ENVIRONMENTAL MONITORING RESULTS OF MULTIFUMIGANT APPLICATIONS IN MANTECA, CALIFORNIA 2005

Study 212

By

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ABSTRACT

Dazomet is one of the three major pesticides that generate methyl isothiocyanate (MITC). It is used as a soil fumigant less widely than metam sodium, but it has been used increasingly in recent years due to more restrictions on metam uses. To implement mitigation for pesticides that generate MITC, Department of Pesticide Regulation (DPR) initiated a pilot air monitoring study to collect information on MITC emissions from a dazomet field application. The study was conducted concurrently with a nursery research experiment on May 6, 2005. The experiment was to evaluate multiple fumigant application efficacies in a pre-plant strawberry field. The fumigant application was a factorial design of four replicates for each of three treatments, methyl bromide/ chloropicrin, Telone only, and Telone + Basamid, randomized on 12 small plots. Each plot was rectangular with dimensions of 100’ x 22’, a total of 0.2 acre for each treatment. DPR collected methyl bromide samples collocated with MITC sampling as a reference. The dazomet application was surface broadcast using a drop spreader, no tarp, and sprinkler irrigation. Its application rate was 235 lb/ac of Basamid (26.1 gram/m^2 of active ingredient of dazomet, equivalent to 11.7 gram/m^2 of MITC). The methyl bromide application was broadcast, shanked to 12 inches depth, and tarped. Its application rate was 370 lb/ac of methyl bromide/ chloropicrin (67/33), i.e. 27.8 gram/m^2 of active ingredient of methyl bromide.

The highest individual sample air concentrations were 129 µg/m^3 for MITC and 133 µg/m^3 for methyl bromide. Both MITC and methyl bromide maximum air concentrations during each sampling period declined over time. The highest 24-hour time-weighted average (TWA) concentration of 66.9 µg/m^3 for MITC (18 hours) and 103 µg/m^3 for methyl bromide (22 hours) occurred during the first sampling day. The highest individual flux estimates were 53.8 µg/m^2-s for MITC and 87.9 µg/m^2-s for methyl bromide during the first 6 and 10 hours after start of MITC and methyl bromide application, respectively. The modeled flux profiles showed a general decline over time. Significant rain and higher relative humidity may have affected the MITC and methyl bromide air concentrations and flux estimates during sampling periods 6 and 8. The highest emission ratio to the application rate in each sampling period was estimated to be 9.93% for MITC during the first 6 hours and the highest 24-hour emission ratio was estimated at 24.1 % for methyl bromide during the first monitoring day of 22 hours. The total amount of MITC released to air from the application field during the 5-day monitoring study was approximately 43.1 % of the equivalent applied amount of MITC and 53.4 % of the applied methyl bromide.

ACKNOWLEDGMENTS

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as an actual or implied endorsement of such products.

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INTRODUCTION

The California Department of Pesticide Regulation (DPR) declared methyl isothiocyanate (MITC) and all pesticidal sources of MITC as toxic air contaminants in June 2003 (DPR, 2003). Metam sodium, metam potassium, and dazomet are three major pesticides that generate MITC. Metam sodium has been widely used as an agricultural soil fumigant and its environmental concentrations have been intensively studied. Metam potassium has a chemical structure similar to metam sodium and would be expected to show similar behavior in the environment. Unlike the metams' open structure, dazomet consists of a heterocyclic ring containing carbon, nitrogen, sulfur, and hydrogen. Therefore it would be expected to have a different degradation rate and pathway. Dazomet use is much less than metam sodium and information on its environmental impact is limited (Wales, 2002). DPR had no field study information on dazomet-related MITC air concentrations or flux before August 2005. DPR initiated studies to determine MITC air concentrations or flux estimates adjacent to dazomet treated fields.

Dazomet is a broad-spectrum soil fumigant used to control soil fungi, nematodes, weeds, and soil insect pests. In moist soil, dazomet decomposes rapidly to methyl (methylaminomethyl) dithiocarbamic acid which further degrades to MITC, formaldehyde, hydrogen sulfide, and methylamine. One manufacturer of dazomet products reported it was this combination of volatile gases that resulted in the fumigant activity (BASF, 1989). The decomposition of dazomet can occur in as little as 10 to 15 minutes (Thomson, 1989). A reported aerobic soil half-life (50% dissipation time) was 18 hours at pH 5.8 in a loamy sand soil (DPR, 1999). Soil moisture may be the key factor in dazomet decomposition. Soil temperature, pH, and soil type all affect on the rate of degradation (Wales, 2002; Munnecke and Martin, 1964; Sczerzenie et al., 1987).

Dazomet agricultural use in California has been increasing every year from 2000 to 2004, according to DPR’s pesticide use database. Of the total reported dazomet use, 202,623 pounds of active ingredient in 2000-2004, 68% was for right of way applications, 24% for crop production, 6% for landscape maintenance, and 2% for other uses. For right of way applications, a major product containing dazomet was Ultrafume. Ultrafume was usually applied around electrical and telephone poles using a deep injection method to protect against pest damage. For crop production, Basamid, a granular soil fumigant, was used with surface or incorporated broadcast applications with or without tarp. From 2000 to 2004, a total of 48,774 pounds (24% of the 202,623 pounds) of active ingredient dazomet was applied for crop production. Ninety-two percent of the 48,774 pounds was used in nurseries (DPR, 2005). Applications in nurseries occur throughout the year.

While Basamid is relatively non-volatile, it produces MITC, which has a high vapor pressure, 16.0 mm Hg at 25 °C (Table 1), and leaves the soil to air via volatilization (Levine et al., 2005). MITC has the potential to drift offsite. DPR’s previous monitoring of metam-sodium under condition that would favor maximum emissions of MITC (Wofford et al, 1994) found that MITC levels exceeded the Office of Environmental Health Hazard Assessment’s 1-hour Reference Exposure Level (REL) for eye irritation of 1.2 micrograms per cubic meter ($\mu g/m^3$) or 0.4 parts per billion (ppb) (Levine et al., 2005).

In efforts to minimize potential adverse human health impacts, DPR is drafting buffer zones for MITC (DPR, 2004). Fumigant studies are conducted to provide a scientific basis for determining effective buffer zones. The Environmental Monitoring (EM) Branch of DPR conducted this dazomet and methyl bromide monitoring in May 2005 at a nursery in Manteca, CA. The objectives of this study were to measure air concentrations of MITC and methyl bromide after a multiple fumigant application, estimate the flux associated with the chemicals and application methods, characterize the flux profiles during the monitoring period, and estimate the emission ratios of MITC and methyl bromide during the first 48 hours (DPR, 2004).

MATERIAL AND METHODS

Pesticides Monitored

The dazomet product monitored in this study was Basamid® Granular soil fumigant. Basamid® Granular contains 99 percent (%) active ingredient of dazomet (tetrahydro-3,5,-dimethyl-2-H-1, 3, 5,-thiadiazine-2-thione) and 1% inert ingredients. It is typically applied by spreader to soil surface and immediately tilled into the soil with a rototiller (Wales, 2002), or applied with a belly grinder to prepared soil, then immediately tarped or irrigated thoroughly, wetting the soil according to the label instruction (BASF, 1998). Basamid® Granular label recommends application rates from 225 to 530 pounds per acre depending on soil texture, pH, organic matter content, and the type of pests to be controlled (BASF, 1998).

The methyl bromide product used in this study was 67-33 Preplant Soil Fumigant, a pressurized liquid composed of 67.0 % methyl bromide and 33.0% chloropicrin. It is applied directly in soil to the desired depth with appropriate equipment. Methyl bromide is biologically active for soil fumigation. Some physical and chemical properties for MITC, dazomet, and methyl bromide are listed in Table 1.

Table 1. Physicochemical properties of MITC, dazomet and methyl bromide[a]

	MITC	Dazomet	Methyl bromide
Molecular formula	C_2H_3NS	$C_5H_{10}N_2S_2$	CH_3Br
Molecular weight	73.12	162.3	94.9
Solubility in water (ppm)	8.61×10^3 (25 ºC)	3.63×10^3 (20 °C)	1.32×10^3 (25 ºC)
Vapor pressure (mm Hg)	16.0 (25 ºC)	9.88×10^{-6} (25 °C)	1.42×10^{3}[b] (25 ºC)
Henry's law constant (atm-m^3/mole)	1.79×10^{-4} (25 ºC)	2.57×10^{-10} (20 °C)	0.134[c] (25 ºC)
Hydrolysis half-life (days)	20.4 (pH 7, 25 ºC)	0.146 (pH 7, 25 °C)	9-29 (18 °C) 8-28 (30 °C)
Aerobic soil half-life (days)	0.5 – 50[d] (25 ºC)	0.75 (pH 5.8, loamy sand)	0.158-20 (23 °C)

[a]All data are from the DPR's Pesticide Chemistry Database, except where denoted.
[b]Merck Index, 13th edition.
[c]calculated
[d]Smelt, 1974

Field Description

The application field was located in the San Joaquin Valley, San Joaquin County, California. The treatment area was approximately 0.5 acre on the southern edge of a 27-acre flat field. The field was open on the north and surrounded by almond orchards on the other three sides. A house was located on the south side. An unoccupied temporary workers' living facility was at the northeast corner of the field and a county road was between the field and almond orchards (Figure 1). There were no reported MITC generating pesticides and methyl bromide applications in the area within this same township between May 3 and May 10, 2005 (Gary Stockel, personal communication).

Pesticide Application

DPR's monitoring study was conducted in cooperation with a nursery research on multiple soil fumigant applications. The research was to evaluate efficacy for three preplant treatments of soil fumigants, methyl bromide / chloropicrin, Telone C35, and Basamid / Telone C35, in a strawberry field. The field plot design was a randomized complete block with four replicates for each of the three pesticide treatments. Twelve rectangular plots were arranged in two columns and six rows. Each plot was 100' x 22' (two passes of the flat-fume rig), approximately 100' apart between the two columns and 13' to 20' between rows (Figure 2). Both the Telone C35 and methyl bromide/chloropicrin were applied using a standard flat-fume soil fumigation rig. The methyl bromide/chloropicrin was shanked in to a 12" depth and tarped. The Telone C35 was shanked in to an 18" depth, but not tarped. Following the application, the shank gap was closed and soil was compacted by a ring roller. The Basamid was broadcast applied using a drop spreader (Figure 3) after the Telone C35 application. Following the Basamid application, sprinkler irrigation was immediately applied from 14:00 to 15:00 for surface sealing and pesticide activation. Post-application irrigation was conducted twice on the next day (May 7, 2005), once in the morning and once in the afternoon. Each ran half an hour with a quarter inch of water (oral communication with nursery research staff). There was another irrigation scheduled in the following morning, but cancelled due to rain. The local weather station (Station MSD of California Data Exchange Center) reported a total of 0.28 inches of rain on May 8, 2005.

The pesticide application rates are listed in Table 2. The application was started on May 6, 2005 with methyl bromide/ chloropicrin treatment from 9:04 to 9:25 am. An equipment problem delayed Telone C35 treatment until 11:42 to 12:42. The Basamid treatment was conducted from 12:43 to 13:22.

Table 2. Pesticide application rates

Pesticide	Total amount applied	Area applied	Application Rate
Basamid	47 lbs.	0.2 ac.	235 lbs./ac.
Telone C35	18.5 gal.	0.4 ac.	46.3 gal./ac.
Methyl bromide/chloropicrin (67/33)	74 lbs.	0.2 ac.	370 lbs./ac.

Figure 1. Application field aerial view (North is at the top)

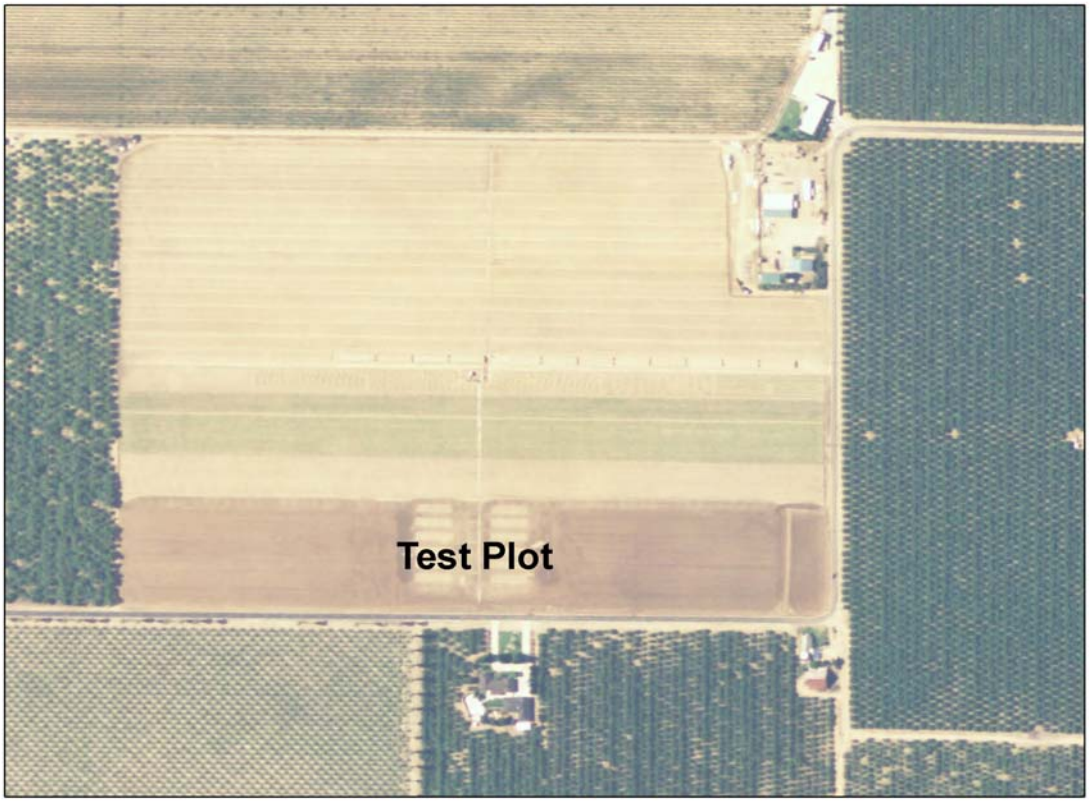
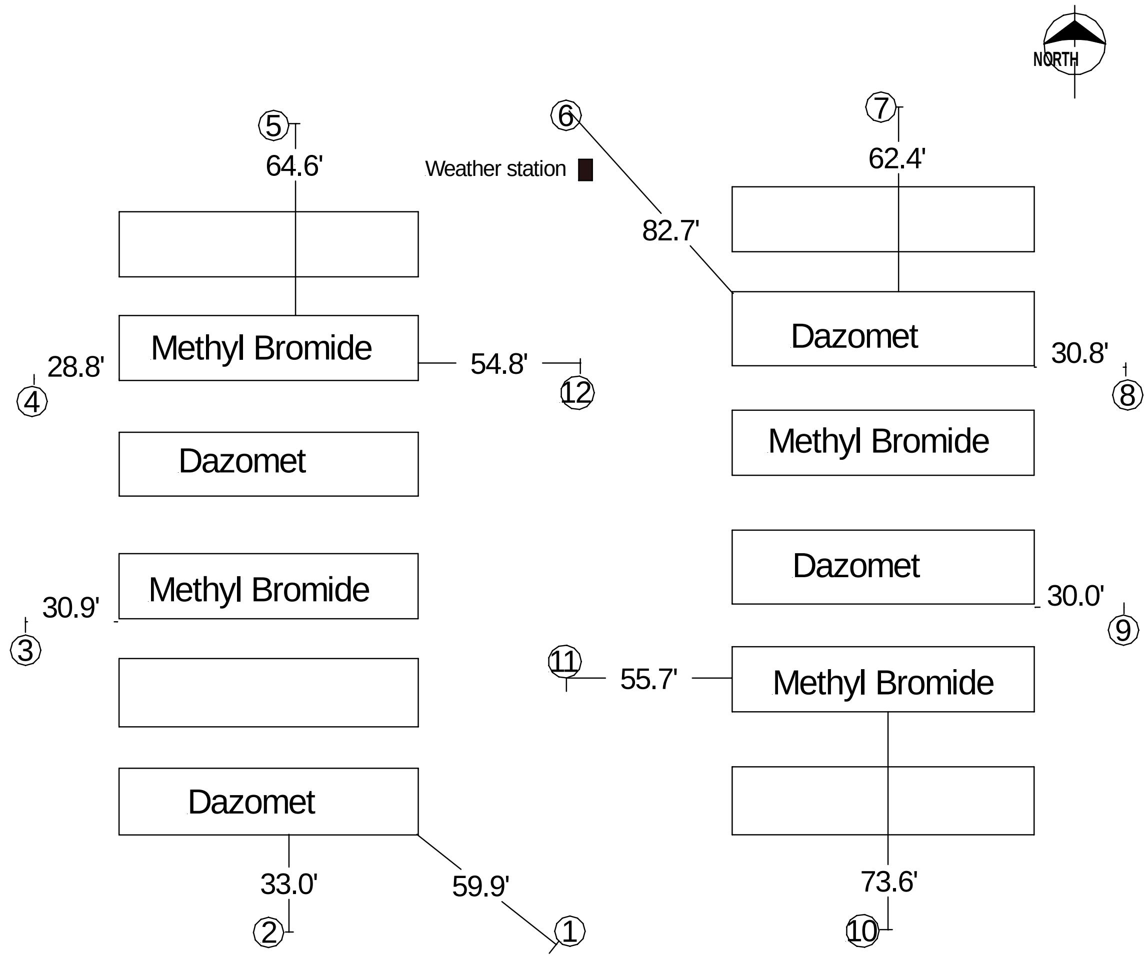


