitor one application site for methyl iodide (Iodomethane, CH_3I). This application monitoring study will be performed during an application of methyl iodide. Methyl iodide 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 methyl iodide as a selective commodity fumigant.

The laboratory analysis method titled “Standard Operating Procedure Sampling and Analysis of Methyl Iodide” dated September 2009, is included as Appendix A.

2.0 Project Goals and Objectives

The goal of this monitoring project is to collect and measure methyl iodide concentrations in ambient air during an application.

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

1. Appropriate application of sampling/monitoring equipment to determine ambient methyl iodide concentrations at a site located by DPR.

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

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

3.0 Contacts

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4.0 Study Location and Design

Methyl iodide is a pre-plant biocide used to control insects, plant parasitic nematodes, soil borne pathogens, and weed seeds. It is a fumigant pesticide, and is proposed to be used as a replacement for methyl bromide. DPR recently approved several field research studies of this pesticide although it has not been registered for use in California. In the event DPR registers methyl iodide, they expect use to be high, and might request further extensive monitoring.

Study Location

The field site for the application of methyl iodide was determined by DPR. The application field is located near 20594 Spence Rd, Corral de Tierra, CA 93908 (Figure 1). For this application, methyl iodide will be applied to a 450 x 95 ft plot. The method of application will be a drip application to tarped beds. The rate will be 200 lb/ac of Midas Gold-EC, which consists of approximately 63 lbs/ac of methyl iodide, plus 127 lbs of Chloropicrin and 10 lbs of emulsifier.

Study Design

DPR will document information pertinent to the fumigation of methyl iodide, including the location, size, and configuration of the site, as well as all other fumigations in use in the same area for the prior two weeks. DPR will document the application method, date, time, rate and total amount of methyl iodide used, and tarp model and manufacturer.

ARB and DPR will conduct the methyl iodide monitoring by two different methods: canisters and sorbent tubes, respectively. Samples will be collected at 4 points around the application area during 4 time periods (12 hrs for each sample), for a total of approximately 48 hours. DPR will compare the measured methyl iodide air concentrations using two methods and decide the efficient sampling method for methyl iodide monitoring.

Sampling Method

For each of sampling method, 4 samplers will be positioned around the application, one on each side or corner of the field. The samplers will be placed approx. 25 feet (or further, as required) from the edge of the application area. Samples will be collected during four 12 hour time periods, for a total of 16 samples (plus spikes, blanks, and collocated samples) for each method.

The sampling/analysis method developed by the ARB Northern Laboratory Branch Special Analysis Section utilizes Silco canisters (Appendix A). During this study, a 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, ±5 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. The inlet heights will be placed at approximately 1.5 meters above the ground.

Because the Tisch sampler can only be configured to sample three (3) canisters with each setup, the study will be divided into two (2) sampling episodes: Background & Fumigation.

Four samplers will be positioned around the application field. One sampler will be located at approximately the midpoint of each side, or at the corners, of the field. A fifth and sixth sampler will be collocated at the expected downwind side (or corner) for a field spike sample and a collocated sample. For each sampling period, one (1) trip spike and one (1) trip blank will be included.

DPR will set up a similar method using sorbent tubes, collocated with the above Tisch samplers.

Background sampling: Four (4) primary samplers, one (1) collocated sampler and one (1) field spike sampler will be deployed prior to methyl iodide fumigation. The four (4) primary samplers will be placed approximately 25 feet away from each side (or corner) of the field. One (1) field spike sampler and one (1) collocated sampler will be located at the expected downwind location. Sampling will occur concurrently. During the Background sampling, one field spike (5 $\mu g/m^3$ CH_3I, ±50%) will be utilized. Sample duration will be configured for a 12 hour period. One (1) trip spike and one (1) trip blank will accompany the background samples to the field and back to the Laboratory. Background air sampling will be completed approximately an hour (1) prior to the application.

Fumigation sampling: Four (4) primary samplers, one (1) collocated sampler and one (1) field spike sampler will be deployed during the methyl iodide fumigation. The four (4) primary samplers will be collocated to the DPR samplers. One (1) field spike and one (1) collocated sampler will be located at the expected downwind location. Sampling will occur concurrently. Sample duration will be configured for three 12-hour periods. One (1) trip spike and one (1) trip blank will accompany the fumigation samples to the field and back to the Laboratory.

The duration of the fumigation process lasts approximately an hour, up to four hours. The application will occur during the first 12 hours of the three fumigation sampling period. The fumigation sampling periods will have staggered start times to coordinate with DPRs sampling start times.

Every attempt will be made to shield all sampled canisters from direct sunlight to help reduce sampled methyl iodide 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.

