

AMBIENT AIR MONITORING FOR PESTICIDES IN
LOMPOC, CALIFORNIA

VOLUME 2: FUMIGANTS

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By

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ABSTRACT

Lompoc is a small city located in a coastal valley of Santa Barbara County, California, with agricultural fields located in the area between Lompoc and the coast. As with most California coastal valleys, the area is cool with frequent fog or low cloudiness, and winds are predominantly from the west or northwest; Lompoc is downwind from the agricultural area. The Department of Pesticide Regulation (DPR) conducted air monitoring in Lompoc to determine whether, and in what amounts, fumigant pesticides occur in air in residential areas of the city. Three fumigant pesticides are used in the Lompoc area: chloropicrin, methyl bromide, and methyl isothiocyanate (MITC, breakdown product of metam-sodium and metam-potassium).

DPR monitored five locations, including two schools in Lompoc, primarily choosing higher-risk sites based on their proximity to agricultural areas. The monitoring plan targeted selected applications, specifically large fumigations in close proximity to Lompoc. DPR monitored six MITC fumigations, and two methyl bromide/chloropicrin fumigations during 2000. For each of the fumigations, DPR monitored for a 72-hour period beginning with the start of fumigation. The 72-hour monitoring period consisted of six alternating 8-hour (day) and 16-hour (night) sequential samples.

The highest concentration of MITC in any sample, 1885 ng/m³, did not exceed the acute health screening level of 66,000 ng/m³. The highest 72-hour air concentration for MITC, 743 ng/m³, did not exceed the subchronic health screening level of 3,000 ng/m³. The highest average MITC concentration (among the five monitoring sites) for all six fumigations combined, 244 ng/m³, did not exceed the chronic health screening level of 300 ng/m³. Only trace levels of methyl bromide were detected and no chloropicrin was detected.

The weather during some of the monitoring was atypical because the fumigations occurred just before or just after storms. Air concentrations for the storm-related fumigations are likely lower than if they had occurred during normal weather conditions because of differences in wind direction. The largest MITC fumigation monitored had normal weather conditions.

Historical pesticide use data indicates that the acute risk for MITC is likely higher than documented here because a few days not monitored have greater amounts applied. Between 1996 and 2000, the highest amount of metam reported for any day was 18,626 pounds, compared to 5,104 pounds on a single day during this study. Since the highest air concentration measured was only three percent of the acute screening level, it's unlikely that MITC air concentrations from fumigations not monitored exceed the acute screening level.

This study may overestimate the subchronic and chronic risk for MITC for several reasons. First, high air concentrations for short periods of time are used to represent longer time periods. A 72-hour air concentration is used to represent a 30 to 90-day subchronic exposure and an 18-day air concentration is used to represent a one-year chronic exposure. In addition, the three-day period chosen for subchronic exposure and 18-day period chosen for chronic exposure are likely among the highest periods between 1996 and 2000.

PREFACE

This report is the second of three volumes describing air monitoring for pesticides in Lompoc, California. Volume 1 is the executive summary. Volume 2 describes air monitoring for individual fumigant pesticides. Volume 3 describes air monitoring for multiple pesticides simultaneously.

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GLOSSARY

Acute: Short term exposure. Acute toxicity can be defined as the toxicity manifested within a relatively short time interval. Acute exposure can be as short as a few minutes or as long as a few days, but is generally not longer than one day. In toxicity testing, exposure is usually for 24 hours or less.

APCD: Air Pollution Control District

ARB: California Air Resources Board

Breakthrough: The desorption and loss of an analyte trapped on sampling media due to too large of a volume of air moving over the sampling media.

Canister: A stainless steel container that has been purged and evacuated with a vacuum pump. The canister is equipped with a flow controller set to fill the canister with ambient air over a set period of time.

Chemigation: The application of pesticides using an irrigation system.

Chronic: Long term exposure. Chronic exposure is generally for a significant portion of an animal's lifetime. Exposure may be through repeated single doses or may be continuous (e.g., food, air, or drinking water).

Concentration: The amount of a chemical in a given amount of air. Concentrations in air can be expressed in units of volume or weight.

Concentration Units and Conversion Factors: These units are all ratios or proportions and refer to the amount of a chemical in a volume of air. Concentrations are expressed as nanograms per cubic meter (ng/m^3). This unit refers to the weight in nanograms of a pesticide contained in one cubic meter of air. A nanogram is one-billionth of a gram.

Confirmation sample: Same as a duplicate sample, but is sent to a different lab for analysis.

DHS: California Department of Health Services

DPR: California Department of Pesticide Regulation

DQO: Data Quality Objectives.

Duplicate sample: Same as a primary sample, but is run on a collocated sampler as a replicate.

Emission Rate: The amount of the chemical (MITC in this study) that volatilizes out of the ground and enters the atmosphere. Expressed in units of mass per area per time ($\text{ug}/\text{m}^2/\text{second}$). Same as flux.

EQL: Similar to detection limit, the Estimated Quantitation Limit is the smallest amount of the chemical that can be measured. Samples with concentrations less than the quantitation limit, but more than detection limit can be identified as containing a trace amount of the analyte, but the concentration cannot be measured reliably with the method employed. When calculating average concentrations or other statistics, samples with a trace concentration are normally assumed to have a concentration of the midpoint between the detection limit and the quantitation limit. As with the detection limit, the quantitation limit is a characteristic of both the method and the chemical. Different methods can have different quantitation limits for the same chemical. The same method can have different quantitation limits for different chemicals.

Exposure: Contact with a chemical. Some common routes of exposure are dermal (skin), oral (by mouth) and inhalation (breathing).

Field Blank: A sample tube broken, capped, covered with foil and left out beside sampler for a single sampling interval, and stored on dry ice with the rest of the samples. The purpose of the field blank is to determine if the field or sample transporting procedures may have contaminated the sample

FFDCA: Federal Food, Drug, and Cosmetic Act

FIFRA: Federal Insecticide, Fungicide, and Rodenticide Act

Flux: the amount of the chemical (MITC in this study) that comes out of the ground and enters the atmosphere. Expressed in units of mass per area per time ($\mu\text{g}/\text{m}^2/\text{second}$). Same as emission rate.

Fortified sample: A sample with a known amount of analyte spiked onto the sample media which is placed next to primary sample and treated to same flow and run time. The fortified spike, in comparison with trip spikes and the respective field sample, provides some information about any change in the ability to recover the analyte during air sampling.

FQPA: Food Quality Protection Act

Half-life: The time it takes for an amount of a compound to be reduced by half through degradation or movement off-site.

HQ: Hazard Quotient. The ratio of an exposure level for a chemical (measured air concentration of a fumigant pesticide) to a reference concentration for the chemical (screening level for that fumigant pesticide) over the same time period. In this case,

$$\text{Hazard Quotient} = \frac{\text{Air Concentration Detected}}{\text{Screening Level}}$$

LIWG: Lompoc Interagency Work Group

LOAEL: Lowest Observed Adverse Effect Level. In a toxicity study, the LOAEL is the lowest dose level that still produces an observable adverse effect.

MDL: The method detection limit is the smallest amount of the chemical that can be identified in a sample with the method employed. If the sample contains no analyte, or may contain the analyte at a concentration less than the detection limit, the sample is designated as containing no detectable amount. When calculating average concentrations or other statistics, samples with no detectable amount are normally assumed to have a concentration of one-half the detection limit. The detection limit is a characteristic of both the method and the chemical. Different methods can have different detection limits for the same chemical. The same method can have different detection limits for different chemicals.

MITC: Methyl isothiocyanate

NOAEL: No Observed Adverse Effect Level. In a toxicity study, the NOAEL is the highest dose level that does not produce an observable adverse effect.

NOI: Notice of Intent. Document submitted to the County Department of Agriculture with information regarding a proposed pesticide application.

ND: None detected. Concentration is below the method detection limit (MDL).

OEHHA: California Office of Environmental Health Hazard Assessment

Primary sample: Sample collected in field to measure fumigant air concentrations.

Public Land Survey System (PLSS)

Section - Basic unit of the system, a square tract of land one mile by one mile containing 640 acres.

Township - 36 sections arranged in a 6 by 6 array, measuring 6 miles by 6 miles. Sections are numbered beginning with the northeast-most section, proceeding west to 6, then south along the west edge of the township and to the east.

Range - Assigned to a township by measuring east or west of a Meridian

Range Lines - North to south lines that mark township boundaries

Township Lines - East to west lines that mark township boundaries

Meridian - Reference or beginning point for measuring east or west ranges. All townships in Lompoc use the San Bernardino Meridian.

Baseline - Reference or beginning point for measuring north or south townships. All townships in Lompoc use the San Bernardino Baseline.

A specific township and section are identified as being north or south of a particular baseline and east or west of a particular principal meridian. For example, township S07N35W is the seventh township north of the San Bernardino baseline in the thirty-fifth range west of the San Bernardino meridian. This particular 36 square-mile area is located west of Lompoc. S07N35W36 is section 36 in this township, a one by one mile area in the southeast corner of the township.

PUR: Pesticide Use Report. California's reporting system that records all agricultural pesticide use in the state.

Range: see Public Land Survey System.

RCD: Risk Characterization Document. DPR's human health risk assessment for a pesticide is presented in the RCD.

RED: Reevaluation Eligibility Document. U.S. EPA's human health risk assessment for a pesticide is presented as part of their RED.

Regression statistics for modeled concentrations:

Linear regression - A line describing the association between two variables (in this case the modeled and measured concentrations), that when graphed, produces a straight line.

r^2 - A measure of the closeness of fit of a graph to its regression line, ranging from zero to one, and a r^2 of one is a perfect fit.

P value - The probability of wrongly rejecting the null hypothesis (that there is no association) when it is true. If the p-value is small (typically, less than 0.05), then the result is said to be statistically significant.

RfD: Reference Dose. The RfD is an estimate of the daily exposure, usually by the oral route, of a chemical to the human population that is likely to be without adverse effects. Initially the term was only used to address chronic exposures, but it is now often used for other exposure lengths. When it is used for exposure lengths other than chronic, that exposure is specified (e.g. "subchronic RfD").

RfC: Reference concentration. The RfC is an estimate of the daily air concentration of a chemical to which the human population can be exposed that is likely to be without adverse effects. Initially the term was only used to address chronic exposures, but it is now often used for other exposure lengths. When it is used for exposure lengths other than chronic, that exposure is specified (e.g. "subchronic RfC").

Risk: Risk is the probability that a toxic effect (adverse health effect) will result from a given exposure to a chemical. It is a function of both the inherent toxicity of the chemical as well as the exposure to the chemical.

Screening Level: Air concentration used to evaluate the possible health effects of exposure to a chemical, based on a chemical's toxicity. Although not a regulatory standard, screening levels can be used in the process of evaluating the air monitoring results. A measured air level that is below the screening level for a given pesticide would not be considered to represent a significant health concern and would not generally undergo further evaluation, but also should not automatically be considered "safe" and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further and more refined evaluation. Different screening levels are determined for different exposure periods (i.e., acute and subchronic)

Section: see Public Land Survey System.

Significant Health Concern: A level of concern regarding health effects that would prompt the consideration of additional regulatory measures.

SOP: Standard Operating Procedure. A document describing the materials and methods used for various monitoring tasks.

Sorbent tube: A glass tube filled with a measured amount of trapping media and sealed. The tube is attached to an air pump and ambient air is drawn through the trapping media in the tube.

Subchronic: Intermediate or medium term. Subchronic exposure is generally for an intermediate, but not significant, portion of an animal's lifetime (e.g., 30 to 90 days). Exposure may be through repeated single doses or may be continuous (e.g., food, air, or drinking water).

TAG: Technical Advisory Group. A subcommittee of the Lompoc Interagency Work Group responsible for planning and evaluating pesticide monitoring.

Tolerance Limit: An estimate of the uncertainty associated with a percentile, the 95th percentile for this study. A tolerance limit expresses the confidence in a percentile estimate, the 90 percent confidence of the 95th percentile for this study.

Township: see Public Land Survey System.

Trip Blank sample: A sample tube broken, capped and stored on dry ice with the rest of the samples. The purpose of the trip blank is to determine if the field or sample transporting or storage procedures may have contaminated the sample.

Trip Spike sample: A sample with a known amount of analyte spiked onto the sample media which is sent with the field technician but stays in an ice chest on dry ice for the duration of the monitoring period. The trip spikes gives some information about any loss or change in the ability to recover the analyte during sample transport or storage.

Units of measurement:

g: Gram. $1 \text{ g} = 1,000 \text{ mg}$

Kg: Kilogram. $1 \text{ Kg} = 1,000 \text{ grams}$

L: Liter.

m: Meter

m^3 : Cubic meter. $1 \text{ m}^3 = 1,000 \text{ L}$

mg: Milligram. $1 \text{ mg} = 1,000 \text{ ug}$

ng: Nanogram.

ppb: Parts per billion.

ppm: Parts per million.

ug: Microgram. $1 \text{ ug} = 1,000 \text{ ng}$

UPS: United Parcel Service

U.S. EPA: United States Environmental Protection Agency

INTRODUCTION

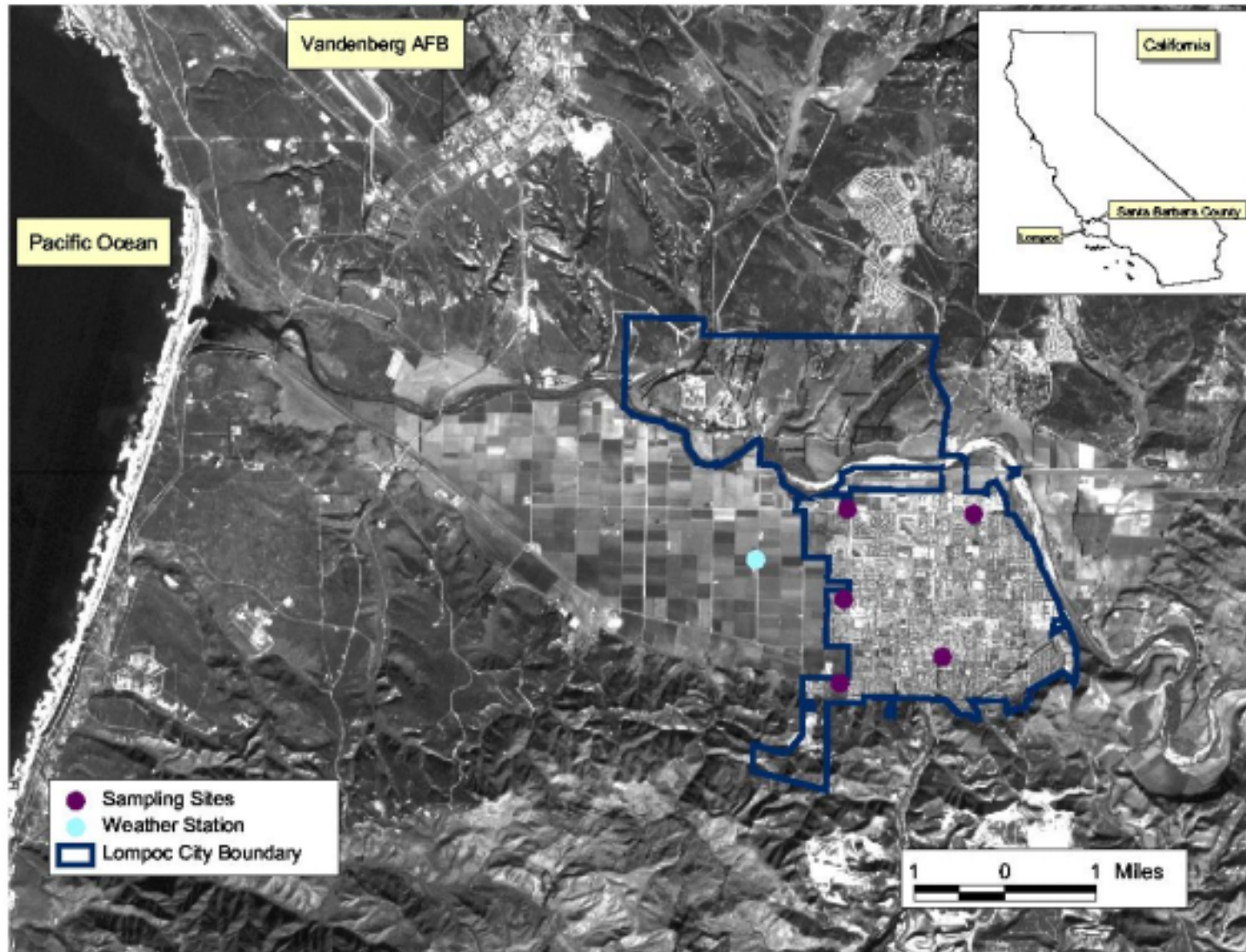
Lompoc is a small city located in a coastal valley of Santa Barbara County, California (Figure 1). The population has been estimated at 41,103 in a U.S. Census conducted in 2000. The city is located approximately seven to eight miles east of the coastline. The valley is oriented roughly northwest to southeast and the surrounding hills form a V shape fanning out towards the ocean. Hills to the east of Lompoc tend to stall air movement as it passes the city, while the air is funneled eastward through the Santa Ynez River basin. Vandenberg Air Force Base (a rocket launch facility) and agricultural fields dominate the area between Lompoc and the coast. Five major crops or crop groups are grown in this area: cole crops (broccoli, cabbage, and cauliflower), lettuce, dried beans, celery, and flowers.

In 1997, the Department of Pesticide Regulation (DPR) formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns (first voiced in 1992) about pesticide use as it relates to community health. The LIWG is composed of staff from federal, state, county and city agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air-monitoring program, and to consider potential exposures from other environmental factors, such as crystalline silica and radon.

The health subgroup of the LIWG analyzed hospital discharge data to determine if there was an increased incidence of specific illnesses in Lompoc compared to other areas. The data from 1991-1994 evaluated by the State's Office of Environmental Health Hazard Assessment (OEHHA) suggests that certain respiratory illnesses occur in Lompoc at higher rates than in other comparison areas. (Wisniewski et al., 1998; Ames and Wisniewski, 1999). The evaluation indicated that the proportion of hospitalizations due to respiratory illnesses, in particular bronchitis and asthma, were elevated in Lompoc relative to the proportion of hospitalizations in the comparison areas, with some differences by age. The incidence of lung and bronchus cancers also was increased above the expected numbers based on regional rates. The purpose of the report was not to speculate on the cause of the illnesses; rather, it was to evaluate the incidence of specific illnesses.

The pesticide exposure subgroup (now called the Technical Advisory Group [TAG]) developed a work plan that recommended comprehensive air monitoring in Lompoc during various seasons to determine whether, and in what amounts, pesticides occur in air in residential areas within the city of Lompoc. The Technical Advisory Group (Appendix A) developed a list of priority pesticides based on their toxicity, use, and volatility. The TAG recommended a comprehensive monitoring program to span peak use periods for the top 23 chemicals (on their list of 46) in a two-phase program. The TAG did not recommend monitoring the remaining 23 pesticides from the original list of 46 because fiscal resources were limited. The first phase of monitoring was recommended for the summer of 1998 (if only partial funding was available), and the second phase for early summer of 1999 (Appendix B). The monitoring recommendation was designed to measure maximum daily pesticide concentrations in air that could be compared to human health "screening levels". The LIWG accepted the TAG recommendations and forwarded them to DPR in April 1998.

Figure 1. Location of Lompoc sampling sites and weather station for fumigant monitoring.



In August 1998, the Legislature passed Senate Bill 661, which provided funding to DPR to conduct the first phase of pesticide air monitoring. The first phase of monitoring was completed in September 1998. The Phase One study was intended to test pesticide sampling and analysis methods and to determine if a subset of the total pesticides used in the area could be measured in air. With some exceptions, these goals were achieved. The study was most successful in developing and demonstrating the multiple-pesticide sampling and analysis method. Due to the limited nature of the Phase One sampling, these results are not appropriate for risk assessment. During phase one both methyl bromide and MITC, the biologically-active breakdown product of metam-sodium, were monitored. The results are considered invalid due to poor sample handling practices and insufficient quality assurance/quality control of the samples.

In May 1999, DPR received a grant from the U.S. Environmental Protection Agency (U.S. EPA) to monitor fumigant applications in the Lompoc area during fall and winter months. Fumigants are a unique class of pesticides. They are highly volatile, applied infrequently, but at higher rates than other pesticides (50 to 400 pounds per acre), and used to control a wide variety of pests and diseases. This document describes the monitoring conducted during the winter months of January - February 2000 and the fall months of October - November 2000 in accordance with the Fumigant Sampling and Analysis Plan (FSAP, Appendix C).

Ambient air concentrations of fumigants were measured within the city of Lompoc during pesticide application events and compared with their respective screening levels. Since screening levels were not available from the U.S. Environmental Protection Agency (U.S. EPA) or OEHHA, who typically generate enforceable human health standards, levels were developed by DPR in consultation with members of the TAG. Screening levels are not equivalent to human health standards and cannot be interpreted as such. The purpose of the monitoring study is to determine what concentrations of the fumigants the people of the city of Lompoc are exposed.

PESTICIDES AND AREA MONITORED

Pesticides Monitored

The pesticides monitored are the fumigants chloropicrin, methyl bromide, and methyl isothiocyanate (MITC), the biologically active breakdown product of metam-sodium and metam-potassium. The degradation rates (half-lives) and potential breakdown products for each are located in Table 1.

MITC is the biologically active product for soil fumigations. Field research has demonstrated that 87 percent to 95 percent of the applied metam-sodium degrades to MITC in various soils; metam-potassium is expected to have similar degradation properties (Smelt et al., 1989; Burnett and Tambling, 1986; Gerstl et al., 1977; Leistra et al., 1974; Leistra, 1974; Smelt and Leistra, 1974; Turner and Corden, 1963). The conversion exhibited a half-life of less than 30 minutes to seven hours, and varied with soil conditions. Depending on conditions present, the

degradation of metam-sodium may also result in release of methyl isocyanate, methylamine, carbon disulfide, sulfur, and hydrogen sulfide. However, due to budgetary constraints, air measurement of additional degradation products could not be addressed in this study.

Table 1. Some physical and chemical properties and breakdown products of fumigants monitored in Lompoc during January through November 2000. All data are from the DPR's Pesticide Chemistry Database, except where indicated.

Analyte	Molecular weight	Solubility ^a in water (mg/L)	Vapor Pressure (mm Hg)	Hydrolysis Half-life (days)	Aerobic Soil Half-life (days)	Photolysis Half-life (days)
Chloropicrin	164.4	2000	23.5, 25 °C	354, pH 7, 25 °C	0.4 - 5.1	1.3 ^d to 20 ^e
MITC	73.12	8610	16, 25 °C	20.4, pH 7, 25 °C	0.5 - 50 ^b	1.1 ^c
Methyl Bromide	94.95	1380	1420, 20 °C	17, pH 8, 25 °C	1.5 - 20	NA

NA = Not applicable. The UV absorption spectra for methyl bromide are below the shortest wavelengths reaching the earth's surface (DowELANCO Study 63792, DPR Library Number 50046-33; Honaganahalli and Seiber, 1997)

^a 25° C

^b Smelt et al., 1989

^c Wales, 2002

^d Wihelm et al., 1997

^e Moilanen et al., 1978

Fumigants are used to treat soil before planting. Most fumigants are injected into the soil with specialized tractor equipment. Fumigants can also be mixed with water and applied through irrigation systems (chemigation). In the Lompoc area, methyl bromide and chloropicrin are usually injected into the soil approximately one foot deep with tractors, and the fumigated soil is covered with plastic tarpaulins to retard volatilization. MITC in the Lompoc area is usually applied through drip irrigation systems.

Pesticide Use

The information regarding amounts of pesticides applied was extracted from DPR's pesticide use report database (PUR). The PUR is the repository for California pesticide use data that has collected data for over 50 years. The current PUR system started in 1990. The PUR contains information on nearly all production agricultural pesticide use and some nonagricultural use in California. The data collected include the pesticide product used, the date it was applied, the amount applied, and application location to a square-mile section. A complete description of the PUR is given in DPR, 1995.

Between 1996 and 1999, in the Lompoc Valley there were 113 applications of the fumigant metam-sodium, 21 of methyl bromide/chloropicrin, and one of 1,3-dichloropropene, compared to approximately 2300 applications for the insecticide chlorpyrifos (DPR 1996,

1997, 1998, 1999, 2000). However, the 135 fumigant applications accounted for almost 221,700 pounds of the 567,000 total pounds of pesticides. In 2000, there were 36 applications of the fumigant metam-sodium, eight methyl bromide/chloropicrin, nine applications of metam-potassium, and none of 1,3-dichloropropene. The 53 fumigant applications made up nearly 155,100 pound of the 233,800 total pound of pesticides. Fumigants are applied prior to planting. Therefore, many applications occur during the fall and winter (Tables 2 and 3). In the Lompoc area, most fumigants are either injected below the soil surface or through drip irrigation systems. Because of their high volatility and high application rates, fumigants are the focus of the monitoring described here. Applications of metam-sodium, metam-potassium, and methyl bromide/chloropicrin were monitored. There were no applications of 1,3-dichloropropene during the study.

Table 2. Fumigants Used for Agricultural Production in the Lompoc Area, 1996 - 2000.

Chemical	Pounds	Acres	Applications	Year	Number of Days	Highest Day
1,3-dichloropropene	5850	19	1	97	1	5850
Chloropicrin	9.3	2	1	96	1	9.3
Chloropicrin	91.1	7	3	97	3	87.5
Chloropicrin	4050	54	4	98	4	2250
Chloropicrin	8711	168	11	99	8	2775
Chloropicrin	7578	108	8	00	6	2716
Metam-sodium	11251	216	19	96	15	4086
Metam-sodium	34126	484	32	97	30	3725
Metam-sodium	42724	398	31	98	25	10541
Metam-sodium	74910	410	31	99	31	18626
Metam-sodium	94536	445	39	00	38	7823
Methyl bromide	681	2	3	96	3	298
Methyl bromide	971	7	3	97	3	696
Methyl bromide	12150	54	4	98	4	6750
Methyl bromide	26175	168	11	99	8	8325
Methyl bromide	19648	108	8	00	6	5574
Metam-potassium	33929	138	8	00	7	9568
Total	377390	2788	217			

Table 3. Fumigants Used for Agricultural Production in the Lompoc Area by Month, 1996 – 2000 (pounds).