Figure 2. Application plots, sampler locations, and approximate distances*



*Only monitored chemicals are shown in the treatment plots. The number in circle indicates the sampler identification.

Figure 3. Basamid application

Air Sampling

Twelve sampling locations were located around the study plots at distances of approximately 30 and 60 feet (ft) from the edge of the treatment plots (Table 3 and Figure 2). On each sampling location, two air sampling pumps (SKC#224-PCXR) were set up. One pump was equipped with a 400/200 mg two-section Anasorb coconut shell charcoal (CSC) tube (SKC #226-09) at an airflow rate of 1.5 liters per minute (L/min) for MITC. The other was connected to two consecutive petroleum charcoal sorbent tubes, a 400 A-tube and a 200 mg B-tube (SKC #226-38-02), and adjusted to an airflow rate of 15 milliliters per minute (ml/min) for methyl bromide. Background air samples were collected the evening prior to the fumigant applications. Application samples were turned on at the scheduled start time of 7:00 am on May 6, 2005. Due to technical problems encountered during application, the methyl bromide/chloropicrin applications started at 9:04 AM and the Basamid application started at 12:43 PM. Samples were collected approximately every 12 hours, one hour before sunset and one hour after sunrise, a total of ten sampling periods for five days (Table 4). At the beginning and the ending of each sampling period, the flow rate for each sampler was measured, recorded and calibrated if necessary. Flow rates were measured with a DryCal® Primary Flowmeter. The sampled sorbent tubes were capped and immediately placed on dry ice. Details of air sampling and equipment operation, calibration, and maintenance are described in DPR's Standard Operation Procedure (Wofford, 2001)

Table 3. Sampler identification and distances from the edge of the application plots

Sampler Identification	Distance (ft)
1	60
2	33
3	31
4	29
5	65
6	83
7	62
8	31
9	30
10	74
11	56
12	55

Table 4. Timing of the sampling periods

Sampling Period	Date and Time On	Date and Time Off	Duration (hours)
background	5-May 16:35	6-May 6:05	13.5
1	6-May 7:00	6-May 18:52	6 (MITC), 10 (methyl bromide)*
2	6-May 18:55	7-May 6:46	12
3	7-May 6:49	7-May 18:50	12
4	7-May 18:52	8-May 7:18	12
5	8-May 6:52	8-May 18:50	12
6	8-May 18:52	9-May 7:02	12
7	9-May 7:08	9-May 18:54	12
8	9-May 18:55	10-May 6:54	12
9	10-May 6:55	10-May18:54	12
10	10-May 18:55	11-May 6:55	12

*Sampling pumps ran for 12 hours. However applications for methyl bromide and MITC started at 9:04 am and 12:43 pm, respectively. The actual sampling duration of the first period was 6 hours for MITC and 10 hours for methyl bromide.

Air Sample Handling and Transportation

Prior to monitoring, sample labels with the study number and sample identification numbers were attached to the sorbent tubes. Preparation of sorbent tubes for use with air sampling pumps is described in DPR's SOP FSAI001.01 (Ganapathy, 2003). Chain of custody forms and sample analysis request forms were supplied to field sampling personnel. Field personnel collected field notes, field measurements, sampler location, application data, and weather observations. During sampling, the tube was covered with aluminum foil to protect from direct sunlight. During irrigation or rain, the tube was placed with the air inlet tip downward and wrapped with an aluminum skirt to protect the sample from water damage. The collected samples were packaged and transported according to procedures in DPR's SOP QAQC004.01 (Jones, 1999). All samples were transported to the laboratory for analysis by May 12, 2005. Each sample was accompanied by chain of custody that was signed by each person handling the sample. All samples followed sample receipt log-in and verification procedures described in SOP QAQC003.01 (Hoffman, 1999).

Soil Sampling

Soil samples were collected at two locations for bulk density and moisture content. The locations were at the southwest side and in the middle of the treatment area. These samples were collected at a depth of 6-12 inches. A composite surface soil sample was randomly collected over the treatment area for soil texture analysis. Samples were collected and analyzed in accordance with DPR's SOP FSSO001.00 and SOP FSSO002.0 (Garretson, 1999a and 1999b).

Meteorological Measurements

Wind direction, horizontal wind speed, temperature, solar radiation, and relative humidity were measured by MetOne® meteorological sensors at a height of 10-meter (32.8 feet). The weather station was installed in the middle of the study field approximately 10 ft north of the treatment block (Figure 2). The meteorological measurements were recorded on a Campbell Scientific CR 21X Data logger as a 1-minute average of 1-second instantaneous readings, except for wind direction which was an instantaneous measurement once every minute. The wind direction measurement was with respect to magnetic north. Therefore a declination angle of 14.5° was added to compute the direction with respect to true north. In addition, amount of cloud cover and/or precipitation was noted at each sampling period.

Chemical Analysis

The MITC and methyl bromide were analyzed by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. MITC in the two-section of 400/200 mg coconut shell charcoal tube was desorbed from the sorbent tubes with 5 ml of 0.1% CS_2 in methylene chloride. The extracts were analyzed on a gas chromatograph equipped with a mass selective detector. Methyl bromide in the 400 mg petroleum charcoal A-tube and 200 mg B-tube was extracted and analyzed separately. The extraction was using 5-10 ml of 0.1% ethyl acetate and measurement was using a gas chromatograph equipped with an electron capture detector. The results of A-tube and B-tube were combined in this report.

QUALITY CONTROL AND QUALITY ASSURANCE MEASURES

Quality control and quality assurance measures followed the Chemistry and Laboratory Quality Control Standard Operating Procedure (Segawa, 1995).

Field Sampling and Sample Handling

Background and Collocated Samples

To measure ambient background concentrations, four background samples, two for each chemical monitored, were collected for a 14-hour period prior to the field application. During the field monitoring, two collocated samples, one at the first sampling period and the other at the ninth period, were collected at sampling location 11 for each chemical. The collocated samples, less than a meter apart, provided an estimate of field sampling precision.

Field Spikes, Trip Spike, and Trip Blank

The field and trip spikes were sorbent tubes spiked with a known amount of MITC or methyl bromide in the laboratory, stored on dry ice, and transported to the field. To provide an estimate of reliability of field sampling process, the field spike was treated the same as a field sample, with air flowing through the spiked tube for a sampling period, stored, transported, and analyzed with other field samples. Two field spikes for each chemical were collected with the background samples to avoid contamination from the application.

The trip spike provided an estimate of the integrity of the sample storage and transportation for the round trip between the laboratory and the field. The trip spike was handled the same as the field spikes but without the field run. One trip spike was collected for each chemical.

The trip blank samples were collected by breaking unused tubes and placing them on dry ice. They were handled, stored, transported, and analyzed with other field samples. The trip blank provides an estimate of any contamination during transportation or storage. One trip blank was collected for each chemical.

Trapping Efficiency

Trapping efficiency for MITC air sampling was conducted by spiking MITC standard onto coconut charcoal tube (SKC #226-09) at three levels, 1, 10, and 100 µg/tube, and three replicates for each level. The spiked sorbent tubes were sampled for 24 hours using personal air sampler pumps (SKC#224-PCXR) with an airflow rate of 1.5 L/min. The average recoveries were 79.8%, 77.6%, and 65.9% for the levels 1, 10, and 100 µg/tube, respectively. The overall recovery was 74.5%. Significant amounts of MITC were detected in all of the second section (B) of the sorbent tubes (Appendix II), indicating the possibility of breakthrough at all levels in a 24-hour sampling period.

Trapping efficiency for methyl bromide air sampling was intensively studied by comparison of charcoal tube and SUMMA canister recoveries (Biermann and Berry, 1999). It was concluded that for most of the data in a humidity range of 20% to 80% and concentrations between 20 ppb and 2000 ppb, no major effects of either humidity or concentration were found. The average recovery was 49% ± 7% (standard deviation) for the sorbent tubes.

Storage Stability

The results of storage stability study (Biermann and Berry, 1999) indicated that frozen air samples of methyl bromide were stable for a week before extraction. MITC samples were reported to be stable for two weeks (Wofford et al., 2003; Leung, 1982)

Chemical Analysis

Method Validation

For validation of the MITC analytical method, the laboratory spiked three sets of tubes at levels of 2, 20, and 200 ppt, respectively. Each set consisted of five replicates. Recoveries ranged from 93 to 111% and overall average was 101% (CDFA, 2004).

Method validation for methyl bromide was conducted by spiking two sets of tubes at levels of 1 and 20 µg/tube, respectively. Each set consisted of three replicates. Recoveries were 85.7%±3.83% and 83.9%±1.99% for 1 and 20 µg/tube, respectively (CDFA, 1994).

In this report, upper and lower control limits and warning limits for QC were determined by adding or subtracting 2X and 3X standard deviations (SD) from the average percent recovery of the method validation. The procedures and definitions for the EM QC program are listed in SOP QAQC001.00 (Segawa, 1995).

MITC validation (15 samples)

Control Limits	Recovery (%)
Upper control limit	117
Upper warning limit	110
Lower warning limit	84.7
Lower control limit	78.2

Methyl bromide validation (6 samples)

Control Limits	Recovery (%)
Upper control limit	107
Upper warning limit	98.4
Lower warning limit	64.2
Lower control limit	55.6

Method Detection Limits and Reporting Limits

The method detection limit (MDL) is the lowest amount of an analyte that a method can detect reliably. MDL for MITC was determined by spiking seven sorbent tubes with small amounts of standard and calculating the mean at 99% of confidence period. For methyl bromide, it was determined with sample size of four. The MDLs were 0.0206 µg/sample for MITC (CDFA, 2004) and 0.2 µg/sample for methyl bromide (CDFA, 1994).

The reporting limit (RL) refers to the smallest amount of a chemical that can be reliably quantified. The laboratory determined RL normally ranges from 1 to 5 times the MDL. The RLs were 0.05 µg/sample for MITC and 0.2 µg/sample for methyl bromide in this study.

Continuing Quality Control and Control Limits

Continuing proficiency of analysis is demonstrated through ongoing analysis of laboratory spiked samples analyzed with each set of up to ten field samples. The control limits are used as a check on the results of the continuing quality control spikes. The upper and lower warning and control limits are set at ±2 and ±3 standard deviations of the percentage recovery using the data from the method validation study for each analyte. The exceedance of a warning limit can indicate a possible problem that should be checked, whereas any spiked sample outside the control limits may require the set of samples associated with the spike to be reanalyzed.

RESULTS AND DISCUSSION

Calculation of Air Concentration

The sample concentrations were calculated as amount of chemical removed from a volume of air moving through the sampling media during a sampling period. The laboratory analytical results were reported in µg/sample. The air concentrations were converted from µg/sample to µg/m^3 with the following calculations:

$$\frac{\text{Sample concentration C (µg/sample) * 1000 (L/m}^3\text{)}}{\text{Flow rate R (L/min)* Time T (minutes/sample)}} = \frac{1000*C}{RT} \text{(µg/m}^3\text{)}$$

Concentrations can be converted from µg/m^3 to ppb:
at 25 ºC (298 ºK) and 1 atmosphere, 1 µg/m^3 = 24.45/molecular weight (MW) ppb

Therefore 1 µg/m^3 MITC = 24.45 /73.12 ppb MITC = 0.3344 ppb MITC

1 µg/m^3 methyl bromide = 24.45/94.9 ppb methyl bromide = 0.2576 ppb methyl bromide

In the following results presentation and discussion, the sampling period numbering refers to sampling sequence. The site numbering is the site identification and its location is shown on Figure 2.

Analytical and calculated results were reported to 2 or 3 significant figures. When a sample was invalid for a known reason, its analytical result was reported as not available (NA). When an analyzed result was below the RL, none detected (ND) was reported, and the quantity of half the (RL + MDL) for MITC or half the RL for methyl bromide was used for concentration calculations unless specified in this study.

When the results were presented as a 24-hour time weighted average (TWA), it was an average of two sampling periods, 12-hour daytime and 12-hour night time for a given day, unless otherwise specified in this study.

Results of Air Monitoring

Figures 4-7 provide a side-by-side graphical comparison of the sample concentrations of MITC and methyl bromide with the wind direction and speed during each sampling period. On the left side of the figure are the wind roses using WRPLOT View v. 3.5 (Lakes Environmental, 2000) for the frequency distribution of wind direction and speed. The spokes represent the direction the wind blew to, while the length represents the duration in that direction. The rings represent different percentages of time that the wind was blowing in a particular direction. The color code refers to the average speed in a given direction. The correspondence of wind speed in unit of meter/second to color code is listed on the figure legend. On the right side are the maps of field plot treatments, sampler locations, and monitoring results. The number in a circle refers to the sampler identity. The sample concentrations in unit of µg/m^3 for MITC and methyl bromide are on the top and bottom, respectively, of the sampler identities. ND means none detected.