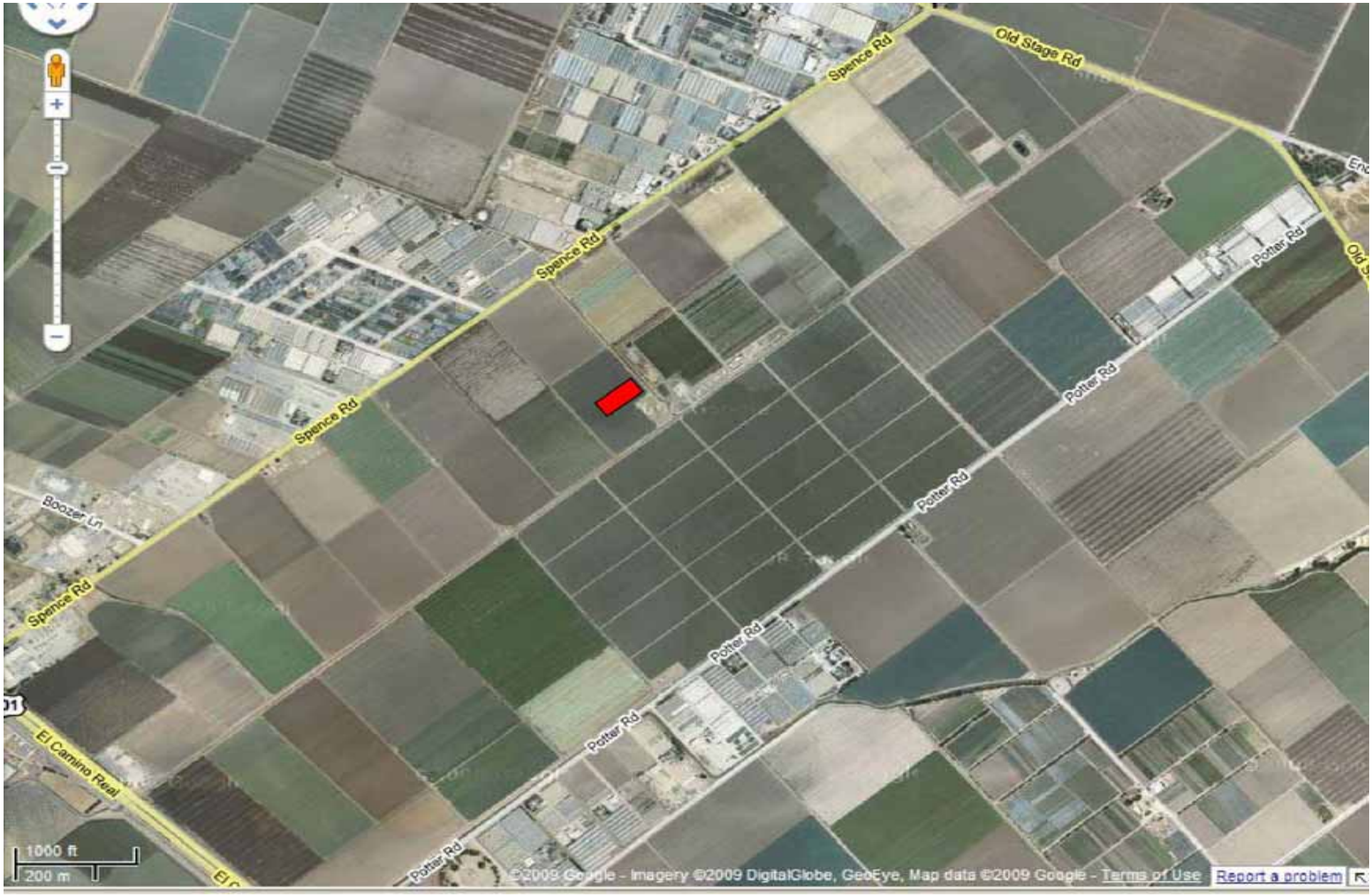

Figure 1: Location of the application field.

TABLE 1: Guidelines for Sampling Schedule

Sample period:	Sample duration time:
Background- ~6pm-6am	6 canisters (total) – 12 hours each
Trip	4 canisters (total) – 2 trip spikes, 2 trip blanks
Fumigation- ~8am-8pm (ending on the following day)	18 canisters (total) – 12 hours each

TABLE 2: Number of Canisters needed

Canister Type:	Total Number of Canisters needed:
Spikes (5 µg/m^3 CH_3I, ±50%)	**7 canisters** (total) – 4 sampled for 12 hours each, 2 trip spikes, 1 spare
Empty	**25 canisters** (total) – 20 sampled for 12 hours each, 2 trip blanks, 3 spare

Data Analysis

DPR will compare the methyl iodide concentrations by the two different methods to test if the two sampling methods can detect the chemical at the same concentration levels. If not, the regression between results of the two methods will be statistically analyzed. The correlation between two methods will also be estimated to demonstrate if they exhibit the same concentration trend along the sampling intervals.

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 the sampling location, and following sample collection, the canisters will be returned 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 provide SPM with cleaned and evacuated Silco canisters, in addition to preparing the necessary canisters spiked with methyl iodide. NLB will perform analyses necessary to measure for methyl iodide 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 Methyl Iodide) 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)	Measuring Wheel
(1)	200 ft measuring tape
(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
(7)	Tisch TE-323 canister samplers
(18)	Sampling inlets (from Tisch to canister)
(6)	DC power cables for Tisch
(6)	Inlet tubing with particulate filter
(6)	Spare particulate filters
(10)	Spare Swagelok/Parker connectors
(6)	Plastic sheeting to wrap analyzers
(32)	Silco canisters (See Table 2 – 25 clean, 7 spikes)
(32)	Sample sheets for each canister
(6)	Tables
(45)	Batteries (12 [2 each] for Background, 30 [5 each] for Fumigation, 3 spares)
(45)	Battery jumper cables
(2)	Hard hat for each individual
(1)	Box of laboratory quality gloves
(2)	Flashlights
(10)	Batteries for flashlights

[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 2: Sample Data Sheet

7.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. State of California, ARB certified transfer standards will be used to measure sample flow rates.

At the request of DPR, metrological sensors will not be utilized.

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 methyl iodide gas into a cleaned and evacuated Silco canister. The field spikes (4 total) will be positioned in parallel with the primary samples. The field spikes 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 methyl iodide 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 and unsampled.

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

Site/Sample Identification

The methyl iodide application sampling sites will be named accordingly for the fumigation as follows:

Site Naming Examples:

N-F-1 = North side fumigation Period 1

W-F-1-CO = collocated west side Period 1

S-F-3 = South side fumigation Period 3

Letter Abbreviations as follows

N = North Side
W = West Side
S = South Side
E = East Side
CO= Collocated
F = Fumigation
FS = Field Spike
TS = Trip Spike
TB = Trip Blank
BK= Background Sample

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 Photographs
4) Sample Summary Table
5) Field Sample Log
6) Laboratory Analysis Reports with calculations in electronic format
7) 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) 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.

APPENDIX A:
Standard Operating Procedure and Analyses for Methyl Iodide

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methyl iodide collected by Silco canister method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of Methyl Iodide.

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure
Sampling and Analysis of Methyl Iodide

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

September 2009

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This method is for the sampling and analysis of methyl iodide in air samples using a six-liter Silco™ canister for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry using an automated cryogenic sampler.