Month	1,3-Dichloro propene	Chloropicrin	Metam Sodium	Methyl Bromide	Metam Potassium	Total
January		0.1	23,868	208		24,076
February	5,850		7,538			13,388
March		4	13,638	883		14,525
April			20,309			20,309
May			33,514			33,514
June			28,126			28,126
July		2	32,744	299		33,045
August			10,626			10,626
September		8,421	19,079	25,264		52,764
October		8,760	30,920	26,325		66,005
November		3,244	19,321	3,601	9,065	35,231
December			11,236	3,044	30,908	45,188
Total	5,850	20,431	250,920	59,624		376,798

The locations (township, range, and sections) of fumigant use for 1996 through 2000, are displayed in Figures 2 through 5. The individual applications used to summarize these figures are listed in Appendix D.

Regulatory Requirements

The labels of all pesticides, including fumigants, have numerous use requirements such as methods of application, application rates, and protective equipment for applicators. In addition, California has statewide regulations regarding the use of methyl bromide that include notification requirements, buffer zones, methods of application, and worker safety requirements. The Santa Barbara Agricultural Commissioner also has local regulatory requirements for MITC, including a one-mile buffer zone between the treated area and occupied structures for MITC applied through sprinkler systems, and a 30-foot buffer zone when applied through drip irrigation systems.

Study Area

The sporadic timing of fumigant applications required that sampling be coordinated with actual applications. For the purpose of this study, the TAG recommended monitoring only applications made in the Lompoc Valley in the sections listed in Table 4 and Figure 6. In addition, metam-sodium fumigations of less than or equal to 150 pounds active ingredient, were not monitored. There were no pound limits for the other fumigants.

Figure 2. 1,3-Dichloropropene use reported from 1996 through 2000.

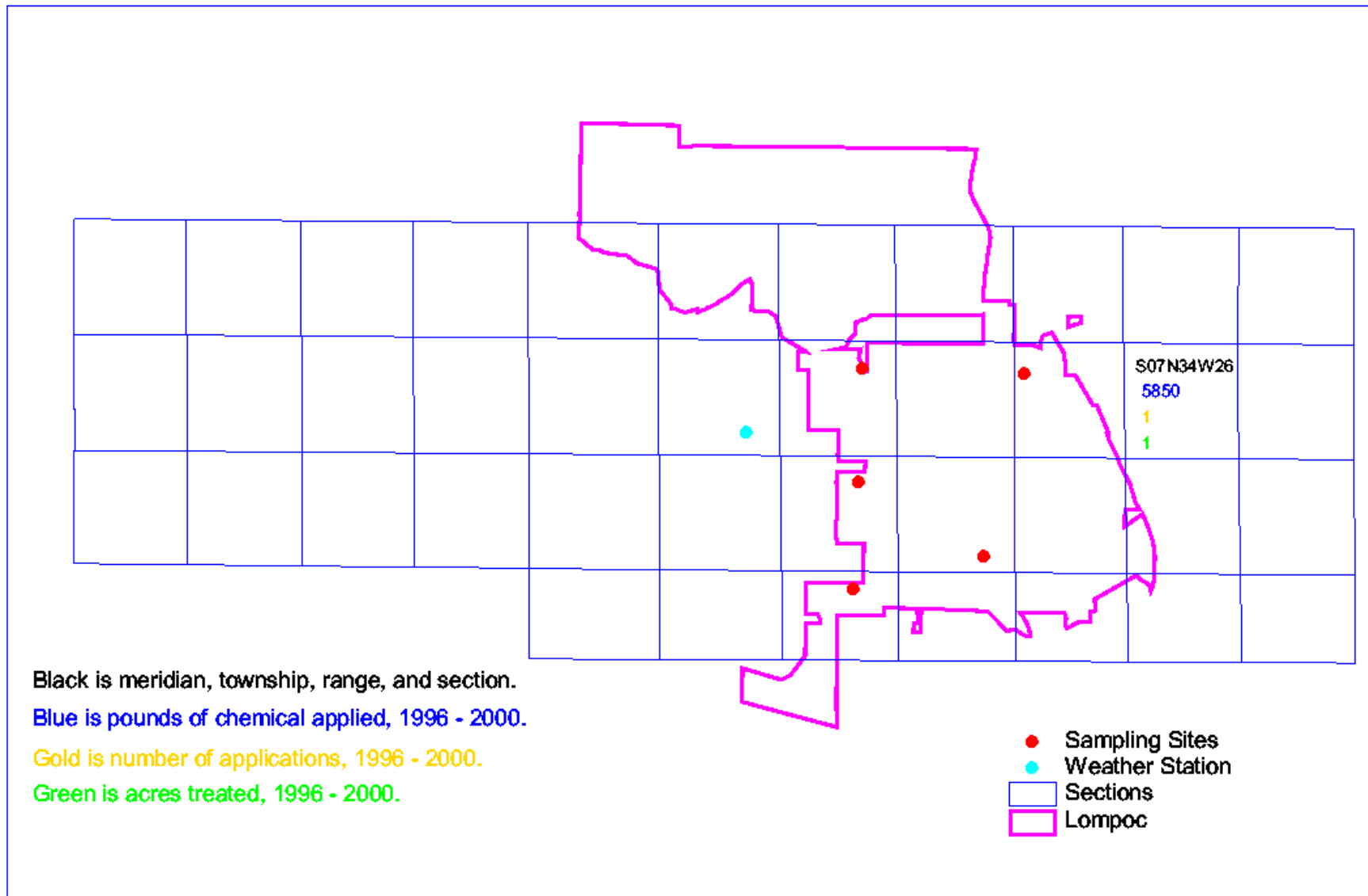


Figure 3. Chloropicrin use reported from 1996 through 2000.

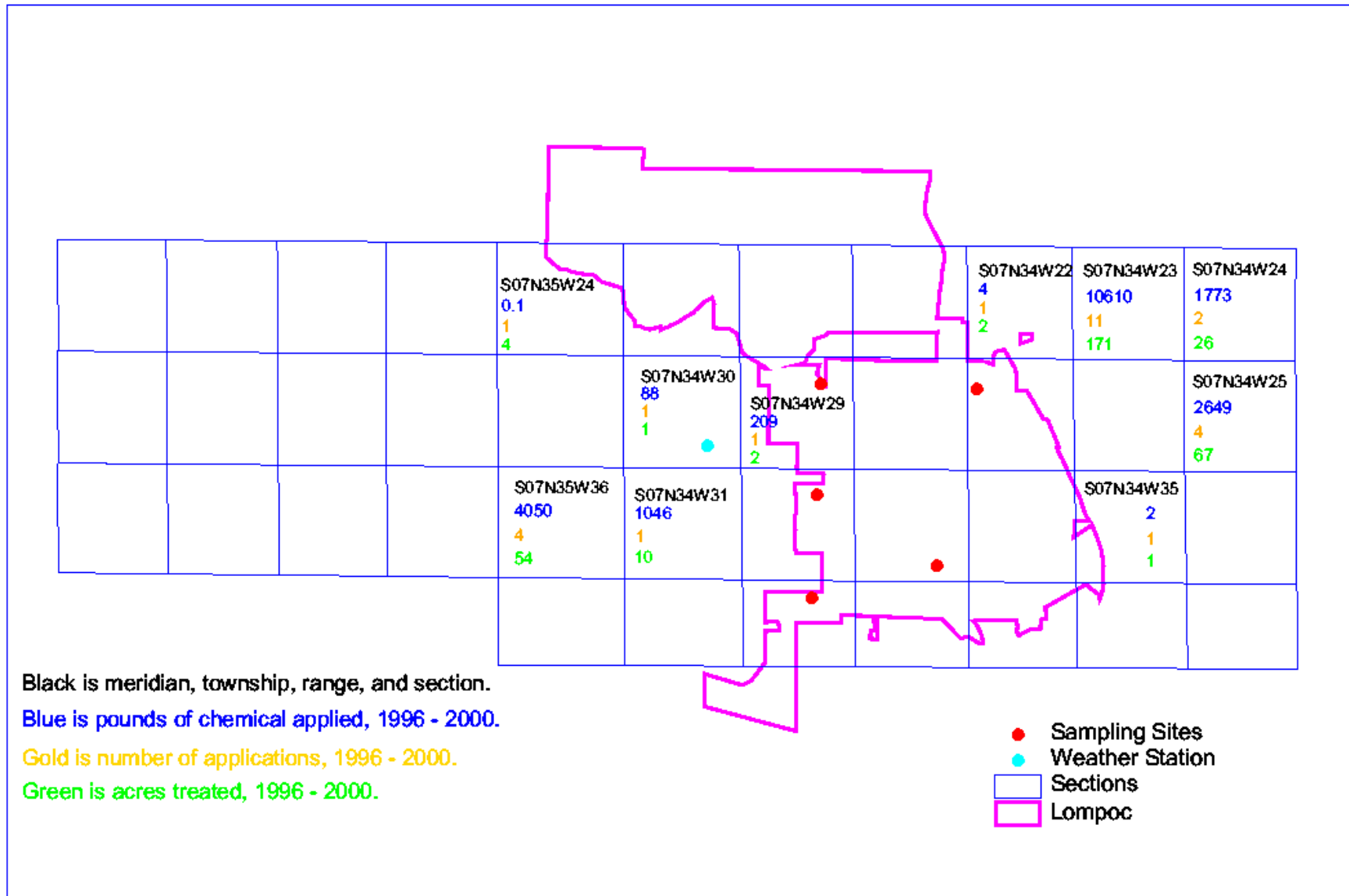


Figure 4. Metam sodium and metam potassium use reported from 1996 through 2000.

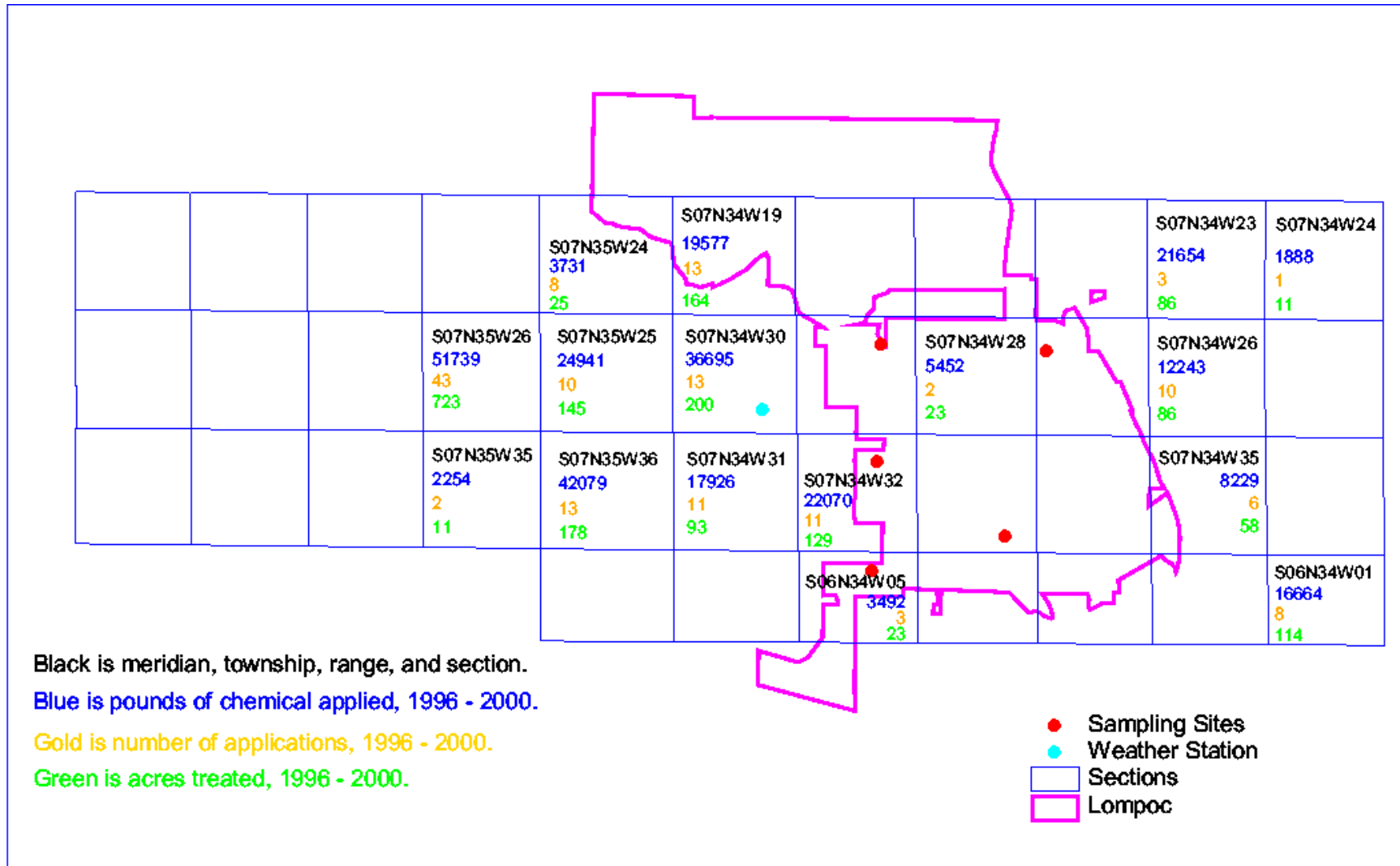


Figure 5. Methyl bromide use reported from 1996 through 2000.

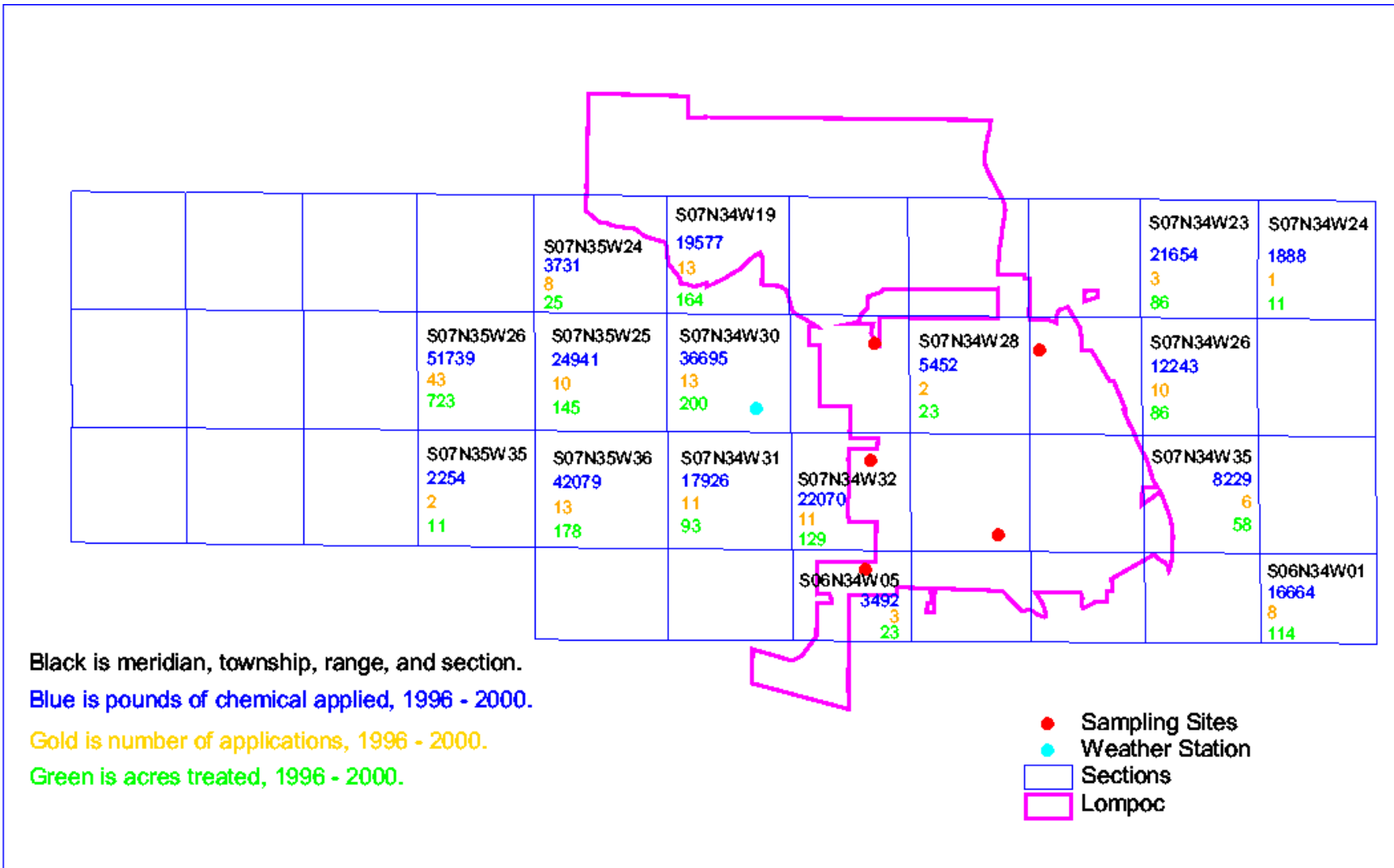
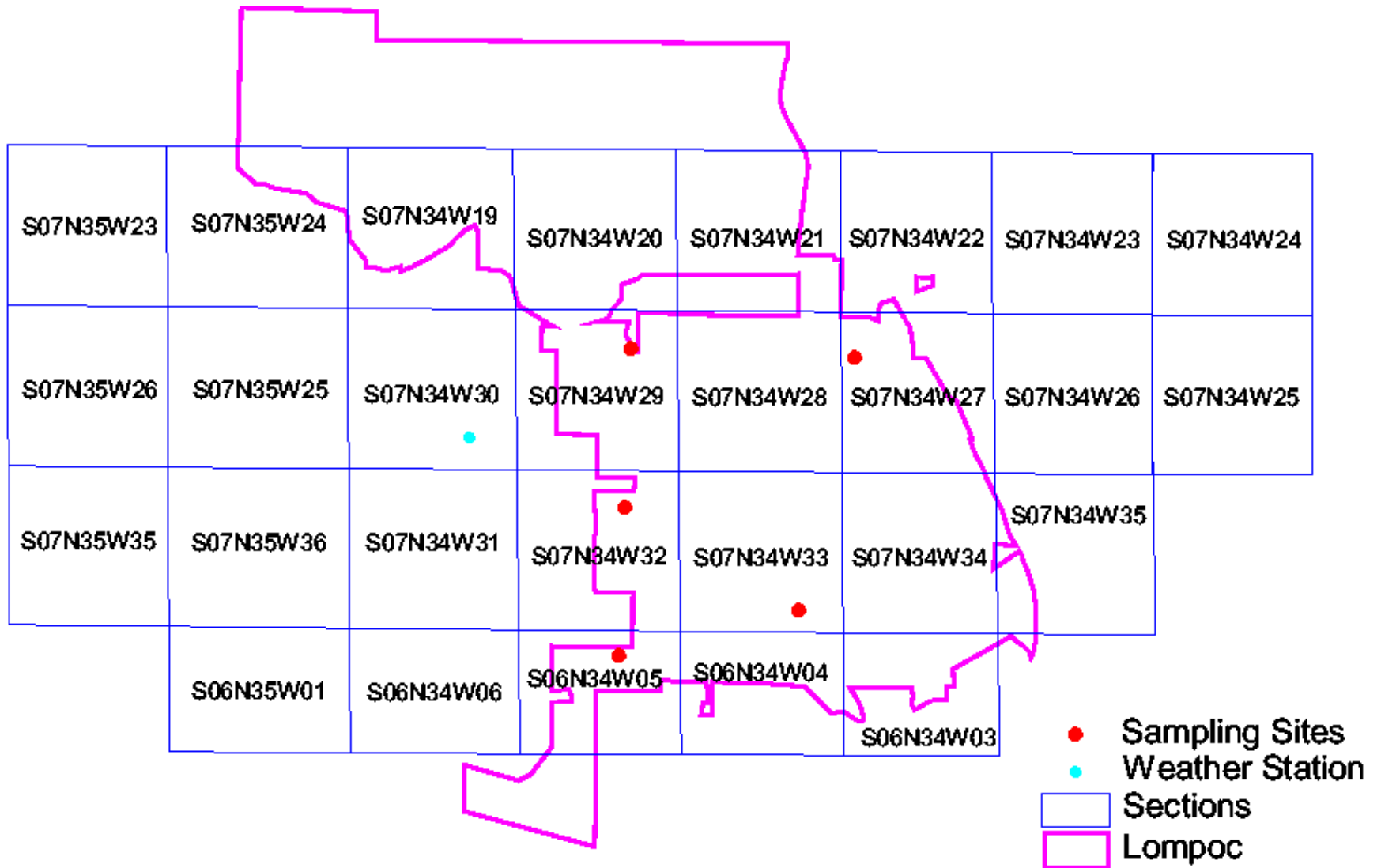


Table 4. Township, range and sections used to select applications for the Lompoc fumigant air monitoring study.^a

Meridian	Township	Range	Section
S	06N	34W	3
S	06N	34W	4
S	06N	34W	5
S	06N	34W	6
S	06N	35W	1
S	07N	34W	19
S	07N	34W	20
S	07N	34W	21
S	07N	34W	22
S	07N	34W	23
S	07N	34W	24
S	07N	34W	25
S	07N	34W	26
S	07N	34W	27
S	07N	34W	28
S	07N	34W	29
S	07N	34W	30
S	07N	34W	31
S	07N	34W	32
S	07N	34W	33
S	07N	34W	34
S	07N	34W	35
S	07N	35W	23
S	07N	35W	24
S	07N	35W	25
S	07N	35W	26
S	07N	35W	35
S	07N	35W	36

^a See Figure 6 for boundaries defined by the above Township-Range-Sections.

Figure 6. Township, range and sections used in selection of applications for the Lompoc fumigant air monitoring study.

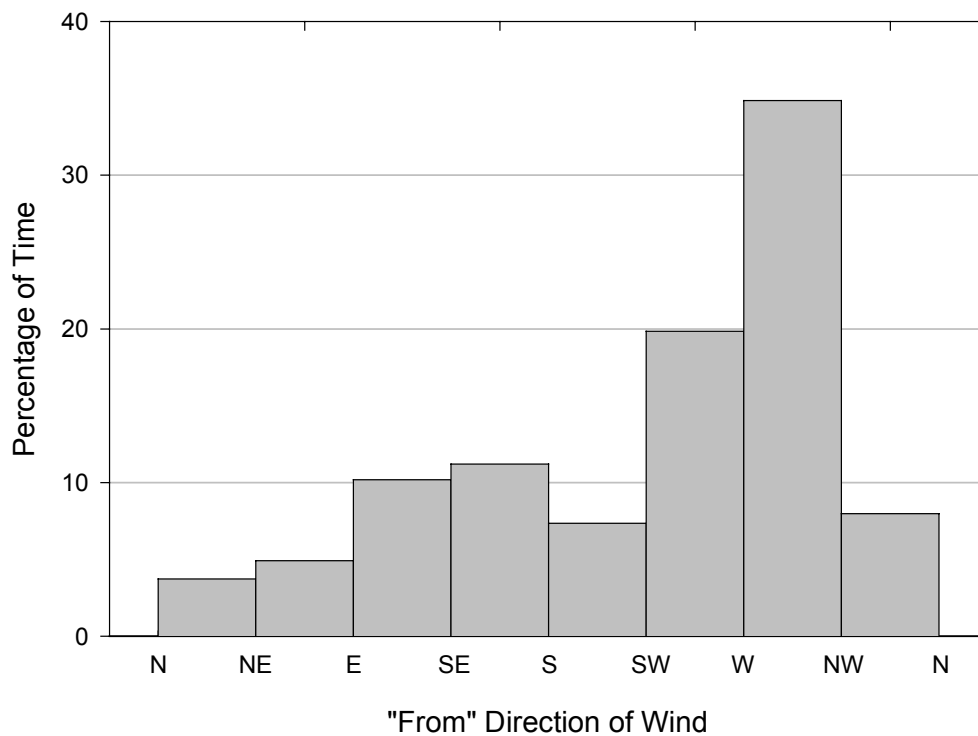


Sample Site Locations

In Phase One sampling, five sites were used to monitor air concentrations in Lompoc (Figure 1). In discussion with the TAG on October 26, 1999, a sampling plan was formulated based on study objectives and monetary constraints. The TAG decided to monitor the original five sites. The sites of primary concern were those along the western edge of the city due to proximity to the majority of the agriculture in the valley and the predominance of wind directions from the west and northwest. Historically, during the months of October through February, the winds are from a western direction just over 50 percent of the time (Figure 7).

The five sampling sites were located within the city limits of Lompoc, one each in the northwest, central-west, southwest, northeast, and near the center of Lompoc (Figures 1 and 6). The sites were selected based on siting criteria, access and security. The sites may not be representative of the areas of maximum concentrations in the community. All sample sites met the U.S. EPA siting criteria for ambient air monitoring sites (Appendix E). Samplers at all locations were on rooftops to ensure the security of the samples. The air column between 2 meters and 15 meters is considered to be uniform.

Figure 7. The percentage of time the wind blows from various directions during the months of October through February. Compiled from weather data collected during 1992-1995 at the H Street weather station located in downtown Lompoc



Locations:

- Northwest - Santa Barbara County Animal Control Shelter
1501 West Central Ave. at V St.
- West- Clarence Ruth School
501 North W St. at College Ave.
- Southwest- Miguelito School
1600 West Olive St. at V St.
- Central- Santa Barbara County APCD monitoring trailer
Between G and H Streets, ½ block south of Ocean Ave.
- Northeast- Lompoc School District Bus Garage
1313 North A St. at Central Ave.

MONITORING METHODS

The design for sample collection is a product of the data quality objectives (DQOs) process as well as a result of community and technical input from the TAG and LIWG. This section describes sampling methods and procedures, quality control and laboratory methods, the applications monitored and meteorological measurements.

Sampling Methods

The most widely used procedure for atmospheric measurement of pesticides is to pass air through a solid sorbent material onto which the pesticide is adsorbed. Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988; Baker, et al., 1996). In this study, sorbent tubes containing XAD resin, coconut charcoal, and petroleum charcoal were used to trap chloropicrin, MITC, and methyl bromide, respectively. The flow rates were set at 0.3, 1.0, and 0.015 L/min for chloropicrin, MITC, and methyl bromide, respectively (Table 5).