Figure 4. Wind-rose diagram along sample concentrations for sampling periods 1-3

(See footnote in Figure 7)

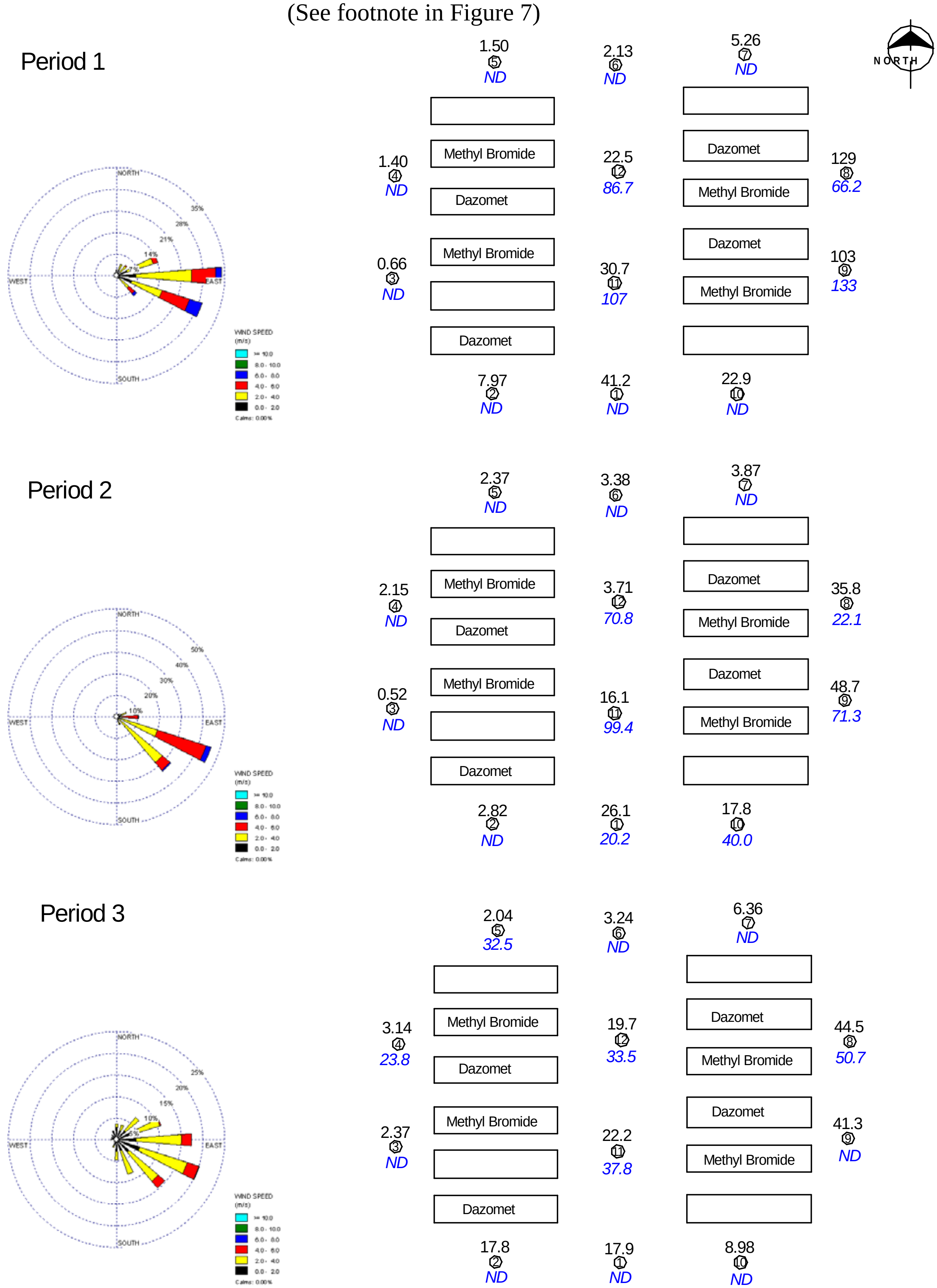


Figure 5. Wind-rose diagram along sample concentrations for sampling periods 4-6

(See footnote in Figure 7)

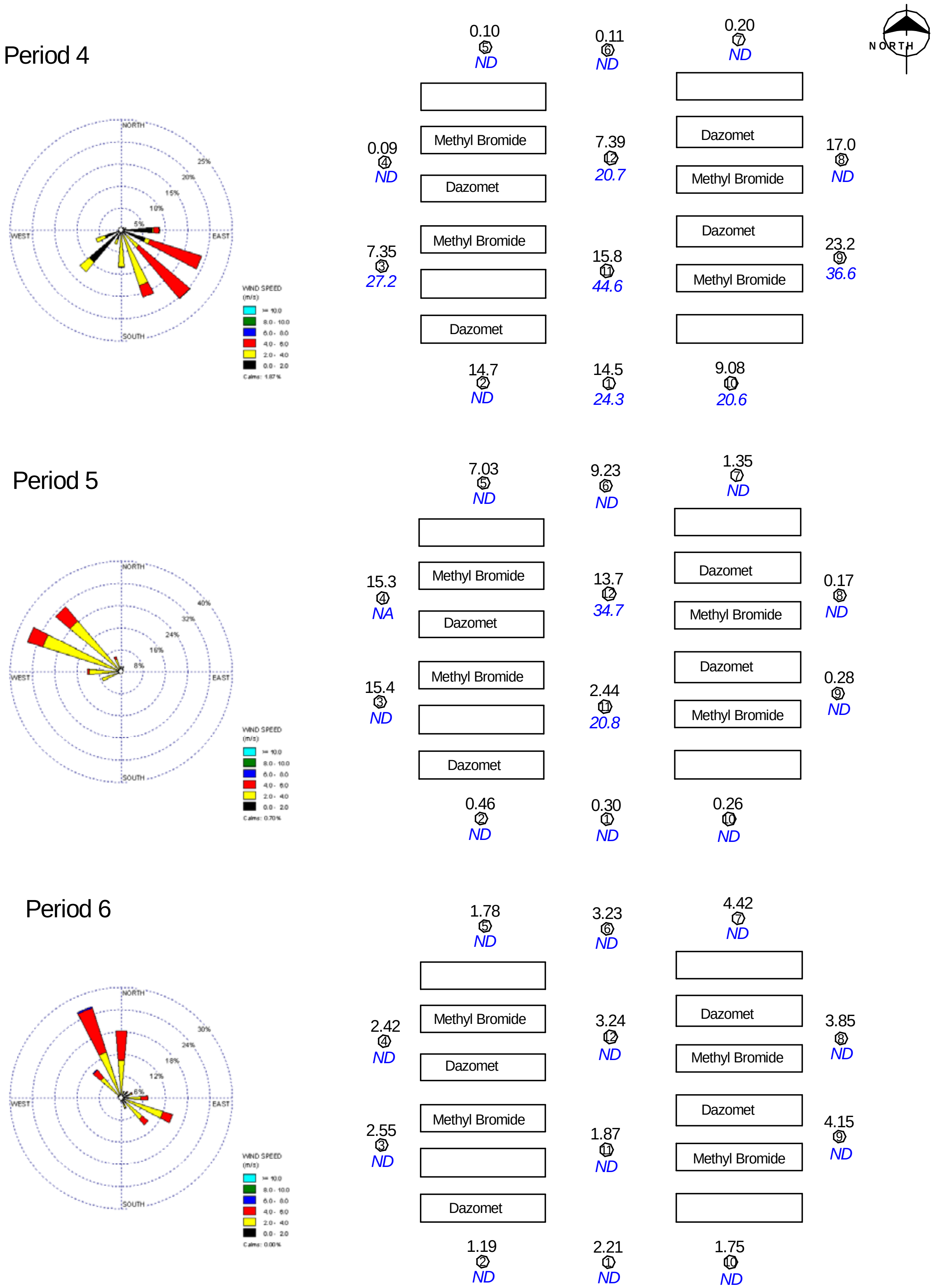


Figure 6. Wind-rose diagram along sample concentrations for sampling periods 7-9

(See footnote in Figure 7)

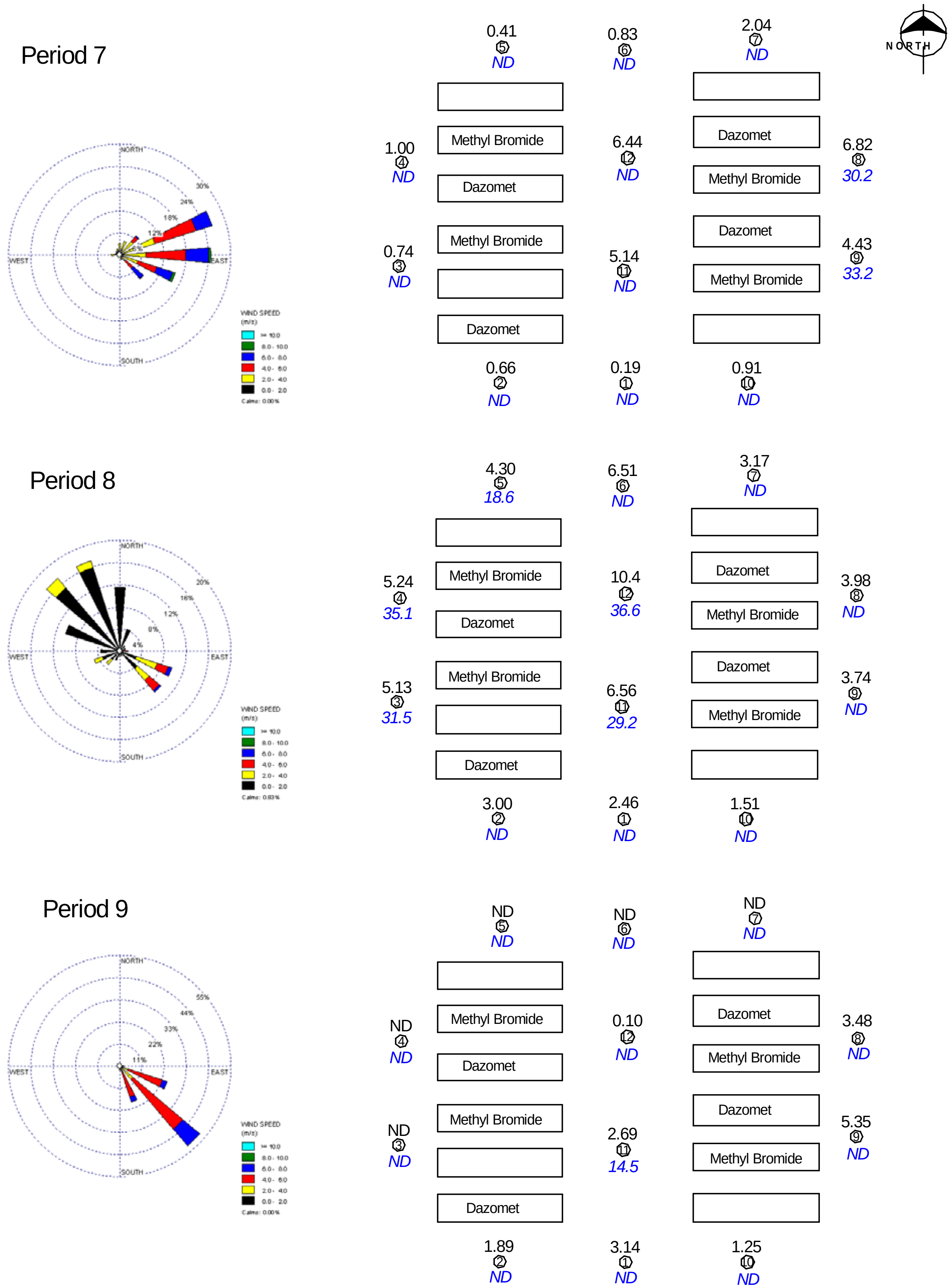
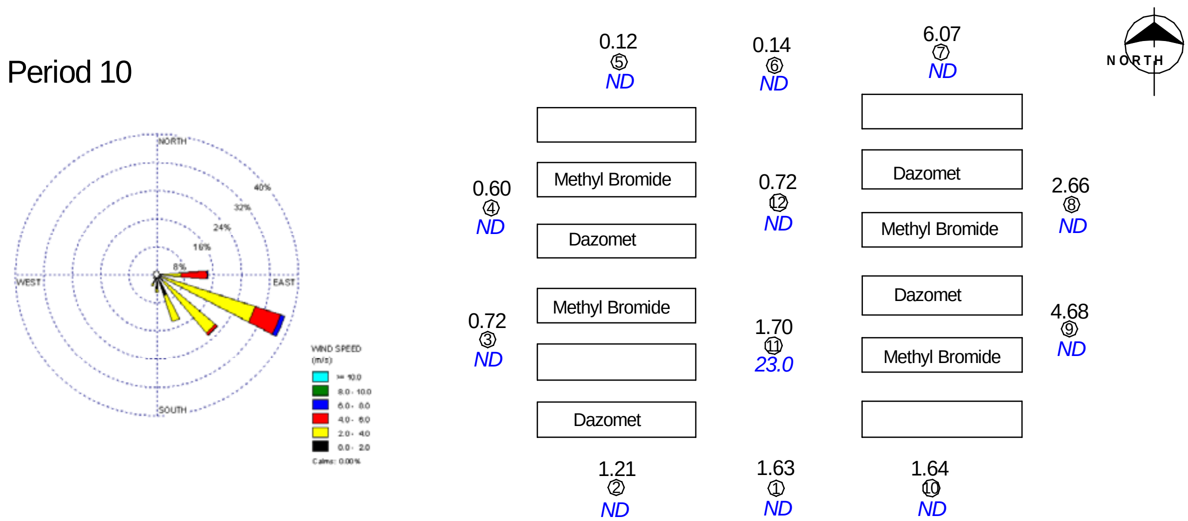


Figure 7. Wind-rose diagram along sample concentrations for sampling period 10*



*On the wind rose, the spoke refers to the direction the wind blew to, the length to the percentage of time the wind blew in the direction, the color code to the average speed in the direction. On the field plot map, the number in a circle refers to the sampler identity, the number on the top or bottom for the sample concentration of MITC or methyl bromide, respectively, in unit of µg/m^3. ND means none detected.

In general, air sample concentrations were strongly affected by wind speed and wind direction. For the monitoring periods with lower wind speeds, such as periods 8 (Figure 6), or wind blowing to two opposite directions, e.g. periods 6 and 8 (Figures 5 and 6), the monitoring results were relatively low and evenly distributed. During periods with dominant wind direction and higher wind speeds, the higher sample concentrations corresponded to the downwind sites, e.g. sites 8 and 9 during the period 1 (Figure 4). Even during periods 9 and 10, both MITC and methyl bromide could still be detected at site 11 (Figures 6 and 7).