2. SUMMARY OF METHOD

Air samples are collected in evacuated six-liter Silco™ canisters. The samples are collected automatically using a Tisch Environmental automatic sample collection system. Final pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. The estimated quantitation level (EQL) for this method is approximately 0.1 parts per billion (ppb).

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler 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. A system 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 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10^{o} C, initial time 1 minute, to 80^{o} C @ 10^{o} C/min, to 200^{o} C @ 25^{o} C/min, hold 1 minute, to 240 ^{o} C @ 50^{o} C/min, hold 2 minutes.
  - Inlet temperature 150^{o} C; split ratio 44.1:1.

- Agilent 5973 mass selective detector (MSD):
  - Acquisition Mode: SIM
  - Tune File: PFTBA Autotune
  - Ions Monitored: 141,142,144,145
  - Quant Ion: 142
  - Internal Standard Ion: 145
  - Solvent Delay: 3.00 min.

- Wasson ECE cryogenic concentrator with Naffion dryer:
  - Cryo Temp #1 at -170°C
  - Cryo Temp #2 at -150°C

- Sample Oven at 200°C
- Transfer Line Temperature at 150°C
- Mass Flow at 35 ml/min
- Line Purge Time 30 seconds

B. Auxiliary Apparatus

Restek six-liter Silco™ canisters with Silco™ valves

C. Reagents

Calibration Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX47999.

Internal Standard: Methyl Iodide-d3 gas at 500 ppb Matheson Tri-Gas cylinder no. SX46440.

Lab Control Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX48752.

D. Gases

Helium, grade 5 or better
Liquid Nitrogen at 22 pounds per square inch (psi)
Nitrogen, grade 5
Compressed air, ultra zero

5. SAMPLE COLLECTION

A. Samples are collected in evacuated six-liter Silco™ canisters using a Tisch Environmental automated sampler set to deliver ambient air over a fixed amount of time.
B. The canisters will be filled so the ending pressure will be above ambient in the range of 5 to 10 psig (psi gauge).

6. ANALYSIS OF SAMPLES

A. Connect each canister to a port on the Wasson ECE cryogenic sample concentrator using a short length of polypropylene tubing. Reserve ports one and two for the blank and calibration standard.
B. For this method the standard volume will be 400 milliliters.
C. Perform an initial calibration curve using the following volumes of known concentrations of methyl iodide: 50, 75, 100, 200, 300, 400 milliliters. At least five (5) points must be analyzed to establish a calibration curve.
D. Prepare a sample sequence for the GC. The sequence should include a system blank and a continuing calibration verification standard (CCV) for every ten (10) samples analyzed. A lab control standard (LCS) should be run prior to field samples to verify that QC criteria have been met.
E. To minimize excessive carry over of contaminants from one analysis to the next, a system blank should be run 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 system blank analysis.

F. Review and edit the quantitation reports as needed.
G. Samples with concentration greater than the upper point of the calibration curve must be run at a smaller volume. Every attempt should be made to have the results fall within the upper half of the calibration curve. If running a volume of 50 ml results in a value greater than the upper calibration point, then the sample will need to be diluted with compressed nitrogen. Either add nitrogen to the original canister being sure to record the beginning and ending pressures, or transfer a known amount of sample from the original canister into a clean fully evacuated canister. Pressurize with nitrogen again recording the final pressure.
H. The final results will be adjusted by an appropriate dilution factor and reported in ppb.
I. The atmospheric concentration is calculated as follows:

$$\text{Sample Conc. (ppb)} = \frac{\text{Sample Vol. (ml)}}{400\ \text{ml}} \times \text{Instrument Result (ppb)} \times \text{Dilution Factor}$$

7. QUALITY ASSURANCE

A. A system blank must be analyzed with each batch of samples. The system blank is a 400 ml sample from a canister pressurized with grade 5 nitrogen. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, after the calibration curve or CCV, and after every tenth sample in the analytical batch.
B. Continuing calibration verification will be run at the beginning of the analytical batch, every tenth sample and at the end of the sample batch to verify system linearity. The calibration verification values must be within 25% of the actual value. Calibration of the entire system occurs if the CCV is outside the acceptable limits.
C. A LCS will be run with every sample batch. The LCS analyte concentration should fall within the lower half of the calibration curve. The LCS stock standard should come from a different source or lot than the daily calibration 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.
D. Run specific quality control samples, such as field spikes, trip spikes, and laboratory spikes prior to the field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over.

8. SAFETY

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 material safety data sheets (MSDS) of any chemicals used in this procedure. Methyl iodide gas is noted as a carcinogen and toxic at levels greater than 1300 mg/kg of body weight. All prep of standards and expected high samples should be performed in a shielded fume hood.

APPENDIX B:
Method Development for the Air Sampling and Analysis of Methyl Iodide

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for methyl iodide collected by Silco canister method.

California Environmental Protection Agency

Air Resources Board

Method Development for the Air Sampling and Analysis of Methyl Iodide

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

September 2009

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

A method was developed for the air sampling and analysis of methyl iodide using a gas chromatograph/mass selective detector (GC/MSD). The 2009 requested estimated quantitation level (EQL) was 0.1 parts per billion (ppb).

2. SUMMARY OF METHOD

Application air samples are collected in evacuated six-liter Silco™ stainless steel canisters. The samples are collected using a Tisch Environmental automatic sample collection system. Final canister pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses external standard method for instrument calibration. The estimated quantitation level for this method is 0.13 ppb.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler 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. A system blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

Instrumentation

- Agilent Technologies 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10^{o} C, initial time 1 minute, to 80^{o} C @ 10^{o} C/min, to 200^{o} C @ 25^{o} C/min, hold 1 minute, to 240 ^{o} C @ 50^{o} C/min, hold 2 minutes.
  - Inlet temperature 150^{o} C; split ratio 44.1:1.

- Agilent 5973 mass selective detector (MSD):
  - Acquisition Mode: SIM
  - Tune File: PFTBA Autotune
  - Ions Monitored: 141,142,144,145
  - Quant Ion: 142
  - Internal Standard Ion: 145
  - Solvent Delay: 3.00 min.