Canisters have been used as an alternative to solid sorbents for air sampling (Keith 1988). In addition, a study by Biermann and Barry (1999) indicated that methyl bromide recovery from canisters was significantly higher than recovery from sorbent tubes. The U.S. EPA TO-15 method for sampling methyl bromide and 1,3-dichloropropene in air using canisters is a validated and peer-reviewed method. For this reason, U.S. EPA staff recommended use of canisters for all fumigants to be monitored in this study. However, at this time, chemical analytical methods using canisters as the air sampling method are available for only three of the four fumigants (1,3-dichloropropene, MITC and methyl bromide). A method for chloropicrin was not available at this time. The number of canister samples collected was limited due to the availability of canisters. Canisters for MITC analysis were available only during the fall sampling period.

Based on historical information for each of the fumigants, the highest concentrations measured around treated fields tend to occur within three days of application (Beard et al., 1996; Ross et al., 1996; Beard, 1994; Fitzell, 1993). Therefore, the TAG recommended three days of monitoring in an attempt to capture the peak air concentrations to which residents of Lompoc might be exposed. Due to historical problems with sorbent tubes and breakthrough of some of the fumigants at long sampling intervals (greater than 12 hours), two samples were collected during a single 24-hour period to equate with the 24-hour screening level. In addition, flow rates were lowered to prevent breakthrough, yet not lowered too much so as to compromise the desired detection limits. In addition to lowering the flow rate, breakthrough problems with methyl bromide were alleviated by adding a secondary tube to the sampling train. Both the secondary and primary tubes were analyzed.

The samples were sent to a chemical laboratory for extraction and analysis. The field sampling protocol is located in Appendix F.

Prior to monitoring, sample labels with the study number and sample identification numbers were attached to the tubes and canisters. Chain of custody forms, log book forms, and sample analysis request forms were supplied to field sampling personnel. Preparation of sorbent tubes for use with air sampling pumps is described in DPR's SOP FSAI001.00 (Appendix G).

The sampling equipment was calibrated in the laboratory prior to delivery to the field. The use, operation, calibration and maintenance of air sampling pumps are described in DPR's SOP EQAI001.00 (Appendix G). The cleaning and certification of canisters for air sampling are described in U.S. EPA Region 9 Laboratory's SOP #312 (Appendix G).

The flow rate for each sampler was measured and recorded before and after each sampling interval. Flows were measured with a DryCal® Primary Flowmeters. All equipment was checked and initially calibrated in the laboratory. Any rotometer used was checked against a calibrator in the laboratory before use.

All sampling equipment and forms were placed in a rental storage locker in Lompoc for easy access for the duration of the study.

Sampling Procedure

For each fumigation event, a minimum of 30 samples (60 for methyl bromide) were collected (two samples per day x three days x five sites, and four samples per day x three days x five sites for methyl bromide). A total of six metam-sodium (or metam- potassium) applications and two methyl bromide/chloropicrin applications were monitored. There were no applications of 1,3-dichloropropene made during 2000. Air samples were run for consecutive eight- and 16-hour intervals during the course of a 24-hour period. The collection times were determined for safety reasons, which allowed for the change of air sampling tubes and canisters during daylight hours. The eight-hour daytime samples were started between 7:00 a.m. and 9:00 a.m. at the first site. The 16-hour nighttime samples were started between at 3:00 p.m. and 5:00 p.m. at the first site. The sequence of air sampling tube changes remained consistent throughout the three sampling days (72 hours of sampling). The site and time of

duplicate sampling, fortified sampling, and confirmation sampling was randomly assigned. The schedule for such sampling, as well as field sampling is located in Appendix F.

Timing of Monitoring

Because all of the fumigants monitored in this study are classified “restricted materials” (a classification that requires pesticide applicators to file a Notice of Intent [NOI] to apply with the county Department of Agriculture prior to pesticide use), the Santa Barbara County Department of Agriculture was able to contact sampling personnel upon notification of a fumigant application. Sampling usually began within 24 hours of notification by the Santa Barbara County Department of Agriculture and was scheduled to include the application time. For example, if field-sampling staff received notice on Tuesday that an application was to occur on Wednesday during the daytime, field sampling was begun between 7:00 and 8:00 a.m. on Wednesday. If field-sampling staff received notice on Saturday that an application was to occur Sunday night, monitoring was begun on Sunday between 3:00 and 4:00 p.m. In summary, monitoring commenced with the daytime or nighttime period during which the application was scheduled to occur. After each application, personnel from the Santa Barbara County Department of Agriculture contacted the applicator to confirm the time and completion of the application

Sample Handling

Samples were collected using the methods described in the previous section and shipped via United Parcel Service (UPS) overnight or delivered to the laboratories by the field personnel. The samples were packaged and shipped according to procedures in DPR’s SOP QAQC004.1 (Appendix G). Each shipment of samples was accompanied by a temperature data-logger that recorded sample temperatures from collection to delivery to the lab as described in DPR’s SOP EQOT001.01 (Appendix G). Samples were shipped or delivered as soon as possible after final sample collection for each fumigation event.

Field personnel delivered most samples to the laboratories, and no problems were reported with sample shipment. Each sample was accompanied by chain of custody record that was signed by each person handling the sample. All samples followed sample receipt log-in and verification procedures described in Appendix H.

Quality Control Methods

During each of the first four metam-sodium applications, two duplicate (collocated) samples, six fortified spikes, four trip spikes, three trip blanks, one field blank and three confirmation samples were collected. During the last two MITC applications, two duplicate samples, two fortified spikes, four trip spikes, and two trip blanks, were collected. No confirmation samples were collected. Two trip spike canisters and one trip blank canister were collected during the last two applications.

During the monitoring of the methyl bromide/chloropicrin applications, two fortified spikes, two trip spikes (only one chloropicrin trip spike was collected during the October 28th application monitoring), and one trip blank were collected for each chemical. No field quality control canisters were collected for methyl bromide due to insufficient preparation time.

The primary laboratory analyzed both duplicate samples. A duplicate sample is a sample that is collocated with a field sample. These samples serve to evaluate overall variation in sample measurement and analysis. Two duplicate samples were analyzed for MITC; three duplicate samples were analyzed for the remaining fumigants.

A fortified spike (also called a sample spike) was a laboratory spike prepared as soon as the primary laboratory was notified of a fumigation. This spike was sent to the field and placed on an air sampler with air flowing through the sorbent tube. The sample spike was kept on dry ice prior to sampling. Once shipped to the field, it was treated just like a field sample, including storage and shipping conditions. The fortified spike, in comparison with trip spikes and the respective field sample, gives information about any change in the ability to recover the analyte during air sampling.

Four trip spikes were generated in the primary laboratory, two at a high concentration and two at a low concentration within the range of concentrations anticipated. Trip spikes were mailed to or picked up by the field technician. Trip spikes were stored on dry ice until all samples for the single fumigation event were collected. Two of the four trip spikes, one high and one low, were sent back to the primary laboratory with the field samples for analysis. The remaining two trip spikes were mailed or delivered to the confirmation laboratory along with the confirmation samples (see below).

The tubes used for trip blanks were taken from the same storage area where all other sampling tubes were kept prior to use. Two trip blanks were sent with the field samples to the primary laboratory for analysis. In addition, one trip blank was sent to the confirmation laboratory along with their respective samples.

Three confirmation samples were shipped with the two trip spikes and one blank sample to the confirmation laboratory for analysis. A confirmation sample is a sample that is collocated with a field sample, yet analyzed by a second (confirmation) laboratory. The number of quality control samples for canisters was limited due to the availability of canisters. Trip spikes and blanks were collected for MITC analysis and a trip blank was collected during methyl bromide monitoring. Only one duplicate MITC canister sample was collected during the study.

Laboratory Audits

Based on the recommendations of the TAG, DPR formed a multi-agency quality assurance team to audit each of the laboratories analyzing samples for this study. The quality assurance team was led by a representative from the ARB, and included members from the U.S. EPA, the Pesticide Action Network (an environmental advocate group), and a DPR representative, employed in a separate division from the personnel directing the study. The quality assurance team performed informal audits prior to the start of the study, as well as formal audits while the study was in progress. A certified industrial hygienist from the U.S. EPA conducted a field evaluation of flow rate measurements during the sixth metam-sodium monitoring event.

Laboratory Methods

Chemical extraction methods for MITC and methyl bromide from sorbent tubes and removal from canisters are referenced below for the primary and confirmation (quality control) laboratories. Chemical extraction methods for chloropicrin from sorbent tubes are referenced below for the primary and confirmation laboratories. At the time of this study there were no analytical methods for chloropicrin sampled using canisters. Since no analysis of 1,3-dichloropropene was necessary, the laboratory methods for analysis are not included in this report.

Department of Health Services Laboratory - Extraction for MITC from sorbent tubes was performed in accordance with the SOP in Appendix I. For canister analysis an aliquot of air is removed and analyzed as described in the SOP in Appendix J.

California Department of Food and Agriculture Laboratory - Extraction for chloropicrin from sorbent tubes was performed in accordance with the SOP in Appendix K. Extraction for MITC from sorbent tubes was performed in accordance with the SOP in Appendix L. Extraction for methyl bromide from sorbent tubes was performed in accordance with the SOP in Appendix M.

U.S. EPA Region 9 Laboratory – For analysis for methyl bromide from canisters, an aliquot of air is removed from the canisters as described in the SOP in Appendix N.

Method calibration

Each laboratory used certified analytical standards. The primary and quality control laboratories exchanged standards for MITC for verification. New standards were prepared at least every six months. New standards were compared with old standards for verification. Standards for fumigants have shown no degradation over a six-month period in prior studies.

Both the primary and confirmation laboratories verify calibration by analyzing a series of standard samples (samples containing known amounts of analyte dissolved in a solvent for the sorbent samples or air for the canister samples). The linear range of calibration is determined by analyzing standards of increasing concentration. Within the linear range, the calibration is determined by regressing the standard concentration on the response of the instrument (peak height or peak area of the chromatogram) using at least five concentrations. The minimum acceptable correlation coefficient of the calibration is given in the SOP for each method, but in general is at least 0.95.

Method detection limits and limits of quantitation

Each laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. This standard is analyzed at least seven times, and the method detection limit is determined by calculating the 99 percent confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The method detection limit for each analyte and method is given in the SOPs.

The limit of quantitation is set a certain factor above the method detection limit. The level of interference determines the magnitude of this factor, and the more interference, the higher the factor. The limit of quantitation for each analyte, along with a summary of chemical analytical and air sampling methods, can be found in Tables 5 and 6.

Calculations of air concentrations

For the sorbent tube samples the air concentrations were calculated as a concentration removed from a volume of air moving through the sampling media. Analytical results are presented in ug/sample. The concentrations are converted from ug/sample to ng/m³ with the following calculations:

$$\frac{\text{sample results (ug)} \times 1000 \text{ L} / \text{m}^3}{\text{flowrate of sampler (L / min)} \times \text{run time (min)}} \times 1000 \text{ ng/ug} = \text{ng/m}^3$$

The analytical canister results are presented in ppbv (parts per billion by volume). The results are converted to ng/m³ with the following calculations:

$$\text{For MITC} = \frac{\text{sample results (ppb)}}{0.3342 \text{ ppb / ug}} \times 1000 \text{ ng/ug} = \text{ng/m}^3$$

$$\text{Methyl bromide} = \frac{\text{sample results (ppb)}}{0.2573 \text{ ppb / ug}} \times 1000 \text{ ng/ug} = \text{ng/m}^3$$

Holding times

Storage stability data for the fumigants can be found in Table 5. All methyl bromide and chloropicrin sorbent tube samples were extracted within seven days of collection. All MITC sorbent tubes were extracted within 14 days.

Table 5. Summary of field sampling parameters and minimum chemical analytical parameters for the fumigants monitored in Lompoc January 2000 - November 2000.

	<u>Analyte</u>		
	Chloropicrin	MITC	Methyl Bromide
Primary Laboratory	CDFA	DHS	CDFA
Confirmation Laboratory	none	CDFA	none
Sorbent Tube Adsorbent	XAD resin	coconut charcoal	petroleum charcoal
Analytical Method ^a	gas chromatography	gas chromatography	gas chromatography
Extraction Solvent	Hexane	CS ₂ /hexane	ethyl acetate
Detector	electron capture	nitrogen/ phosphorous	electron capture
Trapping Efficiency	67%	94%	60%
Desorption Efficiency ^b	77%	69%	49%
Storage Stability	42 days	14 days	14 days
Flow Rate (L/min)	0.3	1.0	0.015
Method Detection Limit (ng/sample)	16	12	35
Method Detection Limit (ng/m ³); 8-hour	111	25	4861
Method Detection Limit (ng/m ³); 16-hour	56	13	2431
Limit of Quantitation (ng/sample)	200	37	200
Limit of Quantitation (ng/m ³); 8-hour	1389	77	28000
Limit of Quantitation (ng/m ³); 16-hour	694	39	14000
Screening levels for acute	10,000 ng/m ³	66,000 ng/m ³	820,000 ng/m ³
Screening levels for subchronic	400 ng/m ³	3,000 ng/m ³	270,000 ng/m ³

^aSee respective appendices for details.

^bDesorption efficiency reported is from primary laboratory results during method validation. Methyl bromide desorption efficiency from Beirmann and Barry, 1999. The desorption efficiency and trapping efficiency obtained during current study are located in Quality Control Results section.

Table 6. Analytical parameters for canisters used for the fumigants monitored in Lompoc January 2000 - November 2000.

	Analyte		
	Chloropicrin	MITC	Methyl Bromide
Primary Laboratory	NA	DHS	EPA Region 9
Analytical Method ^a	NA	gas chromatography	gas chromatography
Detector	NA	mass spectrometer	mass spectrometer
Limit of Detection (ppb)	NA	0.018	NR
Limit of Quantitation (ppb)	NA	0.054	1
Limit of Quantitation (ng/m ³)	NA	162	3890
Percent Recovery	NA	95.7 ^a	NA

NA – Not Applicable

NR – Not Reported

^a Calculated from lab spikes during study

Applications Monitored

Six applications of MITC (five metam-sodium applications and one metam-potassium application) and two methyl bromide/chloropicrin applications were monitored. Maps of the fumigation locations are located in Figures 13 – 20. Monitoring began on an additional application of metam-sodium on January 22, 2000, but was discontinued after eight hours due to rain. The TAG recommended postponing sampling following the fourth application until canisters were available for use, which was not until fall. Therefore, no sampling was conducted during the summer months. The fumigation records for the applications are located in Appendix O.

MITC #1

Date and Approximate Start Time:	1/12/00 7:45 AM
Product:	Vapam HL
Active Ingredient:	metam-sodium
U.S. EPA Registration Number:	5481-468-AA
Township/Range-Section:	07N35W23
Distance and Direction From Lompoc Town Limits:	3 miles west
Method of Application:	Chemigation - drip
Commodity:	Artichokes
Amount of Active Ingredient:	1619 pounds
Area Treated:	19 acres

MITC #2

Date and Approximate Start Time: 1/28/00 4:00 AM
Product: Vapam HL
Active Ingredient: metam-sodium
U.S. EPA Registration Number: 5481-468-AA
Township/Range-Section: 7N34W31
Distance and Direction From Lompoc Town Limits: 0.8 miles west
Method of Application: Chemigation - drip
Commodity: Ornamentals
Amount of Active Ingredient: 3340 pounds
Area Treated: 14 acres

MITC #3

Date and Approximate Start Time: 2/3/00 4:00 AM
Product: Vapam HL
Active Ingredient: metam-sodium
U.S. EPA Registration Number: 5481-468-AA
Township/Range-Section: 7N34W31
Distance and Direction From Lompoc Town Limits: 0.5 miles west
Method of Application: Chemigation - drip
Commodity: Ornamentals
Amount of Active Ingredient: 2386 pounds
Area Treated: 10 acres

MITC #4

Date and Approximate Start Time: 2/5/00 7:00 AM
Product: Vapam HL
Active Ingredient: metam-sodium
U.S. EPA Registration Number: 5481-468-AA
Township/Range-Section: 7N34W31
Distance and Direction From Lompoc Town Limits: 0.5 miles west
Method of Application: Chemigation - drip
Commodity: Ornamentals
Amount of Active Ingredient: 2386 pounds
Area Treated: 10 acres

MITC #5

Date and Approximate Start Time: 10/28/00 15:00 PM
Product: Vapam HL
Active Ingredient: metam-sodium
U.S. EPA Registration Number: 5481-468-AA
Township/Range-Section: 7N34W30/19
Distance and Direction From Lompoc Town Limits: 1 mile west
Method of Application: Chemigation - drip
Commodity: Ornamentals
Amount of Active Ingredient: 4771 pounds
Area Treated: 20 acres

MITC #6

Date and Approximate Start Time: 11/16/00 7:00 AM
Product: K-PAM HL
Active Ingredient: metam-potassium
U.S. EPA Registration Number: 5481-483-AA
Township/Range-Section: 7N34W30
Distance and Direction From Lompoc Town Limits: 1 mile west
Method of Application: Chemigation - drip
Commodity: Ornamentals
Amount of Active Ingredient: 5104 pounds
Area Treated: 20 acres

Methyl bromide/chloropicrin #1

Date and Approximate Start Time: 10/7/00 10:00AM
Product: AmeriBrom 75/25
Active Ingredient: Methyl bromide/chloropicrin
U.S. EPA Registration Number: 8622-15-AA
Township/Range-Section: 7N34W35
Distance and Direction From Lompoc Town Limits: 0.25 miles East
Method of Application: Tarped bed (method #9)
Commodity: Strawberries
Amount of Active Ingredient: 2250 pounds
Area Treated: 10 acres

Methyl bromide/chloropicrin #2

Date and Start Time: 11/16/00 6:00 AM
Product: Tri-Con 67/33
Active Ingredient: Methyl bromide/chloropicrin
U.S. EPA Registration Number: 11220-7-AA
Township/Range-Section: 7N34W23
Distance and Direction From Lompoc Town Limits: 0.75 miles East
Method of Application: Tarped broadcast (method #4)
Commodity: Flower Seed
Amount of Active Ingredient: 1072 pounds
Area Treated: 5 acres

Meteorological Measurements

In addition to air samples, a MetOne® meteorological station was located in the agricultural areas approximately 0.75 miles west of the city of Lompoc (Figures 1 and 6) in a fenced maintenance yard. The station was set up according to DPR's SOP EQWE001.00 (Appendix G) in November 1999 prior to the start of sampling. The MetOne® meteorological sensors were placed on a trailer mast at a height of 10 meters. The sensors recorded wind direction, horizontal wind speed, temperature, and relative humidity. The manufacturer calibrated the MetOne® sensors on October 5, 1999 to fit within the equipment specifications. The meteorological data was recorded on a Campbell Scientific CR 21X datalogger every five

minutes. In addition, the Santa Barbara County Air Pollution Control District maintains a weather station at the H Street sampling site in central Lompoc for comparison with the meteorological data collected by DPR.

The MetOne® meteorological station was checked periodically (at least once a month) against hand-held sensors (Appendix G). Data were downloaded and batteries were exchanged approximately once a month.

DATA ANALYSIS METHODS

Methods for Computer Modeling and Statistical Analysis

DPR attempted to use computer modeling to estimate ambient air concentrations from pesticide application made (but not monitored). Modeling can be used to supplement measured air concentrations in the event a large application, close to the city limits, does not occur within the specified monitoring period. The strength of this approach is the flexibility afforded by modeling. It can provide air concentration estimates within city limits given application scenarios that occur outside of the monitoring period.

For this study, applications were modeled with the U.S. EPA gaussian plume dispersion model, Industrial Source Complex Short Term (ISCST) model, version 3 (U.S. EPA 1995). The ISCST model was developed by the U.S. EPA to simulate the effects of emissions from a wide variety of industrial sources. DPR and others have used this model to estimate air concentrations from agricultural pesticide applications. This model estimates air concentrations based on three main factors: 1) characteristics of the pollution source, such as rate of emission and size of field; 2) weather conditions at the time of emission, such as wind speed and direction; and 3) terrain over the downwind area, such as urban or rural geography. For this study, data was collected for field size, weather, terrain, and air concentrations, but not emission rate. Since emission rate is a key model input, DPR used the measured air concentrations to "back-calculate" an emission rate (Ross, et al. 1996). The back-calculated emission rate, weather station measurements, and other monitoring data can then be used to map out the air concentrations of MITC that would be expected for the whole city.

Air concentrations for other applications were also evaluated by examining various factors influencing air concentrations. Air concentrations may be correlated with the amount of fumigant applied, distance of application to the monitoring sites, or other factors. The analysis of data determined if there is a significant correlation between air concentration and application parameters.

Even with large numbers of samples, it is never likely that the highest measured value is the highest that is possible. DPR used statistical methods to estimate the percentiles of air concentrations from sample data. In order to estimate the "upper bound" of daily exposure, DPR used the estimated population 95th percentile of daily exposure. The 95% tolerance limit is the concentration that, with given probability, will be exceeded in no more than 5% of

future samples (Hahn and Meeker, 1991). It is equivalent to a 90% upper confidence limit on the population 95th percentile. For the lognormal distribution, it is calculated as:

95% tolerance limit =

$$\exp\{\text{arithmetic mean of } \log_e \text{ concentrations} + g_{(0.90;0.95; n)} * (\text{sd of } \log_e \text{ concentrations})\}$$

The multiplier *g* for 90% probability is tabled in Hahn and Meeker (1991).

Methods for Deriving Screening Levels

No state or federal government agency has established human health standards for ambient air concentrations for these pesticides. Therefore, DPR and a subcommittee of the LIWG's TAG developed health screening levels for these pesticides to place the results in a health-based context (Appendix P). Although not regulatory standards, these screening levels can be used in the process of evaluating the air monitoring results. A measured air level that is below the screening level for a given pesticide would not be considered to represent a significant health concern and would not generally undergo further evaluation, but also should not automatically be considered "safe" and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further and more refined evaluation. Significant exceedances of the screening levels could be of health concern and would indicate the need to explore the imposition of mitigation measures.

Acute toxicity can be defined as the toxicity manifested within a relatively short time interval, generally not longer than one day, from a single exposure. In this document, unless specifically noted, acute screening levels are for 24 hours. Subchronic toxicity can be defined as the toxicity manifested within a more extended interval, but not one that constitutes a significant portion of the lifespan of the species in question. In subchronic toxicity testing using mammalian test species, the period of exposure is generally 30 to 90 days. Chronic toxicity is manifested over a long-term period, generally for a significant portion of a lifetime.

One quantitative descriptor of the results of a toxicity study is the No Observed Effect Level (NOEL). The NOEL can be defined as the highest dose level of a chemical (in this case, a pesticide) that causes no observable adverse or toxic effect in the animal test species in the study. A related term, the Lowest Observed Effect Level (LOEL), can be defined as the lowest dose of a chemical that still causes an observable adverse or toxic effect. In some cases, a study will demonstrate adverse effects at all dose levels, and a NOEL will not be readily apparent. In these situations, an Estimated No Effect Level (ENEL) can be generated by applying an uncertainty factor (generally 10-fold or less) to the LOEL. The units of the NOEL, LOEL, and ENEL, will depend on the route and method of exposure in the animal study. In the current application, all studies are by the inhalation route, with the pesticides delivered in the air. Therefore, these dose levels are expressed in terms of air concentrations, such as parts per million (ppm), parts per billion (ppb), or micrograms per cubic meter (ug/m³).

The toxicology database for a pesticide contains a series of toxicity studies. The particular study and corresponding NOEL that is selected as the basis for the risk calculations or screening level derivations can be described as the "critical" study or NOEL. These studies

are performed on a variety of experimental animals, including rats, rabbits, and dogs. In the case of inhalation studies, due to logistical reasons, the period of exposure is for less than a full 24-hour period, and the resulting NOEL is usually normalized to a 24-hour period. Likewise, subchronic inhalation studies are often conducted for 5 days per week, and the results are normalized to a 7-day week. In addition, since the experimental animals have different respiration rates than humans, different amounts of toxicant will be inhaled over the same time period. Therefore, the air concentrations from the animal studies are generally adjusted to account for the differential respiration rates in order to derive an “human equivalent” concentration. It should be noted that this adjustment does not factor in potential differences in toxicologic sensitivity. This potential differential toxicologic sensitivity is taken into account in the application of uncertainty factors. The human equivalent concentration is calculated, taking the above factors into account, according to the following equation.

$$\text{ppm or ug/m}^3 \text{ (human)} = \text{ppm or ug/m}^3 \text{ (animal)} \times \frac{\text{animal respiration rate}}{\text{human respiration rate}} \times \frac{\text{hours exposed}}{24 \text{ hours}} \times \frac{\text{days exposed per week}}{7 \text{ days}}$$

The term for “days exposed per week/7 days” is used in the calculation only for subchronic inhalation studies. Unless otherwise noted, the default respiration rates used are: 0.20 m³/kg/day for adult humans, 0.76 m³/kg/day for children, 0.96 m³/kg/day for rats, 0.54 m³/kg/day for rabbits, and 0.39 m³/kg/day for dogs.

Table 7 presents acute (24-hour) and subchronic screening levels agreed upon by DPR, OEHHA and DHS toxicologists for each fumigant monitored and the recommended response for each level of concern. The recommended responses state that if the maximum 24-hour time-weighted average air concentration is below the acute screening level, no immediate action will be taken. However, DPR would still consider further analysis (e.g., additional modeling, further monitoring, and/or a more detailed analysis of the health effects data). If the maximum 24-hour time-weighted average air concentration is equal to or greater than the acute screening level then DPR would respond immediately with development of a plan for further analysis and/or interim regulatory action. Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study. The same decision rules apply to calculated concentrations made to estimate subchronic exposures.

Screening Levels

For methyl bromide and MITC, the quantitation and detection limits for both analytical methods are below the acute and subchronic screening levels (Figures 8 and 9). For chloropicrin the detection limit and quantitation limit are below the acute screening level, whereas the quantitation limit of 930 ng/m³ is above the subchronic screening level of 400 ng/m³ (Figure 10). The screening levels and correspondence on the determination of the screening levels is located in Appendix P.

