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AIR RESOURCES BOARD

Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Loomis, CA Summer- 2004

Prepared by
Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

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Monitoring Report Approval

Title: Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Loomis, CA – Summer 2004

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

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Executive Summary

Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Loomis, CA– Summer 2004

This report presents air monitoring results during fumigation of a home using the pesticides sulfuryl fluoride and chloropicrin. The monitoring was conducted at the request of the Department of Pesticide Regulation (DPR) to support their toxic air contaminant identification program. The testing occurred in Placer County, from June 29 through July 4, 2004, around a sulfuryl fluoride fumigation of an approximately 45,000 cubic foot house. The product label for sulfuryl fluoride (Vikane®) requires that chloropicrin be used as a warning agent (lachrymator) during the fumigation. The study was conducted during the fumigation for powderpost beetles. Powderpost beetle fumigation requires a higher concentration of sulfuryl fluoride relative to other types of fumigation using this pesticide.

In general, structural fumigations in California consist of the following steps:

1. Sealing the structure with tarps.
2. Introduction of the fumigant gas (and warning agent).
3. Exposure period (normally from 36 to 72 hours for powderpost beetle).
4. First opening of the tarp seal. This is referred to as the "mechanical vent." The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from the structure for release through a vent pipe near the eaves. This vent process generally lasts from 10 to 30 minutes and is followed immediately by the removal of the tarps. For the purposes of this monitoring study, the "mechanical vent" period has been defined as ending and aeration as starting when the tarps are completely removed.
5. Aeration (minimum of eight hours in California).
6. Clearing; a verification that sulfuryl fluoride concentrations are less than 5 ppmv inside the structure. This allows the structure to be re-occupied.

Per DPR recommendations, the test consisted primarily of sampling at multiple sites (13) around the structure at distances ranging from 5 feet to 40 feet from the structure. Samples were collected based on the following schedule:

1. A 24-hour background at four sites (i.e., collected prior to the fumigation).
2. During fumigant introduction and the exposure period. This sampling was divided into daytime and overnight periods.
3. During the "mechanical vent" period.
4. During aeration. This sampling was divided into daytime and overnight periods.

Samples were collected for a total of 10 periods. Two additional samplers were used at downwind locations during the mechanical vent period as ambient sulfuryl fluoride concentrations were expected to be the highest during this process. No samples were collected inside the structure after the structure was cleared for re-entry.

Sulfuryl Fluoride

The sulfuryl fluoride results ranged from less than the method detection limit (<MDL) to 29,000 ug/m^3 (6900 ppbv). The highest concentration was observed at the sampling site closest to and downwind from the mechanical vent during sampling period five.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable levels greater than the estimated quantitation limit (>EQL) were also observed during all of the fumigation exposure periods. Only one sample had a quantifiable result during the first aeration sampling period (period six) and no quantifiable levels were observed during the remaining aeration periods (seven through nine). The test results are shown in a bar graph included in this Executive Summary.

All test results reported as "detected" (>MDL but less than EQL) are questionable due to low level fluoride contamination in the sampling cartridges. Quantifiable levels (i.e., >EQL) are not considered affected.

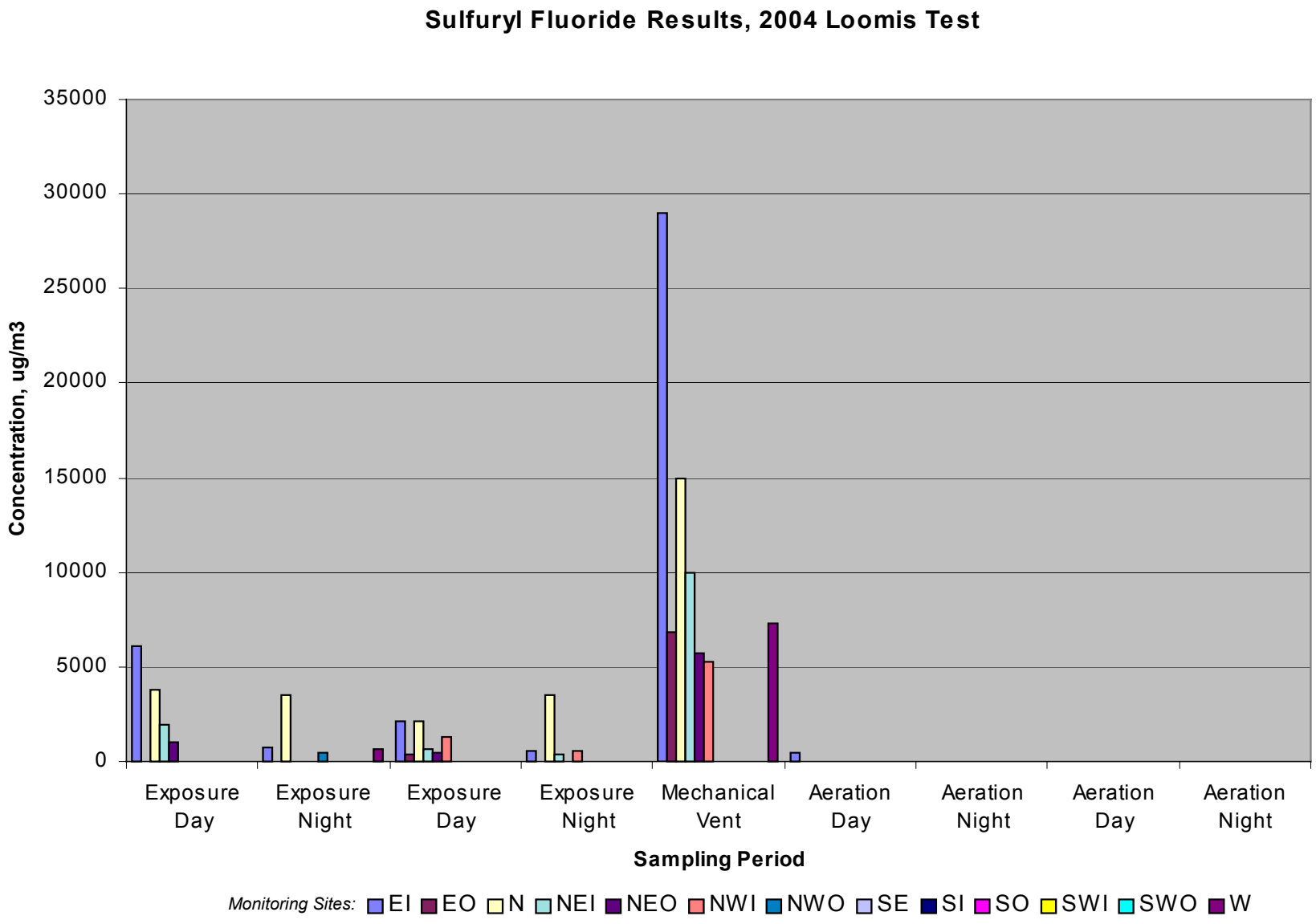
We collected 132 samples for sulfuryl fluoride (includes four background and nine collocated samples). Of these, approximately 24 percent (31) had quantifiable concentrations above the EQL, 71 percent (94) were "detected," five percent (6) were <MDL, and one result was determined to be invalid. The sulfuryl fluoride results from the four background samples were all "detected." The background results are not included on the following bar graphs.