- Wasson ECE cryogenic concentrator with Naffion dryer:
    - Cryo Temp #1 at -170°C
    - Cryo Temp #2 at -150°C
    - Sample Oven at 200°C
    - Transfer Line Temperature at 150°C
    - Mass Flow at 35 ml/min
    - Line Purge Time 30 seconds

5. METHOD DEVELOPMENT

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the methyl iodide instrument reproducibility.

Table 1: Instrument Reproducibility
Methyl Iodide

Concentration	Low	Medium	High
Amount (ppb)	0.0794	0.3666	0.7609
	0.0814	0.3669	0.7766
	0.0803	0.3753	0.7815
	0.0742	0.3700	0.7755
	0.0743	0.3669	0.7826
Average	0.0779	0.3691	0.7754
Standard Deviation	0.0034	0.0037	0.0087
Relative Standard Deviation	4.3949	1.0061	1.1182

B. Linearity

A six-point external calibration is performed. Calibration standards ranging from at or near the EQL to approximately eight times higher are used. A linear regression with an r^2 of 0.995 or higher is required for a calibration to be acceptable. Continuing calibration verifications (CCV) will be run at the start of each analytical batch and after every tenth sample to verify system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicate spikes of a low-level standard, the MDL and EQL for methyl iodide is calculated as follows:

Table 2: MDL and EQL Determination

Amount (ppb)	0.096, 0.091, 0.092, 0.094, 0.095, 0.082, 0.094
Average	0.092
Standard Deviation	0.005
MDL = 3.143*STD EQL= 5*MDL	0.015 0.134

The calculated MDL for methyl iodide is 0.015 ppb. The EQL for methyl iodide assuming a 1:1.79 dilution of the sample is 0.13 ppb.

D. Storage Stability

Storage stability will be performed in triplicate using evacuated canisters spiked with methyl iodide and pressurized to approximately 7 psi. The project will be run for 28 days during September 2009 with canisters analyzed at 0, 1, 7, 14, 21 and 28 days.

Appendix C

Methyl Iodide Analytical Results for Application Air Monitoring Samples

California Environmental Protection Agency

Air Resources Board

Methyl Iodide Analytical Results for Application Air Monitoring Samples

November 2010

Prepared by
Karen Fletcher
Air Pollution Specialist

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Reviewed and Approved by

Russell Grace, Manager
Special Analysis Section

Table of Contents

1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) conduct application air monitoring for methyl iodide. This report covers the analytical and quality assurance results for methyl iodide during an application study in Monterey County in 2009. DPR requested a method estimated quantitation limit (EQL) of 0.1 parts per billion (ppb). The EQL achieved during this project was approximately 0.13 ppb.

2.0 METHOD DEVELOPMENT

2.1 Overview

Silco™ canisters are used to collect the air samples. Samples are analyzed using a cryogenic sample concentrator and gas chromatograph/mass selective detector operated in the single ion monitoring mode. Sample quantitation uses external standard method for instrument calibration. Appendix A contains the standard operating procedure (SOP) and the method development results for methyl iodide.

2.2 Calibration Curve

Standard volumes of approximately 50, 75, 100, 200, 300, and 400 ml are used to produce a six-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 external standard, and whenever the continuing calibration verification standard (CCV) does not fall within $\pm$ 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 MDL's. Using the analysis of seven low-level matrix analyses (50 ml), the MDL and EQL are calculated as follows:

s = the standard deviation of the concentration calculated for the seven replicate spikes.
For methyl iodide: s = 0.005
MDL = (3.14) x (s) = (3.14) x (0.005) = 0.015 ppb
EQL = (5) x (MDL) = (5) x (0.015) = 0.134 ppb

Results at or above the EQL will be reported to two significant figures. Results below the EQL but greater than or equal to the MDL are reported to one (1) significant figure. Results less than MDL are reported as less than the calculated MDL to one (1) significant figure.

3.0 METHYL IODIDE APPLICATION AIR MONITORING SAMPLE RESULTS

The laboratory received a total of 20 application samples plus four field spikes, one trip blank, one field blank, and two trip spikes on October 30, 2009. In addition, one laboratory spike was prepared and analyzed with the field samples. Table 1 presents the results of the analysis of the methyl iodide application air samples by site.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch, after each CCV, after every tenth sample, and after samples containing high levels of methyl iodide or co-extracted contaminants. Staff defines the analytical batch as all the samples analyzed together, but not to exceed 20 samples. The system blank is run 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.

4.2 Laboratory Control Samples (LCS)

Laboratory staff analyzed a LCS with each analytical batch. The stock standard used to prepare the LCS was from a different lot number than the stock standard used for method calibration. The LCS was prepared at 0.42 ppb, approximately 50% of the calibration standard concentration. The LCS recoveries averaged 91.8% with a standard deviation of 7.5%. The acceptable LCS range was 69.2% to 114.5%. All LCS results were within this range.

4.3 Continuing Calibration Verification Standards (CCV)

Following standard lab 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 $\pm$ 25% of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV standard volume is 400 ml. The CCV recoveries averaged 96.6% with a standard deviation of 8.6%. All the CCV's were within the 25% acceptance range.

4.4 Laboratory Duplicates

Three pairs of laboratory duplicates were run with this project. The duplicate pairs are made up of two samples run from the same canister in succession. The relative percent difference for each pair is reported in Table 2.

4.5 Collocated Field Samples

Three pairs of collocated samples were analyzed during this study. All of the collocated samples had values above the requested EQL. The collocated samples from the application sampling period were reanalyzed to confirm the results. The relative percent difference for each pair is reported in Table 3.

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

During the Monterey County 2009 project, four field and two trip spikes along with one laboratory spike, one trip and one field blank were analyzed. Laboratory staff prepared the spikes with a target of 0.44 ppb of methyl iodide assuming the canister was pressurized to approximately 5 psi after sampling.

5.1 Laboratory Spike

Table 4 presents the results of the laboratory spike. The methyl iodide recovery was 88.9%.

5.2 Trip Spikes

Table 4 presents the results of the trip spikes. The average methyl iodide recovery was 97.0% with a standard deviation of 1.6%.