Chloropicrin

A risk assessment of chloropicrin has been initiated at DPR, but has not been completed. However, as part of the air Toxics Hot Spots Program, OEHHA has generated an acute REL of 4.4 ppb (29 ug/m³) derived for a 1-hour human exposure. This value was based on decreased respiratory rates in an acute mouse inhalation study in a 10-minute exposure. Assuming a maximal sensitivity within eight hours, the 24-hour REL of 10 ug/m³ (2 ppb) is used for acute exposure. It should be noted that this REL would also apply to time periods between 8 and 24 hours. A chronic REL of 0.4 ug/m³ (0.06 ppb) was derived for chronic human inhalation exposure from a rat inhalation study. A subchronic REL was not derived as part of the Hot Spots program; therefore, the chronic REL of 0.4 ug/m³ (0.06 ppb) is used as a surrogate (conservative) for subchronic exposure.

Methyl Bromide

DPR has completed an RCD for methyl bromide. It should be noted that for the methyl bromide RCD, a child breathing rate of 0.46 m³/kg/day and an adult breathing rate of 0.26 m³/kg/day were used. The RCD uses an acute NOEL of 40 ppm (156 mg/m³) for developmental effects from a rabbit inhalation developmental toxicity study as the critical NOEL for acute exposure. This value of 40 ppm is equivalent to a human NOEL of 21 ppm (82 mg/m³), after adjusting for differences in breathing rate and exposure period. A human child equivalent NOEL of 25 ppm (97 mg/m³) was derived from a dog neurotoxicity study (exposure 7 hours per day, NOEL of 55 ppm), so children would be protected by the use of the NOEL of 21 ppm (82 mg/m³; 82,000 ug/m³). In another inhalation rabbit developmental toxicity study, the NOEL was 20 ppm (78 mg/m³). The equivalent child NOEL is 7 ppm (27 mg/m³; 27,000 ug/m³) and can be used for subchronic exposures of shorter duration (1 week). Applying the conventional uncertainty factor of 100 for results based on animal studies (10-fold uncertainty factors for both interspecies and intraspecies variability) to the acute NOEL of 21 ppm results in an acute screening level of 210 ppb (820,000 ng/m³). For reference, the corresponding acute screening levels for 8 and 16 hours can be calculated to be 63 and 32 ppb, respectively. Applying the 100-fold factor to the subchronic NOEL of 7 ppm (27 mg/m³) results in a short duration subchronic screening level of 70 ppb (270,000 ng/m³).

MITC

DPR has prepared a health evaluation of MITC for the Toxic Air Contaminant Program. The evaluation was based on a rat inhalation study which demonstrated severe lung damage at the high dose of 34 ppm, accompanied by far milder expressions of such damage at 1.7 and 6.8 ppm. The final NOEL, with the use of an uncertainty factor of three to estimate a NOEL from a LOEL, was 100 ppb. This, then, resulted in a REL for subchronic exposure of 1 ppb (3,000 ng/m³). This is the value that should be used as the subchronic screening level to evaluate subchronic exposure to air levels of MITC.

Methods for Estimating Health Risks

The risk or health significance of a chemical(s) in air is a function of both the inherent toxicity of the chemical(s) as well as the level of exposure to the chemical(s). The potential health significance of the measured levels of fumigant pesticides in Lompoc air can be evaluated by comparing the air concentration measured over a specified time (e.g. eight hours, 16 hours, 24

hours, three days) with the screening level derived for a similar time (acute, subchronic). In these calculations, the screening level is used in the same manner as the RfC.

The ratio of an exposure level for a chemical (measured air concentration of a fumigant pesticide) to a RfC for the chemical (screening level for that fumigant pesticide) over the same time period is called the Hazard Quotient (HQ). In this case,

$$\text{Hazard Quotient} = \frac{\text{Air Concentration Over Specified Time Period}}{\text{Screening Level for Same Time Period}}$$

As stated previously, a measured air level that is well below a screening level for a given pesticide is not considered to represent a significant health concern and will not generally undergo further evaluation, but also will not be automatically considered “safe.” By the same token, a measured air level that is above a screening level will not necessarily be a significant health concern, but will indicate the need for a further and more refined evaluation. Put another way, if the HQ exceeds one, there may be concern for the occurrence of toxic effects, while HQs below one indicate a low risk. The lower the value of HQ is below one, the greater the health protection. Conversely, the greater the value of the HQ is above one, the greater the level of concern.

This discussion on the HQ approach was excerpted from portions of documents listed in Appendix Q, all of which are available online.

To evaluate the potential health risk of acute exposure to the individual monitored fumigants, the highest [24-hour] concentration at any site at any time was used. If a pesticide was not detected at any time, a default value of one-half the minimum detection limit concentration was used. If only a trace amount was detected, the value used was the concentration halfway between the minimum detection limit and the estimated quantitation limit. For these calculations we used the highest concentration measured during any one interval (eight or 16-hour). This resulted in a more conservative comparison since a 24-hr time-weighted average concentration will be lower.

To evaluate the potential health risk of subchronic exposure to the individual monitored fumigants, the highest 30 to 90-day time-weighted average concentration at any site should be used. Similar to the previous calculations, if a pesticide was not detected at any time, a default value of one-half the minimum detection limit concentration would be used. If only a trace detection was measured, the value used would be the concentration halfway between the minimum detection limit and the estimated quantitation limit. In this study the highest three-day air levels were used to evaluate the potential health effects from subchronic exposure to the monitored fumigants. Since subchronic exposure is considerably longer than three days, this is a significant overestimate of subchronic exposure.

This study was not designed to determine chronic exposure. However, metam-sodium is used in the Lompoc area throughout the year, so a simple evaluation of chronic exposure to MITC was attempted. DPR estimated chronic exposure by using the average air concentration at one

site. The average of the MITC air concentrations, on all of the 18 monitored days, was calculated for each monitoring site. Similar to the previous calculations, if a pesticide was not detected at any time, a default value of one-half the minimum detection limit concentration would be used. If only a trace detection was measured, the value used would be the concentration halfway between the minimum detection limit and the estimated quantitation limit. The site with the highest 18-day average concentration was used to estimate chronic exposure.

Table 7. Screening levels for each fumigant monitored.

Analyte	No Observable Effect Level	Screening Level	Ambient Air Concentration ^a	Recommended Response ^b
Chloropicrin	Acute (24 hour) Not available ^c	10,000 ng/m ³ (2 ppb)	< 10,000 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis
			≥ 10,000 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.
	Subchronic Not available	400 ng/m ³	< 400 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 400 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.
Methyl Bromide	Acute (24 hour) 82,000,000 ng/m ³	820,000 ng/m ³ (210 ppb)	< 820,000 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 820,000 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.
	Subchronic 27,000,000 ng/m ³	270,000 ng/m ³ (70 ppb)	< 270,000 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 270,000 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.
MITC	Acute (24 hour) 660,000 ng/m ³	66,000 ng/m ³ (22 ppb)	< 66,000 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 66,000 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.
	Subchronic 300,000 ng/m ³	3,000 ng/m ³ (1 ppb)	< 3,000 ng/m ³	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 3,000 ng/m ³	Not necessarily a health concern. Initiate a more refined analysis. Significant exceedances of health concern, indicate the need to explore mitigation measures.

^a Ambient air concentrations were averaged as described above.

^b A more refined analysis could include, but not be limited to atmospheric dispersion modeling, more air monitoring and a more refined risk analysis. Mitigation measures could include, but not be limited to permit conditions, statewide regulations, and label changes.

^c See Appendix O for description of screening level decisions.

Figure 8. MITC Detection Limit, Quantitation Limit, and Screening Levels. (The numbers in parenthesis are the values for the related concentrations)

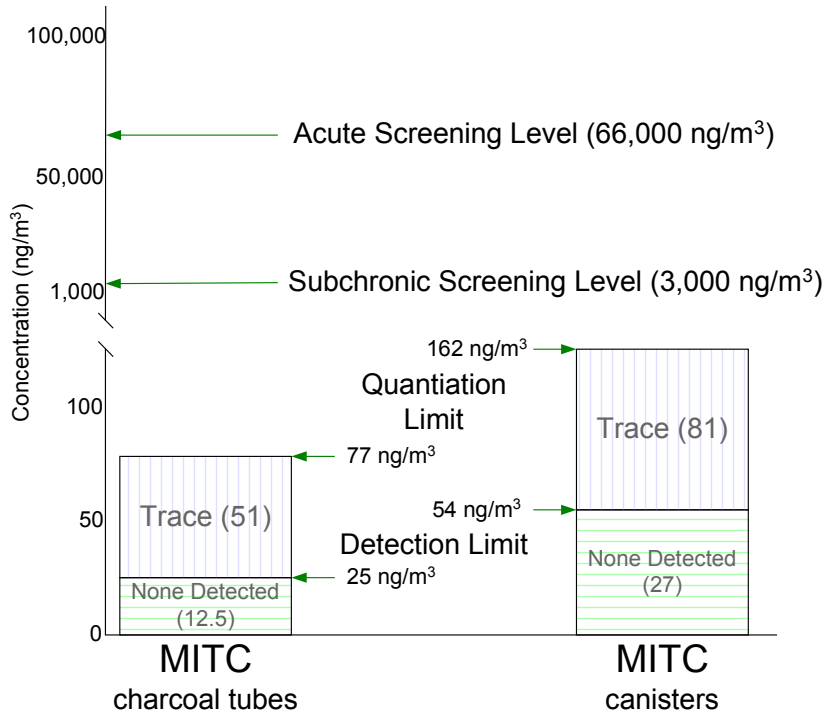


Figure 9. Methyl Bromide Detection Limit, Quantitation Limit, and Screening Levels. (The numbers in parenthesis are the values for the related concentrations)

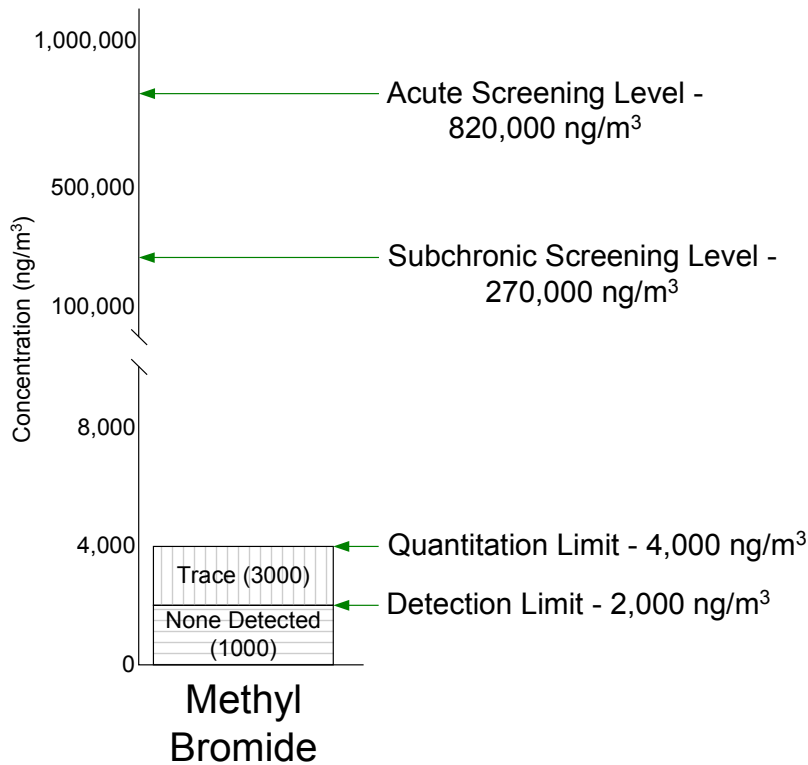
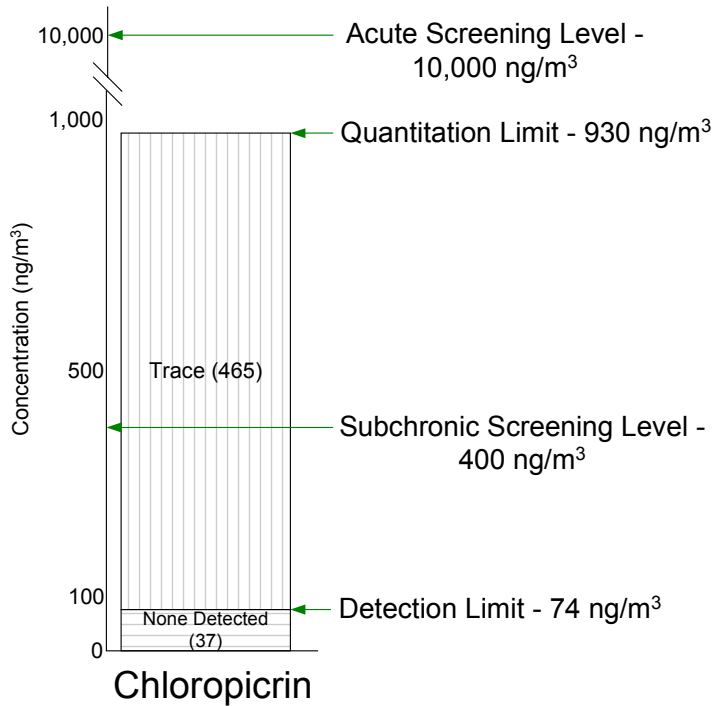


Figure 10. Chloropicrin Detection Limit, Quantitation Limit, and Screening Levels. (The numbers in parenthesis are the values for the related concentrations)



RESULTS AND DISCUSSION

Results of Air Monitoring

DPR collected and analyzed 293 of the 300 samples described in the monitoring plan. Five of the planned MITC samples were not collected due to the short time between the third and fourth fumigations monitored. Two days separated the third and fourth fumigation, insufficient time for the three days of monitoring according to the plan. In addition, one duplicate and two primary samples were lost during field sampling. An adjusted concentration was calculated for each sorbent tube result to account for the 30% loss in desorption efficiency in the method validation.

Of the 293 samples collected and analyzed, 102 had detectable concentrations, 100 for MITC, two for methyl bromide, and none for chloropicrin (Table 8). The highest concentration detected in any sample for MITC was 920 ng/m³ using sorbent tubes and 1885 ng/m³ using canisters (Table 9). The highest three-day average concentration measured was 616 ng/m³, using canister samples (Table 10). All MITC concentrations were less than the acute health screening level of 66,000 ng/m³ and the subchronic health screening level of 3,000 ng/m³ (Figure 11). Only trace levels were detected for methyl bromide, and chloropicrin had no detectable concentrations (Table 8). Individual results of all 293 samples are given in Appendix R. The measurement error determined from the duplicate samples is ±11 percent.

The peak concentrations for five of the six fumigations occurred within the first two days on monitoring (Figure 12), indicating that the 3 days of sampling captured the peak air concentrations. Rain occurred the day after application for the third and fifth applications monitored. High soil moisture can affect the volatilization rate of pesticides from soil; MITC is more likely to volatilize at a slower rate with high soil moisture. In addition, airborne MITC may be scavenged from the air by rain drops and returned to the soil surface.

In general, the highest MITC concentrations were detected at the northwest and west monitoring locations (Table 11). Figures 13 through 18 indicate the sampling interval with the highest concentrations for each application monitored. On each map is a wind rose that indicates the wind speed and direction the wind is blowing “to” for the sampling interval. The locations of the highest concentrations are consistent with the wind direction at the time of sampling. Although the wind pattern during the fifth metam sodium application (figure 17) was mainly to the north west, the relatively high concentrations detected were probably due to slower wind speeds and more stable conditions during the nighttime sampling period.

Figures 19 and 20 indicate the location of the methyl bromide/chloropicrin applications. The wind rose indicates the wind speed and direction the wind is blowing “to” for the entire monitoring period. The methyl bromide and chloropicrin results (two trace detections for methyl bromide, no detections for chloropicrin) are consistent with the wind patterns. The fumigated fields are east of Lompoc and downwind of the monitoring site for nearly the entire monitoring period.

Table 8. Percent of samples with detected pesticides.

Pesticide	None	Trace	Quantified
	Detected (%)		
MITC (173 samples)	42	19	39
Methyl Bromide-sorbent tubes (60 samples)	100	0	0
Methyl Bromide-canisters (33 samples)	94	6	0
Chloropicrin (60 samples)	100	0	0

Table 9. Highest air concentrations detected.

Fumigation (date)	Maximum Concentration (ng/m ³)	Adjusted Sorbent Tube Concentration (ng/m ³) ^a	Acute Screening Level ^b (ng/m ³)
MITC #1 (1/12/00)	150 ^c	195	66,000
MITC #2 (1/28/00)	340 ^d	442	66,000
MITC #3 (2/3/00)*	47 ^c	61	66,000
MITC #4 (2/5/00)	300 ^c	390	66,000
MITC #5 (10/28/00)*	800 (1885**) ^c	1040	66,000
MITC #6 (11/16/00)	920 (1017**) ^d	1196	66,000
Methyl Bromide 1 (10/7/00)	None Detected (<2000)	None Detected	820,000
Methyl Bromide 2 (11/18/00)	Trace (<4000**) ^c	Trace	820,000
Chloropicrin 1 (10/7/00)	None Detected (<74)	None Detected	10,000
Chloropicrin 2 (11/18/00)	None Detected (<74)	None Detected	10,000

^a MITC sorbent tube concentrations adjusted to account for 70% recovery.

^b Acute screening level is based on a 24-hr exposure. The 24-hour time weighted average sample would be lower by definition than the individual 8- and 16-hour samples.

^c 16-hour sample

^d 8-hour sample

* Rain on day after fumigation

** Concentration from canister sample

Table 10. MITC concentrations detected at sites with the highest three-day average.

Fumigation (site)	Three-Day Time Weighted Average Concentration (ng/m ³)	Adjusted Three-Day Time Weighted Average Concentration (ng/m ³) ^a	Subchronic Screening Level (ng/m ³)
MITC #1 (NE)	110	142	3,000
MITC #2 (W)	87	109	3,000
MITC #3 (W)	35	45	3,000
MITC #4 (W)	95	117	3,000
MITC #5 (NW)	288 (616*)	371	3,000
MITC #6 (NW)	573 (615*)	743	3,000

^a MITC sorbent tube concentrations adjusted to account for 70% recovery.

* Concentration from canister samples

Figure 11. Maximum and average MITC concentration detected during each application monitoring.

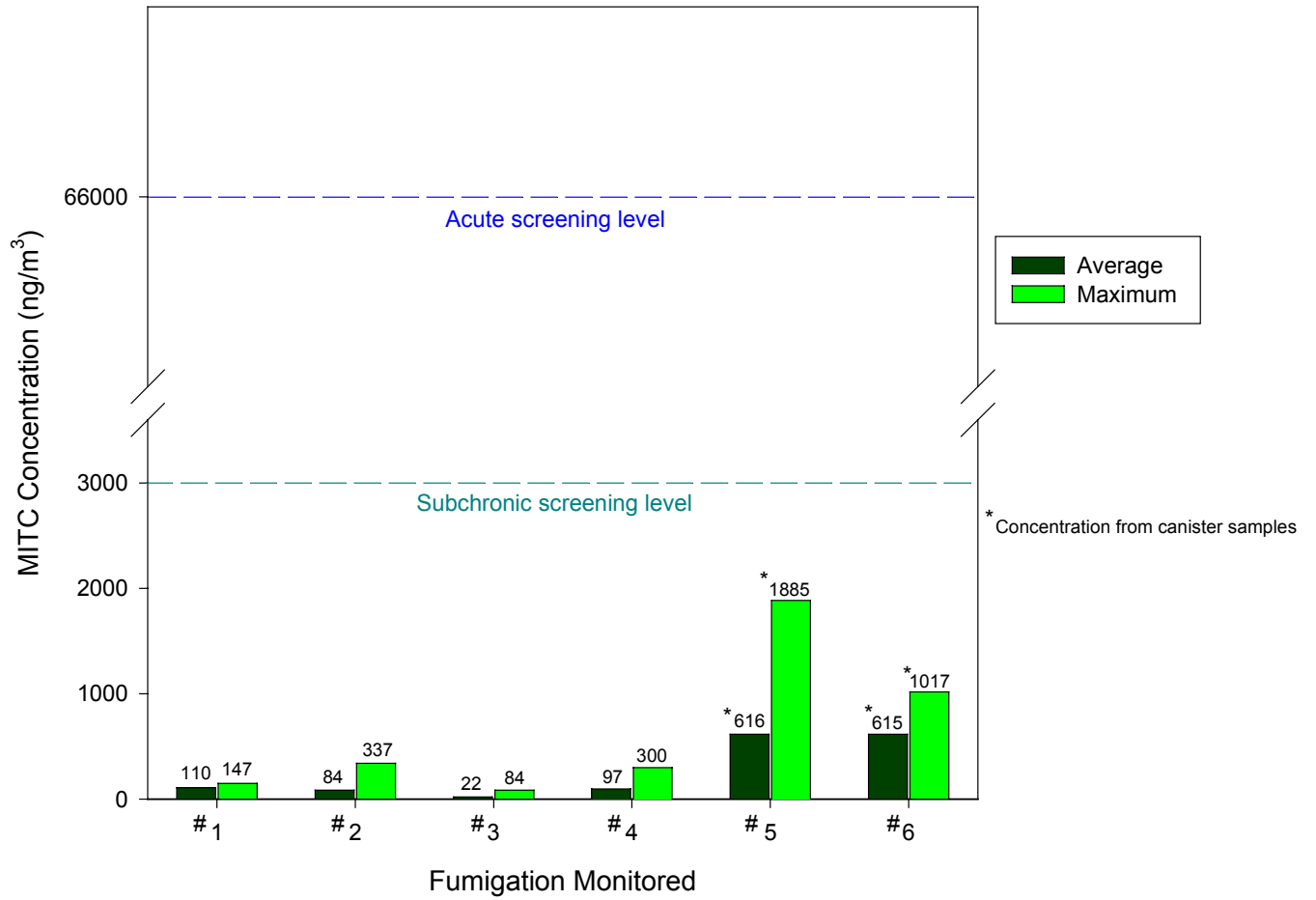


Figure 12. Highest MITC concentration measured for each sampling period over time (includes canister results).

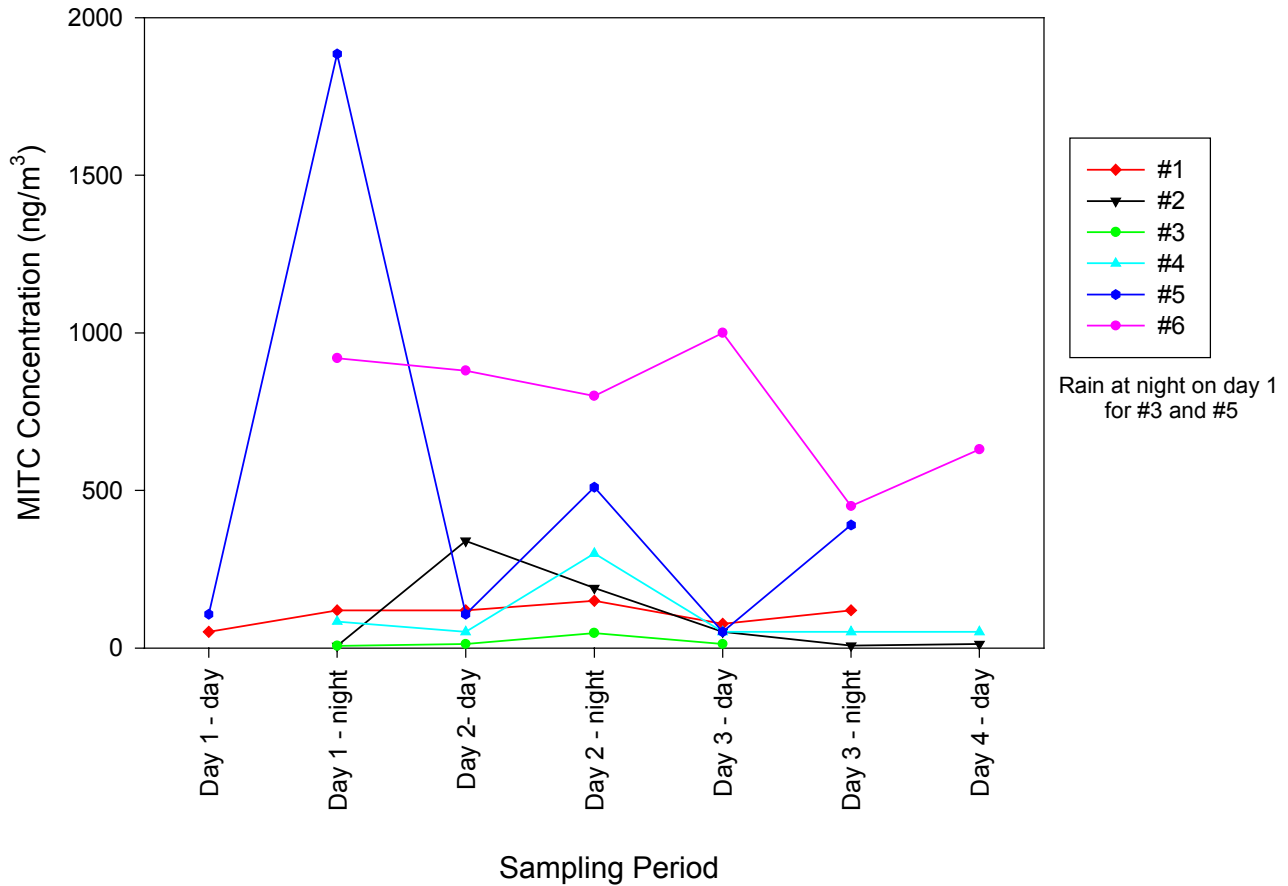


Table 11. MITC concentrations detected by location. Average of all samples collected at each site over entire study period.

Location	Maximum Concentration (ng/m ³)	Adj. Max. Sorbent Conc. (ng/m ³) ^a	Average Concentration (ng/m ³)	Adj. Average Concentration (ng/m ³) ^a
Central	260 ^b	338 ^b	27	47
Northeast	230 ^c	299 ^c	59	82
Northwest	880 (1885*) ^c	1144 (1885*) ^c	183	244
Southwest	340 ^b	442 ^b	30	50
West	920 ^b	1196 ^b	117	160

^a MITC sorbent tube concentrations adjusted to account for 70% recovery.