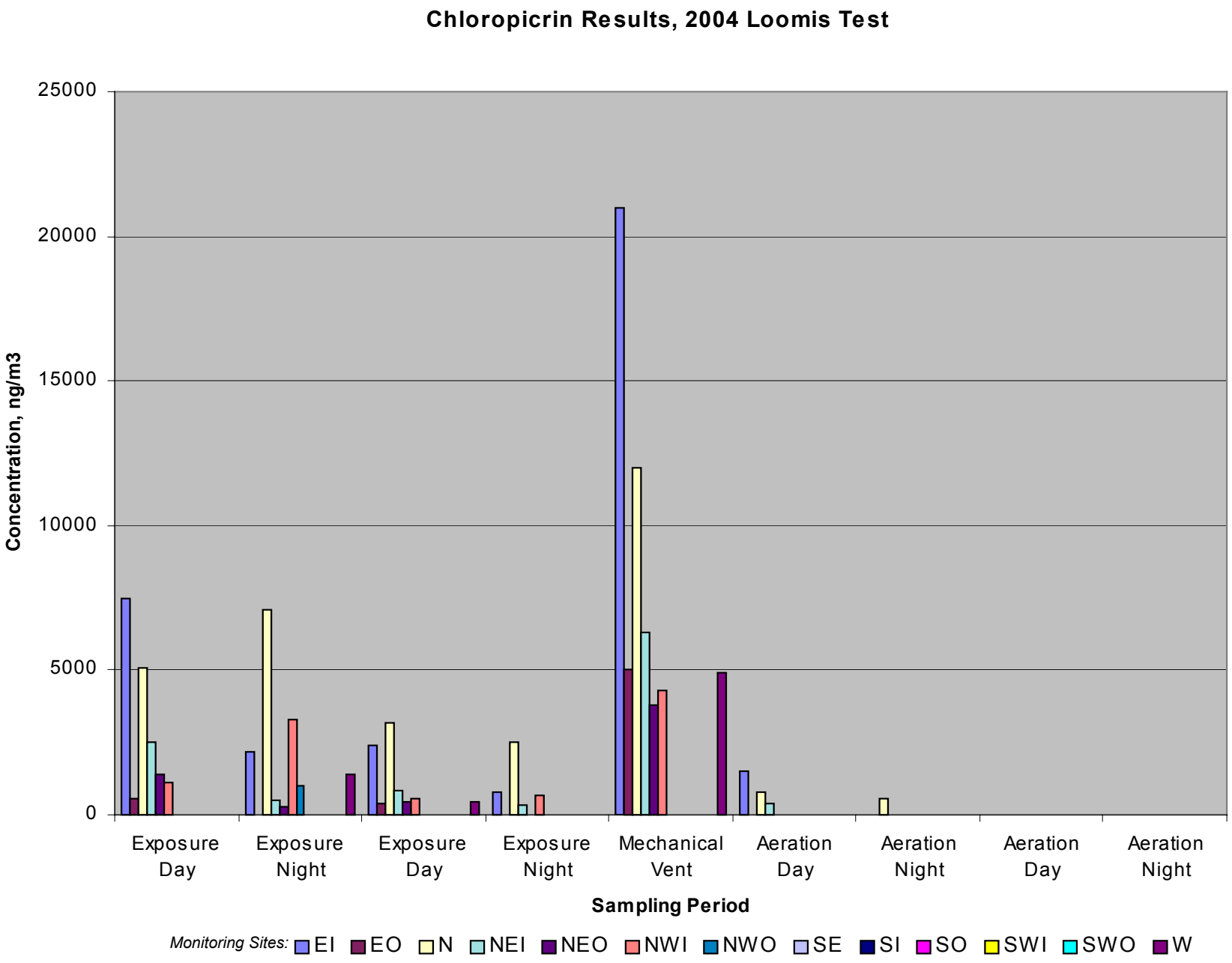
Chloropicrin

The chloropicrin results ranged from <MDL to 21,000 ng/m^3 (3100 pptv). The highest concentration was observed at the sampling site closest to and downwind from the mechanical vent during the mechanical vent sampling period (period 5).

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable results (>EQL) were observed during all of the fumigation exposure periods. A total of four samples had quantifiable results during the first two aeration sampling periods (periods six and seven) and no quantifiable levels were observed during the remaining aeration periods (eight and nine). The test results are shown in a bar graph included in this Executive Summary.

We collected 132 samples for chloropicrin (includes four background samples and nine collocated samples), approximately 32 percent (42) sample results had quantifiable concentrations above the EQL, 25 percent (33) were "detected," and 43 percent (57) of the sample results were <MDL. The chloropicrin results from the four background samples were all <MDL. Background results are not included on the following graphs.