MITC

A total of 128 samples for MITC were collected during the study, including two background, two collocated, two field spikes, one trip spike, and one trip blank sample. The two background samples did not contain any detectable amount of MITC.

The results for MITC at each sampling location in each sampling period are listed on Table 5. The highest individual sample concentration, 129 µg/m^3, occurred during the first sampling period at sampling site 8 (Table 5), located 31 ft from the east edge of the application block (Figures 2 and 4). The maximum air concentration of MITC during each sampling period (12 hours except for the first period which was 6 hours) is listed on Table 7. In general, the maximum air concentration declined with time after application except that the lowest one occurred during the sampling period 6 and increased slightly during periods 7 and 8 (Figure 8). The highest maximum 24-hour of TWA concentration was 66.9 µg/m^3 (18 hours) during the first sampling day (Table 8), at sampling site 8.

Table 5. MITC concentration (µg/m^3) in each sampling period at each site

Sampling Site	Sampling Period 1	2	3	4	5	6	7	8	9	10
1	41.21	26.09	17.94	14.53	0.30	2.21	0.19	2.46	3.14	1.63
2	7.97	2.82	17.81	14.68	0.46	1.19	0.66	3.00	1.89	1.21
3	0.66	0.52	2.37	7.35	15.43	2.55	0.74	5.13	ND*	0.72
4	1.40	2.14	3.14	0.09	15.29	2.42	1.00	5.24	ND	0.60
5	1.50	2.37	2.04	0.10	7.03	1.78	0.41	4.30	ND	0.12
6	2.13	3.38	3.24	0.11	9.23	3.23	0.83	6.51	ND	0.14
7	5.26	3.87	6.36	0.20	1.35	4.42	2.04	3.17	ND	0.07
8	129.23	35.76	44.51	17.00	0.17	3.85	6.82	3.98	3.48	2.66
9	102.79	48.69	41.26	23.21	0.28	4.15	4.43	3.74	5.35	4.68
10	22.85	17.76	8.98	9.08	0.26	1.75	0.91	1.51	1.25	1.64
11	30.74[1]	16.09	22.22	15.80	2.44	1.87	5.14	6.56	2.69[1]	1.70
12	22.51	3.71	19.71	7.39	13.69	3.24	6.44	10.43	0.10	0.72

*None detected. MDL for 6-hour sample = 0.04 µg/m^3, 12-hour sample = 0.02 µg/m^3
[1]average of collocated samples.

Methyl Bromide

A total of 128 samples for methyl bromide were collected from field including two background, two collocated, two field spikes, one trip spike, and one trip blank samples. Two samples were invalid due to loss of their A-tube samples during laboratory extraction. On two other samples, their B tube samples were lost during extraction. The results of A-tubes were used for these two samples since most of B-tubes were nondetectable. The two background samples did not contain any detectable amount of methyl bromide.

The results for each sampling location in each sampling period are listed on Table 6. Approximately 75% of the samples were non-detects. In part, this may have been due to the small application areas and consequent, low application mass. The highest individual sample concentration, 133 µg/m^3, occurred during the first sampling period at sampling site 9 (Table 6), located 30 ft from the east edge of the application block (Figures 2 and 4). The maximum 12-hour (10 hours for the first sampling period) air concentration of methyl bromide during each sampling period is listed on Table 7. In general, the maximum air concentration declined with time after application except for periods 7 and 8 (Figure 8). The pattern of the maximum air concentration was similar to MITC with the lowest during the sampling period 6 and increasing during periods 7 and 8. The highest maximum 24-hour of TWA concentration was 103 µg/m^3 (22 hours) during the first sampling day (Table 8), at site 11 located in the middle of the application block and 55.7 ft from the closest edge of the methyl bromide application plot (Figure 2 and 4).

Table 6. Methyl bromide concentration (μg/m^3) in each sampling period at each site

Sampling Site	Sampling Period 1	2	3	4	5	6	7	8	9	10
1	ND	20.15	ND	24.28	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	ND	ND	27.20	NA*	ND	ND	31.51	ND	ND
4	ND	ND	23.79	ND	NA	ND	ND	35.10	ND	ND
5	ND	ND	32.54	ND	ND	ND	ND	18.55	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	66.21	22.11	50.71	ND	ND	ND	30.18	ND	ND	ND
9	132.66	71.32	ND	36.60	ND	ND	33.16	ND	ND	ND
10	ND	39.94	ND	20.61	ND	ND	ND	ND	ND	ND
11	107.47[1]	99.40	37.75	44.63	20.77	ND	ND	29.17	14.47[1]	23.01
12	86.71	70.84	33.54	20.66	34.68	ND	ND	36.59	ND	ND

*Not available. MDL for 10-hour sample = 22.2 μg/m^3, 12-hour sample = 18.5 μg/m^3
[1]average of collocated samples.

Figure 8. Maximum air concentrations at each sampling period

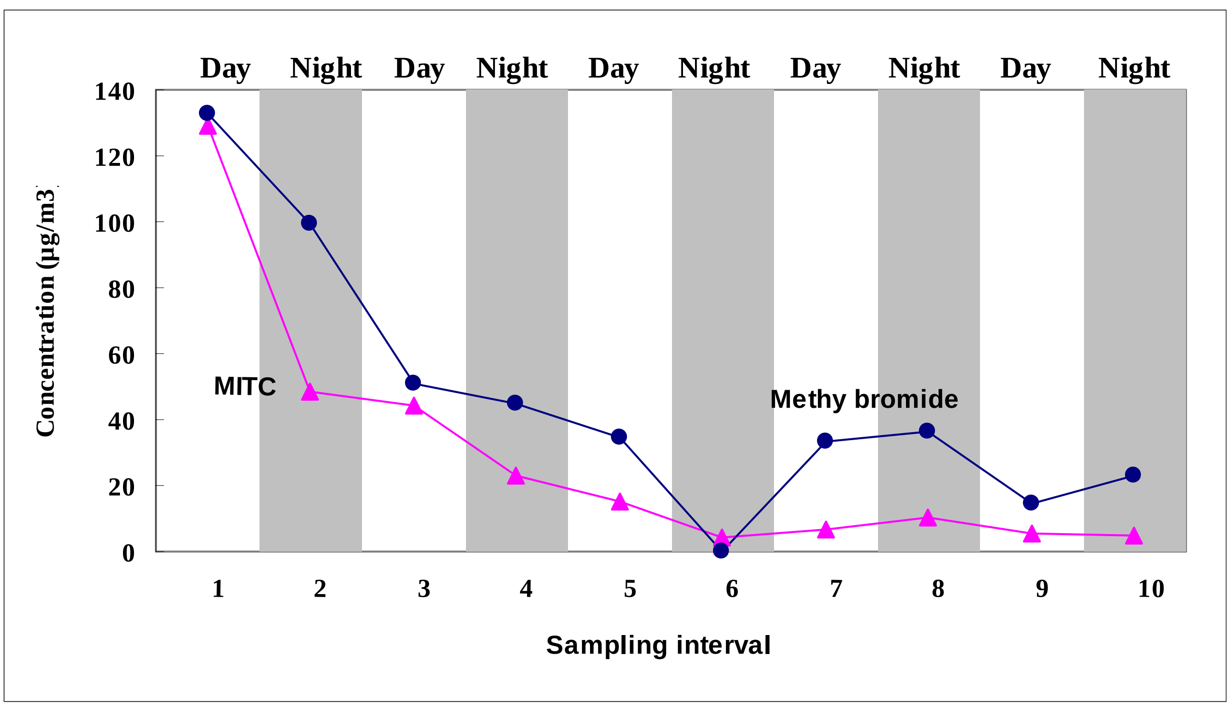


Table 7. 12-hour* maximum concentrations (µg/m^3)

Day (D)/night (N)	1st D	1st N	2nd D	2nd N	3rd D	3rd N	4th D	4th N	5th D	5th N
Hours after start of MITC application	0-6	6-18	18-30	30-42	42-54	54-66	66-78	78-90	90-102	102-114
MITC concentration	129	48.7	44.5	23.2	15.4	4.42	6.82	10.4	5.35	4.68
Hours after start of methyl bromide application	0-10	10-22	22-34	34-46	46-58	58-70	70-82	82-94	94-106	106-118
Methyl bromide concentration	133	99.4	50.7	44.6	34.7	ND**	33.2	36.6	14.5	23.0

*The first sampling period was 6 hours for MITC and 10 hours for methyl bromide.
**none detectable

Table 8. 24-hour* TWA of maximum concentrations

Day	1	2	3	4	5
Hours after start of MITC application	0-18	18-42	42-66	66-90	90-104
MITC concentration (µg/m^3)	66.9	32.2	8.99	8.44	5.02
Hours after methyl bromide application	0-22	22-46	46-70	70-94	94-118
Methyl bromide concentration (µg/m^3)	103	41.2	22.0	22.9	18.7

*The first sampling day was 18 hours for MITC and 22 hours for methyl bromide.

Soil and Weather Characteristics

Soil texture was characterized as loamy sand consisting of 86.5% sand, 7% silt, and 6.5% clay in the particle size diameter less than 2.00 mm portion (96.65%) of the soil sample. There were 3.35% of total soil particles with diameter greater than 2.00 mm. Bulk density was 1.87 g/cm^3. Soil moisture was 8.44% and pH was 7.25. All soil sample results were averages of duplicate samples.

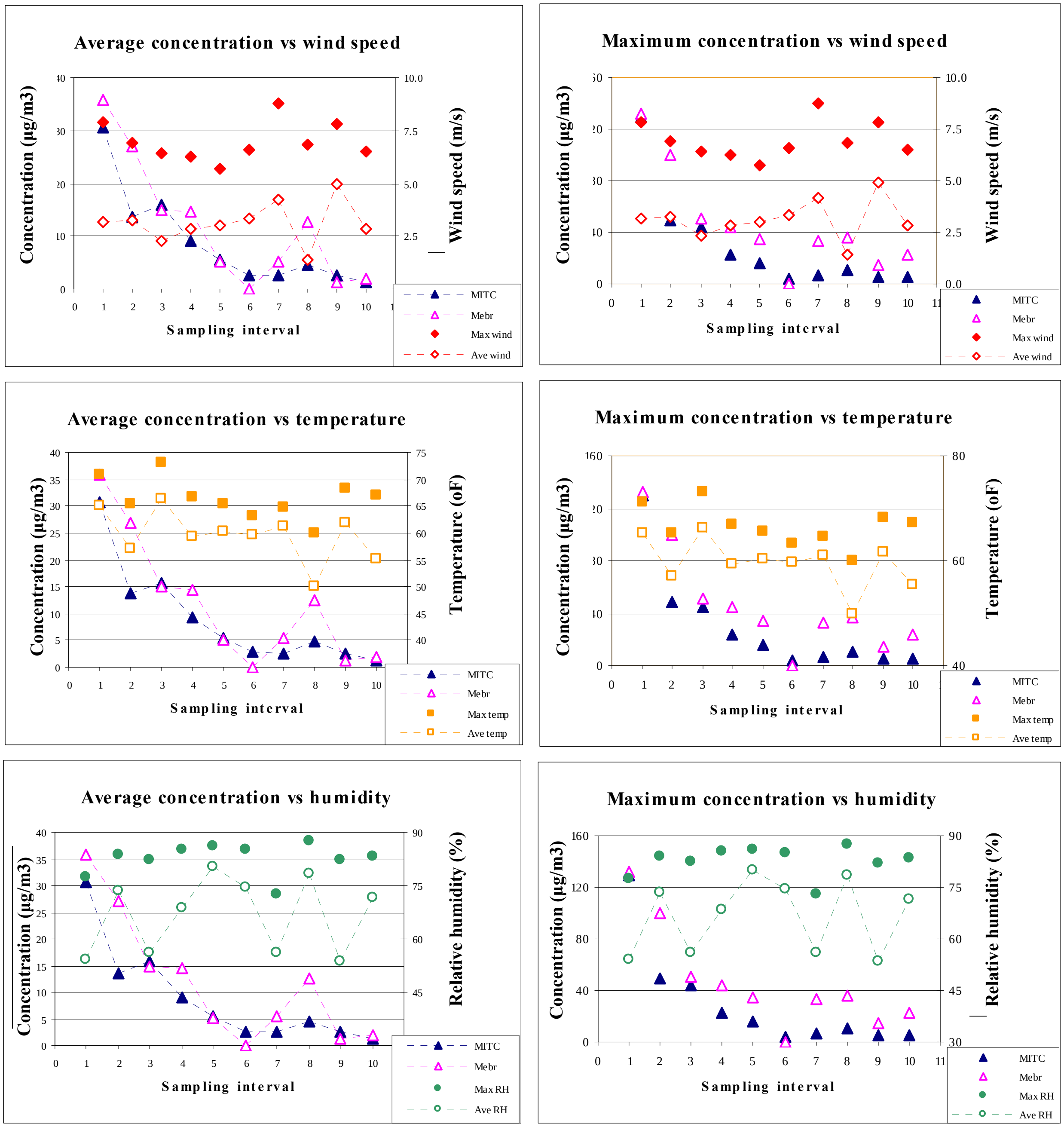
Sky cover during sampling ranged from clear and sunny to overcast (Table 9). On the third day, May 8, 2005, sampling periods 5 and 6, it rained intermittently with hourly precipitation from 0 to 0.08 inch and a total of 0.28 inches of rain that day according to regional weather station (Location: San Joaquin River at Mossdale Bridge, Station ID: MSD, Sensor number: 2, CDWR, 2005). Average wind speed, wind direction, air temperature and relative humidity during each sampling period are listed in Table 9 and detailed records in one-minute increments measured by MetOne® meteorological sensors are available upon request. There was no apparent relationship between average and maximum air concentrations of MITC or methyl bromide versus average and maximum wind speed, temperature, and relative humidity of each sampling period (Figure 9) over time because the dominant effect was the chemical depletion.

Table 9. Average wind speed, wind direction, air temperature and relative humidity

Sampling Period		Cloud cover	Wind speed m/s	Wind speed difference (night-day)	Wind from Direction 0-360°	Temperature °F	Relative Humility %
1	day	Overcast	3.19		269	65.2	54.2
2	night	Partial cloudiness	3.29	0.10	295	57.2	73.5
3	day	Sunny, partial cloudiness	2.31		253	66.2	55.9
4	night	Partial cloudiness	2.84	0.53	241	59.2	68.6
5	day	Raining	2.99		122	60.3	80.1
6	night	Raining	3.35	0.36	214	59.6	74.3
7	day	Sunny, partial cloudiness	4.20		250	61.1	56.0
8	night	Cloudy	1.41	-2.79	176	50.0	78.5
9	day	Clear, partial cloudiness	4.93		311	61.8	53.7
10	night	Clear, sunny	2.85	-2.08	280	55.3	71.5

Figure 9. Air concentrations versus weather measurements

Average and maximum air concentrations of MITC and methyl bromide versus average and maximum wind speed, temperature and relative humidity from each sampling period



Results of Modeling

To estimate MITC and methyl bromide flux and emission ratio during this study, the U.S. EPA ISCST3 model was used to calculate MITC and methyl bromide flux as described by Johnson et al. (1999). The model requires input of location of the treatment areas (source), sampling locations (receptors), and the meteorological data (Met1® data). The treatment areas and sampling locations were mapped in an x and y coordinate system. The meteorological data were collected with a Met1® weather station near the field, and were averaged over 1-hour periods. The model results and measured results were compared through linear regression analysis for each sampling period. The slope of the regression line was used to estimate flux. Detailed modeling information is provided in Appendix III.