5.3 Field Spikes

Table 4 presents the results of the field spikes. Four field spikes were analyzed during this study, one during each sampling period. The spike collected during the field background sampling period had a recovery of 102.3%. The result of the unspiked collocated background sample was less than the MDL. The recovery of the field spikes collected during and following the application could not be determined due to the extremely high methyl iodide recovery. The results of the collocated application samples ranged from 28.2 to 256.7 times the spike concentration.

5.4 Trip and Field Blanks

Table 4 presents the results of the trip and filed blanks. One trip and one field blank were received during this project and both results were less than the MDL.

6.0 DISCUSSION

The Laboratory received 20 field samples and 8 field quality control samples on October 30, 2009. Four field spikes and two trip spikes along with one field and one trip blank were received. One additional spike was prepared in the laboratory. Results for the spikes ranged from less than the MDL to 82.2 ppb methyl iodide. The five background field sample results and one fumigation sample result were less than the MDL. The

fumigation sample with the result less than the MDL was reanalyzed to confirm the result. All of the other field samples were above the 0.10 ppb EQL requested by DPR. The values ranged from 1.6 to 80.7 ppb. The highest results came from the samples taken during the first fumigation period on the south side of the field.

Due to the EQL requested by DPR and subsequent calibration range, the fourteen field samples with results above the EQL required dilution. Five samples were analyzed at a lower volume to obtain values within the calibration range. Nine samples were pressurized to approximately 29.5 psi and no more than 500 mls were injected into evacuated canisters. The canisters were then pressurized between 5 and 10 psi. Samples ranging from 200 and 400 mls were analyzed.

No other anomalous events occurred.

Table 1: Application Air Monitoring Results
Monterey County 2009

Site	Log Number	Sample Identification	Date Received	Date Analyzed	Methyl Iodide (ppb)	Total Dilution Factor	Methyl Iodide MDL (ppb)
East	1	E-BK	10/30/2009	11/9/2009	<0.02	1.00	0.02
	2	E-F-1	10/30/2009	11/23/2009	13	31.88	0.48
	3	E-F-2	10/30/2009	11/10/2009	6.2	8.00	0.12
	4	E-F-3	10/30/2009	11/10/2009	4.1	8.00	0.12
North	5	N-BK	10/30/2009	11/9/2009	<0.02	1.00	0.02
	6	N-F-1	10/30/2009	11/24/2009	<0.02	1.00	0.02
	7	N-F-2	10/30/2009	11/23/2009	27	72.82	1.10
	8	N-F-3	10/30/2009	11/17/2009	3.7	8.00	0.12
	8d	N-F-3d	10/30/2009	11/17/2009	3.8	8.00	0.12
West	9	W-BK	10/30/2009	11/9/2009	<0.02	1.00	0.02
	10	W-F-1	10/30/2009	11/23/2009	21	38.37	0.58
	11	W-F-2	10/30/2009	11/10/2009	1.6	8.00	0.12
	12	W-F-3	10/30/2009	11/10/2009	2.0	4.00	0.06
South	13	S-BK	10/30/2009	11/16/2009	<0.02	1.00	0.02
	14	S-F-1	10/30/2009	11/25/2009	64	104.36	1.57
	15	S-F-2	10/30/2009	11/25/2009	13	45.98	0.69
	16	S-F-3	10/30/2009	11/24/2009	7.5	34.13	0.51
	16d	S-F-3d	10/30/2009	11/24/2009	7.8	34.13	0.51
	17	S-CO-BK	10/30/2009	11/16/2009	<0.02	1.00	0.02
	18	S-CO-F-1	10/30/2009	11/24/2009	81	118.23	1.78
	19	S-CO-F-2	10/30/2009	11/24/2009	15	26.17	0.39
	20	S-CO-F-3	10/30/2009	11/25/2009	7.2	30.60	0.46

Table 1 Notes: Application Monitoring Results, Monterey County 2009

If the analytical result is <MDL it is reported as less than the established method detection limit multiplied by the dilution factor. Results are reported to one significant figure. If the analytical result is ≥ MDL and < EQL it is reported in the table as the measured value to one significant figure. Levels at or above the EQL are reported as the actual measured value and are reported to two significant figures.

ppb = parts per billion

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

Sample ID numbers followed by the letter d are duplicate samples for the samples with the corresponding number.

Site location identification:

E: East Side
N: North Side
W: West Side
S: South Side

Table 2: Duplicate Results
Monterey County 2009

Log Number	Sample ID	Date Analyzed	Methyl iodide concentration (ppb)	Relative Percent Difference
8	N-F-3	11/17/09	3.66	
8d	N-F-3d	11/17/09	3.76	-2.48
16	S-F-3	11/24/09	7.51	
16d	S-F-3d	11/24/09	7.83	-4.23
24	S-FS-F-3	11/24/09	8.45	
24d	S-FS-F-3d	11/24/09	8.32	1.60

Notes:

d designates the duplicate analysis
ppb parts per billion

Relative %Difference: Result A-Result B / (Average of Result A and B)* 100
Due to rounding of results, calculated values may not match values presented in table.

Table 3: Field Collocated Sample Results
Monterey County 2009

Log Number	Sample Identification	Date Analyzed	Results (ppb)	Relative %Difference
13	S-BK	11/16/2009	<0.02	N/A
17	S-CO-BK	11/16/2009	<0.02	
14	S-F-1	11/25/2009	63.85	-23.29
18	S-CO-F-1	11/24/2009	80.68	
15	S-F-2	11/25/2009	13.17	-9.89
19	S-CO-F-2	11/24/2009	14.54	
16	S-F-3	11/24/2009	7.51	3.94
20	S-CO-F-3	11/25/2009	7.22	

Notes:

CO designates the collocated sample
ppb parts per billion

Relative %Difference: Result A-Result B / (Average of Result A and B)* 100
Due to rounding of results, calculated values may not match values presented in table.