Sulfuryl Fluoride Results, 2004 Loomis Test
Concentration, ug/m3
35000
30000
25000
20000
15000
10000
5000
0
Exposure Day
Exposure Night
Exposure Day
Exposure Night
Mechanical Vent
Aeration Day
Aeration Night
Aeration Day
Aeration Night
Sampling Period
Monitoring Sites:
EI
EO
N
NEI
NEO
NWI
NWO
SE
SI
SO
SWI
SWO
W


Chloropicrin Results, 2004 Loomis Test
Concentration, ng/m3
25000
20000
15000
10000
5000
0
Exposure Day
Exposure Night
Exposure Day
Exposure Night
Mechanical Vent
Aeration Day
Aeration Night
Aeration Day
Aeration Night
Sampling Period
Monitoring Sites:
EI
EO
N
NEI
NEO
NWI
NWO
SE
SI
SO
SWI
SWO
W

Acknowledgments

Staff of the Special Purpose Monitoring Section collected the samples. Steve Rider coordinated the field work. Jim Omand and Michael Orbanosky of the ARB Special Analysis Section laboratory performed the method development and chemical analyses. Lynn Baker of the ARB Stationary Source Division provided comments on the monitoring protocol and report.

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Report for the Air Monitoring
Around a Structural Application of Sulfuryl Fluoride
in Loomis, CA - Summer 2004

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (October 17, 2003, Memorandum, Helliker to Lloyd, and April 15, 2004, Memorandum, Sanders to Cook), the Air Resources Board (ARB) staff conducted pesticide air monitoring to determine concentrations of sulfuryl fluoride and chloropicrin during a structural application. The monitoring was done to fulfill the requirements of Assembly Bill 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions…of pesticides which may be determined to pose a present or potential hazard..." when requested by DPR.

The monitoring was conducted in Placer County, from June 29 to July 4, 2004, around a sulfuryl fluoride fumigation of an approximately 45,000 cubic foot house. The product label for sulfuryl fluoride (Vikane®) requires that chloropicrin be used as a warning agent (lachrymator) during the fumigation. The study was conducted during a fumigation for powderpost beetles, which requires an elevated level of the fumigant relative to structural fumigation for other pests (e.g., termites).

The sampling and analysis followed the procedures outlined in 1) the monitoring protocol (page 1 of the separate volume of Appendices), 2) the quality assurance guidelines described in the “Quality Assurance Plan for Pesticide Air Monitoring” (May 11, 1999 version), 3) the “Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography” (page 12 of the Appendices), and 4) the “Standard Operating Procedure, Sampling, and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector,” (page 19 of Appendices).

II. Fumigation Process and Test Overview

In general, structural fumigations in California consist of the following steps:

1. Sealing the structure with tarps.
2. Introduction of the fumigant gas (and warning agent).
3. Exposure period.
4. First opening of the tarp seal. This is referred to as the “mechanical vent.” The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from the structure for release through a vent pipe near the eaves. This vent process generally lasts from 10 to 30 minutes and is followed immediately by the removal of the tarps. For this

monitoring study, the "mechanical vent" period has been defined as ending and aeration as starting when the tarps are completely removed.

5. Aeration (minimum of eight hours in California).
6. Clearing; a verification that sulfuryl fluoride concentrations are less than 5 ppmv inside the structure. This allows the structure to be re-occupied.

Per DPR recommendations, the test consisted primarily of sampling at multiple sites around the structure at distances ranging from 5 feet to 40 feet from the structure. Samples were collected based on the following schedule.

1. A 24-hour background at four sites (i.e., collected prior to the fumigation).
2. During fumigant introduction and the exposure period. This sampling was divided into daytime and overnight periods.
3. During the "mechanical vent" period.
4. During aeration. This sampling was divided into daytime and overnight periods.

The study included the background sampling period at four positions outside the house and nine fumigation/post-fumigation sampling periods at 13 positions (1 collocated) outside the house. Samples were also collected at two additional positions outside the house for the mechanical vent (period 5) sampling period. No indoor samples were collected.

III. Fumigation Monitoring

A single-family house in Loomis, California, was chosen for the fumigation monitoring site. Refer to Figure 1 for a rough map of the site and to Figure 2 for a more detailed diagram of the site. Refer to Appendix IV (page 72 of Appendices) for a copy of the fumigation log.

Fumigation Site, Application Rate, and Fumigation Information

The DPR's monitoring recommendation (April 15, 2004 memo, Sanders to Cook,) directed that:

> "The application dosage of sulfuryl fluoride can vary, for a typical single-family house fumigation, from 6 – 16 ounces per 1,000 cubic feet for termites to a higher application rate necessary to control Powderpost beetle." It further indicated "The label rate for chloropicrin use as a "warning agent" is one ounce per 10,000 cubic feet of space to be fumigated."
>
> "DPR recommends selecting a site with a volume of at least 26,000 cubic feet, no obstructions between the samplers and the structure, and an exposure time of at least 36 hours but no more than 48 hours that will be treated for the Powderpost beetle to assure a higher application rate."

Table 1 summarizes the actual fumigation conditions and information.

Table 1
Fumigation Information

Location:	5860 Laird Road, Loomis CA
Type of Structure:	Two story house
Size of Structure:	Approximately 45,000 cubic feet
Applicator:	The Ultratech Division
Pest controlled:	Powderpost Beetle
Product Applied:	Vikane®, chloropicrin
Type of Application:	Structural, tarped, "monitored"
Application Rate:	126.3 lbs. Vikane® initial; 44.9 oz./1000 $ft.^3$ Added 45.5 lbs Vikane® at 21 hours 3 oz. chloropicrin total
Duration of Fumigation:	43.5 hours (Amount of Vikane® was calculated assuming 36-hour duration)
Duration of Vent	50 minutes (including tarp removal)
Duration of Aeration:	Approx. 72 hours due to the holiday weekend
Terminal reading:	17 oz. Vikane®/1000 $ft.^3$ at 06:15 on 7/2/04
Method of Introduction:	Vikane® is released into the structure as a gas via a leak-proof tube and disbursed using one or more fans with a minimum capacity of 1000 cubic feet per minute for each pound of Vikane® released per minute. Chloropicrin, when used as a warning agent during structural fumigation with Vikane®, is applied in liquid form within structures five to ten minutes prior to fumigation. Chloropicrin is dispensed into a shallow plastic or non-aluminum metal pan with a wicking agent (e.g., cotton) and is placed in the direct air stream of a fan to hasten evaporation.