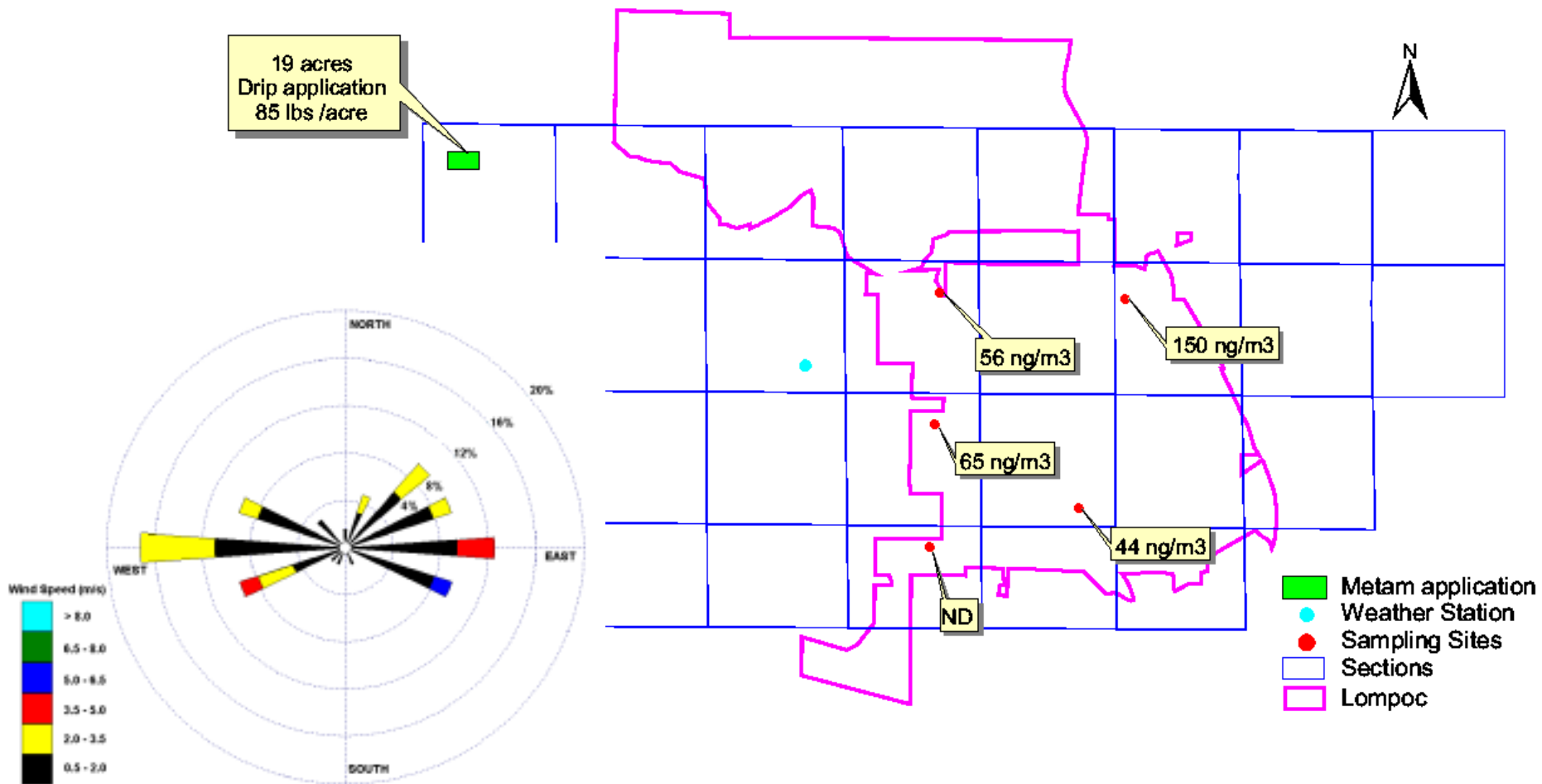
^b 8-hour sample

^c 16-hour sample

* Concentration from canister sample (see Quality Control results for discussion of difference from tubes)

Figure 13. Interval with highest concentrations of MITC for metam sodium application January 12, 2000.

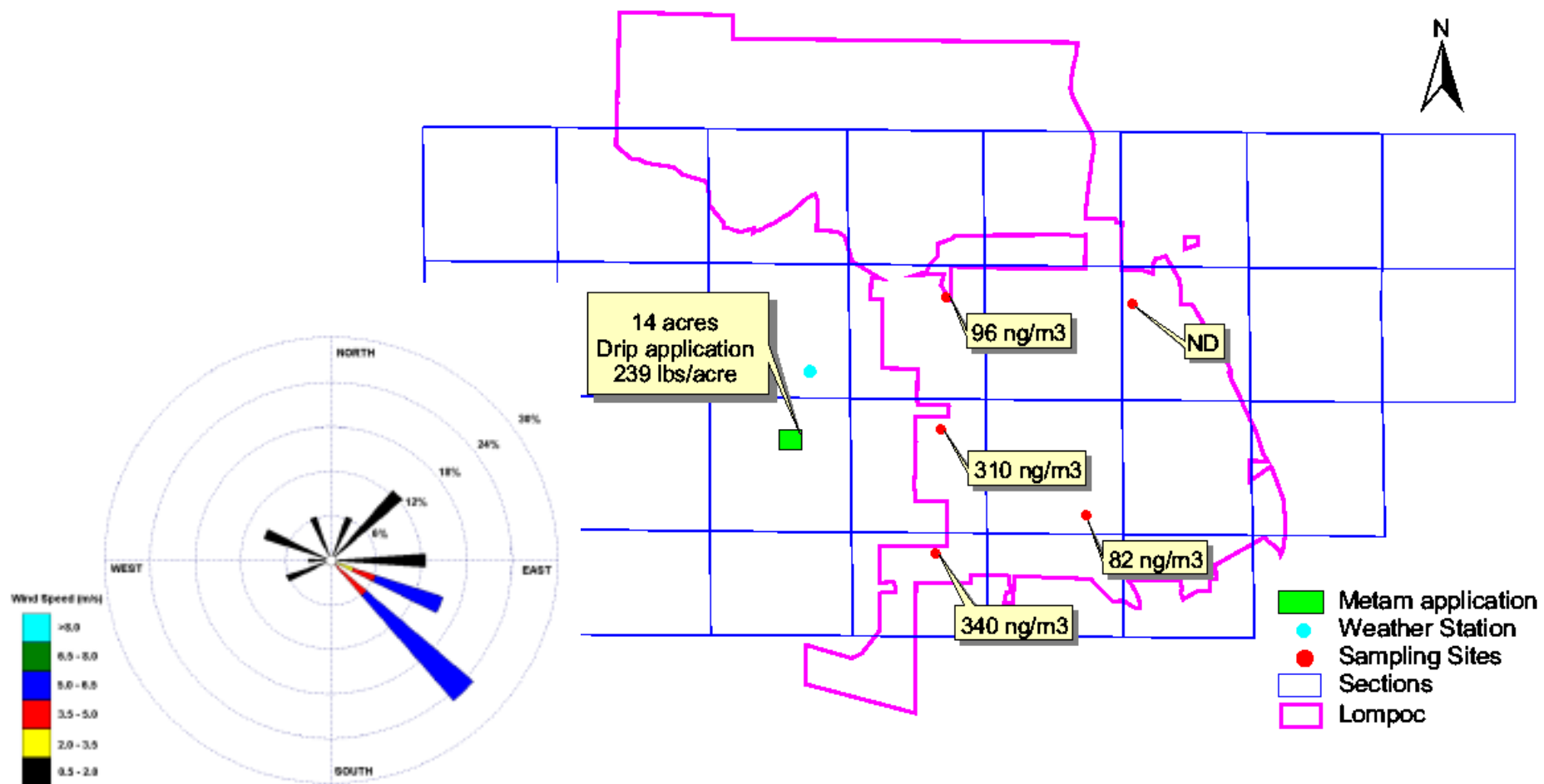
Sampling interval 1/13/00 15:00 - 1/14/00 07:00



Direction wind is blowing "to"

Figure 14. Interval with highest concentrations of MITC for metam sodium application January 28, 2000.

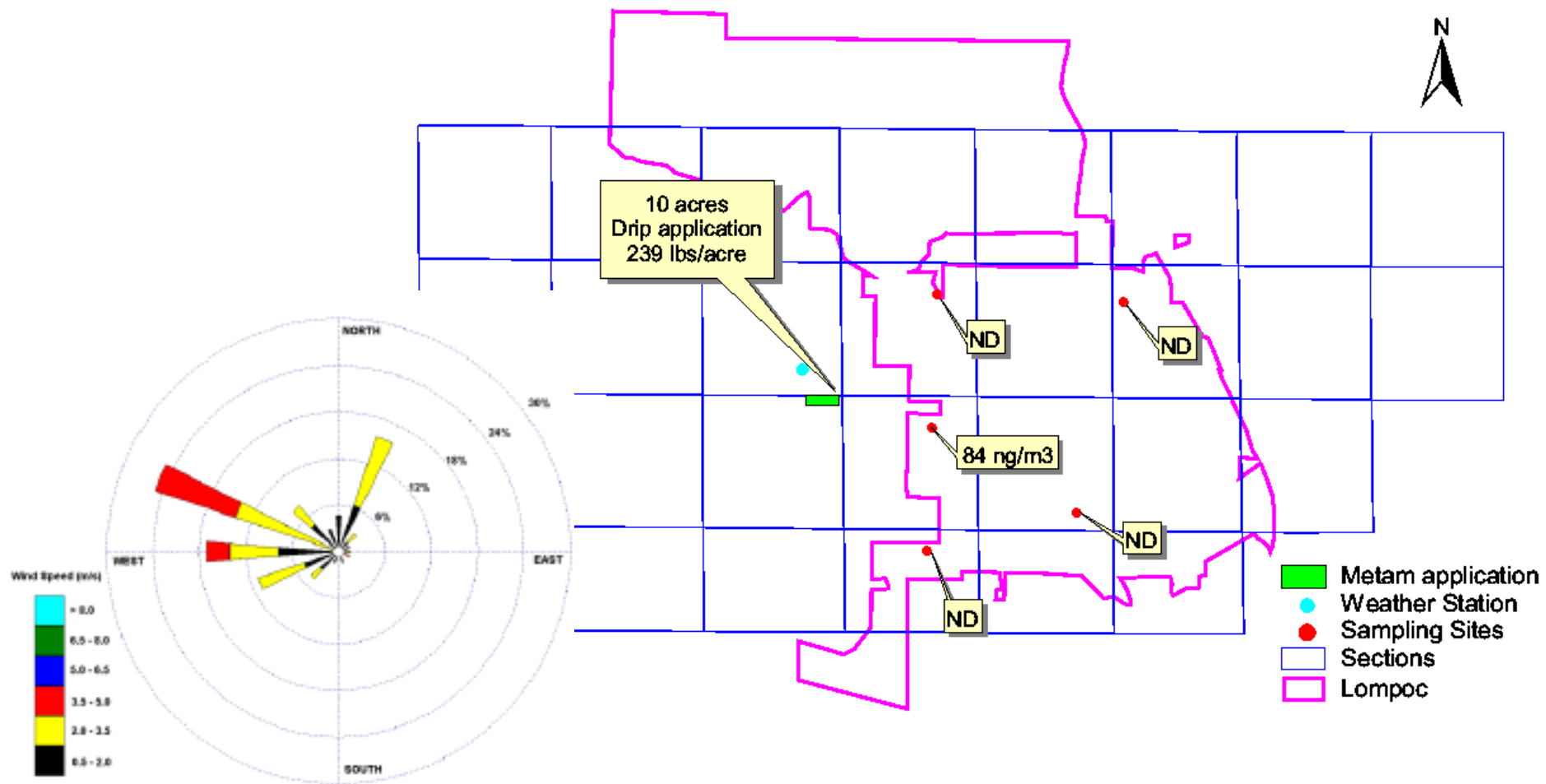
Sampling interval 1/28/00 07:00 - 1/28/00 15:00



Direction wind is blowing "to"

Figure 15. Interval with highest concentrations of MITC for metam sodium application February 3, 2000.

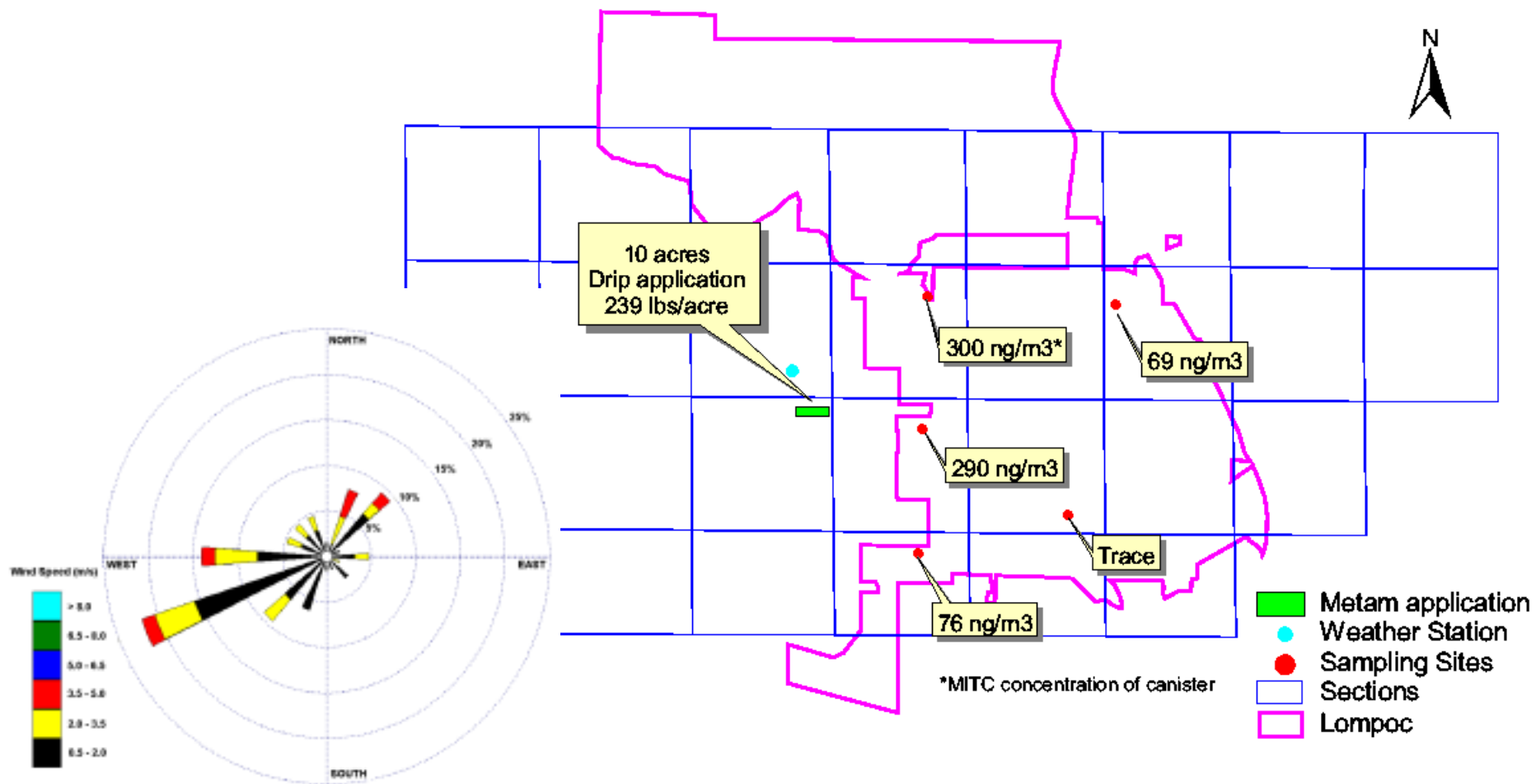
Sampling interval 2/4/00 16:00 - 2/5/00 08:00



Direction wind is blowing "to"

Figure 16. Interval with highest concentrations of MITC for metam sodium application February 5, 2000.

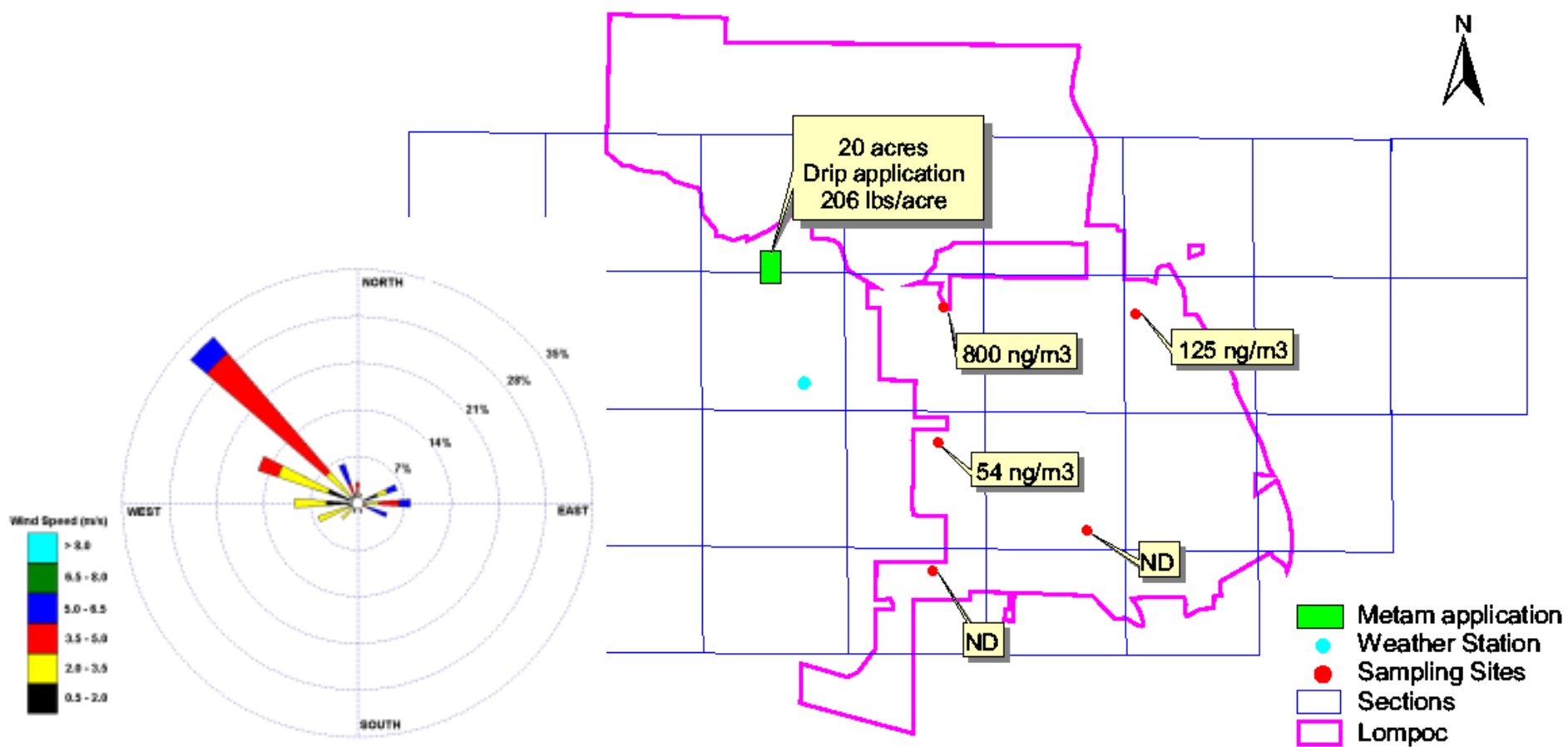
Sampling interval 2/5/00 16:00 - 2/6/00 08:00



Direction wind is blowing "to"

Figure 17. Interval with highest concentrations of MITC for metam sodium application October 28, 2000.

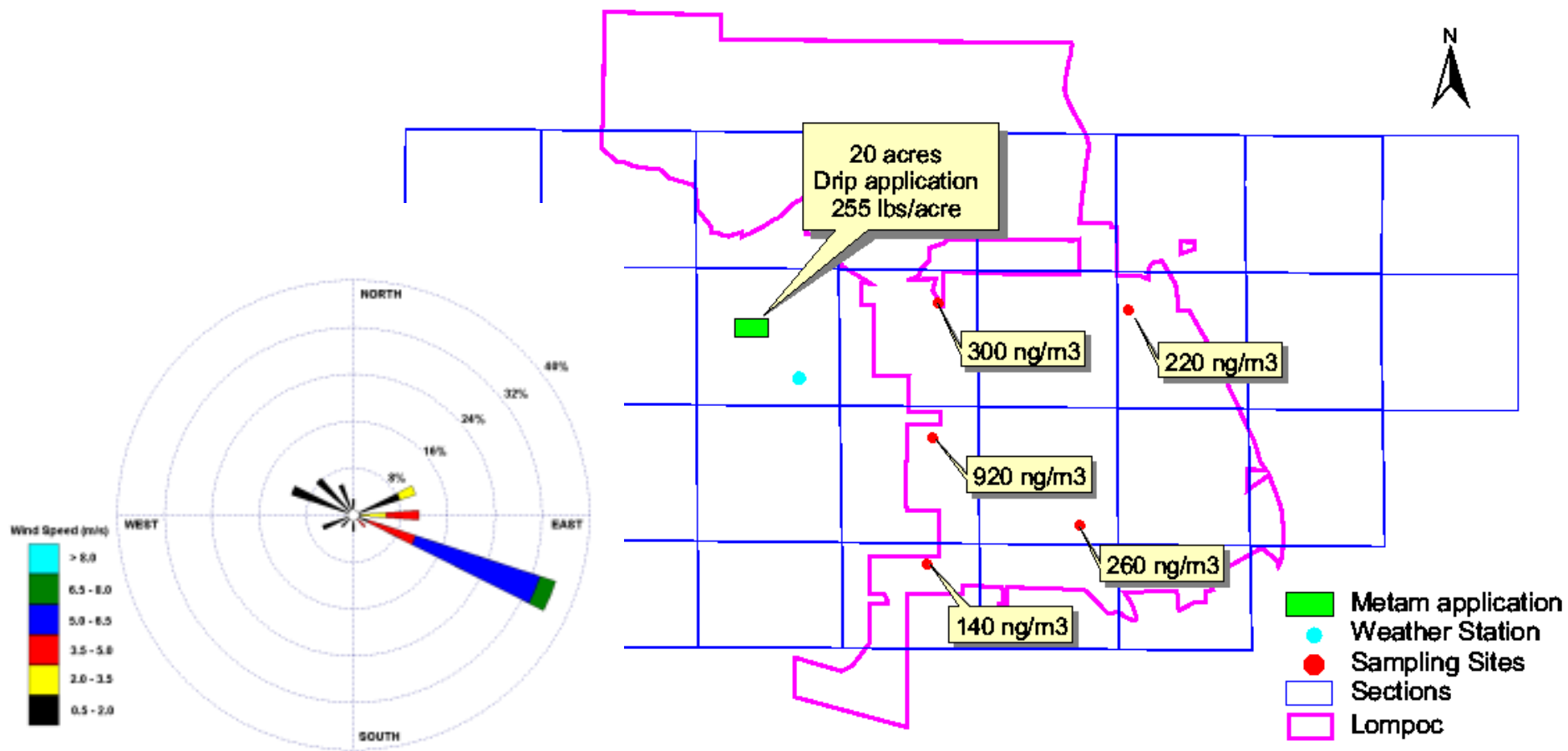
Sampling interval 10/28/00 17:00 - 10/29/00 09:00



Direction wind is blowing "to"

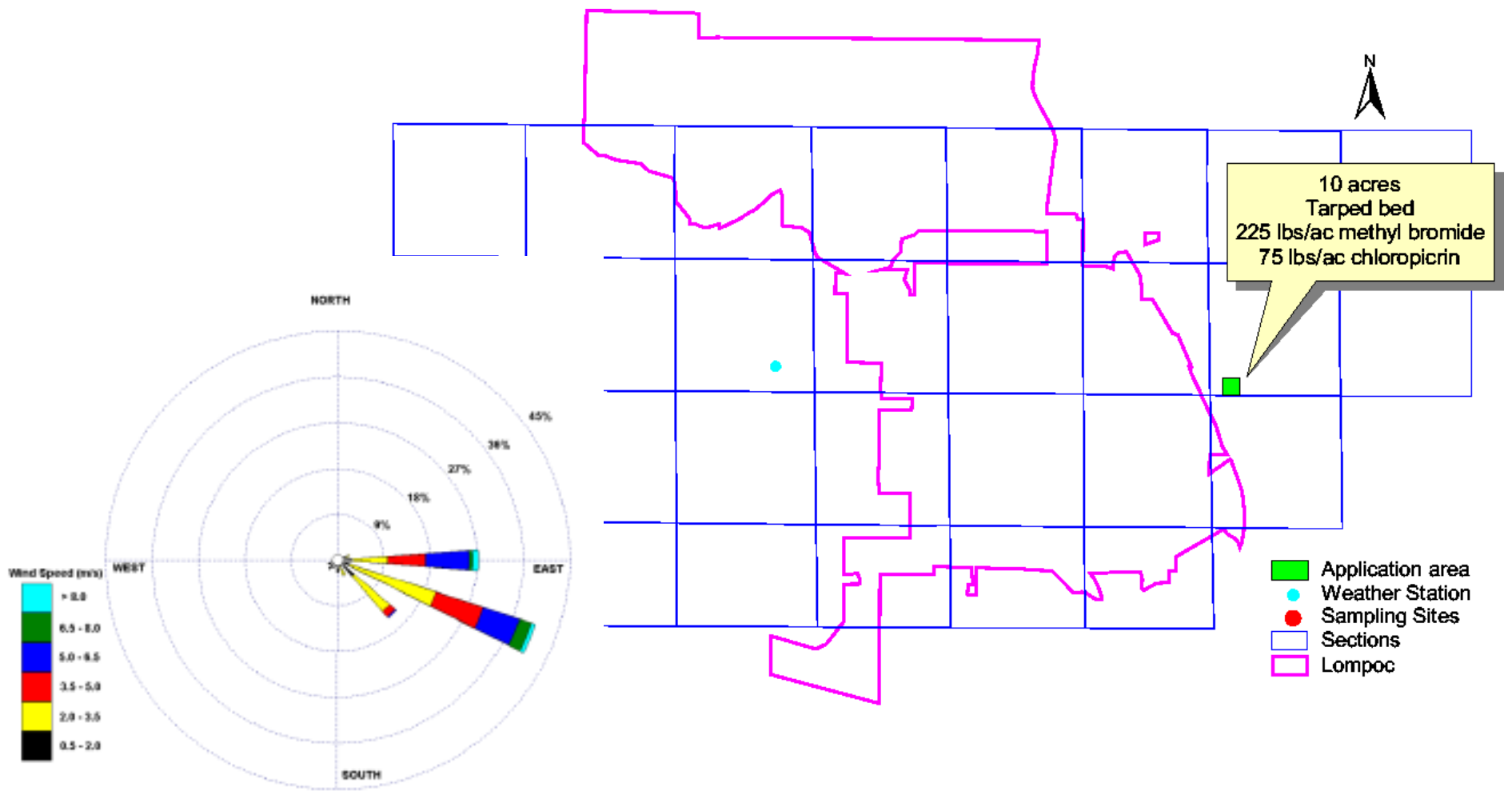
Figure 18. Interval with highest concentrations of MITC for metam sodium application November 16, 2000.