Table 4: Field and Laboratory Quality Control Sample Results Monterey County 2009

Quality Control Type	Log Number	Sample Identification	Date Received	Date Analyzed	Methyl Iodide (ppb)	Spiked Concentration (ppb)	Percent Recovery
Field Spike	21	S-FS-BK	10/30/2009	11/17/2009	0.28	0.27	102.26
	22	S-FS-F-1	10/30/2009	11/24/2009	82.15	0.32	N/A
	23	S-FS-F-2	10/30/2009	11/24/2009	14.37	0.30	N/A
	24	S-FS-F-3	10/30/2009	11/24/2009	8.45	0.30	N/A
	24d	S-FS-F-3d	10/30/2009	11/24/2009	8.32	0.30	N/A
Trip Spike	25	TS-BK	10/30/2009	11/17/2009	0.39	0.40	95.93
	27	TS-F	10/30/2009	11/17/2009	0.40	0.41	98.17
Lab Spike	NA	NA	10/30/2009	11/3/2009	0.37	0.42	88.93
Trip Blank	26	TB	10/30/2009	11/3/2009	<0.02	--	--
Field Blank	28	FB	10/30/2009	11/3/2009	<0.02	--	--

Notes:

ppb parts per billion
d designates the duplicate analysis
N/A not applicable, background field levels too high to determine recovery

Percent Recovery: (Actual Recovery/Spiked Concentration)*100
Due to rounding of results, calculated values may not match values presented in table.

Appendix A:

Standard Operating Procedure and Method Development for Methyl Iodide

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure
Sampling and Analysis of Methyl Iodide

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

September 2009

Version 1

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.

1. SCOPE

This method is for the sampling and analysis of methyl iodide in air samples using a six-liter Silco™ canister for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry using an automated cryogenic sampler.

2. SUMMARY OF METHOD

Air samples are collected in evacuated six-liter Silco™ canisters. The samples are collected automatically using a Tisch Environmental automatic sample collection system. Final pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. The estimated quantitation level (EQL) for this method is approximately 0.1 parts per billion (ppb).

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler 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. A system 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 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10^{o} C, initial time 1 minute, to 80^{o} C @ 10^{o} C/min, to 200^{o} C @ 25^{o} C/min, hold 1 minute, to 240^{o} C @ 50^{o} C/min, hold 2 minutes.
  - Inlet temperature 150^{o} C; split ratio 44.1:1.

- Agilent 5973 mass selective detector (MSD):

- Acquisition Mode: SIM
- Tune File: PFTBA Autotune
- Ions Monitored: 141,142,144,145
- Quant Ion: 142
- Internal Standard Ion: 145
- Solvent Delay: 3.00 min.

- Wasson ECE cryogenic concentrator with Naffion dryer:
  - Cryo Temp #1 at -170°C
  - Cryo Temp #2 at -150°C
  - Sample Oven at 200°C
  - Transfer Line Temperature at 150°C
  - Mass Flow at 35 ml/min
  - Line Purge Time 30 seconds

B. Auxiliary Apparatus

Restek six-liter Silco™ canisters with Silco™ valves

C. Reagents

Calibration Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX47999.

Internal Standard: Methyl Iodide-d3 gas at 500 ppb Matheson Tri-Gas cylinder no. SX46440.

Lab Control Standard: Methyl Iodide gas at 10 ppb Matheson Tri-Gas cylinder no. SX48752.

D. Gases

Helium, grade 5 or better
Liquid Nitrogen at 22 pounds per square inch (psi)
Nitrogen, grade 5
Compressed air, ultra zero

5. SAMPLE COLLECTION

A. Samples are collected in evacuated six-liter Silco™ canisters using a Tisch Environmental automated sampler set to deliver ambient air over a fixed amount of time.
B. The canisters will be filled so the ending pressure will be above ambient in the range of 5 to 10 psig (psi gauge).

6. ANALYSIS OF SAMPLES

a) Connect each canister to a port on the Wasson ECE cryogenic sample concentrator using a short length of polypropylene tubing. Reserve ports one and two for the blank and calibration standard.
b) For this method the standard volume will be 400 milliliters.

c) Perform an initial calibration curve using the following volumes of known concentrations of methyl iodide: 50, 75, 100, 200, 300, 400 milliliters. At least five (5) points must be analyzed to establish a calibration curve.
d) Prepare a sample sequence for the GC. The sequence should include a system blank and a continuing calibration verification standard (CCV) for every ten (10) samples analyzed. A lab control standard (LCS) should be run prior to field samples to verify that QC criteria have been met.
e) To minimize excessive carry over of contaminants from one analysis to the next, a system blank should be run 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 system blank analysis.
f) Review and edit the quantitation reports as needed.
g) Samples with concentration greater than the upper point of the calibration curve must be run at a smaller volume. Every attempt should be made to have the results fall within the upper half of the calibration curve. If running a volume of 50 ml results in a value greater than the upper calibration point, then the sample will need to be diluted with compressed nitrogen. Either add nitrogen to the original canister being sure to record the beginning and ending pressures, or transfer a known amount of sample from the original canister into a clean fully evacuated canister. Pressurize with nitrogen again recording the final pressure.
h) The final results will be adjusted by an appropriate dilution factor and reported in ppb.
i) The atmospheric concentration is calculated as follows:

$$\text{Sample Conc. (ppb)} = \frac{\text{Sample Vol. (ml)}}{400\ \text{ml}} \times \text{Instrument Result (ppb)} \times \text{Dilution Factor}$$

7. QUALITY ASSURANCE

A. A system blank must be analyzed with each batch of samples. The system blank is a 400 ml sample from a canister pressurized with grade 5 nitrogen. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, after the calibration curve or CCV, and after every tenth sample in the analytical batch.
B. Continuing calibration verification will be run at the beginning of the analytical batch, every tenth sample and at the end of the sample batch to verify system linearity. The calibration verification values must be within 25% of the actual value. Calibration of the entire system occurs if the CCV is outside the acceptable limits.
C. A LCS will be run with every sample batch. The LCS analyte concentration should fall within the lower half of the calibration curve. The LCS stock standard should come from a different source or lot than the daily calibration 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.

D. Run specific quality control samples, such as field spikes, trip spikes, and laboratory spikes prior to the field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over.