Exposure Period: The fumigation process for powderpost beetles was expected to consist of a 36 to 72 hour exposure period and the intention of this study was to target a fumigation using a shorter exposure period (i.e., 36 hours rather than 72 hours) as higher Vikane® application rates are required to meet the 10x fumigation ounce hours (higher rate for powderpost beetles relative to rates used for other pests such as termites). The Vikane® application rate for this study was calculated using an assumption of a 36-hour exposure. However, due to scheduling problems by the fumigation company, the actual exposure period was 43.5 hours.

Mechanical Vent Period: The "mechanical vent" period is a short aeration conducted at the end of the exposure period just prior to removal of the tarps. The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from

between the tarp and the structure for release through a small vent pipe near the eaves. The vent is pulled through at a tarp seam, usually located just below the height of the roof overhang. An air inlet opening is normally located on the opposite side of the structure.

For this study, the mechanical vent sampling period included the time during removal of the tarp covering the structure. The time required for mechanical venting and tarp removal was approximately 50 minutes. However, due to the length of time required for sample change-out, this sampling period actually lasted for approximately 1.25 hours. Referring to Figure 1, the mechanical vent was located on the east side of the structure between the garage and the main part of the house.

Aeration Period: Aeration was defined as starting when the tarps were completely removed. The aeration period required by the product label is a minimum of eight hours. However, fumigation companies may choose to aerate the structure for a longer period of time, e.g., up to 48 hours. In any case, a fumigated structure cannot be re-entered until it is "cleared" as having Vikane® concentrations of less than five parts per million by volume (ppmv). The fumigator uses a Miran or Interscan gas analyzer to measure the Vikane® concentration to clear the structure for re-entry.

The intention of this study was to target a fumigation using a twenty-four hour aeration period (i.e., re-entry would be cleared and post aeration sampling would begin after twenty-four hours of aeration). However, this was not accomplished. Due to scheduling issues (i.e., Fourth of July weekend) the applicator did not return to "clear" the structure until July 5, 2004. Due to this no indoor samples were collected during this study. This issue was discussed and agreed to with DPR staff prior to the test.

Sampling Locations

The DPR's monitoring recommendation (April 15, 2004, memo, Sanders to Cook) directed that:

> "The structure selected for monitoring must have enough clearance surrounding it to allow for sampler placement at a distance of 5 and 10 feet from the edge of the structure. Four background samples should be taken prior to application. Twelve samplers should be placed surrounding the structure as 3 rings. The first ring consists of four samplers located at the middle of and 5 feet from each side of the structure. The second ring consists of four samplers 10 feet out from each corner of the structure. The third ring contains four samplers which would be placed 30 to 50 feet from each side or corner of the structure. A thirteenth sampler will be collocated with one sampler in the first ring and at the site expected to be downwind during aeration. The collocated sample will be collected at this site during each sampling interval. Sample intake should be 1.5 to 2.0 meters above the ground. There should be no large obstructions between the structure and the furthest samplers."

Table 2 below lists the site identifications. Referring to Figure 1, in addition to the samplers recommended by DPR, one more sampler was placed on the downwind side of the structure (site EO). Also, two samplers were used during the "mechanical vent" (period 5) sampling period and were placed downwind of the structure at a distance of approximately 80 feet. These two samplers were located in a small vineyard. These samplers were placed on two-foot tall stands to bring the cartridge inlet height (7 feet) just above the height of the grape leaves.

Table 2 Loomis Sampling Site Identification

Descriptive Name	***Abbreviation***	***Approx. Distance from House (ft)***
East Outer	EO	40
East Inner	EI	5
Southeast	SE	10
South Outer	SO	40
South Inner	SI	5
Southwest Inner	SWI	10
Southwest Inner Field Spike	SWI-FS	10
Southwest Outer	SWO	40
West	W	5
Northwest Inner	NWI	10
Northwest Inner Field Spike	NWI-FS	10
Northwest Outer	NWO	40
North	N	5
North Collocated	N-C	5
Northeast Inner	NEI	11
Northeast Outer	NEO	40
Extra Northeast	XNE	83
Extra Northwest	XNW	80

The "NWO" sampler was in a small hole and so was raised by 1.5 feet by installing pallets and configuring the sampler to get closer to the same elevation as the structure. All other samplers were positioned at the same elevation relative to the house. All sampler inlets were approximately five feet ($\pm$0.5 feet) above the ground.

The collocated sampler was positioned at the north side of the house. For this test, no samplers were placed inside the structure for collection of post-aeration indoor samples. Background samples were collected at the four corner (2nd ring) locations for 24 hours prior to the fumigation.

Sampling Periods

The fumigation process for powderpost beetles was expected to consist of a 36 to 72 hour exposure period, followed by a one to two hour mechanical vent period and an eight to forty-eight hour aeration period.

The DPR's monitoring recommendation also directed that:

> "For both sulfuryl fluoride and chloropicrin, samples should be taken before application, during application (exposure period), during mechanical and tarp removal aeration (alternate Daytime/Overnight sampling according to the duration of aeration), and post aeration for two Daytime/Overnight sampling periods. Additionally, after completion of aeration, two 24-hour samples should be taken at each of two different locations inside the fumigated structure for 48-hours sampling duration (total of four samples inside structure)."

The sampling schedule listed in the monitoring protocol (Appendix I) was provided as a guide. Table 3 lists the actual fumigation test sampling periods. The sample times listed are approximate. Refer to the field log sheets for the exact start and stop times for each sample. All times are in Pacific Standard Time (PST).