The flux estimate was used to calculate the emission ratio, which is the amount of chemical released into air during a given period as a percentage of the effective application rate. The effective application rate is the amount (g) of the target chemical applied to the area (m^2). In this study, the target chemical MITC was assumed to be in 1:1 stoichiometric relationship to the active ingredient of dazomet, which comprised 99% of the formulated product, Basamid. The target chemical methyl bromide comprised 67.0% of the formulation of 67-33 Preplant Soil Fumigant product.

$$MITC\ emission(\%) = 100 * \left[\frac{flux\left(\frac{ug}{m^2 s}\right) * 10^{-6}\left(\frac{g}{ug}\right) * time(\text{seconds})}{effective\ application\ rate, 11.7\left(\frac{g}{m^2}\right)} \right]$$

where the effective application rate was calculated as:
Basamid application rate = 47 pounds * 453.4 g/pound/ (0.2 acre* 4047 m^2/acre) = 26.3 g/m^2.
Active ingredient dazomet application rate = 26.3 g/m^2 * 99% = 26.08 g/m^2.
Since molecular weight of dazomet and MITC is 162.3 and 73.1, respectively,
the effective MITC application rate = 26.08 g/m^2 * 73.1/162.3 = 11.7 g/m^2.

$$Methylbromide\ emission(\%) = 100 * \left[\frac{flux\left(\frac{ug}{m^2 s}\right) * 10^{-6}\left(\frac{g}{ug}\right) * time(\text{seconds})}{effective\ application\ rate, 27.8\left(\frac{g}{m^2}\right)} \right]$$

where the effective application rate was calculated as:
Soil fumigant application rate = 74 pounds * 453.4 g/pound / (0.2 acre * 4047 m^2/acre)
= 41.5 g/m^2.
Active ingredient methyl bromide (67%) application rate = 41.5 g/m^2 * 67% = 27.8 g/m^2

MITC

The four plots treated with Basamid and Telone C35 were represented as four separate sources of MITC. Modeling was conducted with an initial emission rate of 100 µg/m^2-s at ground level, and weather data measured from 1:00 pm, May 6 to 7:00 am, May 11 because the Basamid application started at approximately 12:45 pm, May 6, 2005.

The modeling results are listed in Table 10. The regressions of the measured and modeled concentrations were significant at P=0.05 for each sampling period except for the Period 8. The data for the Period 8 were sorted, and the sorted values were regressed. The flux estimate was highest (53.8 µg/m^2-s) during the application period (Period 1) and decreased over time except for periods 7 and 9. The 18-hour time weighted average (TWA) flux estimate for the first two sampling periods was 33.8 µg/m^2-s (Table 10).

The emission ratio for each sampling period, 24-hour, and cumulative period (Table 11 and Figure 10) was calculated based on the flux estimate and the effective application rate of 11.7 g/m^2 of MITC (235 lb/ac of Basamid, 26.1 g/m^2 of dazomet). The highest emission ratio (9.93%) occurred in the first 6 hours during and after Basamid application although the duration time (6 hours) for this period was only half of those (12 hours) for other periods. The emission ratio for the first 18, 30, and 42 hours was 18.7%, 26.0%, and 30.5%, respectively (Table 11). The cumulative emission for 5 days of the study period was 43.1% of the applied MITC equivalent Basamid (Table 11 and Figure 10).

Table 10. Modeling estimates of MITC flux for air monitoring in Manteca

Sampling Period	Duration (hrs)	Time of Day	Flux (µg/m^2-s)	24-hour TWA flux (µg/m^2-s)
1	6	Day	53.8	
2	12	Night	23.8	33.8*
3	12	Day	19.7	
4	12	Night	12.3	16.0
5	12	Day	11.8	
6	12	Night	1.56	6.69
7	12	Day	9.37	
8	12	Night	3.78	6.57
9	12	Day	6.06	
10	12	Night	1.56	3.81

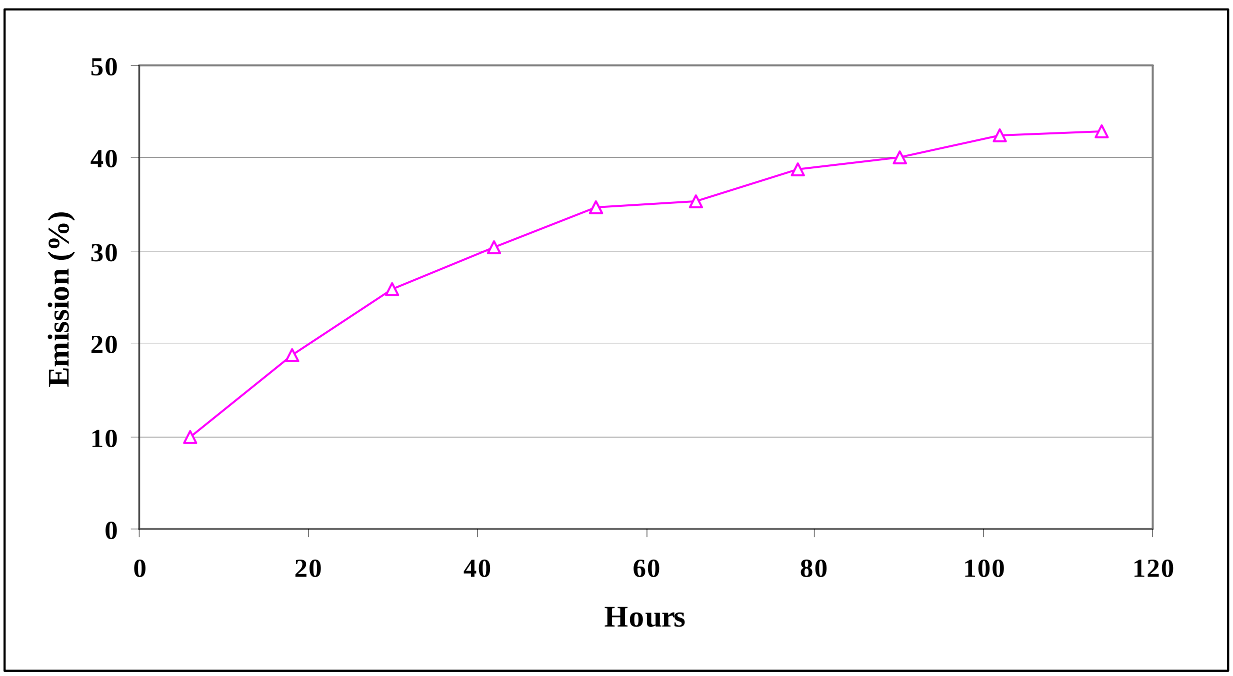
*18 hours for the first day

Table 11. MITC emission for each sampling period, 24-hour, and cumulative period

Sampling		Time of Day	Emission				
Period	Duration Hours		Each Period		24-hour	Cumulative	
			g/m^2	%	%	Hours	%
1	6	Day	1.16	9.93		6	9.93
2	12	Night	1.03	8.79	18.7*	18	18.7
3	12	Day	0.85	7.27		30	26.0
4	12	Night	0.53	4.54	11.8	42	30.5
5	12	Day	0.51	4.36		54	34.9
6	12	Night	0.07	0.58	4.93	66	35.5
7	12	Day	0.40	3.46		78	38.9
8	12	Night	0.16	1.40	4.86	90	40.3
9	12	Day	0.26	2.24		102	42.6
10	12	Night	0.07	0.58	2.81	114	43.1

*18 hours for the first day

Figure 10. Cumulative MITC emission



Methyl Bromide

The model represented the four plots treated with methyl bromide and chloropicrin as four separate sources. Weather data for modeling started from 9:00 am, May 6 and ran to 7:00 am, May 11, 2005.

The modeling fluxes are listed in Table 12. The regressions of the measured and modeled concentrations were significant at P=0.05 for four of the ten sampling periods (Periods 1, 2, 4, and 7), but not significant for periods 3, 5, 8, 9, and 10. The data for these periods were sorted and regressed. Period 10 still could not achieve a significant regression, so the flux was estimated by dividing the sum of the measured concentrations by the sum of the modeled concentrations. During sampling Period 6, no measurable concentrations were detected and the flux was estimated to be 0. Flux was the highest (87.9 µg/m^2-s) during the first period (application) and decreased over time except for periods 5 and 7. The 22-hour maximum TWA flux for sampling periods 1 and 2 was 84.6 µg/m^2-s (Table 12).

The emission ratio for each sampling period, 24-hour, and cumulative period (Table 13 and Figure 11) was calculated based on the estimated flux and the effective application rate of 27.8 g/m^2 of methyl bromide (370 lb/ac of 67-33 Preplant Soil Fumigant with 67.0% methyl bromide). The highest emission ratio was 12.7% in the second sampling period. Although the highest flux was estimated during the first period, its duration time (10 hours) was 2 hours shorter than the second and other periods (12 hours). The emission ratio for the first 22, 34, and 46 hours was 24.1%, 31.3%, and 35.7%, respectively. The cumulative emission for 5 days of the study period was 53.4% of the applied methyl bromide equivalent 67-33 Preplant Soil Fumigant (Table 13 and Figure 11). No flux estimates or emission ratios were adjusted for trapping efficiency which was 50% for the charcoal tube method based on Biermann and Barry (1999).

Table 12. Modeling estimates of methyl bromide flux for air monitoring in Manteca

Sampling Period	Duration (hours)	Time of day	Flux (µg/m^2-s)	24-hour TWA flux (µg/m^2-s)
1	10	Day	87.9	
2	12	Night	81.8	84.6***
3	12	Day	46.2*	
4	12	Night	28.2	37.2
5	12	Day	37.1*	
6	12	Night	0	18.6
7	12	Day	37.9	
8	12	Night	23.7*	30.8
9	12	Day	10.5*	
10	12	Night	5.00**	7.75

* Flux was estimated after concentrations were sorted.

**Flux was estimated by dividing sum of the measured concentrations by the sum of the modeled concentrations.

***22 hours for the first day

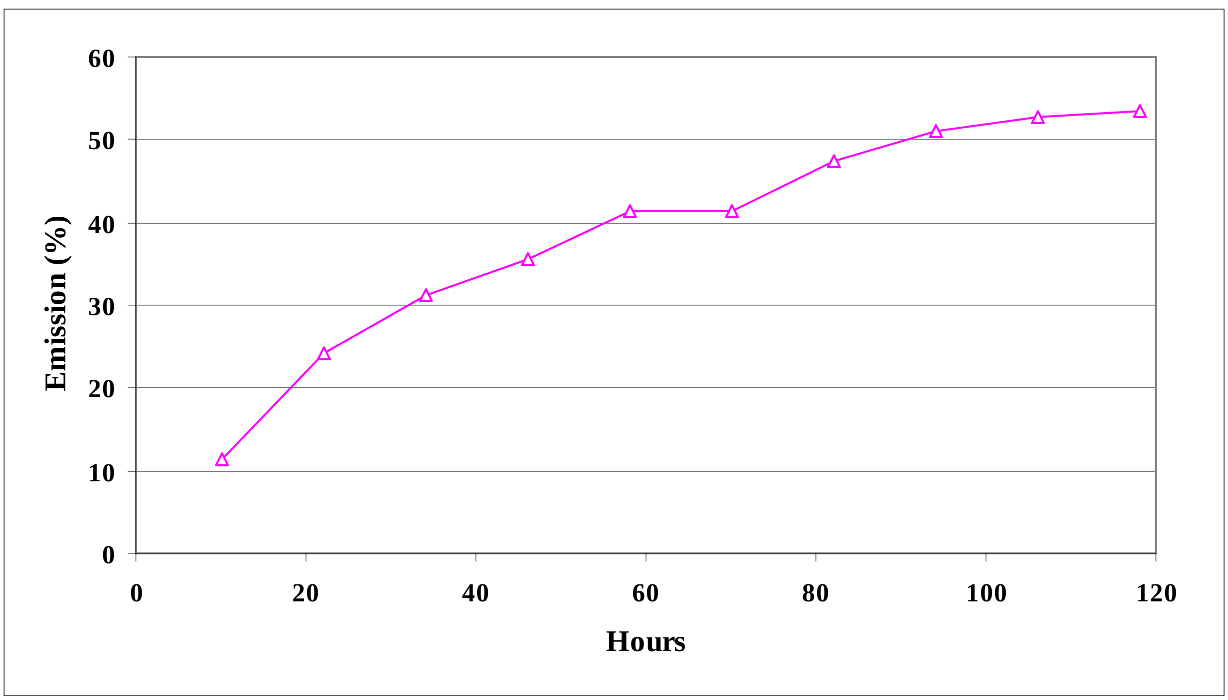
Table 13. Methyl bromide emission for each period, 24-hour, and cumulative periods

Sampling		**Time of Day**	**Emission**				
			Each Period		**24-hour**	**Cumulative**	
Period	**Duration Hours**		**g/m^2**	**%**	**%**	**hours**	**%**
1	10	Day	3.16	11.4		10	11.4
2	12	Night	3.53	12.7	24.1*	22	24.1
3	12	Day	2.00	7.18		34	31.3
4	12	Night	1.22	4.38	11.6	46	35.7
5	12	Day	1.60	5.77		58	41.4
6	12	Night	0.00**	0.00	5.77	70	41.4
7	12	Day	1.64	5.89		82	47.3
8	12	Night	1.02	3.68	9.57	94	51.0
9	12	Day	0.454	1.63		106	52.7
10	12	Night	0.216	0.777	2.41	118	53.4

*22 hours for the first day

**When all the measured concentrations were none detectable during a sampling period, zero emission was used for calculation purpose.

Figure 11. Cumulative methyl bromide emission (unadjusted)



Discussion of Measured and Modeled Results

MITC

The DPR's 8-hour exposure target level is 660 µg/m^3 for MITC. In this study at a Basamid application rate of 235 lbs/ac, the highest individual air concentration was 129 µg/m^3 during a 6-hour sampling period (Table 5). This result showed MITC air concentrations were lower than the DPR's 8-hour exposure target level. In another Basamid surface application study (Certis, 2003) with application rate of 307 lbs/ac (14.8 g/m^2 of equivalent MITC), the highest individual air concentration was 348 µg/m^3 during a 4-hour sampling period (Table 14). In another DPR study (Gurusinghe et al. 2008) the highest 4-hour concentration was 560 ug/m^3.

The highest 24-hour TWA of measured MITC concentration (Table 8) and estimated flux (Table 10) occurred during the first sampling day. This pattern was similar to results from metam sodium studies (Wofford et al., 1994; ARB 1997; Saeed et al., 2000; Barry et al., 2004; Li 2004; and Levine et al., 2005). Another pattern similar to other MITC studies was that the measured air concentration (Figure 8) and the estimated flux (Figure 12) decreased dramatically after the first 24 hours, which indicates that dazomet conversion to MITC occurred rapidly although its molecular structure is more complicated than metam. This result was consistent with the reported dazomet hydrolysis half-life of 0.146 day at pH 7, 25 °C and aerobic soil half-life of 0.75 day in a pH 5.8, loamy sand soil (Table 1).