Sampling interval 11/16/00 07:00 - 11/16/00 16:00



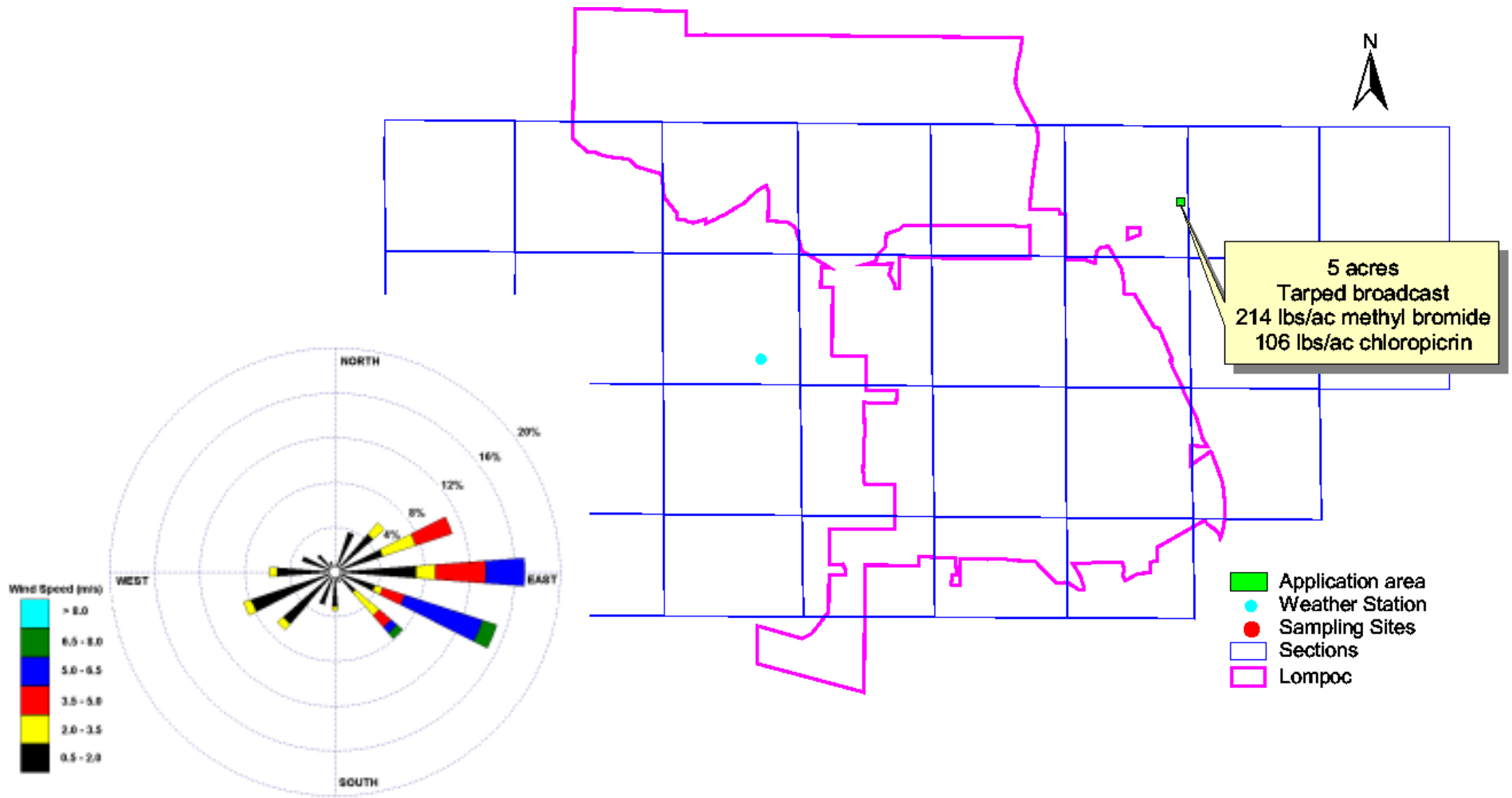
Direction wind is blowing "to"

Figure 19. Wind direction and application site for methyl bromide/chloropicrin application October 7, 2000.



Direction wind is blowing "to"

Figure 20. Wind direction and application site for methyl bromide/chloropicrin application November 18, 2000.



Direction wind is blowing "to"

Results from Meteorological Stations

A summary of the meteorological data recorded for each application monitored is given in Table 12 and Figures 21 - 24. Weather conditions during the applications monitored were typical for the winter and fall seasons in Lompoc, as documented in Johnson, 1998.

Table 12. Summary of weather data for each fumigant application. All rain measurements obtained from National Weather Service from location in Lompoc unless otherwise noted.

Fumigant	Monitoring Period	Wind Speed (mph)		Temperature (°F)		Wind Direction Figure	RH (%) Range
		range	average	Range	average		
Metam-sodium	1/12/00 07:00 - 1/15/00 07:00	0.5 - 17.9	5.0	37 - 78	51	21	N/A
Metam-sodium	1/27/00 15:00 - 1/30/00 15:00	0.5 - 24.7	8.6	39 - 67	52	21	40 - 97 ¹
Metam-sodium	2/2/00 16:00 - 2/5/00 08:00	0.6 - 29.3	9.6	45 - 72	57	22	30 - 95 ²
Metam-sodium	2/5/00 08:00 - 2/8/00 08:00	0.5 - 20.6	6.5	42 - 81	58	22	54 - 97
Metam-sodium	10/28/00 09:00 - 10/31/00 09:00	0.5 - 22.2	6.9	42 - 71	56	23	58 - 93 ³
Metam-potassium	11/16/00 05:30 - 11/19/00 08:00	0.5 - 16.9	5.0	28 - 72	46	23	22 - 88
methyl bromide	10/7/00 10:30 - 10/10/00 09:00	0.5 - 22.1	7.6	54 - 68	60	24	68 - 92 ⁴
methyl bromide	11/18/00 08:00 - 11/21/00 08:00	0.5 - 36.6	11.2	28 - 66	44	24	29 - 67

¹ During the last sampling interval there was very light rain, 0.06 inches measured from 10:00 January 30th to 10:00 January 31th.

² During the day and night following the application there was approximately 0.5 inches of rain measured at nearby Vandenberg Air force Base.

³ During the night and morning immediately following application (sampling interval 2) it rained approximately 0.7 inches.

⁴ During the third night (interval 6) it rained a total of 0.1 inches.

Figure 21. Wind Speed and Direction wind is blowing to during the first and second MITC applications monitored.

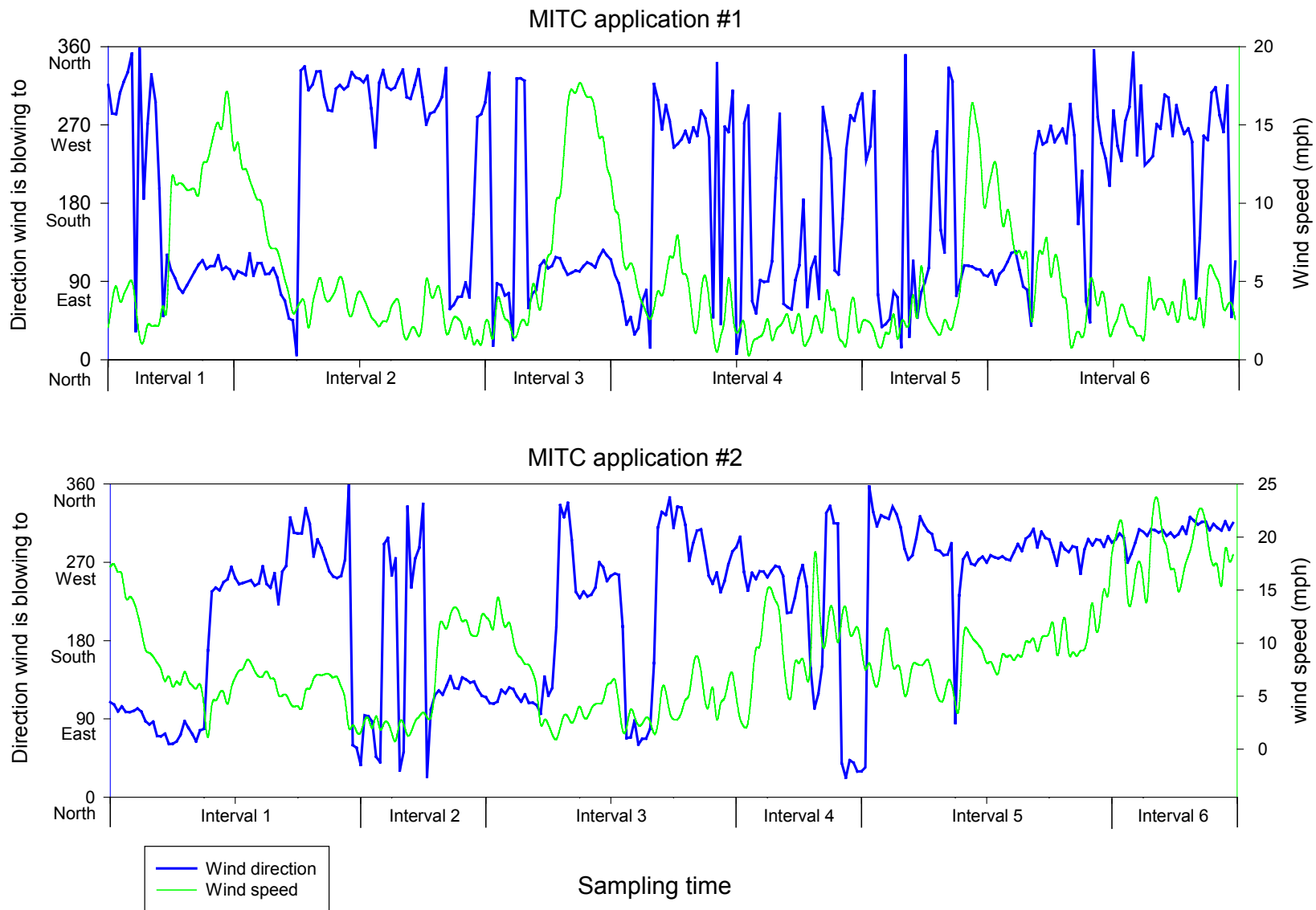


Figure 22. Wind Speed and Direction wind is blowing to during the third and fourth MITC applications monitored.

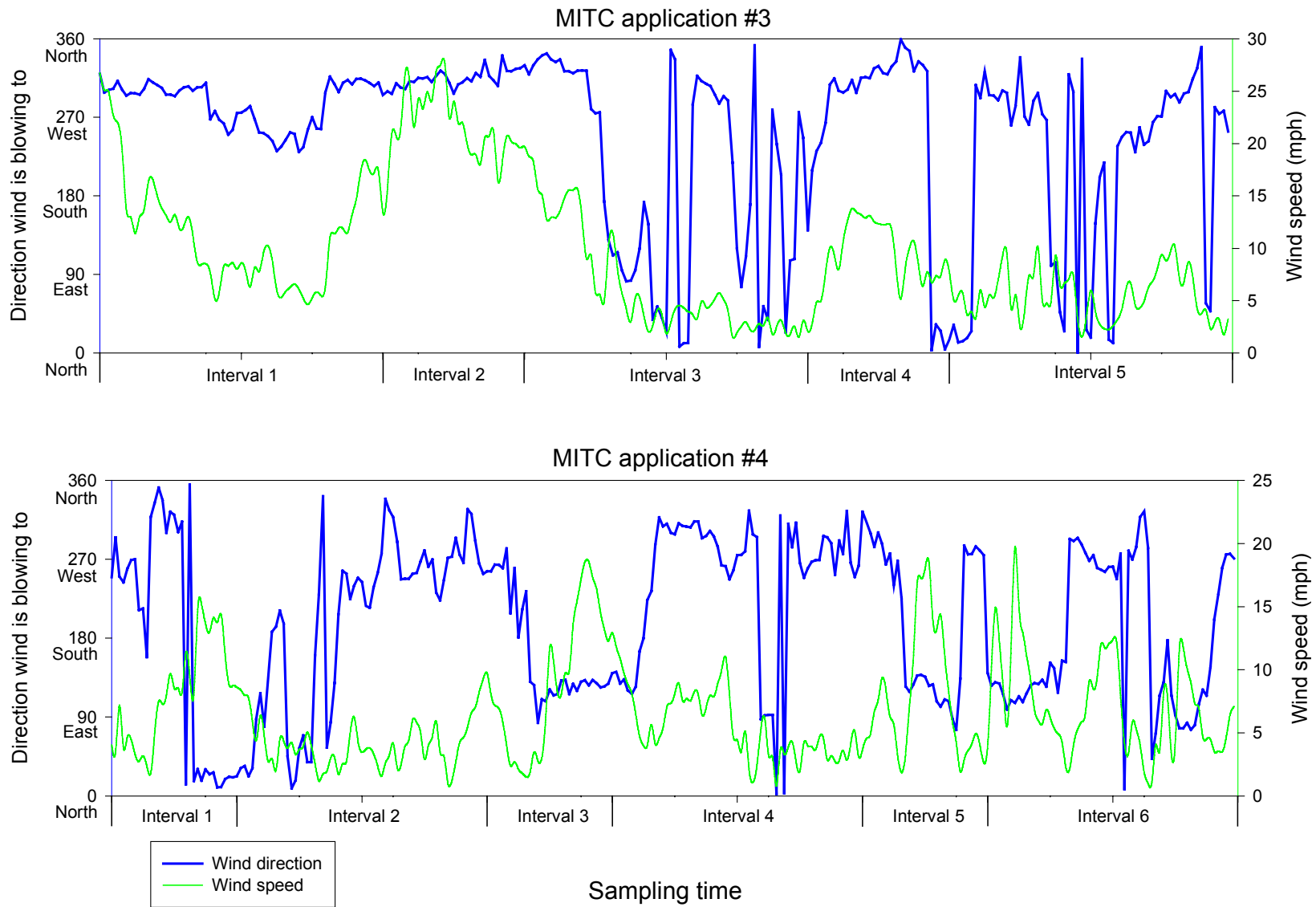


Figure 23. Wind Speed and Direction wind is blowing to during the fifth and sixth MITC applications monitored.

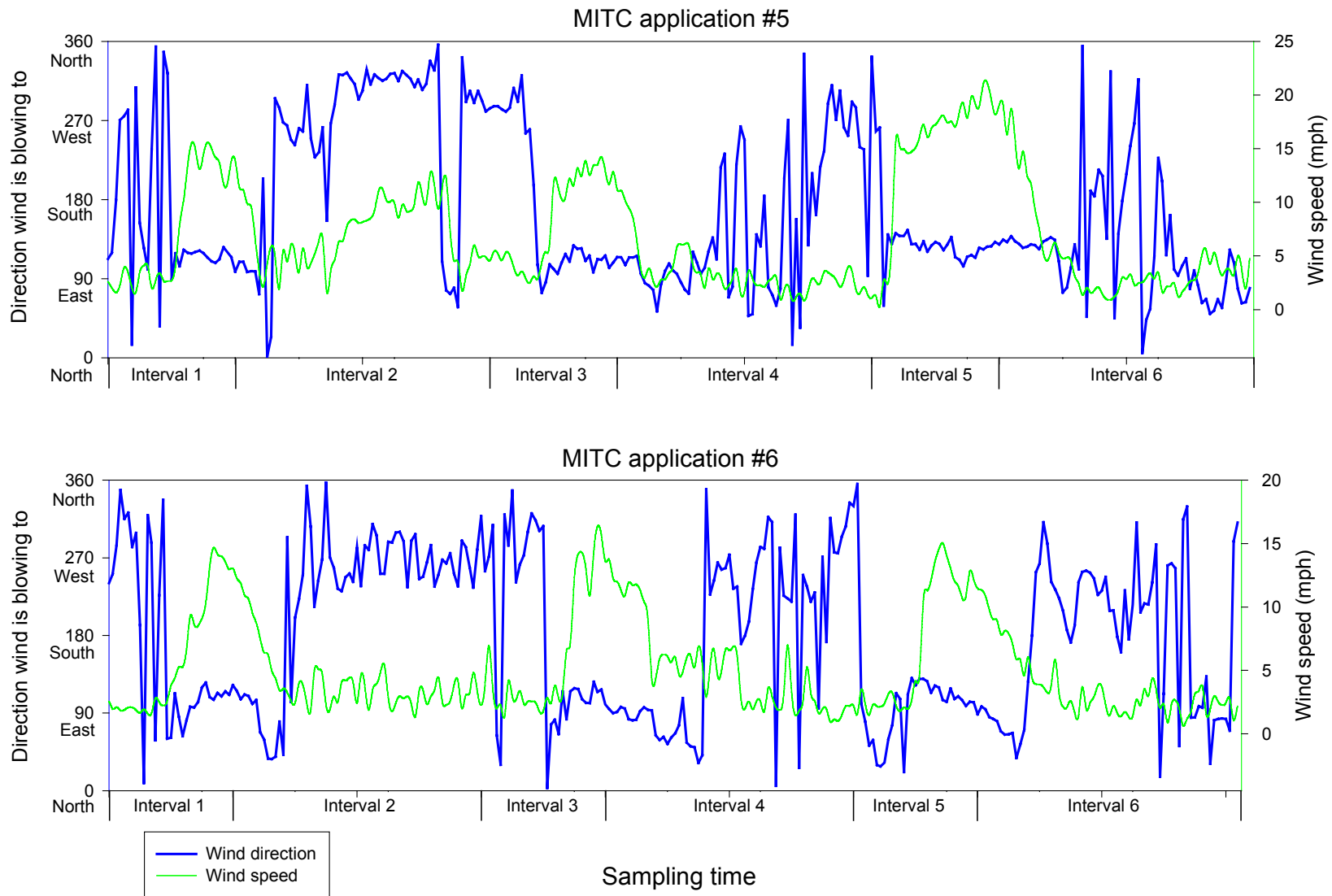
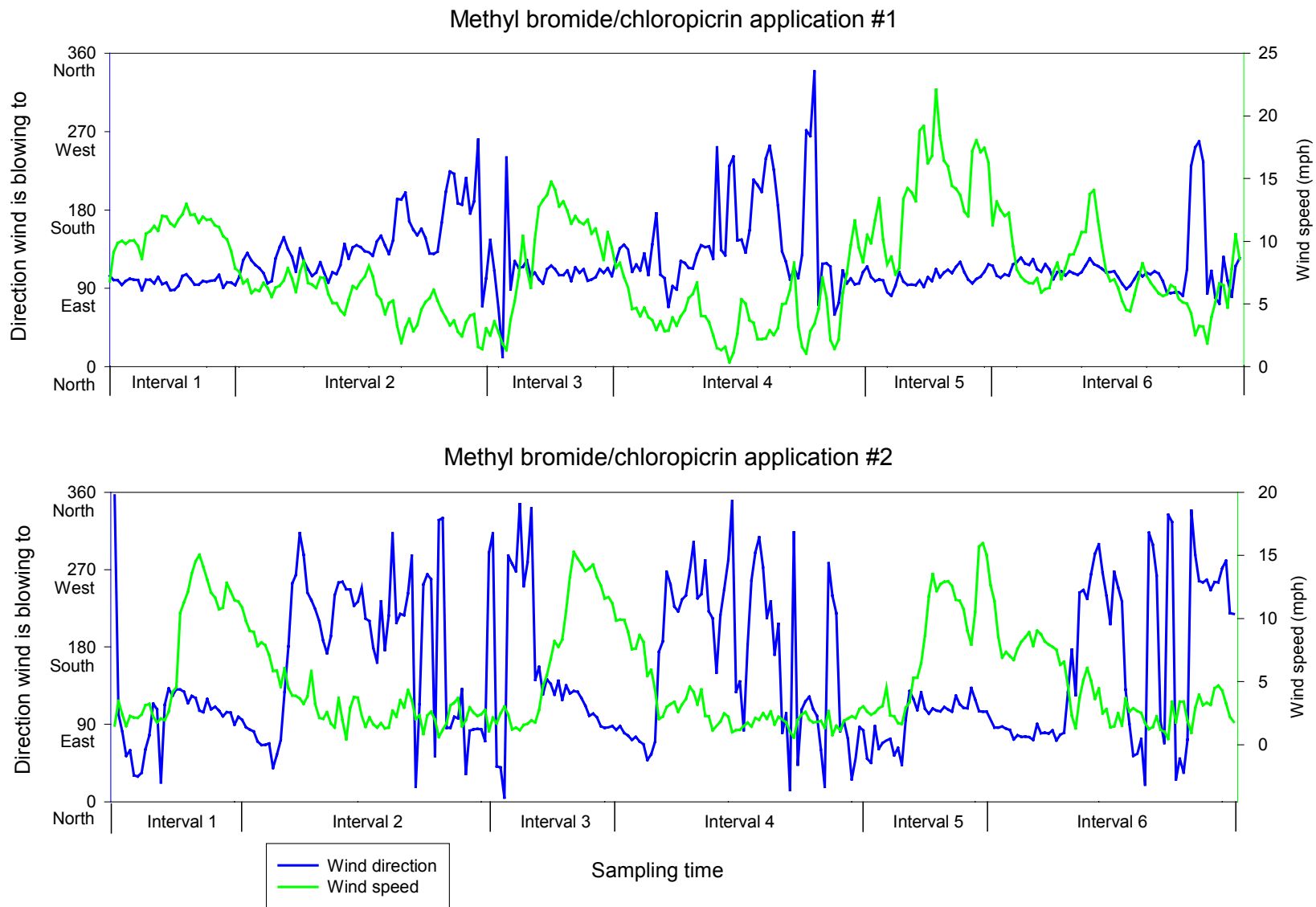


Figure 24. Wind Speed and Direction wind is blowing to during the first and second methyl bromide/chloropicrin applications monitored.



As a quality control check on the meteorological data collected by the MetOne® station, weather data was compared to data collected by the Santa Barbara County Air Pollution Control District (APCD) station at the H Street sampling site. Regressions of the wind speeds during each of six MITC monitoring periods between the two meteorological stations were all highly statistically significant ($p < .001$). On average the H Street wind speeds were 59 percent of the DPR wind speeds. The APCD station is located in a central business district of Lompoc and is surrounded by trees and buildings that could alter wind speeds measured at the site, while the DPR weather station is located west of the city in an open agricultural area. It was difficult to compare the wind directions measured by the two weather stations because different methods were used by the systems to average measurements. A regression of corresponding hourly wind directions from the APCD and DPR was not statistically significant. Lack of statistical significance was probably due to differences in the computational algorithms, as well as the siting differences mentioned above. The presence of buildings and trees at the H Street station may cause local variations in wind direction, not observed in the more open site of the DPR station. Another factor contributing to the differences in wind direction may have been the localized topography. The DPR site was more in the center of the valley. The H Street site was two miles east of the DPR site, closer to the southeastern end of the valley that terminates in hilly terrain. Although no formal audit of the weather station was conducted, the DPR weather station was checked monthly against hand held instruments.

Results of Computer Modeling and Statistical Analysis

The magnitude of pesticide air concentrations depends on numerous factors such as the amount of pesticides applied, distance from applications, volatility of the pesticides, method of application, terrain, and weather. The monitoring results discussed in this report are based on sampling of a few applications, at a few locations, during a few time periods. Additional analysis of the data is necessary to estimate air concentrations for applications, locations, and time periods that were not monitored. Only MITC has sufficient monitoring data to attempt additional analysis.

All six of the metam applications were modeled with the U.S. EPA gaussian plume dispersion model, ISCST, version 3 (U.S. EPA 1995) to attempt to estimate air concentrations for locations and time periods not monitored. Unfortunately, the regressions of the modeled concentrations versus the measured concentrations did not show a significant relationship for most of the sampling intervals. In other words, the air concentrations predicted by the model did not match the air concentrations measured in the field, no matter what emission rate was used. It was not possible to use the computer model to estimate air concentrations for other locations and time periods. The regression statistics for the intervals with the highest concentrations measured during each application versus the modeled concentrations for those intervals are listed in Table 13.

Table 13. Regression statistics for modeled MITC concentrations

Application	Interval	r^2	<i>P</i> value	Slope
1/12/00	4	0.127	0.557	
1/28/00	2	0.381	0.267	
2/3/00	5	0.063	0.685	
2/5/00	2	0.190	0.463	
10/28/00	2	0.994	<0.001	0.052
11/16/00	1	0.008	0.884	

Because regression equations could not be adequately determined, an emission rate estimate was not possible. Additional attempts to determine the emission rate for two of the applications (three and four) were unsuccessful (Appendix S). Since it was not possible to determine a correlation between the measured concentrations and modeled concentrations, it would be inappropriate to attempt further estimations.

There may be several reasons why the modeled air concentrations did not match the measured air concentrations. First, this modeling approach assumes a constant emission rate for the entire eight or 16-hour sampling period. Modeled and measured air concentrations may not correlate if the emission rate varies during the sampling period. Second, the data from the DPR weather station was used for the model inputs. As discussed earlier, there are significant differences in weather measurements between DPR's weather station and the H Street station. The difference in weather conditions between the agricultural area (source) and Lompoc (monitoring stations) may account for the lack of correlation. Attempts to model air concentrations using the H Street weather data were also not successful.