Table 3
Loomis Fumigation Test Sampling Periods

Period	Approx. # Hours	Date	Time
Background	24 hours	6/29-30/04	0735 to 0735
1 (exposure/daytime)	5.75 hours	6/30/04	1305 to 1845
2 (exposure/overnight)	11 hours	6/30-7/1/04	1845 to 0550
3 (exposure/daytime)	13 hours	7/1/04	0550 to 1840
4 (exposure/overnight)	11.25 hours	7/1-2/04	1840 to 0605
5 (mechanical vent)	1.25 hours	7/2/04	0850 to 1005
6 (aeration/daytime)	8.5 hours	7/2/04	1005 to 1840
7 (aeration/overnight)	11.25 hours	7/2-3/04	1840 to 0555
8 (aeration/daytime)	13 hours	7/3/04	0555 to 1850
9 (aeration/overnight)	11 hours	7/3-4/04	1850 to 0555

The house was fumigated at 1315 on 6/29/04. Mechanical venting started at 0855 and ended at 0920 on 7/2/04. Tarp removal started at 0925 and was finished at 0943 on 7/2/04. Due to the length of time required for sample change-out, the actual sampling period was longer than the mechanical vent period. Aeration was extended during this fumigation and lasted for approximately 72 hours. No indoor samples were collected during this test.

Meteorological Monitoring

The meteorological station (oriented toward true north) was positioned 845 feet to the southeast of the southeast corner of the house. The meteorological station was set up, at a height of 21 feet, to determine wind speed and direction, air temperature, barometric pressure and relative humidity. The raw meteorological station data are available in comma delimited text format. Appendix V (page 74 of the Appendices) lists the meteorological station data in 1-minute averages for the "mechanical vent" test period. Appendix VI (page 78 of the Appendices) lists the meteorological station data in

5-minute averages for the remainder of the test period. Data collected during the background sampling period were lost due to an internal error occurring when the datalogger memory was cleared. ARB staff noted the degree of cloud cover on the sample log sheet whenever sample cartridges were changed.

IV. Sampling Procedures

Air sampling for sulfuryl fluoride and chloropicrin was conducted with sampling tubes. For sulfuryl fluoride, the tubes were 8 mm x 110 mm, coconut shell charcoal with 800 mg in the primary section and 200 mg in the secondary (SKC special order). For chloropicrin, the tubes were 8 mm x 140 mm, XAD-4 with 400 mg in the primary section and 200 mg in the secondary section (SKC special order).

Sample collection for sulfuryl fluoride was conducted at a flow rate of 50 standard cubic centimeters per minute (sccpm). For chloropicrin, a flow rate of 100 sccpm was used.

Two sulfuryl fluoride cartridges in series were used for sample collection at all sites during the "mechanical aeration" sampling period. Doubling of the cartridges during the mechanical vent period was intended as a precaution to address possible breakthrough at higher concentrations.

Each sample train consisted of an adsorption tube, Teflon® fittings and Tygon® tubing, rain/sun shield, needle valve, train support and a 12 volt DC vacuum pump (Figure 3). Tubes were prepared for use by breaking off the sealed glass end and immediately inserting the tube into the Teflon® fitting. The tubes were oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. Needle valves with a range of 0-100 ccpm and 50-500 ccpm were used to control sample flow for sulfuryl fluoride and chloropicrin sampling, respectively. The flow rates were set using calibrated digital mass flow meters (MFM) before each sampling period. A MFM scaled from 0-200 sccpm was used for both sulfuryl fluoride and chloropicrin samplers. The flow rate was also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates was recorded on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included in Appendix I (page 25 of Appendices).

Immediately after sampling, the tubes were capped, labeled, placed in a culture tube and stored and transported in an insulated container with dry ice to the ARB laboratory in Sacramento.

Caution was used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

V. Analytical Methodology

The sampling and analysis method (SOP) and validation results for sulfuryl fluoride are included in Appendix I. The sulfuryl fluoride method consists of sampling with charcoal cartridges at a flow rate of 50 sccpm followed by extraction with 40 millimolar sodium hydroxide and anion exchange ion chromatography. The DPR recommended a target 24-hour estimated quantitation limit (EQL) of 30 ug/m^3 for sulfuryl fluoride. The SOP specifies an EQL of 11.5 ug/sample, which corresponds to 160 ug/m^3 for a 24-hour sample collected at 50 sccpm.

With respect to sample stability, analytical validation work conducted prior to the study indicated that sulfuryl fluoride samples are stable for at least six weeks. All sample analyses for sulfuryl fluoride were conducted with a six-week timeframe.

The SOP for chloropicrin is included in the Appendices. The chloropicrin method consists of sampling with XAD-4 cartridges, extraction with three milliliters of methylene chloride and analysis using gas chromatography/mass selective detector operated in the selected ion-monitoring mode. The DPR recommended a target 24-hour EQL of 0.1 ug/m^3 for chloropicrin. The SOP specifies an EQL of 19.8 ng/sample, which corresponds to 138 ng/m^3 (0.138 ug/m^3) for chloropicrin for a 24-hour sample collected at 100 sccpm.

Analytical method validation work conducted prior to the study indicated that chloropicrin stability was within acceptable limits for at least six weeks. All sample analyses for chloropicrin were conducted with a six-week timeframe.

VI. Monitoring Results

A total of 132 samples each (including background and collocated samples; excluding spikes and blanks) were collected for sulfuryl fluoride and chloropicrin. One sulfuryl fluoride sample (log #s 95/96) was not valid due to a probable error in sample labeling.

Sample results for sulfuryl fluoride and chloropicrin are discussed below. Tables 5 and 8 of this report present the results of air monitoring for sulfuryl fluoride and chlorpicrin in units of ug/m^3 and ng/m^3, respectively, and in units of parts per billion by volume (ppbv) and parts per trillion by volume (pptv), respectively. A summary of the sulfuryl fluoride and chloropicrin results is presented in Tables 6 and 9, respectively. A summary of the sulfuryl fluoride and chloropicrin results are also presented in Figures 4 through 12 and 13 through 21, respectively, as associated with wind roses for each sampling period.