The maximum MITC air concentration (Figure 8) was mainly driven by the emission flux (Figure 12). The maximum MITC air concentration decreased over time regardless of day or night except following the lowest concentrations during period 6 (Figure 8). This contrasts with most metam sodium studies where MITC followed a diurnal pattern with air concentration increasing slightly during night sampling periods. The pattern of increased nighttime concentration in part may be due to nighttime stable atmospheric conditions accompanied by a surface based inversion (Barry, 2004; Levine et al. 2005). The lack of day/night diurnal pattern in this study is probably due to slightly higher average wind speed at nighttime than daytime in the first three days after application (Table 9) and due to generally decreasing fluxes (Table 10 and Figure 12). At the fourth night (period 8), maximum air concentration was higher than the preceding daytime maximum concentration (period 7) as shown in Figure 8. The average wind speed dropped by 2.79 meters/second correspondingly (Table 9). In another MITC study (Levine et al, 2005), no diurnal pattern occurred during the second treatment of metam sodium application to an untarped bedded field. The lowest concentration in period 6 (Figure 8) of this study was probably due to significant rain during sampling periods 5 and 6.

In comparing this study with other dazomet applications, the 6-hour maximum flux of this study was higher than 4-hour maximum fluxes of the two studies conducted by Certis (Table 14). The flux estimates for all three studies were confirmed through independent calculations (Wofford and Johnson, 2006). It appears that the differences of the two surface application studies conducted independently by Certis and DPR was larger than the two studies with different application methods and both conducted by Certis (Table 14). However, these comparisons could not be conclusive. During the two studies conducted by Certis, the calm winds may have added uncertainty to the ISCST3 modeling and made it difficult to produce strong regressions between the measured concentrations and the modeled concentrations (Certis, 2003). The maximum flux in this study was comparable to the maximum flux in Gurusinghe et al. (2008).

Several factors may contribute to high flux estimates in this monitoring study. The soil with low organic matter content and coarse texture of loamy sand promoted diffusion of MITC from soil to air due to larger pore space, lower moisture-holding capacity and number of adsorption binding sites. In addition, this study was conducted on 4 small, narrowed rectangular plots with dimensions of 100'x 22' and area of 0.05 acre each. The narrowed rectangular plots coupled with fairly consistent wind direction during application period (Figure 4), resulted in localized high concentrations downwind with a steep concentration gradient along the direction of longer sides of the plots. However, varying the wind direction to test the sensitivity of regressions indicated the fluxes were evidently not sensitive to these localized air concentrations. Detailed modeling for this pilot dazomet study was thoroughly discussed by Wofford and Johnson (2006). The higher edge to area ratio of the small plots compared to large fields may have some effects. For example, the application of dazomet through a spreader can lead to spills outside the intended area (Gurusinghe et al. 2008). In Gurusinghe et al. (2008) it was thought that an inadvertent spill near one of the monitors led to exaggerated concentrations. The high concentrations occurred when the monitor was upwind from the application area. If dazomet applications result in deposition of material outside of the measured boundaries of the plots, then this would more greatly impact the results in smaller plots compared to larger plots because the edge to area ratio is higher. For this reason, it would be preferable to conduct future studies on commercial scale fields (5-10 acres).

Table 14. Comparison of estimated flux and emission from four dazomet applications

Application type	Effective application rate of MITC (g/m^2)	Maximum 4-hour TWA concentration (µg/m^3)	Maximum 4-hour Emission (µg/m^2-s)	%
Incorporated (Certis, 2003)	29.1	1107	24.1-36.1[a]	1.19-1.79
Surface (Certis, 2003)	14.8	348	6.81-23.0[a]	0.66-2.24
Surface (DPR, 2005)	11.7	129[b]	53.8[b]	6.62[c]
Surface (DPR, 2006)	22.2	560[b]	79[b]	5.3[c]

[a]maximum 4-hour flux estimates from various regression analysis techniques (Wofford and Fan, 2006)
[b]maximum 6-hour flux or concentration
[c]calculated 4-hour emission using the maximum 6-hour flux

Methyl Bromide

The DPR 24-hour exposure target level was 815 µg/m^3 for methyl bromide. In this study at methyl bromide application rate of 248 lbs/ac, the highest individual air concentration was 133 µg/m^3 during a 10-hour sampling period (Table 6) and a maximum 24-hour TWA air concentration of 103 µg/m^3 (Table 8). These results showed methyl bromide air concentrations were lower than the DPR's 24-hour exposure target level.

Based on modeled flux, the estimated 24-hour maximum TWA emission of 26.3% was the highest among 14 methyl bromide studies with the same application method (Table 15). The estimated 24-hour maximum TWA emission for other 13 studies ranged from 4.9% to 24% and averaged 13%. Possible reasons for the high emission estimates relating to the soil properties in this monitoring study were discussed previously in the MITC section. Not surprisingly, the maximum 24-hour TWA concentration of this study was the lowest even though the application rate was the second highest among all studies listed in Table 15. This was due to the small field size (0.2 acre) of the application area. The higher flux for methyl bromide suggests the possibility that there are difficulties inherent to the small plot size, which could lead to higher measured flux values. However, unlike dazomet, methyl bromide was not applied via a spreader and therefore, it is more difficult to find mechanisms relating to plot size which may have induced higher flux estimates. It is possible that the higher flux estimates were an artifact of the many non-detects, which were at least partially due to the small plot size generating correspondingly small air concentrations. As with MITC, it would seem prudent to conduct future studies on larger plots.

Table 15. Comparison of estimated maximum 24-hour emission to other methyl bromide applications[a] (Data source: Segawa et al., 2000)

Study ID	Application area and rate		Measured maximum 24-hour TWA concentration at 30 feet	Estimated 24-hour Emission[b]
	acres	pounds/acre	Ppb	%
TC 199	20	396	340 (at 0 foot)	13
EH 127-1	10	235	150	7.9
EH 150-6	10	200	82	4.9
EH 163-2	9	180	55	20
EH 164-5	12	205	187	18
EH 164-10A	1	231	69	18
EH 164-10C	1	234	60	15
EH 164-10E	1	231	53	8.7
EH 164-10G	1	226	46	8.5
TC324.1	5	216	52 (at 60 feet)	3.4
EH 163-4	2	214	100	13
BR787.1A	1	186	49	9.8
BR787.2A	1	178	190	24
EM 212-Manteca	0.2	248	27 (at 56 feet)	26.3[c]

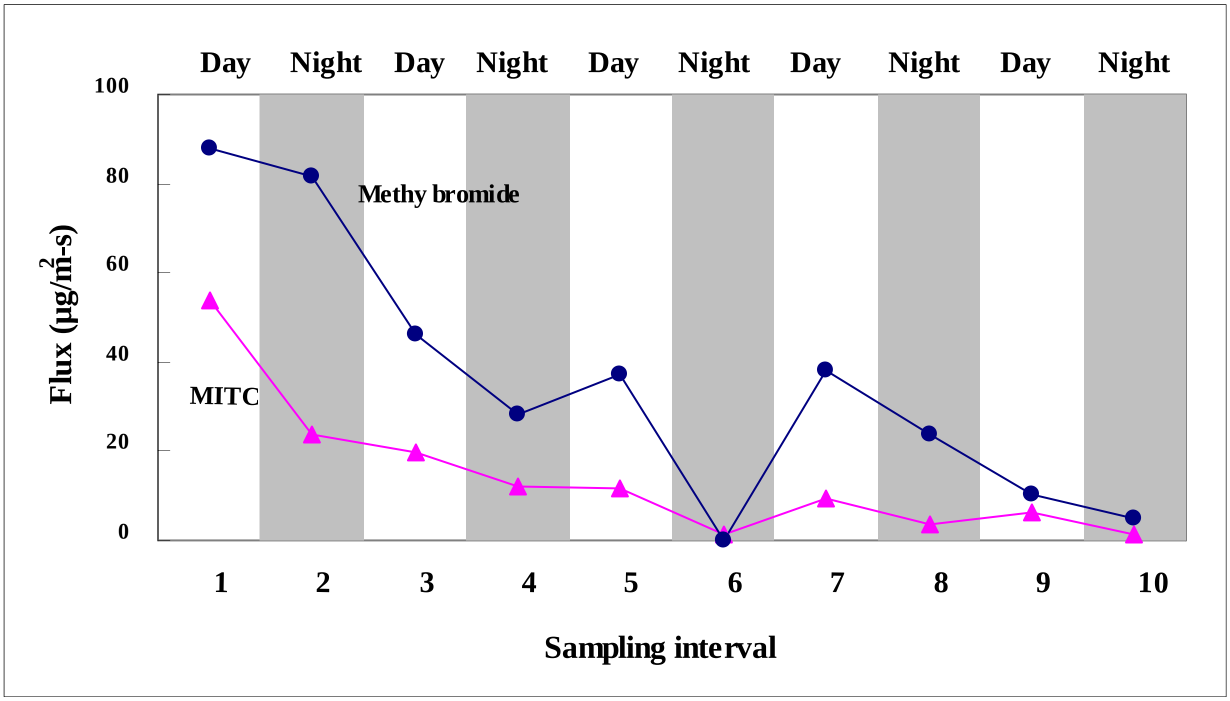
[a]broadcast, shank application with Nobel Plow chisel, injected to 12 inches, no tractor implement, tarped with high barrier tarpaulin.

[b]Estimated as percentage of applied methyl bromide, and unadjusted for 50% of trapping efficiency (Biermann and Barry, 1999).

[c]Calculated 24-hour emission using the maximum TWA 22-hour flux.

One objective for monitoring methyl bromide in this study was as a reference to dazomet regarding their emission patterns. Sampling for these two chemicals was collocated throughout the entire monitoring period. Statistical analysis showed that the measured MITC and methyl bromide air concentrations were significantly correlated ($p<0.001$, $r=0.63$, $n=122$). Their maximum concentrations during each sampling period were also significantly correlated ($p<0.001$, $r=0.935$, $n=10$). Similar to dazomet, the highest 24-hour TWA of measured methyl bromide concentration (Table 8) and modeled flux (Table 12) occurred during the first sampling day. The concentrations (Figure 8) and estimated flux (Figure 12) decreased dramatically after the first 24 hours although the decline rates were slightly different from dazomet.

Figure 12. Model estimated flux for MITC and methyl bromide



CONCLUSION

For MITC, the highest individual sample concentration, 129 μg/m^3, in the first 6-hour during and after Basamid application were lower than the DPR's 8-hour MITC exposure target level, 660 μg/m^3. Based on the modeling flux estimates, the highest emission ratio, 9.89%, occurred in the first 6 hours during and after Basamid application. The cumulative emission for 5 days of the study period was 43.1% of the applied MITC equivalent Basamid.

Similar to other MITC studies including metam sodium studies, the highest 24-hour TWA of measured MITC concentration and estimated flux occurred during the first sampling day, and decreased dramatically after the first 24 hours. This indicates that dazomet conversion to MITC occurred rapidly. Unlike most of other MITC studies which followed an apparent diurnal pattern with air concentration increasing slightly during night sampling periods due to wind speed decrease at nighttime, the dominant pattern of maximum MITC air concentration in this study was declining over time because of declining of the estimated fluxes and slightly higher average wind speed at nighttime than daytime in the first three days after application.

For methyl bromide, the highest maximum 24-hour of TWA concentration, 103 μg/m^3, during the first sampling day (22 hours), was lower than the DPR's 24-hour exposure target level, 815 μg/m^3. Based on modeled flux, the estimated 24-hour maximum TWA emission of 26.3% was twice as high as the average of the other 13 methyl bromide studies. The cumulative emission for 5 days of the study period was 53.4% of the applied methyl bromide.

For both MITC and methyl bromide, the patterns of measured concentrations and modeled emission fluxes over time were parallel and significantly correlated. Their maximum concentrations during each sampling period were also significantly correlated. In addition, the modeled flux and emission ratio of both chemicals were higher than other MITC and methyl bromide studies, respectively.

The small size and configuration of the application area may have impacted study results. The large fraction of methyl bromide samples below the detection limit was probably due to the small size of the application areas and the consequent small mass of methyl bromide that was applied.. The non-detect samples made it difficult to produce significant regressions for the purposes of flux analysis. For MITC, the small plots may have led to higher flux estimates because the method of dazomet application may lead to inadvertent spillage at the plot edges. This could have a relatively larger effect on small plots, where the perimeter-to-area ratio is relatively higher than in larger fields. Future studies should probably utilize larger plots, more consistent with commercial applications.

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APPENDIX I. Field Sample Results

MITC

Sampling			Flow Rate (ml/min)			Time			Results	
Date	Site	Period	Start	End	Average	Start	End	Minutes	µg/sample	$\mu g/m^3$
5/5/05	11	Bg[1]	1522	1499	1510.5	16:41	6:05	804	ND[2]	ND
5/5/05	10	Bg	1460	1417	1438.5	16:35	6:14	819	ND	ND
5/6/05	1	1	1491	1469	1480.0	7:00	18:47	707	22.200	41.209
5/6/05	2	1	1501	1482	1491.5	7:00	18:48	708	4.340	7.972
5/6/05	3	1	1505	1525	1515.0	7:01	18:55	714	0.374	0.664
5/6/05	4	1	1518	1631	1574.5	7:02	19:06	724	0.842	1.396
5/6/05	5	1	1503	1471	1487.0	7:02	19:15	733	0.876	1.503
5/6/05	6	1	1500	1489	1494.5	7:02	19:15	733	1.250	2.134
5/6/05	7	1	1597	1550	1573.5	7:01	19:17	736	3.260	5.258
5/6/05	8	1	1498	1521	1509.5	7:01	19:09	728	75.300	129.233
5/6/05	9	1	1496	1495	1495.5	7:00	18:59	719	57.800	102.791
5/6/05	10	1	1424	1485	1454.5	7:00	18:47	707	12.100	22.854
5/6/05	11	1	1461	1441	1451.0	7:01	18:56	715	16.600	30.671
5/6/05	11c	1	1483	1546	1514.5	7:10	18:56	706	17.400	30.801
5/6/05	12	1	1529	1548	1538.5	7:01	19:07	726	13.300	22.512
5/7/05	1	2	1425	1404	1414.5	18:55	6:45	710	26.200	26.088
5/7/05	2	2	1457	1476	1466.5	18:55	6:46	711	2.940	2.824
5/7/05	3	2	1487	1511	1499.0	19:05	6:59	714	0.551	0.516
5/7/05	4	2	1481	1518	1499.5	19:10	7:05	715	2.290	2.148
5/7/05	5	2	1489	1510	1499.5	19:20	7:11	711	2.530	2.370
5/7/05	6	2	1427	1417	1422.0	19:20	7:00	700	3.360	3.380
5/7/05	7	2	1499	1420	1459.5	19:23	7:18	715	4.040	3.871
5/7/05	8	2	1421	1438	1429.5	19:15	7:07	712	36.400	35.763
5/7/05	9	2	1478	1474	1476.0	19:05	6:57	712	51.100	48.693
5/7/05	10	2	1396	1391	1393.5	18:55	6:47	712	17.600	17.764
5/7/05	11	2	1441	1450	1445.5	19:05	6:51	706	16.400	16.093
5/7/05	12	2	1491	1490	1490.5	19:13	6:55	702	3.880	3.708
5/7/05	1	3	1410	1373	1391.5	6:49	18:50	721	18.000	17.941
5/7/05	2	3	1533	1512	1522.5	6:55	18:53	718	19.500	17.813
5/7/05	3	3	1543	1555	1549.0	7:00	18:57	717	2.630	2.375
5/7/05	4	3	1553	1562	1557.5	7:06	19:01	715	3.480	3.143
5/7/05	5	3	1540	1513	1526.5	7:15	19:07	712	2.200	2.038
5/7/05	6	3	1450	1407	1428.5	7:02	19:02	720	3.330	3.238
5/7/05	7	3	1560	1425	1492.5	7:21	19:11	710	6.740	6.360
5/7/05	8	3	1531	1477	1504.0	7:09	19:03	714	47.600	44.513
5/7/05	9	3	1585	1470	1527.5	6:59	18:54	715	45.000	41.260
5/7/05	10	3	1452	1430	1441.0	6:49	18:45	716	9.250	8.978
5/7/05	11	3	1460	1415	1437.5	6:54	18:54	720	23.000	22.222
5/7/05	12	3	1519	1525	1522.0	6:58	18:58	720	21.600	19.711
5/8/05	1	4	1500	1548	1524.0	18:52	6:50	718	15.900	14.531