8. SAFETY

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 material safety data sheets (MSDS) of any chemicals used in this procedure. Methyl iodide gas is noted as a carcinogen and toxic at levels greater than 1300 mg/kg of body weight. All prep of standards and expected high samples should be performed in a shielded fume hood.

Calibration Standard Preparation for Methyl Iodide

The certified gas standard used for calibration was purchased from Matheson Tri-Gas, Inc., Morrow, Georgia and has the following specification:

Cylinder No:	SX47999
Expiration date:	March 3, 2010
Methyl Iodide:	0.01 $\pm$ 5% ppm

The calibration standard is made by taking an aliquot of the stock standard (10ppb) and diluting in a six liter Silco™ canister with nitrogen. A typical dilution is as follows:

1500ml of Methyl Iodide at 10ppb

Pressurize canister to approximately 29.4 psig
[Volume in ml = (Final Pressure (psig)/14.7 psig x 6000ml) + 6000ml]

Resulting concentration in can is approximately 0.83 ppb
Final concentration ppb= vol of std/vol in canister x std conc (ppb)

A minimum of six sample volumes are used to generate the calibration curve, with the standard at 50 ml being the low point. The sample volumes for the calibration curve are 50, 75, 100, 200, 300, and 400 ml. The 400ml represents a concentration of 0.83 ppb. The low point (50ml) equates to approximately 0.10 ppb.

All continuing calibration verification standards (CCV) and samples are run at 400 ml.

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

California Environmental Protection Agency

Air Resources Board

Method Development for the Air Sampling and Analysis of Methyl Iodide

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

October 2009

Version 2

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.

1. SCOPE

A method was developed for the air sampling and analysis of methyl iodide using a gas chromatograph/mass selective detector (GC/MSD). The 2009 requested estimated quantitation level (EQL) was 0.1 parts per billion (ppb).

2. SUMMARY OF METHOD

Application air samples are collected in evacuated six-liter Silco™ stainless steel canisters. The samples are collected using a Tisch Environmental automatic sample collection system. Final canister pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses external standard method for instrument calibration. The estimated quantitation level for this method is 0.13 ppb.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler 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. A system blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

Instrumentation

- Agilent Technologies 6890 Series gas chromatograph:
  - Column: Agilent 113-4332 GS GasPro, 30 meter, 0.32mm I.D., with helium as carrier gas at constant flow
  - GC temperature program: initial -10^{o} C, initial time 1 minute, to 80^{o} C @ 10^{o} C/min, to 200^{o} C @ 25^{o} C/min, hold 1 minute, to 240 ^{o} C @ 50^{o} C/min, hold 2 minutes.
  - Inlet temperature 150^{o} C; split ratio 44.1:1.

- Agilent 5973 mass selective detector (MSD):
  - Acquisition Mode: SIM
  - Tune File: PFTBA Autotune

- Ions Monitored: 141,142,144,145
- Quant Ion: 142
- Internal Standard Ion: 145
- Solvent Delay: 3.00 min.

- Wasson ECE cryogenic concentrator with Naffion dryer:
  - Cryo Temp #1 at -170°C
  - Cryo Temp #2 at -150°C
  - Sample Oven at 200°C
  - Transfer Line Temperature at 150°C
  - Mass Flow at 35 ml/min
  - Line Purge Time 30 seconds

5. METHOD DEVELOPMENT

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the methyl iodide instrument reproducibility.

Table 1: Instrument Reproducibility
Methyl Iodide

Concentration	Low	Medium	High
Amount (ppb)	0.0794	0.3666	0.7609
	0.0814	0.3669	0.7766
	0.0803	0.3753	0.7815
	0.0742	0.3700	0.7755
	0.0743	0.3669	0.7826
Average	0.0779	0.3691	0.7754
Standard Deviation	0.0034	0.0037	0.0087
Relative Standard Deviation	4.3949	1.0061	1.1182

B. Linearity

A six point external calibration is performed. Calibration standards ranging from at or near the EQL to approximately 8 times higher are used. A linear regression with an r^2 of 0.995 or higher is required for a calibration to be acceptable. Continuing calibration verifications (CCV) will be run at the start of each analytical batch and after every tenth sample to verify system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicate spikes of a low-level standard, the MDL and EQL for methyl iodide is calculated as follows:

Table 2: MDL and EQL Determination

Amount (ppb)	0.096, 0.091, 0.092, 0.094, 0.095, 0.082, 0.094
Average	0.092
Standard Deviation	0.005
MDL = 3.143*STD EQL= 5*MDL	0.015 0.134

The calculated MDL for methyl iodide is 0.015 ppb. The EQL for methyl iodide assuming a 1:1.79 dilution of the sample is 0.13 ppb.

D. Storage Stability

Storage stability was performed in triplicate using evacuated canisters spiked with methyl iodide and pressurized to approximately 7 psi. The project was run for 28 days with canisters analyzed at 0, 1, 7, 14, 21 and 28 days. Table 3 lists the results for the storage stability study.

Table 3: Storage Stability Study

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Deviation
0	90.43	94.68	90.18	91.76	2.53
1	90.59	94.16	88.64	91.13	2.80
7	103.61	107.50	103.57	104.89	2.26
14	100.11	102.99	99.09	100.73	2.02
21	91.43	119.84	116.42	109.23	15.51
28	108.22	113.72	110.71	110.88	2.75