Laboratory results are reported to three significant figures and the sample results (in air concentration units) equal to and above the estimated quantitation limit (EQL) are reported to two significant figures. Results equal to or above the method detection limit (MDL), but less than the EQL, are reported as “detected.”

Sulfuryl Fluoride
The sulfuryl fluoride results ranged from <MDL to 29,000 ug/m^3 (6900 ppbv). The highest concentration was observed at the "east inside" (EI) sampling site during the mechanical vent sampling period (period 5). The "EI" site was closest to and downwind from the mechanical vent.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable levels (>EQL) were observed during all of the fumigation exposure periods. Only one sample had a quantifiable result during the first aeration sampling period (period six) and no quantifiifiable levels were observed during the remaining aeration periods (seven through nine).

The laboratory report states: "Because all system blanks were <MDL and most extraction blanks were DET it seems probable that the charcoal collection tubes contain a small amount of fluoride. Blank values were not subtracted from the monitoring data." Thus, all "detect" results from this study should be considered as questionable due to low level contamination. Since quantifiable results (i.e., above the EQL) were not found in any cartridge (extraction) blanks, the sample results above the EQL should not be affected by this low level contamination issue.

Of the 132 samples collected for sulfuryl fluoride (includes four background samples and nine collocated samples), 31 sample results were found to have quantifiable concentrations above the EQL, 94 sample results were "detected," six sample results were <MDL, and one result (log #95) was determined to be invalid due to a probable labeling error (see Appendix II, page 50).

Four samples were collected for the background period (i.e., prior to application) from the "northeast inside" (NEI), "northwest inside" (NWI), southeast (SE) and "southwest inside" (SWI) sites. The sulfuryl fluoride results from the four background samples were all "detected."

Backup cartridges (a second cartridge in series behind the primary cartridge) were collected at all sites during the "mechanical vent" period. Of the 16 backup cartridges collected, 14 sample results were "detected," one sample result was <MDL, and one sample (log #96) was invalid due to a probable labeling error (refer to the laboratory report, Appendix II, page 50).

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples.

Chloropicrin
The chloropicrin results ranged from <MDL to 21,000 ng/m^3 (3100 pptv). The highest concentration was observed at the "east inside" (EI) sampling site during the mechanical vent sampling period (period 5). The "EI" site was closest to and downwind from the mechanical vent.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable results (>EQL) were observed during all of the fumigation exposure periods. A total of four samples had quantifiable results during the first two aeration sampling periods (periods six and seven) and no quantifiable levels were observed during the remaining aeration periods (eight and nine).

Of the 132 samples collected for chloropicrin (includes four background samples and nine collocated samples), 42 sample results were found to have quantifiable concentrations above the EQL, 33 sample results were "detected," and 57 sample results were <MDL.

Four samples were collected for the background period (i.e., prior to application) from the "northeast inside" (NEI), "northwest inside" (NWI), southeast (SE) and "southwest inside" (SWI) sites. The chloropicrin results from the four background samples were all <MDL.

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples.

VII. Field Quality Control

Field quality assurance for the application monitoring included the following:

1) Two field spikes for chloropicrin obtained by sampling ambient air at the application monitoring site. The field spikes were obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample).

2) Two field spikes for chloropicrin and two dynamic field spikes (see page 12 for description) for sulfuryl fluoride collected by sampling ambient air at the ARB 13th and T street facility.

3) Four trip spikes each for sulfuryl fluoride and chloropicrin. The trip spikes were labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

4) Four lab spikes prepared at the same level as the field and trip spikes. The lab spikes remained in the laboratory freezer and were extracted and analyzed along with the field and trip spikes.

5) Collocated (replicate) samples taken for all sampling periods (except the background period) at one sampling location (N).

6) One trip blank each for sulfuryl fluoride and chloropicrin. Each trip blank

was obtained, labeled, recorded on the field log-sheet, and transported and submitted along with the field and trip spikes and application samples.

7) The battery operated mass flow meters used to set and check the sampling flow rate were calibrated by the ARB's Quality Assurance Section.

VIII. Quality Control Results

A. Trip Blanks

The result for the sulfuryl fluoride trip blank was "detected." The result for the chloropicrin trip blank was <MDL.

B. Collocated Sample Results

The relative percent difference (RPD) of the collocated results provides an indication of the precision of the monitoring method (i.e., the lower the RPD the better the precision). RPD is calculated as follows: RPD=(| difference |/average) x 100.

Referring to Table 7, five collocated pairs of samples for the fumigation study had both sulfuryl fluoride results above the EQL. The RPD of the data pairs ranged from 3 to 17 percent, with an average of 11percent, indicating acceptable precision for the sampling and analyses.

Referring to Table 10, seven collocated pairs of samples for the fumigation study had both chloropicrin results above the EQL. The RPD of the data pairs ranged from 2 to 15 percent, with an average of 9.9 percent, indicating acceptable precision for the sampling and analyses.

C. Laboratory, Trip and Field Spikes

The purpose of collecting spiked samples is to assess the accuracy (% recovery) of the sampling and analytical methods. Laboratory, trip, and field spikes were prepared by spiking a known amount of the target compound onto the appropriate cartridges. Field spikes are collected by sampling ambient air through a previously spiked cartridge at one sampling site during the background sampling. Thus, the field spikes provide an assessment of the accuracy of the entire method and are collected under the same environmental and experimental conditions as those occurring at the time of ambient sampling. The lab and trip spikes are used to confirm the field spike results or to help identify the source of losses (or other problems) when they occur in the field spikes.

The laboratory spikes were placed immediately in a freezer and kept there until extraction and analysis. The trip and field spikes were kept in the lab freezer until transported to the field. The trip spikes were kept on dry ice in an ice chest (the same

one used for samples) during transport to and from the field and at all times while in the field except log-in and labeling. The extraction and analysis of each set of laboratory, trip and field spikes normally occurs at the same time. The collocated (unspiked) background sample result, if above the EQL, is subtracted from the field spike sample result before calculation of percent recovery of the analytes.