DPR also attempted to estimate air concentrations for other applications by correlating the measured air concentrations with some application parameters. DPR found a correlation between the amount of metam applied and maximum air concentration detected (Table 14). However, the TAG is not in agreement that this correlation is robust enough to estimate air concentrations for other metam applications. This correlation is based on monitored applications that may not be representative of other applications. There was no correlation found between distance of application and the measured air concentrations (Table 15).

Table 14. Concentration, pesticide use and distance from application to the Lompoc city limits.

Fumigation (date)	Maximum Concentration* (ng/m ³)	Amount Applied (lbs)	Distance (mi)
MITC 1 (1/12/00)	150	1619	3.00
MITC 2 (1/28/00)	340	3340	0.75
MITC 3 (2/3/00)	47	2386	0.70
MITC 4 (2/5/00)	300	2386	0.60
MITC 5 (10/28/00)	800	4771	1.00
MITC 6 (11/16/00)	920	5104	1.50
Methyl bromide 1 (10/7/00)	ND (<2000)	2250	0.15
Methyl bromide 2 (11/18/00)	Trace (<4000)	1072	1.25
Chloropicrin 1 (10/7/00)	ND (<74)	750	0.15
Chloropicrin 2 (11/18/00)	ND (<74)	528	1.25

*Sorbent tube results

Even though the computer modeling was not successful, information on additional fumigant applications made during 2000 are listed in Table 15 for a comparison to monitored applications. Figures 25 and 26 show the location and information for each of the fumigations in 2000 that were not monitored. A metam-sodium application made on the east side of Lompoc on January 15th occurred on the last day of monitoring the January 12th application. The methyl bromide application on November 20th probably occurred during the fifth sampling interval in the same section as the application monitored.

Table 15. Additional fumigant applications during the study that were not monitored.

Fumigant	Number of Applications	Pounds Applied (a.i.)	Acres
Chloropicrin	9	7300	113
Metam-sodium	36	7263	379
Metam-potassium	7	28893	118
Methyl bromide	9	20826	113

Figure 27 presents the amount of metam (metam-sodium and metam-potassium) applied during each application made in 2000 for comparison to the applications monitored by the study. The largest metam application monitored by DPR was 5,104 pounds. Figure 27 shows that of the 49 metam fumigations in the Lompoc area during 2000, two used more than 5,104 pounds of metam (9,568 pounds and 6,043 pounds).

The maximum measured 24-hr concentration was 845 ng/m³. The estimated 95th percentile 24-hr air concentration was 3,624 ng/m³. The 90 percent tolerance limit for the 95th percentile was 10,880 ng/m³. That is, if these concentrations do come from a lognormal population, the probability is 0.90 that at least 95 percent of 24-hr MITC concentrations are below 10,880 ng/m³.

Figure 25. Additional methyl bromide/chloropicrin applications during 2000 which were not monitored.

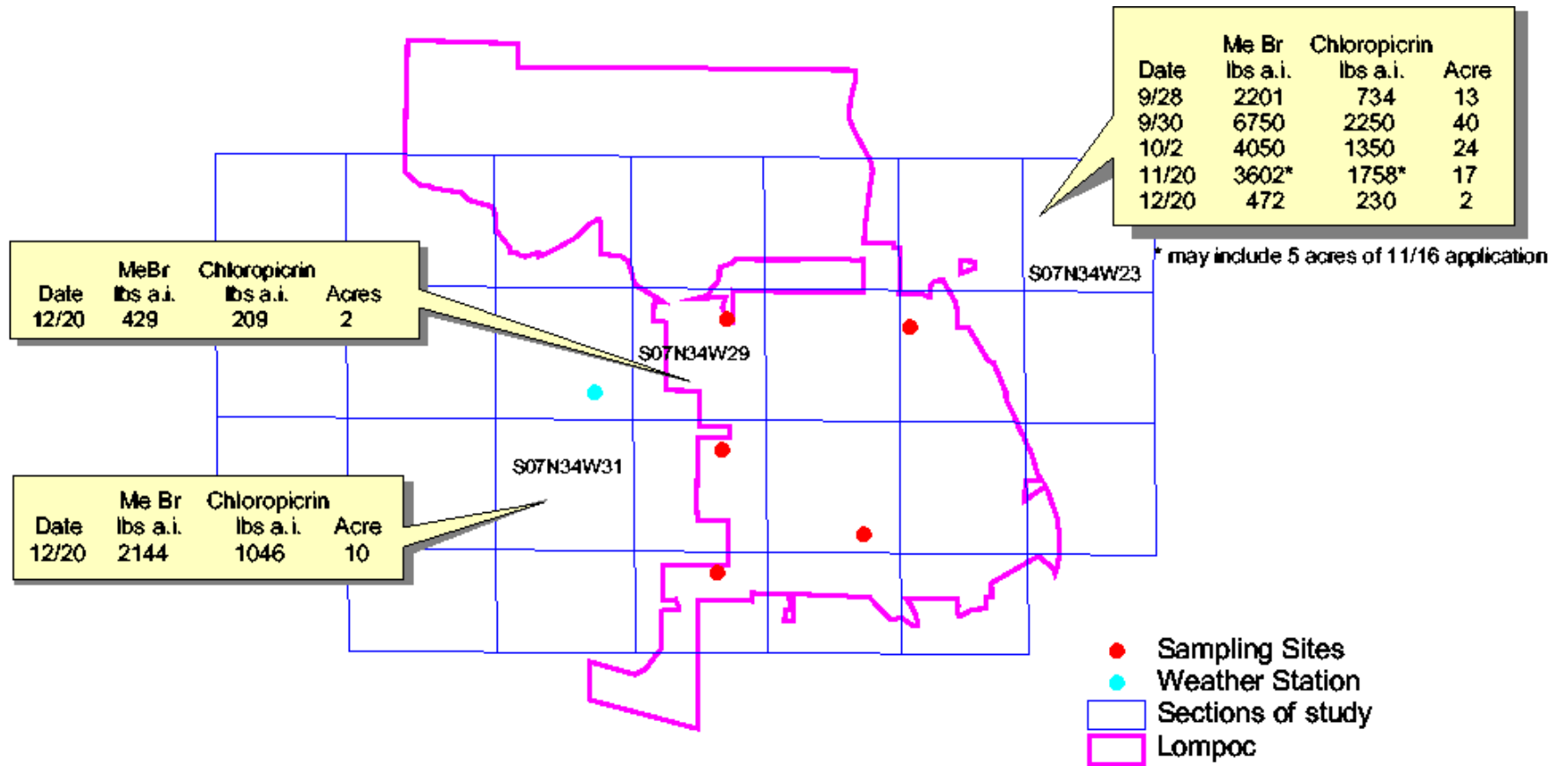
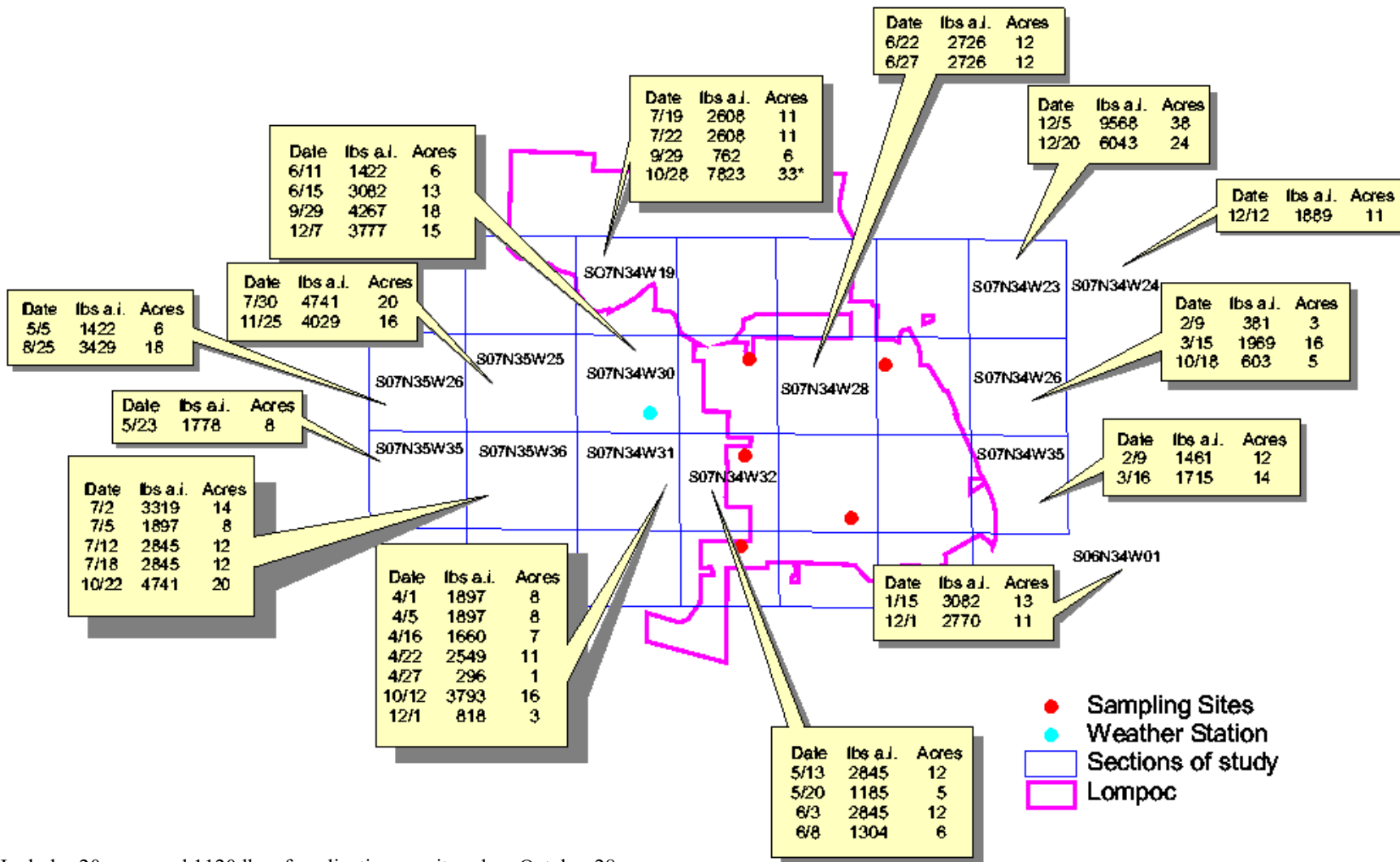
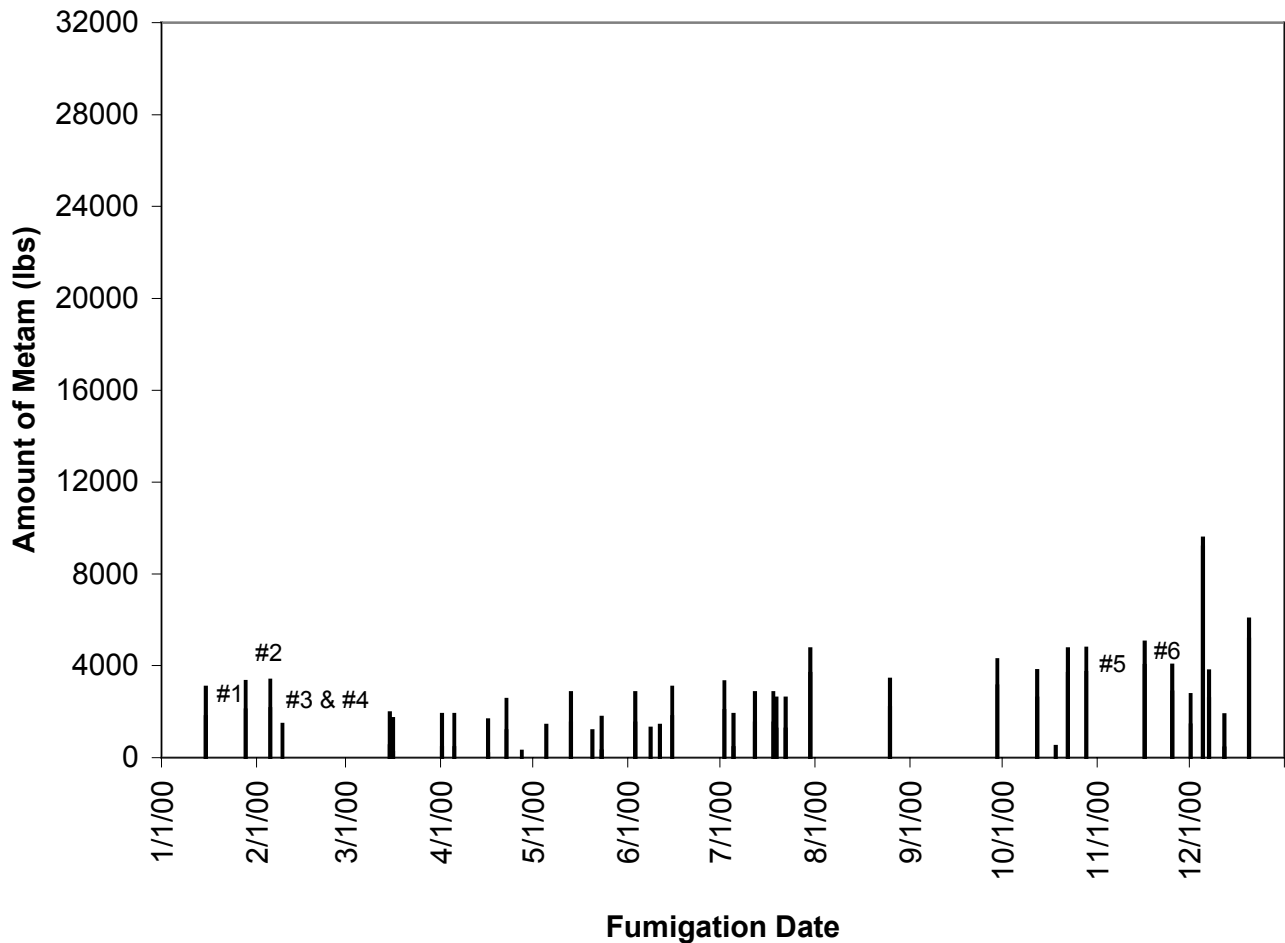


Figure 26. Additional MITC (metam sodium and metam potassium) applications during 2000 which were not monitored.



*Includes 20 acres and 1120 lbs of application monitored on October 28, additional acreage treated on October 25

Figure 27. Metam (metam-sodium and metam-potassium) applications in 2000 and amount applied.



Comparisons to Other Monitoring in California

Both methyl bromide and MITC were monitored during phase one sampling in Lompoc in 1998, but due to poor sample handling practices and insufficient quality assurance/quality control of the samples are considered invalid and are not included in this section. Toxic Air Contaminant program studies conducted by the ARB, in consultation with DPR, has measured other ambient air concentrations of fumigants in California. Monitoring for pesticides is conducted in counties with the highest use for a particular pesticide during the season of highest use. The following summarizes information from air sampling conducted under the toxic air contaminant program.

Chloropicrin was measured in Monterey County in September 1986 using sorbent resin and analyzed by gas chromatography and an electrolytic conductivity detector (Baker et al., 1996). Three sites were measured over the course of 16 days with 28 percent of the samples above the minimum quantitation level of 85 ng/m³. The maximum four-hour concentration was

4600 ng/m³, the average was 640 ng/m³, and the mean urban background concentration was <85 ng/m³. No samples collected in Lompoc contained a detectable amount of chloropicrin.

Methyl bromide was measured in Monterey County in September 1986 using petroleum-based sorbent and analyzed by gas chromatography and an electron capture detector (Baker et al., 1996). The maximum four-hour concentration was 4400 ng/m³, the average was 4100 ng/m³, and the mean urban background concentration was <4200 ng/m³. Methyl bromide was measured in Monterey and Santa Cruz Counties in the fall of 2000 and 2001 and Kern County in the summer of 2000 and 2001 using sorbent tubes and canisters (ARB 2001, 2002a, 2002b). The maximum 24-hour concentration measured in Monterey and Santa Cruz Counties in 2000 was 119,000 ng/m³, the maximum average over 8 weeks was 28,900 ng/m³, and the eight-week mean urban background concentration was 5250 ng/m³. In 2001 the maximum 24-hour concentration measured in Monterey and Santa Cruz Counties was 142,000 ng/m³, the maximum average over 8 weeks was 23,800 ng/m³, and the eight-week mean urban background concentration was 5400 ng/m³. In Kern County the maximum concentration measured in 2000 was 55,000 ng/m³, the maximum average over eight weeks was 9,020 ng/m³, and the eight-week mean urban background concentration was 692 ng/m³. In 2001 the maximum 24-hour concentration measured was 98,300 ng/m³, the maximum average over eight weeks was 11,000 ng/m³, and the eight-week mean urban background concentration was 455 ng/m³. Two samples collected in Lompoc contained methyl bromide at levels below a quantifiable amount.

MITC was measured in Kern County in July 1993 using sorbent tubes and analyzed by gas chromatography and a nitrogen-phosphorous detector (Baker et al., 1996). Four sites were measured over the course of eight days with 83 percent of the samples above the minimum quantitation level of 10 ng/m³. The maximum 24-hour concentration was 18,000 ng/m³, the average was 5800 ng/m³, and the mean urban background 24-hour concentration was 2100 ng/m³. In Kern County in the summer of 1997 and winter of 1998 (Seiber et al., 1999), 12-hour ambient samples were collected at several indoor and outdoor locations. Each sampling period was one week long and one sampling period occurred each month over the course of four months. During the summer of 1997, the maximum concentration indoors was 1800 ng/m³, 1060 ng/m³ for the outdoor house samples near the houses, and 3110 ng/m³ for outdoor ambient "environmental samples". Over 75 percent of the samples collected in the summer of 1997 had measurable concentrations of MITC. During the winter of 1998, the maximum concentration was 3690 ng/m³ for the indoor samples, 4530 ng/m³ for the outdoor house samples, and 4060 ng/m³ for the outdoor ambient samples. Nearly 67 percent of the samples collected in the winter of 1998 had measurable concentrations of MITC. The University of Nevada, Reno conducted this monitoring. They also conducted the analysis of the Phase One fumigant samples from Lompoc. The laboratory problems associated with Phase One may or may not have occurred with this monitoring.

Ambient air monitoring of fumigant applications in Lompoc resulted in a measurable concentration of MITC in 57 percent of the samples. Maximum 24-hour concentrations measured on sorbent tubes in the previous studies were: 18,000 ng/m³ in 1993, 3110 ng/m³ in the summer of 1997, and 4530 ng/m³ during the winter of 1998. The highest concentration measured during the Lompoc study on a sorbent tube was 920 ng/m³ for a nine-hour sample.

As a comparison to previous studies, the highest 24-hour time-weighted average on sorbent tubes measured in Lompoc was 677 ng/m³ (Table 16). Although none of the previous MITC monitoring studies had used canisters, the highest 24-hour time-weighted average measured on canisters in the Lompoc study was 1292 ng/m³. The difference in concentration is in part due to the difference in use in the study areas. The results from phase one monitoring in Lompoc are considered invalid to poor sample handling practices and insufficient quality assurance/quality control of the samples.

Table 16. Highest 24-hour MITC concentrations measured in Lompoc and previous monitoring studies.

Year	County	Maximum 24-hour Concentration (ng/m ³)	Percent of Samples with Measurable Concentrations	Metam-Sodium Use in County During Year of Study (lbs a.i.)
1993	Kern	18,000	83	1,028,870
1997	Kern	3,110	75	3,866,530
1998	Kern	4,530	67	3,261,010
2000	Lompoc	677	57	664,440

Results of Health Evaluation

As mentioned earlier in this report, the risk or health significance of a chemical(s) in air is a function of both the inherent toxicity of the chemical(s) as well as the level of exposure to the chemical(s). The potential health significance of the measured levels of fumigant pesticides in Lompoc air can be evaluated by comparing the air concentration measured over a specified time (e.g. eight hours, 16 hours, 24 hours, three days) with the screening level derived for a similar time (acute, subchronic).

Acute Exposure

For these calculations DPR used the highest concentration measured during any one interval (eight or 16-hour). This resulted in a more conservative comparison since a 24-hr time-weighted average concentration will be lower. As can be seen from the “Acute Hazard Quotient” column in Table 17, the HQs for MITC are ten times less than one or lower. HQs below one indicate low risk.

Subchronic Exposure

To evaluate the potential health risk of subchronic exposure to the individual monitored fumigants, the highest 30 to 90-day time-weighted average concentration at any site should be used. In this study the highest three-day air levels were used to evaluate the potential health effects from subchronic exposure to the monitored fumigants. Since subchronic exposure is considerably longer than three days, this is an overestimate of subchronic exposure.

As can be seen from the “Subchronic Hazard Quotient” column in Table 17, the HQs for MITC are nearly ten times less than one. Therefore, no further refinement of the estimate of the subchronic exposure period is necessary.

Chronic Exposure

As a simple attempt to estimate a chronic exposure to MITC, an average of air concentrations on all the monitored days, was calculated for each monitoring site. The highest average air concentration of 244 ng/m³ (adjusted for recovery) is from the Northwest site (unadjusted value is 183 ng/m³). The completed TAC Health Evaluation Document for MITC established a subchronic REL of 3000 ng/m³ based on respiratory irritation in a 4-week rat inhalation study. The TAC Health Evaluation Document is available online at www.cdpr.ca.gov/docs/emprm/pubs/mitc/augfinl02/augexs.pdf. Since a chronic inhalation study was not available, the TAC document established a chronic REL by applying a 10-fold uncertainty factor to the subchronic REL, resulting in a chronic REL of 300 ng/m³. This chronic REL can be used as the chronic screening level for MITC.

As can be seen from the “Chronic Hazard Quotient” column in Table 17, the HQs for MITC are less than one. Therefore, no further refinement of the estimate of the chronic exposure period is necessary.

Hazard quotients were not calculated for the methyl bromide results since the concentrations were not quantifiable (trace amounts). To determine a hazard quotient from a trace result would be misleading since the actual concentration is not known, but only a range can be given. With that noted, even if the highest concentration of the range of a trace detection is used, the resulting hazard quotient would be significantly less than one.

Table 17. Hazard quotient calculations.

		MITC (sorbent tube)		MITC
		unadjusted	adjusted ^a	(canister)
Acute (8 or 16 hours)	Screening Level (ng/m ³)	66,000	66,000	66,000
	Concentration (ng/m ³)	920 ^b	1196 ^b	1885 ^c
	Hazard Quotient	0.014	0.018	0.029 ^c
Subchronic (3 days)	Screening Level (ng/m ³)	3,000	3,000	3,000
	Concentration (ng/m ³)	573	743	619
	Hazard Quotient	0.191	0.248	0.206
Chronic (18 days)	Screening Level (ng/m ³)	300	300	NA
	Concentration (ng/m ³)	183	244	NA
	Hazard Quotient	0.610	0.813	NA

^a MITC sorbent tube concentrations adjusted to account for 70% recovery.

^b 8-hour sample

^c 16-hour sample

NA - Not applicable

The screening levels initially included as part of the Fumigant Sampling and Analysis Plan were discussed in a November 29, 1999 memorandum (see Appendix P) and agreed upon by DPR, OEHHA, and DHS toxicologists. OEHHA suggested that an additional uncertainty factor of 10 be included for methyl bromide to account for the potential increased sensitivity of children. At the time, the DPR risk assessment on methyl bromide was undergoing peer review by the National Academy of Sciences (NAS). Since the NAS peer review was not completed, the additional factor of 10 was incorporated into the screening levels for methyl bromide. Since that time, the NAS review has been concluded. In that review, NAS was asked among other things to review the endpoints that DPR selected and whether an additional 10-fold factor was appropriate. The NAS supported the toxicological endpoints selected by DPR and stated that the additional 10-fold factor was not appropriate. Therefore, the additional factor has been removed, raising the original screening levels by a factor of 10.

The acute screening level for MITC described in the November 29 memorandum was based on the results of a human study, but at the request of OEHHA incorporated an additional uncertainty factor of 10 to address more sensitive individuals. Since the November 29 memorandum, DPR has prepared the health evaluation of MITC for the Toxic Air Contaminant (TAC) Program. This evaluation has been peer reviewed and accepted by the Science Review Panel (SRP). The TAC document that was accepted by the SRP uses an acute REL without this additional factor. Therefore, the screening level no longer incorporates this additional factor. As part of this TAC review process, a different inhalation study was selected for evaluating subchronic exposure to MITC in the air. This study and the resulting screening level is now used. The basis for the initial selection and subsequent modification of the screening levels is described in more detail in the memoranda contained in Appendix P.

The screening levels, modified as described above are included in Table 7.

DATA VALIDATION/QUALITY ASSURANCE

Data Review

Before any statistical or other evaluation of the data took place, the entire set of field logbook sheets and laboratory quality assurance data was reviewed to determine the strength of the data for final assessment. The field logbook records were checked for any notations of flow faults or stoppage in sample collection, or any changes in the flow over the sampling interval greater than 25 percent. Any problems encountered during sampling are noted in the raw data results (Appendix R).

Sample Shipment Quality Assurance

Measurements collected by the temperature recorders located in the sample shipment containers were reviewed for any occurrence of temperature changes during shipment that would adversely affect the samples. No unusual temperature changes were found.

Pesticide Use Report Validation

The methods used in the validation of the DPR's pesticide use reporting database are located in the DPR report PM 01-02 entitled "Final Report to the California Department of Food and Agriculture for Contract Agreement No. 98-0241 Data Quality of California's Pesticide Use Report" (Wilhoit et al, 2001).

Audit Results

The quality assurance team performed informal audits prior to the start of the study, as well as formal audits while the study was in progress. The quality assurance team performed the pre-study audits on October 12 - 13, 1999. The pre-study audit recommended several minor procedural changes, which were implemented (Appendix T).

The quality assurance team performed the first study audits on February 16, 2000. The quality assurance team again found some procedures that could be improved, most significantly a couple of procedures that could potentially lead to cross-contamination of samples. The laboratories revised their procedures to address these issues (Appendix T). The quality assurance team performed a second audit on November 30, 2000, to review the new canister method for MITC, and to review the procedures at the U.S. EPA Region 9 laboratory that had not been involved in the study previously. The second audit found that the U.S. EPA Region 9 laboratory had insufficient time to prepare trip spikes, and the laboratories could not obtain standards from a second source for verification. The quality assurance team also found that the canisters did not work properly in some cases, and that DPR placed samplers less than one meter above the roof; a one meter minimum is required by the siting criteria (Appendix E).