Appendix D

Methyl Iodide Canister Field Log Sheets

METHYL IODIDE CANISTER FIELD LOG SHEET

Log #	Sample Name	Sampler ID Number	Canister ID Number	PST Date & Time Start	PST Date & Time End	Sampler Elapsed Time	Canister Vacuum Display Start	Canister Vacuum Display End	Mass Flow Meter Display Start	Mass Flow Meter Display End	Corrected Average Flow	Comment Number	Weather K,P,C,F&R Start	Weather K,P,C,F&R End	Initials Start	Initials End
001	E-BK	114	1127	10/27/09 17:00	10/28/09 5:00		-29.5	21.0	17.4	21.2	22.9		K	K	MM	MM
002	E-F-1	114	1171	10/28/09 6:30	10/28/09 18:30	719.59	-28.0	11.0	16.0				K	K	MM	MM
003	E-F-2	114	1055	10/28/09 18:30	10/29/09 6:30	719.58	-29.0	11.0					K	K	MM	MM
004	E-F-3	114	1074	10/29/09 6:30	10/28/09 18:30	719.59	-27.0	11.0		11.9	17.2		K	P	MM	MM
005	N-BK	118	2811	10/27/09 17:10	10/28/09 5:10		-29.5	17.5	16.0	21.0	22.0		K	K	MM	MM
006	N-F-1	118	1113	10/28/09 6:40	10/28/09 18:40	719.59	-28.0	7.0	16.0				K	K	MM	MM
007	N-F-2	118	1060	10/28/09 18:40	10/29/09 6:40	720.00	-30.0	7.0					K	K	MM	MM
008	N-F-3	118	2809	10/29/09 6:40	10/29/09 18:40	719.59	-29.0	6.0		13.9	18.2		K	P	MM	MM
009	W-BK	119	1149	10/27/09 17:20	10/28/09 5:20		-30.0	15.5	15.9	22.2	22.6		K	K	MM	MM
010	W-F-1	119	1102	10/28/09 6:50	10/28/09 18:50	719.58	-30.0	8.0	16.0			1	K	K	MM	MM
011	W-F-2	119	1087	10/28/09 18:50	10/29/09 6:50	697.36	-30.0	1.0				1	K	K	MM	MM
012	W-F-3	119	1169	10/29/09 6:50	10/29/09 18:50	710.36	-30.0	9.0		16.6	19.7	1	K	P	MM	MM
013	S-BK	113	1177	10/27/09 17:30	10/28/09 5:30		-31.0	20.5	16.1	19.8	21.5		K	K	MM	MM
014	S-F-1	113	1165	10/28/09 7:00	10/28/09 19:00	719.58	-30.0	11.0	16.0				K	K	MM	MM
015	S-F-2	113	1083	10/28/09 19:00	10/29/09 7:00	719.58	-29.5	12.0					K	K	MM	MM
016	S-F-3	113	1142	10/29/09 7:00	10/29/09 19:00	719.58	-30.0	10.0		14.3	18.4		K	P	MM	MM
017	S-CO-BK	115	1067	10/27/09 17:30	10/28/09 5:30		-31.0	18.5	17.3	19.1	21.7		K	K	MM	MM
018	S-CO-F-1	115	1075	10/28/09 7:00	10/28/09 19:00	719.59	-30.0	15.0	16.0			2	K	K	MM	MM
019	S-CO-F-2	115	1088	10/28/09 19:00	10/29/09 7:00	719.59	-29.5	11.0				2	K	K	MM	MM
020	S-CO-F-3	115	1064	10/29/09 7:00	10/29/09 19:00	719.56	-30.0	13.0		14.5	18.6	2	K	P	MM	MM
021	S-FS-BK	116	1057	10/27/09 17:30	10/28/09 5:30		-28.0	16.5	16.0	17.3	20.1		K	K	MM	MM
022	S-FS-F-1	116	1172	10/28/09 7:00	10/28/09 19:00	719.58	-27.0	14.0	16.0				K	K	MM	MM
023	S-FS-F-2	116	1135	10/28/09 19:00	10/29/09 7:00	719.58	-28.0	11.0					K	K	MM	MM
024	S-FS-F-3	116	1186	10/29/09 7:00	10/29/09 19:00	719.58	-29.0	13.0		13.1	17.8		K	P	MM	MM

MFM Used #: **20005345** **Slope:** **1.073** **Intrcpt:** **2.194**

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

METHYL IODIDE CANISTER FIELD LOG SHEET

Log #	Sample Name	Sampler ID Number	Canister ID Number	Date & Time			Canister Vacuum Display		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
				Start	End		Start	End	Start	End			Start	End	Start	End
025	TS-BK	-	1146	-	-		-28.5	-	-	-	-		-	-	MM	MM
026	TB	-	1071	-	-			-	-	-	-		-	-	MM	MM
027	TS-F	-	1173	-	-		-28.4	-	-	-	-		-	-	MM	MM
028	FB	-	1101	-	-			-	-	-	-		-	-	MM	MM

Comments:

1= battery failure, not full flow or run times, fixed for 3rd fumigation sample

2= final flow check didn't sound correct, pump not running well, better after running for a while

which resulted in higher flows that slowly drifted back to initial flow value

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

Appendix E

Calibration/Certification Reports

CALIFORNIA AIR RESOURCES BOARD

FLOW CALIBRATION REPORT

TO: *TESTING AND EVALLUATIONS*
STEVE RIDER

LOG NUMBER : *2009 216*

FROM: ROBERT RUSSELL\BRIAN SPREADBOROUGH
Program Evaluation & Standards

CALIBRATION DATE: *11/10/2009*
REPORT DATE : *11/10/2009*

IDENTIFICATION

Instrument : *AALBORG 100 cc/min*
Position number : *1*
Property No. : 20005345
Serial No. : *G18861*
Previous Log No.: *2008 223*
Bar Code No. : *20005345*
Elevation : *25.00'*
Inst. Prop. Of : *TESTING AND EVALUATIONS BRANCH / MLD*

Site Name : *MLD Standards Lab*
Site Number : *34-299*
Location : *1309 T-Street*
Sacramento, CA 95814

CALIBRATION STANDARDS	ID NUMBER
molbox	20021121

CALIBRATION RESULTS

Component	FLOW
Instrument Range	0-100 SCCM
Initial Zero Setting	
Initial Span Setting	
Final Zero Setting	
Final Span Setting	
Slope	0.932
Intercept	-2.046 ✓
Correlation Coefficient	1.00000 ✓
Change From Previous Calibration (%)	-6.459
Date Of Last Calibration	10/20/2008

Calibration Equation:

Calibration Expires: *11/10/2010*

Std. FLOW = 1.073 * (Net Display) + 2.194

Comments:

CALIBRATED BY: RSS

CHECKED BY: RR