The lab, trip and field spike results (average percent recovery) are summarized in Table 4 and discussed below.

Table 4
Spike Results
Average Percent Recovery

	Sulfuryl Fluoride	Chloropicrin
Lab	100	87
Trip	95	87
Field	83	77

Sulfuryl Fluoride: The sulfuryl fluoride laboratory, trip, and field spike results are listed in Tables 11, 12, and 13, respectively. Each of the lab and trip spike cartridges was spiked with 55.2 ug/sample of sulfuryl fluoride.

For sulfuryl fluoride, method development work showed that use of a dynamic spiking procedure was necessary to accurately reflect sampling conditions (i.e., to generate field spikes) for sulfuryl fluoride in ambient air. The dynamic spiking system mixes a known volume of standard gas, from a certified gas standard, with ambient air prior to passing into the sampling cartridge. Thus, a known concentration of sulfuryl fluoride in ambient air is generated that can be sampled through a charcoal cartridge for the sampling duration and at the sampling flow rate used for fumigation tests. However, it is not generally feasible to run the dynamic field spike procedure at the application test sites. For this test, two 24-hour "dynamic" field spikes were generated at the ARB's 13th and T Street facility during the time period that the test in Loomis was being conducted. The first field spike was collected from 6/29/04 to 6/30/04 and the second from 6/30/04 to 7/1/04.

The concentration of the sulfuryl fluoride gas standard used was 137,400 micrograms per cubic meter (ug/m^3)(33.0 ppmv; Scott Marrin, 3/21/01, $\pm$2%). By adding two sccpm of standard gas into 48 sccpm of ambient air for a total sampling flow rate of 50 sccpm, the resulting sulfuryl fluoride concentration was 5,496 ug/m^3 (2/50 x 137,400 ug/m^3 = 5,496 ug/m^3). The expected amount of sulfuryl fluoride spiked onto the cartridge using this approach for a 24-hour sample was 396 ug.

The average recovery of the two field spikes was 83 percent. The field spike results are consistent with the lab and trip spike results and indicate that the sampling, sample transport, storage and analytical procedures used in this study produce acceptable results for sulfuryl fluoride.

Chloropicrin: The chloropicrin laboratory, trip, and field spike results for the fumigation study are listed in Tables 14, 15, and 16, respectively. Each of the spike cartridges was spiked with 228 ng/sample of chloropicrin. Two of the field spikes were collected at the test site and two were collected at the same time as the dynamic spikes collected for sulfuryl fluoride at the ARB 13th and T Street facility. The field spike results are consistent with the lab and trip spike results and indicate that the sampling, sample transport, storage and analytical procedures used in this study produce acceptable results for chloropicrin.

D. Breakthrough

The following is in reference to the evaluation of samples collected in the field for breakthrough. See laboratory reports in Appendix for additional details.

Sulfuryl Fluoride: All samples collected during period five (mechanical vent), which included samples 67 through 98, were evaluated for breakthrough. These samples were collected using two charcoal tubes in series. The primary beds of the front and back tubes were analyzed and none of the back tube primary beds had quantifiable levels of sulfuryl fluoride. For those samples that had quantifiable levels in the primary bed in the front tube, the secondary bed in the front tube was analyzed and no quantifiable sulfuryl fluoride was detected. In addition, the secondary bed of a select group of samples other than those in period five (i.e., samples 28, 41, 55, and 56) were analyzed and found to have no quantifiable amounts of sulfuryl fluoride. These results indicate that breakthrough was not a problem in this study.

Chloropicrin: A total of 132 application samples were analyzed for chloropicrin. Two samples (29 and 30) were found to have levels beyond the high calibration point of the analytical instruments. The back sections of these collection tubes were analyzed to determine if breakthrough had occurred. Chloropicrin was not detected in either back section of the samples 29 and 30. The chloropicrin levels in the field samples, together with the evaluation of the back sections of samples 29 and 30, indicate that breakthrough was not a problem in this study.