The quality assurance team also reviewed the canister data for MITC, comparing the data to sorbent tube data. The quality assurance team found that canister values ranged from 0.84 to 3.46 times the values of the sorbent tubes. The quality assurance team recommended that canister data be used to assess any possible risk (Appendix T). Since the canisters were not the primary monitoring method, they were not used for all samples. Therefore, the canister data cannot be used in all cases to estimate exposure and risk. A more detailed explanation of the exposure and risk estimates using both canisters and sorbent tubes is given in the health evaluation methods section of data analysis methods.

A field investigation of flow rate measurements was conducted by a certified industrial hygienist from the U.S. EPA during the sixth metam-sodium application monitoring event (Appendix U). The field investigator found that DPR made good efforts to provide field reliable measurements for flow rate. The flow rate results were within limits expected for this event.

Quality Control Results

Methyl Bromide

All sorbent tubes were analyzed by CDFA. Canisters were analyzed by the U.S. EPA Region 9 laboratory.

The spike level for the trip and field sorbent tube spikes was 2000 ng/sample. The laboratory samples were spiked at a 1000 ng/sample and 5000 ng/sample level. The field spike recoveries ranged from 56.5 to 63.0 percent, with a median of 61.0 percent (four samples). Two of the three 16-hour sampling period spikes demonstrated migration (movement from the first sampling tube to the second tube) with an average migration of 26.1 percent (Table 18). There was no migration in the eight-hour or the other 16-hour spike sample. All samples for methyl bromide included a second backup tube for analysis. The trip spike recoveries ranged from 61.0 to 65.0 percent, with a median of 62.25 percent (four samples). There is no significant difference between the field and trip spike recoveries. The laboratory spike recoveries ranged from 65.0 to 78.0 percent, with a median of 73.3 percent (four samples). There was no difference in recoveries between the 1000 ng and 5000 ng/sample spike levels. There was a significant difference between the laboratory spikes and the trip spikes ($P < 0.001$) indicating there may be some loss in transport. The difference between the average laboratory spike recovery (16 samples) and average trip spike recovery (four samples) is 10.5%.

Table 18. Analytical results from the methyl bromide field and trip spikes.

Type of Spike	Date On	Duration (hours)	Results			Spike Level (ug)	Recovery %	Migration %
			Front tube (ug)	Back tube (ug)	Total (ug)			
Field	10/8/00	16	0.96	0.3	1.26	2	63.0	23.8
Field	10/8/00	16	0.86	0.34	1.2	2	60.0	28.3
Field	11/20/00	8	1.24	0	1.24	2	62.0	0.0
Field	11/20/00	16	1.13	0	1.13	2	56.5	0.0
Trip			1.24	0	1.24	2	62.0	0.0
Trip			1.25	0	1.25	2	62.5	0.0
Trip			1.3	0	1.3	2	65.0	0.0
Trip			1.22	0	1.22	2	61.0	0.0

All primary and duplicate sorbent tubes contained no detectable amount of methyl bromide. No methyl bromide was detected in any trip blank or lab blank.

There were no spiked canisters of methyl bromide. There were no methyl bromide detections in the trip blank (one sample) or laboratory blank samples (seven samples). Of the 20 canisters collocated with a sorbent tube sample, two contained detectable amounts of methyl bromide, both levels were below the reporting limit for analysis on sorbent tubes. The collocated sorbent tubes contained no detectable amounts of methyl bromide.

Chloropicrin

All sorbent tubes were analyzed by CDFA.

The spike level for all sorbent tube spike samples was 2000 ng/sample. Field spike recoveries ranged from 69.5 to 97.0 percent, with a median of 79.0 percent (four samples). Trip spike recoveries ranged from 73.0 to 93.5 percent, with a median of 85.0 (three samples). Laboratory spikes ranged from 71.9 to 88.0, with a median of 73.5 percent (nine samples). Recoveries for the field spikes, trip spikes, and laboratory spikes were virtually identical with overall means \pm standard deviation of 81.1 ± 12.3 percent, 83.8 ± 10.3 percent, and 76.4 ± 6.4 percent, respectively. Consequently these data indicate that analytical recoveries were unaffected by the field and transportation procedures

All primary and duplicate sorbent tubes contained no detectable amounts of chloropicrin. No chloropicrin was detected in any trip blank or lab blank.

MITC

For the first four applications, only sorbent tubes were used, canisters were not available. DHS was the primary laboratory and CDFA was the quality control laboratory for the first four applications. For the last two applications, DHS analyzed both canister and sorbent tube samples.

Sorbent tube field spike recoveries ranged from 45 to 80 percent, with a median of 67.9 percent. The longer 16-hour sampling period demonstrated greater MITC migration (movement from the first sampling tube to the second tube) than the eight-hour sampling period (mean of 19.6 versus 1.8 percent, respectively). Fifteen of these samples were also equipped with a third tube to evaluate “total breakthrough” from the first two tubes. MITC was detected in five of these fifteen “third” tubes. Only two of the fifteen tubes with a detectable amount of MITC contained more than two percent of the total initial spike (4.0 and 7.4 percent). However, mean recoveries for the eight- and 16-hour sampling periods were not significantly different (Figure 28) indicating that although some small amount of breakthrough did occur in some of the 16-hour field spikes, this breakthrough did not cause any significant recovery differences between the 16- and eight-hour sampling periods.

Recoveries for the sorbent tube field spikes, trip spikes, and laboratory spikes were virtually identical with overall means \pm standard deviation of 66.1 ± 9.3 percent, 70.5 ± 11.3 percent, and 70.4 ± 5.6 percent, respectively. Consequently these data indicate that analytical recoveries were unaffected by the field and transportation procedures.

The primary and duplicate samples yielded comparable results (Table 19). The MITC levels in most of the primary samples were either below the method detection limit or limit of quantitation. Consequently, quantitative estimation of any potential variation between the primary and duplicate analysis is not possible. However it is apparent that the two data sets qualitatively yielded similar results.

The primary and confirmation samples yielded comparable results (Table 20). The MITC levels in most of the primary samples were either below the method detection limit or limit of

quantitation. Consequently, quantitative estimation of any potential variation between the primary and confirmation analysis is not possible. However it is apparent that the two data sets qualitatively yielded similar results.

No MITC was detected in any trip blank or lab blank.

Figure 28. Comparison of recovery by sample time.

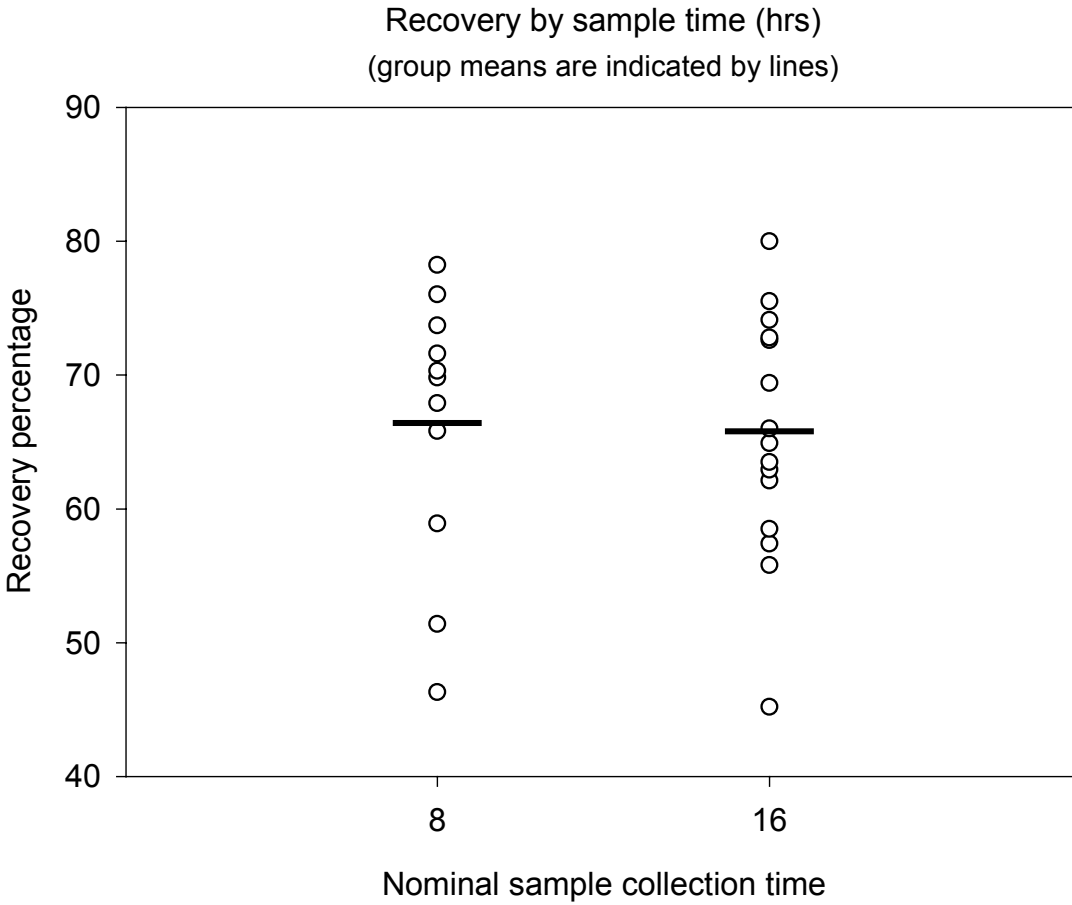


Table 19. Comparison of primary MITC samples and duplicate (collocated) samples.

Primary sample (ng/m ³)	Duplicate sample (ng/m ³)
Trace (25 – 77)	Trace (25 – 77)
120	110
ND (MDL 13)	trace (13 - 37)
ND (MDL 13)	ND (MDL 13)
ND (MDL 13)	ND (MDL 13)
ND (MDL 13)	ND (MDL 13)
ND (MDL 25)	ND (MDL 25)
ND (MDL 25)	ND (MDL 25)
230	300
ND (MDL 25)	ND (MDL 25)
Trace (25 – 77)	Trace (25 – 77)
230	240
180	170

ND = no detectable amount, MDL = method detection limit

Table 20. Comparison of primary and confirmation (collocated) MITC samples.

Primary laboratory (ng/m ³)	Confirmation laboratory (ng/m ³)
Trace (13 – 39)	Trace (21 – 210)
56	Trace (21 – 210)
Trace (25 – 77)	Trace (41 – 410)
96	Trace (21 – 210)
310	Trace (21 – 210)
Trace (25 – 77)	ND (MDL 21)
ND (MDL 13)	ND (MDL 21)
ND (MDL 25)	ND (MDL 41)
ND (MDL 25)	ND (MDL 41)
Trace (25 – 77)	Trace (41 – 410)
ND (MDL 25)	ND (MDL 41)
Trace (25 – 77)	ND (MDL 41)

ND = no detectable amount, MDL = method detection limit

The average recovery for the MITC canister trip spikes was 97.2 percent (five samples). The average recovery for the lab spikes was 95.7 percent (five samples). The trip and lab spikes were spiked at two levels, with no significant difference between the two spike levels for either the trip spikes (P=0.286) or the lab spikes (P=0.078). There were no MITC detections in any of the trip blank or laboratory blank samples.

There were measurable MITC concentrations reported for both canister and collocated sample tubes in 14 sample pairs (Table 21). The canister values ranged from 0.85 to 3.50 times the values of the sorbent tubes. The initial regression analysis revealed the variance was not constant but instead appeared to be a function of the mean, so a logarithmic transformation of

the data is appropriate. Linear regression of the log 10 value of the canister concentrations on the log 10 value of the tube concentrations for those data yields:

$$\text{Log10 (canister concentration)} = -0.134 + (0.626 * \text{log10 (tube concentration)})$$

R²=0.73, Figure 29

Table 21. Collocated sample results of sorbent tubes and canisters. Only the 14 sample pairs with quantifiable concentrations are shown.

<u>MITC concentration</u>		
Sorbent tube (ng/m ³)	Canister (ng/m ³)	Ratio (Canister / tube)
797.7	1885.1	2.36
53.7	179.5	3.34
315.3	508.7	1.61
97.8	269.3	2.75
142.6	269.3	1.89
193.3	389.0	2.01
212.9	389.0	1.83
882.4	748.1	0.85
230.9	807.9	3.50
834.6	1017.4	1.22
430.8	418.9	0.97
313.3	448.8	1.43
629.4	628.4	1.00
386.7	807.9	2.09

The tube results were consistently less than its collocated canister results as illustrated in Figures 30 and 31. The difference between the tube and its collocated canister varies with concentration.

The spike recoveries for the canisters (mean = 96.4 percent, 10 samples) and tubes (mean = 68.6 percent, 66 samples) were compared and found to be significantly different (t = -8.612, p = <0.001, difference = 27.8, Figure 32). The difference in recoveries appears to account for most of the difference between the canister and tube concentrations.

Figure 29. Comparison of canister vs tube MITC results.

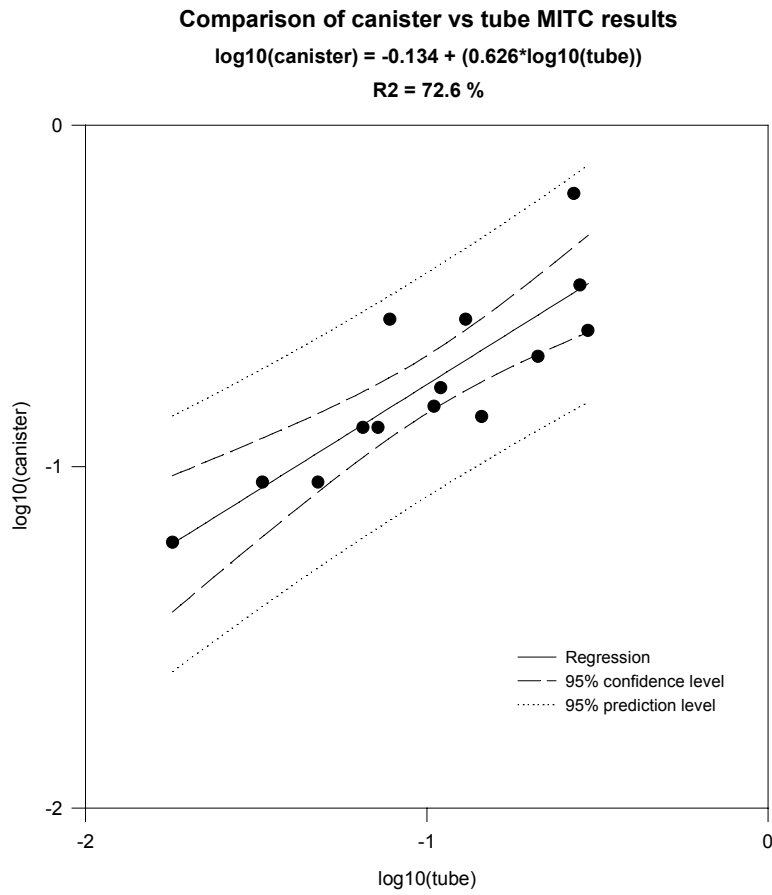


Figure 30. Comparison of tube concentration vs the difference between tube and canister concentration.

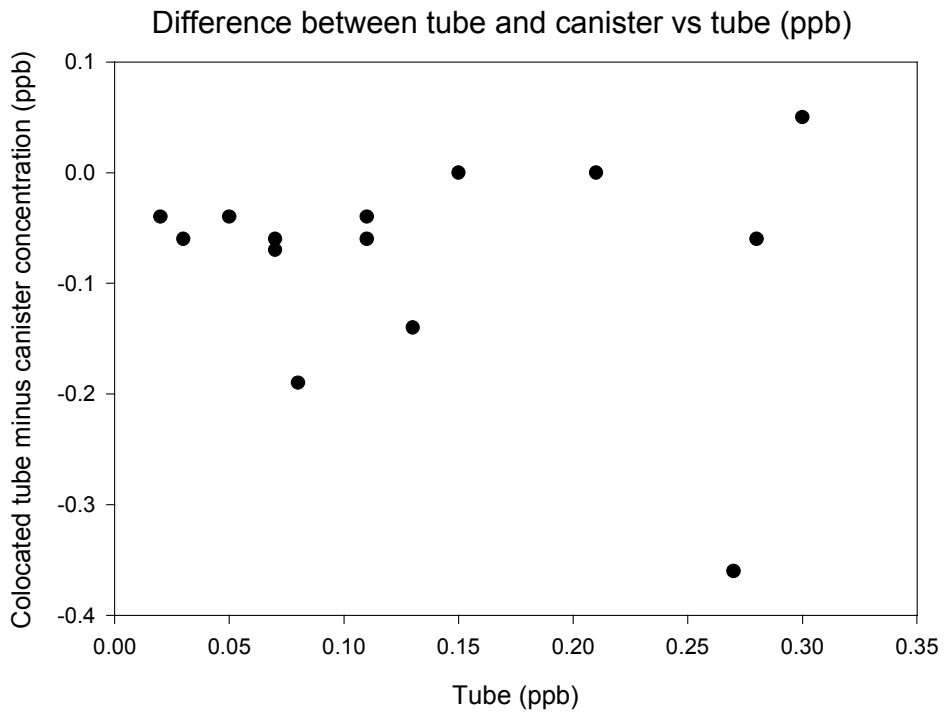


Figure 31. Comparison of canister and tube analysis of paired samples.

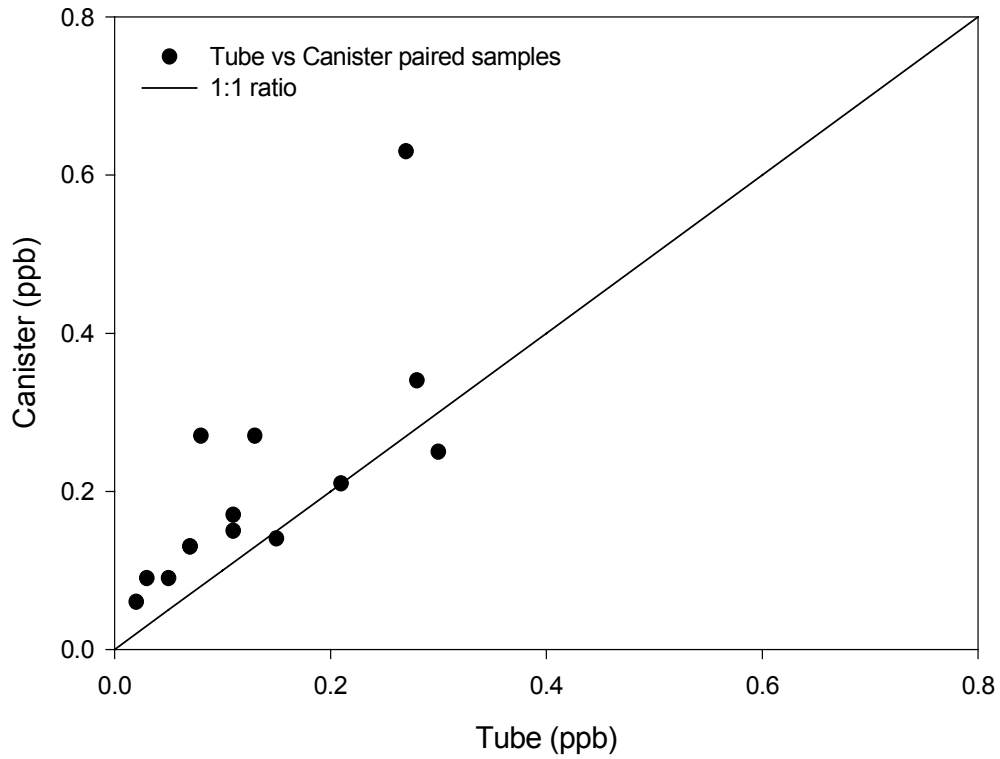
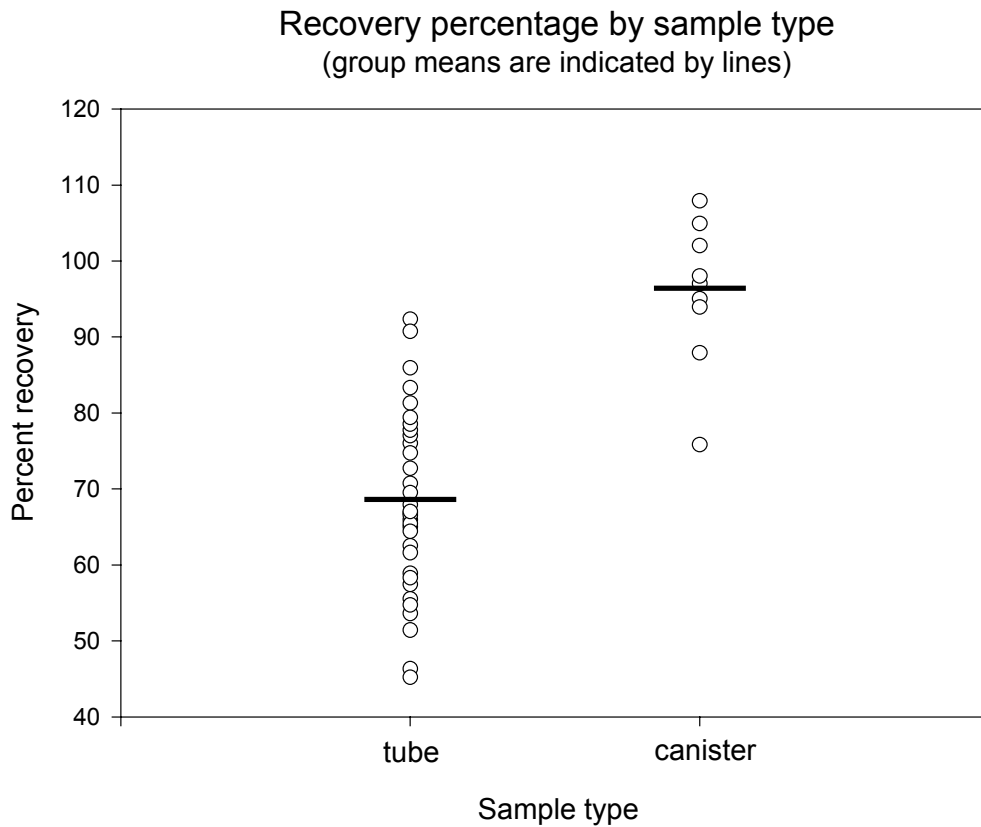


Figure 32. Comparison of recovery means between canisters and tubes.



CONCLUSIONS AND RECOMMENDATIONS

Ambient air concentrations in the city of Lompoc during eight fumigant applications did not exceed screening levels, even with a series of health-protective assumptions and overestimates of exposure. The highest risk estimated was the chronic exposure for MITC. The highest 18-day (chronic) air concentration was 244 ng/m³, or 81 percent of the screening level. However, the chronic exposure estimate may not be reliable because an 18-day concentration is used to estimate a one-year exposure. Only trace levels of methyl bromide were detected and no chloropicrin was detected.

The weather at the time of the monitoring was variable. During four of the fumigations, the weather was consistent with normal patterns in the Lompoc area, and the wind direction from the northwest-west. Wind direction during the other two fumigations monitored was variable because the fumigations occurred just before or just after storms. Air concentrations for the storm-related fumigations are likely lower than if they had occurred during normal weather conditions. The largest MITC fumigation monitored had normal weather conditions. During the two methyl bromide/chloropicrin fumigations, wind was from the normal northwest-west direction. Since these fumigations occurred east of Lompoc, the air monitoring locations were upwind and had lower air concentrations than if the wind direction had been in the opposite direction.

While concentrations for other locations and time periods cannot be quantified, some qualitative conclusions are possible. Few other areas within the city of Lompoc should have higher risk than documented here. The monitoring sites encompass an area approximately 2.3 square miles, or approximately 36% of the area of the city south of the airport. Approximately 0.15 square miles, or two percent of the city south of the airport is located to the west of the monitoring sites and may have higher air concentrations than those documented here due to closer proximity of the agricultural area.

The risk from other methyl bromide and chloropicrin fumigations is difficult to estimate. In addition to the low or no amounts detected, the pesticide use and weather patterns compound the difficulty. Almost all methyl bromide and chloropicrin is applied east of Lompoc, downwind of the city during normal weather conditions. With the available data, estimating the probability that the wind direction will be opposite of normal, and estimating the air concentration is problematic.

For MITC, the acute risk is likely higher than documented here because a few days not monitored have greater amounts applied. Between 1996 and 2000, the highest amount of metam reported for any day was 18,626 lbs, compared to 5,104 lbs on a single day during this study. Eight (6%) of the days with fumigations between 1996 and 2000 used more metam than the largest amount monitored during this study. Since the highest air concentration measured was only three percent of the screening level, it's unlikely that MITC air concentrations from fumigations not monitored exceed the acute screening level.

This study may overestimate the subchronic and chronic risk for MITC for several reasons. First, high air concentrations for short periods of time are used to represent longer time

periods. The highest 72-hour air concentration is used to represent a 30 to 90-day subchronic exposure and the highest 18-day air concentration is used to represent a one-year chronic exposure. In addition, the three-day period chosen for subchronic exposure and 18-day period chosen for chronic exposure are likely among the highest periods between 1996 and 2000.

The only fumigant with air concentrations that approach its screening levels is MITC. Monitoring in other areas of the state (although not in Lompoc) indicates that air concentrations exceed the screening level and DPR's regulatory goal under some circumstances. DPR is working with the pesticide manufacturers and other agencies to develop and implement statewide regulatory measures to reduce exposure to MITC. Santa Barbara County's current requirements for MITC provide more protection than other areas of the state. DPR will evaluate Santa Barbara's requirements during the development of the statewide measures.

This study and monitoring from other areas in the state indicate that fumigant air concentrations in the Lompoc area are less than other areas. DPR manages pesticides statewide based on the areas or populations at greatest risk. Monitoring and control of fumigants in the higher-risk areas will provide adequate protection for Lompoc. No further fumigant monitoring or investigation in the Lompoc area is warranted.

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