5/8/05	2	4	1499	1492	1495.5	18:56	6:50	714	15.700	14.683
5/8/05	3	4	1538	1507	1522.5	19:01	6:57	716	8.010	7.348
5/8/05	4	4	1555	1547	1551.0	19:06	7:02	716	0.100	0.090
5/8/05	5	4	1472	1482	1477.0	19:10	7:06	716	0.108	0.102
5/8/05	6	4	1503	1520	1511.5	19:04	7:02	718	0.116	0.107
5/8/05	7	4	1454	1479	1466.5	19:12	7:07	715	0.211	0.201
5/8/05	8	4	1500	1503	1501.5	19:04	7:02	718	18.300	16.998
5/8/05	9	4	1480	1504	1492.0	18:56	6:54	718	24.900	23.211
5/8/05	10	4	1432	1448	1440.0	18:46	6:50	724	9.470	9.083
5/8/05	11	4	1520	1600	1560.0	18:56	6:54	718	17.700	15.802
5/8/05	12	4	1495	1560	1527.5	19:00	6:58	718	8.110	7.395
5/8/05	1	5	1510	1476	1493.0	6:52	18:50	718	0.323	0.301
5/8/05	2	5	1474	1465	1469.5	6:55	18:50	715	0.483	0.460
5/8/05	3	5	1526	1509	1517.5	7:01	18:55	714	16.700	15.435
5/8/05	4	5	1564	1522	1543.0	7:09	19:01	712	16.800	15.292
5/8/05	5	5	1515	1482	1498.5	7:11	19:04	713	7.510	7.029
5/8/05	6	5	1530	1487	1508.5	7:04	19:02	718	10.000	9.233
5/8/05	7	5	1467	1410	1438.5	7:09	19:06	717	1.390	1.350
5/8/05	8	5	1530	1502	1516.0	7:03	19:02	719	0.190	0.175
5/8/05	9	5	1560	1529	1544.5	6:57	18:55	718	0.311	0.280
5/8/05	10	5	1480	1448	1464.0	6:52	18:51	719	0.269	0.256
5/8/05	11	5	1570	1565	1567.5	6:56	18:54	718	2.750	2.443
5/8/05	12	5	1560	1533	1546.5	7:00	18:58	718	15.200	13.689
5/9/05	1	6	1460	1488	1474.0	18:52	7:02	730	2.380	2.209
5/9/05	2	6	1477	1551	1514.0	18:59	7:00	721	1.300	1.191
5/9/05	3	6	1516	1550	1533.0	19:00	7:06	726	2.840	2.552
5/9/05	4	6	1544	1607	1575.5	19:03	7:11	728	2.780	2.424
5/9/05	5	6	1511	1566	1538.5	19:17	7:15	718	1.990	1.777
5/9/05	6	6	1528	1508	1518.0	19:04	7:22	738	3.610	3.231
5/9/05	7	6	1461	1484	1472.5	19:07	7:17	730	4.750	4.419
5/9/05	8	6	1519	1510	1514.5	19:03	7:12	729	4.250	3.849
5/9/05	9	6	1523	1506	1514.5	18:57	7:08	731	4.600	4.149
5/9/05	10	6	1475	1442	1458.5	18:52	7:03	731	1.870	1.754
5/9/05	11	6	1585	1583	1584.0	18:56	7:10	734	2.170	1.866
5/9/05	12	6	1532	1527	1529.5	19:00	7:15	735	3.650	3.242
5/9/05	1	7	1449	1510	1479.5	7:08	18:54	706	0.193	0.185
5/9/05	2	7	1509	1542	1525.5	7:05	18:55	710	0.709	0.656
5/9/05	3	7	1565	1587	1576.0	7:11	19:00	709	0.823	0.736
5/9/05	4	7	1597	1538	1567.5	7:15	19:05	710	1.120	1.005
5/9/05	5	7	1547	1548	1547.5	7:18	19:10	712	0.455	0.414
5/9/05	6	7	1510	1560	1535.0	7:23	19:02	699	0.874	0.826
5/9/05	7	7	1497	1537	1517.0	7:18	19:02	704	2.180	2.041
5/9/05	8	7	1502	1570	1536.0	7:14	18:59	705	7.390	6.824
5/9/05	9	7	1591	1503	1547.0	7:09	18:56	707	4.840	4.431
5/9/05	10	7	1457	1517	1487.0	7:05	18:51	706	0.955	0.911
5/9/05	11	7	1604	1675	1639.5	7:13	18:56	703	5.920	5.144

5/9/05	12	7	1503	1587	1545.0	7:18	18:59	701	6.960	6.436
5/10/05	1	8	1514	1470	1492.0	18:55	6:54	719	2.640	2.461
5/10/05	2	8	1547	1538	1542.5	18:59	6:59	720	3.320	3.002
5/10/05	3	8	1591	1520	1555.5	19:05	7:01	716	5.720	5.129
5/10/05	4	8	1533	1579	1556.0	19:09	7:05	716	5.840	5.242
5/10/05	5	8	1515	1526	1520.5	19:14	7:10	716	4.680	4.299
5/10/05	6	8	1500	1499	1499.5	19:03	7:02	719	7.020	6.511
5/10/05	7	8	1533	1470	1501.5	19:02	7:02	720	3.420	3.172
5/10/05	8	8	1559	1555	1557.0	18:59	6:58	719	4.450	3.981
5/10/05	9	8	1473	1588	1530.5	18:57	6:55	718	4.110	3.740
5/10/05	10	8	1449	1444	1446.5	18:54	6:52	718	1.570	1.512
5/10/05	11	8	1513	1589	1551.0	18:57	6:56	719	7.320	6.564
5/10/05	12	8	1549	1517	1533.0	19:00	6:59	719	11.500	10.433
5/10/05	1	9	1460	1400	1430.0	6:55	18:54	719	3.230	3.142
5/10/05	2	9	1550	1519	1534.5	7:01	18:55	714	2.060	1.888
5/10/05	3	9	1585	1566	1575.5	7:05	18:57	712	ND	ND
5/10/05	4	9	1605	1588	1596.5	7:09	19:01	712	ND	ND
5/10/05	5	9	1543	1505	1524.0	7:12	19:03	711	ND	ND
5/10/05	6	9	1499	1555	1527.0	7:03	19:02	719	ND	ND
5/10/05	7	9	1491	1539	1515.0	7:03	19:00	717	ND	ND
5/10/05	8	9	1570	1595	1582.5	6:59	18:57	718	3.950	3.476
5/10/05	9	9	1541	1529	1535.0	6:56	18:54	718	5.900	5.353
5/10/05	10	9	1476	1544	1510.0	6:53	18:51	718	1.350	1.245
5/10/05	11	9	1592	1584	1588.0	6:57	18:56	719	3.050	2.671
5/10/05	11c	9	1527	1566	1546.5	6:57	18:56	719	3.000	2.698
5/10/05	12	9	1538	1620	1579.0	7:00	19:00	720	0.109	0.096
5/11/05	1	10	1492	1450	1471.0	18:55	6:55	720	1.730	1.633
5/11/05	2	10	1495	1538	1516.5	18:56	6:54	718	1.320	1.214
5/11/05	3	10	1526	1542	1534.0	19:00	6:55	715	0.795	0.724
5/11/05	4	10	1505	1580	1542.5	19:02	6:59	717	0.665	0.603
5/11/05	5	10	1502	1540	1521.0	19:05	7:01	716	0.134	0.123
5/11/05	6	10	1540	1510	1525.0	19:03	7:03	720	0.152	0.138
5/11/05	7	10	1479	1490	1484.5	19:01	6:59	718	0.074	0.069
5/11/05	8	10	1538	1540	1539.0	18:58	6:56	718	2.940	2.661
5/11/05	9	10	1540	1542	1541.0	18:55	6:54	719	5.190	4.684
5/11/05	10	10	1493	1418	1455.5	18:52	6:52	720	1.720	1.644
5/11/05	11	10	1559	1560	1559.5	18:58	6:58	720	1.910	1.701
5/11/05	12	10	1561	1503	1532.0	19:01	7:01	720	0.798	0.723

Methyl bromide

Sampling			Flow Rate			Time			Results	
Date	Site	Period	Start	End	Average	Start	End	Minutes	µg/sample	µg/m^3
5/5/05	11	Bg	13.84	10.89	12.4	16:40	5:55	795	ND	ND
5/5/05	10	Bg	14.98	10.47	12.7	16:50	6:20	810	ND	ND
5/6/05	1	1	15.33	16.6	16.0	7:00	18:49	585	ND	ND
5/6/05	2	1	14.56	14.47	14.5	7:00	18:45	581	ND	ND
5/6/05	3	1	13.68	14.4	14.0	7:01	18:57	593	ND	ND
5/6/05	4	1	15.4	15.92	15.7	7:02	19:06	602	ND	ND
5/6/05	5	1	13.77	12.23	13.0	7:02	19:15	611	ND	ND
5/6/05	6	1	15.13	15.38	15.3	7:02	19:15	611	ND	ND
5/6/05	7	1	13.29	14.52	13.9	7:01	19:17	613	ND	ND
5/6/05	8	1	14.86	14.40	14.6	7:01	19:09	605	0.586	66.206
5/6/05	9	1	19.13	13.05	16.1	7:00	18:59	595	1.270	132.657
5/6/05	10	1	13.93	14.91	14.4	7:00	18:47	583	ND	ND
5/6/05	11	1	15.06	13.14	14.1	7:01	18:56	592	0.963	115.368
5/6/05	11c	1	14.6	12.07	13.3	7:10	18:56	592	0.786	99.565
5/6/05	12	1	16.28	16.54	16.4	7:01	19:07	603	0.858	86.708
5/7/05	1	2	15.81	13.69	14.8	18:55	6:45	710	0.211	20.148
5/7/05	2	2	15.28	14.62	15.0	18:55	6:47	712	ND	ND
5/7/05	3	2	14.73	14.5	14.6	19:05	6:59	714	ND	ND
5/7/05	4	2	15.92	16.63	16.3	19:10	7:05	715	ND	ND
5/7/05	5	2	14.5	13.85	14.2	19:20	7:11	711	ND	ND
5/7/05	6	2	15.01	13.19	14.1	19:20	7:00	700	ND	ND
5/7/05	7	2	14.43	16.16	15.3	19:23	7:18	715	ND	ND
5/7/05	8	2	14.07	11.59	12.8	19:15	7:07	712	0.202	22.113
5/7/05	9	2	14.54	16.89	15.7	19:05	6:57	712	0.798	71.320
5/7/05	10	2	16.11	16.29	16.2	18:55	6:47	712	0.460	39.937
5/7/05	11	2	16.01	14.57	15.3	19:05	6:51	706	1.070	99.404
5/7/05	12	2	16.23	15.46	15.8	19:13	6:55	702	0.788	70.843
5/7/05	1	3	15.3	15.99	15.6	6:49	18:50	721	ND	ND
5/7/05	2	3	15.77	15.64	15.7	6:55	18:53	718	ND	ND
5/7/05	3	3	15.86	19.04	17.5	7:40	18:57	677	ND	ND
5/7/05	4	3	14.03	17.9	16.0	7:10	19:01	711	0.270	23.786
5/7/05	5	3	12.29	14.83	13.6	7:15	19:07	712	0.312	32.544
5/7/05	6	3	14.97	13.74	14.4	7:02	19:02	720	ND	ND
5/7/05	7	3	15.27	10.85	13.1	7:21	19:11	710	ND	ND
5/7/05	8	3	16.23	15.33	15.8	7:09	19:03	714	0.569	50.715
5/7/05	9	3	15.34		15.3	6:59	18:54	715	ND	ND
5/7/05	10	3	15.68	11.69	13.7	6:49	18:45	716	ND	ND
5/7/05	11	3	16.29	14.1	15.2	6:54	18:54	720	0.413	37.750
5/7/05	12	3	15.95	15.69	15.8	6:58	18:58	720	0.382	33.573
5/8/05	1	4	15.72	15.6	15.7	18:52	6:50	718	0.273	24.280
5/8/05	2	4	15.32	14.13	14.7	18:56	6:50	714	ND	ND
5/8/05	3	4	15.8	15.93	15.9	19:01	6:57	716	0.309	27.202