Figure 1
Loomis Fumigation Site Map

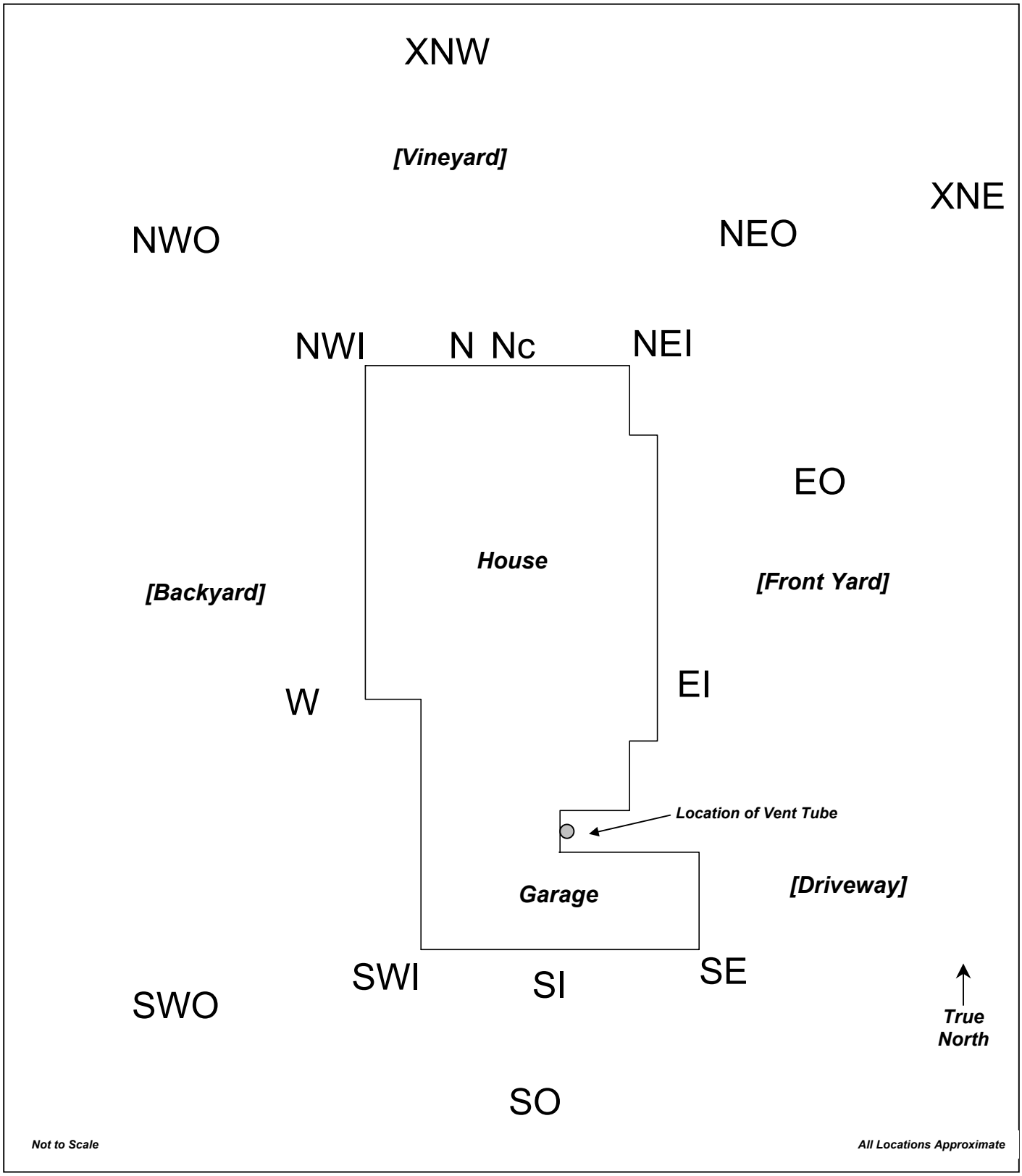

Figure 2
Loomis Fumigation Site Diagram

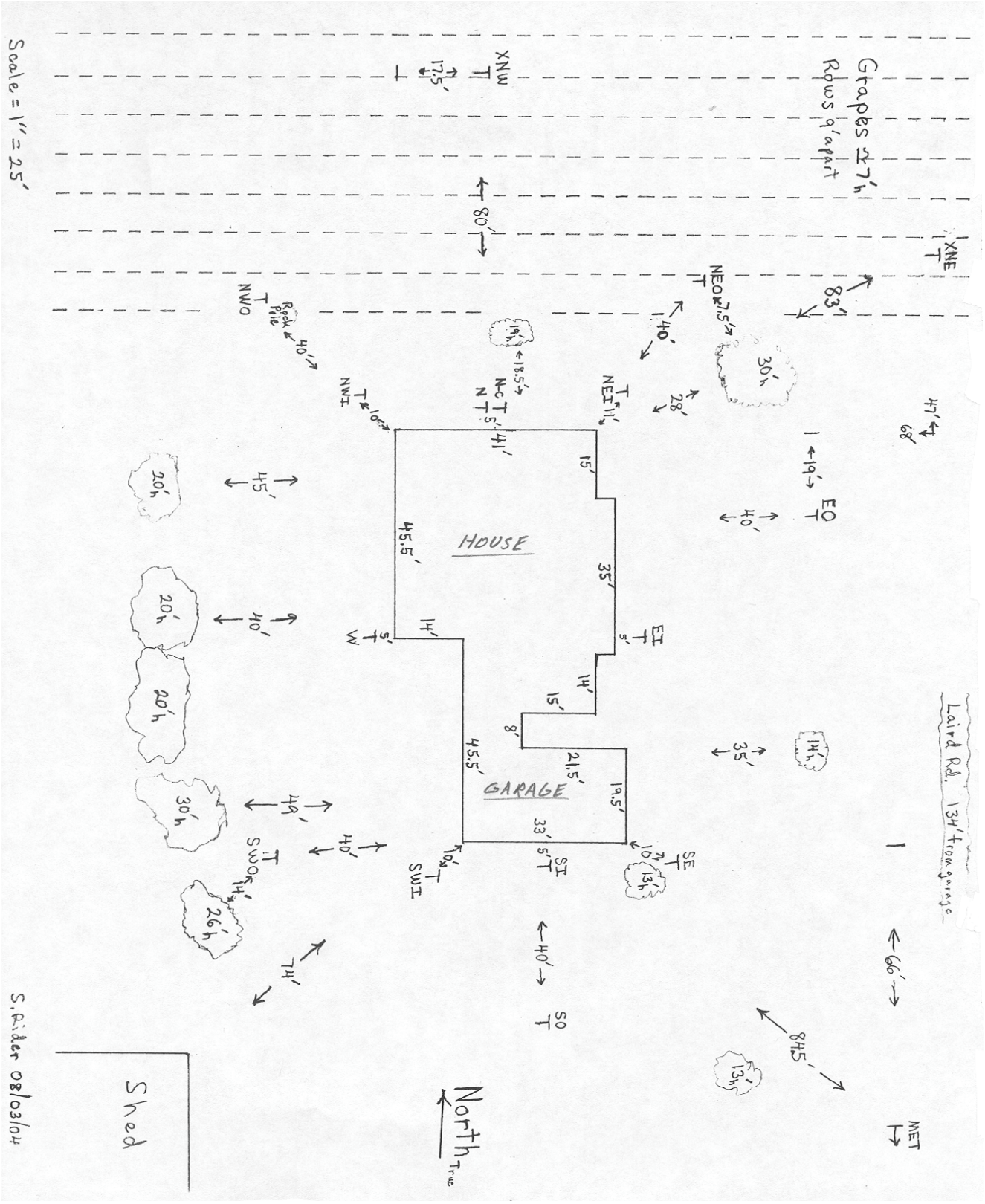

Figure 3
Cartridge Sampling Manifolds