5/8/05	4	4	15.69	14.94	15.3	19:06	7:02	716	ND	ND
5/8/05	5	4	14.69	13.61	14.2	19:10	7:06	716	ND	ND
5/8/05	6	4	13.94	14.9	14.4	19:04	7:02	718	ND	ND
5/8/05	7	4	15.66	15.48	15.6	19:12	7:07	715	ND	ND
5/8/05	8	4	14.42	15.57	15.0	19:04	7:02	718	ND	ND
5/8/05	9	4	14.81	15.74	15.3	18:56	6:54	718	0.402	36.603
5/8/05	10	4	15.55	15.55	15.6	18:46	6:50	724	0.232	20.607
5/8/05	11	4	14.83	15.94	15.4	18:56	6:54	718	0.493	44.630
5/8/05	12	4	14.71	14.81	14.8	19:00	6:58	718	0.219	20.665
5/8/05	1	5	15.97	15.83	15.9	6:52	18:50	718	ND	ND
5/8/05	2	5	14.05	14.84	14.4	6:55	18:50	715	ND	ND
5/8/05	3	5	15.82	16.17	16.0	7:01	18:55	714	NA[3]	NA
5/8/05	4	5	15.31	15.43	15.4	7:09	19:00	711	NA	NA
5/8/05	5	5	14.24	14.28	14.3	7:11	19:04	713	ND	ND
5/8/05	6	5	15.06	15.04	15.1	7:04	19:02	718	ND	ND
5/8/05	7	5	15.51	15.62	15.6	7:09	19:06	717	ND	ND
5/8/05	8	5	15.86	15.81	15.8	7:03	19:02	719	ND	ND
5/8/05	9	5	16.01	15.91	16.0	6:57	18:55	718	ND	ND
5/8/05	10	5	15.63	15.72	15.7	6:52	18:51	719	ND	ND
5/8/05	11	5	16.26	16.33	16.3	6:56	18:54	718	0.243	20.770
5/8/05	12	5	15.03	14.77	14.9	7:00	18:58	718	0.371	34.679
5/9/05	1	6	15.63	15.49	15.6	18:52	7:02	730	ND	ND
5/9/05	2	6	14.55	14.26	14.4	18:59	7:00	721	ND	ND
5/9/05	3	6	15.97	16.23	16.1	19:00	7:06	726	ND	ND
5/9/05	4	6	15.47	15.63	15.6	19:03	7:11	728	ND	ND
5/9/05	5	6	14.32	14.12	14.2	19:07	7:15	728	ND	ND
5/9/05	6	6	15.11	14.82	15.0	19:04	7:22	738	ND	ND
5/9/05	7	6	16.03	15.26	15.6	19:07	7:17	730	ND	ND
5/9/05	8	6	15.99	15.38	15.7	19:03	7:12	729	ND	ND
5/9/05	9	6	16.09	15.53	15.8	18:57	7:08	731	ND	ND
5/9/05	10	6	16.05	14.94	15.5	18:52	7:03	731	ND	ND
5/9/05	11	6	15.45	15.13	15.3	18:56	7:10	734	ND	ND
5/9/05	12	6	15.06	14.6	14.8	19:00	7:15	735	ND	ND
5/9/05	1	7	15.55	16.08	15.8	7:08	18:54	706	ND	ND
5/9/05	2	7	14.9	15.32	15.1	7:05	18:55	710	ND	ND
5/9/05	3	7	14.14	15.29	14.7	7:11	19:00	709	ND	ND
5/9/05	4	7	15.63	15.73	15.7	7:15	19:05	710	ND	ND
5/9/05	5	7	14.25	14.73	14.5	7:18	19:10	712	ND	ND
5/9/05	6	7	14.85	15.34	15.1	7:23	19:02	699	ND	ND
5/9/05	7	7	16.51	16.07	16.3	7:18	19:02	704	ND	ND
5/9/05	8	7	16.17	16.17	16.2	7:14	18:59	705	0.344	30.176
5/9/05	9	7	15.52	16.43	16.0	7:09	18:56	707	0.374	33.161
5/9/05	10	7	15.69	16.36	16.0	7:05	18:51	706	ND	ND
5/9/05	11	7	15.68	15.47	15.6	7:13	18:56	703	ND	ND
5/9/05	12	7	15.22	15.24	15.2	7:18	18:59	701	ND	ND
5/10/05	1	8	15.22	15.36	15.3	18:55	6:54	719	ND	ND

5/10/05	2	8	15.14	15.36	15.3	18:59	6:59	720	ND	ND
5/10/05	3	8	15.56	14.36	15.0	19:05	7:01	716	0.338	31.511
5/10/05	4	8	14.54	14.59	14.6	19:09	7:05	716	0.366	35.096
5/10/05	5	8	15.01	15.1	15.1	19:14	7:10	716	0.200	18.554
5/10/05	6	8	15.71	14.36	15.0	19:03	7:02	719	ND	ND
5/10/05	7	8	15.97	14.55	15.3	19:03	7:02	719	ND	ND
5/10/05	8	8	16.05	15.32	15.7	19:00	6:58	718	ND	ND
5/10/05	9	8	15.69	15.94	15.8	18:57	6:55	718	ND	ND
5/10/05	10	8	16.28	14.99	15.6	18:54	6:52	718	ND	ND
5/10/05	11	8	15.27	14.58	14.9	18:57	6:56	719	0.313	29.168
5/10/05	12	8	15.08	14.04	14.6	19:00	6:59	719	0.383	36.585
5/10/05	1	9	15.90	16.62	16.3	6:55	18:54	719	ND	ND
5/10/05	2	9	14.81	15.32	15.1	7:01	18:55	714	ND	ND
5/10/05	3	9	14.69	15.02	14.9	7:05	18:57	712	ND	ND
5/10/05	4	9	15.63	15.83	15.7	7:09	19:01	712	ND	ND
5/10/05	5	9	14.01	14.8	14.4	7:12	19:03	711	ND	ND
5/10/05	6	9	14.66	15.15	14.9	7:03	19:02	719	ND	ND
5/10/05	7	9	14.92	16.62	15.8	7:03	19:00	717	ND	ND
5/10/05	8	9	16.01	16.24	16.1	6:59	18:57	718	ND	ND
5/10/05	9	9	15.95	16.65	16.3	6:56	18:54	718	ND	ND
5/10/05	10	9	15.60	16.08	15.8	6:53	18:51	718	ND	ND
5/10/05	11	9	15.56	15.76	15.7	6:57	18:56	719	ND	ND
5/10/05	11c	9	16.14	15.65	15.9	6:57	18:56	719	0.225	19.688
5/10/05	12	9	14.66	15.41	15.0	7:00	19:00	720	ND	ND
5/11/05	1	10	16.30	15.17	15.7	18:55	6:55	720	ND	ND
5/11/05	2	10	15.66	15.32	15.5	18:56	6:54	718	ND	ND
5/11/05	3	10	14.92	15.02	15.0	19:00	6:55	715	ND	ND
5/11/05	4	10	14.28	15.83	15.1	19:02	6:59	717	ND	ND
5/11/05	5	10	14.62	14.8	14.7	19:05	7:01	716	ND	ND
5/11/05	6	10	15.13	14.26	14.7	19:03	7:03	720	ND	ND
5/11/05	7	10	16.14	14.67	15.4	19:01	6:59	718	ND	ND
5/11/05	8	10	16.11	15.21	15.7	18:58	6:56	718	ND	ND
5/11/05	9	10	16.35	15.18	15.8	18:55	6:54	719	ND	ND
5/11/05	10	10	15.98	14.73	15.4	18:52	6:52	720	ND	ND
5/11/05	11	10	15.56	15.22	15.4	18:58	6:58	720	0.255	23.013
5/11/05	12	10	15.19	14.24	14.7	19:01	7:01	720	ND	ND

[1]Background, [2]None detected, [3]Not available.

APPENDIX II. Quality Control Measurement Results

MITC Trapping Efficiency in SKC Coconut Charcoal (24 hours trapping)

Sample number	Pump type	Run Time minutes	Flow Rate on	Flow Rate off	Flow Rate average	Spike Level µg	Recovery A µg	Recovery B µg	Recovery A+B %
14	PCXR	1402	1566	1599	1583	1.0	0.59	0.22	81.5
15	PCXR	1440	1537	1612	1575	1.0	0.46	0.33	79.0
16	PCXR	1440	1594	1627	1611	1.0	0.51	0.28	79.0
13	PCXR	1424	1563	1607	1585	0.0	nd	nd	nd
17	PCXR	1441	1540	1569	1555	10.0	5.07	2.74	78.1
18	PCXR	1440	1566	1590	1578	10.0	3.59	3.82	74.1
19	PCXR	1441	1539	1558	1549	10.0	6.24	1.83	80.7
20	PCXR	1441	1560	1599	1580	100	28.40	37.80	66.2
21	PCXR	1441	1575	1575	1575	100	27.80	37.10	64.9
22	PCXR	1427	1470	1457	1464	100	31.80	34.90	66.7
						Overall average			**74.5**
						Average for the level of 1.0 µg			79.8
						Average for the level of 10.0 µg			77.6
						Average for the level of 100 µg			65.9

Field spike, trip spike, and trip blank

Date	Sampling Site	Sampling Type	Spike (µg)	Flow Rate Start	Flow Rate End	Flow Rate Average	Time Start	Time End	Minutes	Recovery µg/sample	Recovery %
MITC											
5/5/05	1	FS[1]	10	1540	1548	1544	16:35	6:15	820	8.65	86.5
5/5/05	12	FS	100	1471	1416	1444	16:41	6:05	804	49.10	49.1
		TS[2]	10							7.02	70.2
		TB[3]								ND	
Methyl bromide											
5/5/05	1	FS	10	15.83	14.18	15.0	16:40	5:55	797	1.77	17.7
5/5/05	12	FS	1	14.10	10.47	12.3	16:50	6:21	810	0.301	30.1
		TS	1							0.603	60.3
		TB								ND	

[1]Field spike; [2]Trip spike; [3]Trip blank

APPENDIX III. Modeling Results

TO: Shifang Fan
Environmental Scientist
Department of Pesticide Regulation
Environmental Monitoring Branch

FROM: Pam Wofford
Senior Environmental Scientist
(916) 342-4297

DATE: May 12, 2008

SUBJECT: MODELING RESULTS FOR THE 2005 DAZOMET AND METHYL BROMIDE MONITORING STUDY IN MANTECA.

General

The U.S. EPA ISCST3 dispersion model was used, as described by Johnson (1999), to estimate metam sodium and methyl bromide flux associated with a dazomet and methyl bromide application in Manteca, CA in 2005. The model requires data input for the treatment areas (source), sampling locations (receptors) and meteorological data (Met1® data). The treatment areas and receptors were mapped out with an x and y coordinate system. The Met1® meteorological weather data collected was averaged over 1 hour intervals. The model results and measured results were compared through regression analysis to determine the multiplying factor (the slope of the regression line) used to calculate the flux factor. There was significant rain during intervals 5 and 6.

MITC modeling results

The treatment areas were represented as four separate sources, with an initial emission rate of 100 ug/m^2s at ground level. Meteorological data was measured near the field with a Met1® weather station. Application to the four treatment areas commenced at approximately 12:45 pm, therefore, the met file data for period 1 started at 1:00 pm. The results of the regression analysis of the measured concentrations and the modeled concentrations are listed in Table 1. The regressions were significant for most of the sampling intervals. Sampling interval 8 did not result in a regression with a significant relationship so the concentrations were sorted from lowest to highest and reanalyzed. The 18-hour time weighted average (TWA) for sampling intervals 1 and 2 was 33.8 $\mu g/m^2$-s (Table 2). The flux rate was highest during the application interval and decreased over time (Figure 2).

Table 1. Regression results for 2005 MITC monitoring in Manteca

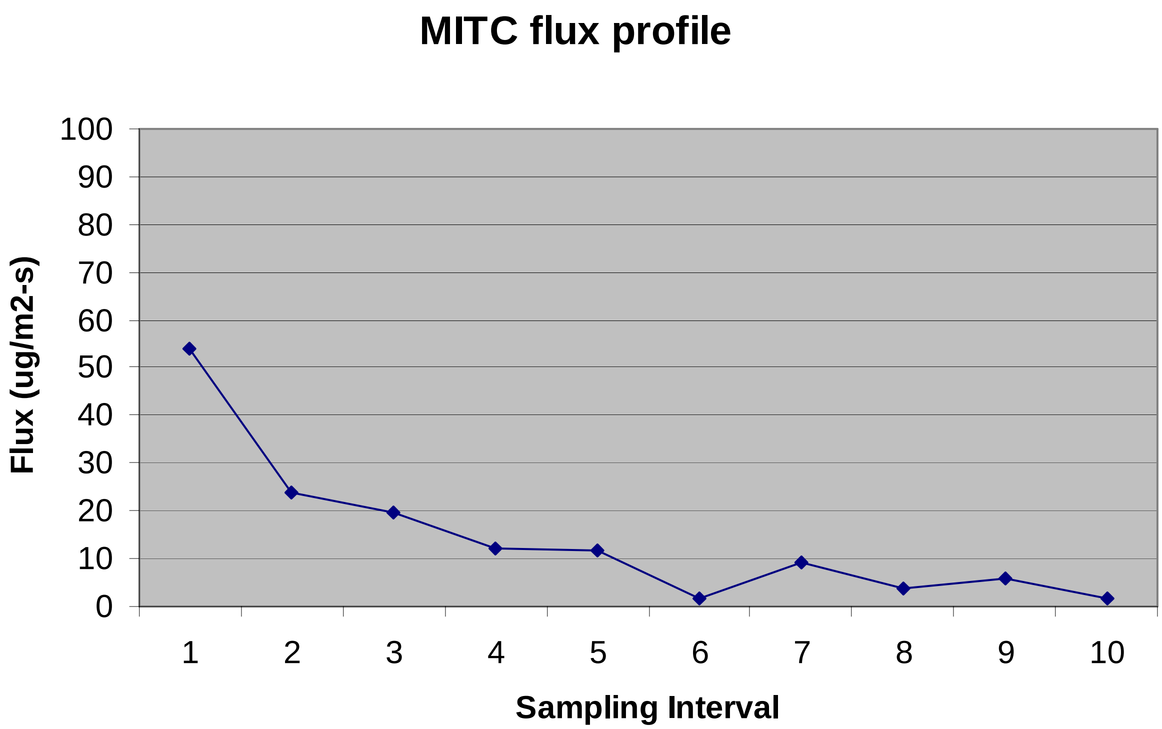
Sampling Interval	Duration (hrs)	Flux (μg/m^2-s)	R^2	F-test p-value	Time of Day
1	6	53.79	0.93	<0.001	Day
2	12	23.76	0.86	<0.001	Night
3	12	19.65	0.76	<0.001	Day
4	12	12.25	0.90	<0.001	Night
5	12	11.82	0.89	<0.001	Day
6	12	1.561	0.36	0.040	Night
7	12	9.369	0.73	<0.001	Day
8	12	3.777	0.88*	**	Night
9	12	6.062	0.79	<0.001	Day
10	12	1.556	0.81	<0.001	Night

*Concentrations were sorted before regression analysis.
**p value cannot be calculated using conventional statistics.

Table 2. 18-hour Time Weighted Average of flux calculation for MITC monitoring.

Sampling Interval	Duration (hrs)	24-hr TWA flux (μg/m^2-s)
1	6	
2	12	33.8

Figure 1. Flux profile for MITC at each sampling interval.



Methyl bromide modeling results

The treatment areas were represented as four separate sources, with an initial emission rate of 100 ug/m^2-s at ground level. Application to the four treatment areas commenced at approximately 9:00 am, therefore, the met file data for period 1 started at 9:00. The results of the regression analysis of the measured concentrations and the modeled concentrations are listed in Table 3. The regressions were significant to the 5% level for four of the sampling intervals (Intervals 1, 2, 4, and 7). Sampling intervals 3, 5, 8, 9 and 10 did not result in a regression with a significant relationship so the concentrations were sorted from lowest to highest and reanalyzed. The regression of interval 10 did not result in a significant relationship. During interval 6 there were no measurable concentrations of methyl bromide detected, therefore, the flux was estimated to be 0. The 22-hour time TWA for sampling intervals 1 and 2 was 84.6 µg/m^2-s (Table 2). The flux rate was highest during the first night following application and decreased over time (Figure 2).

Table 3. Regression results for 2005 methyl bromide monitoring in Manteca

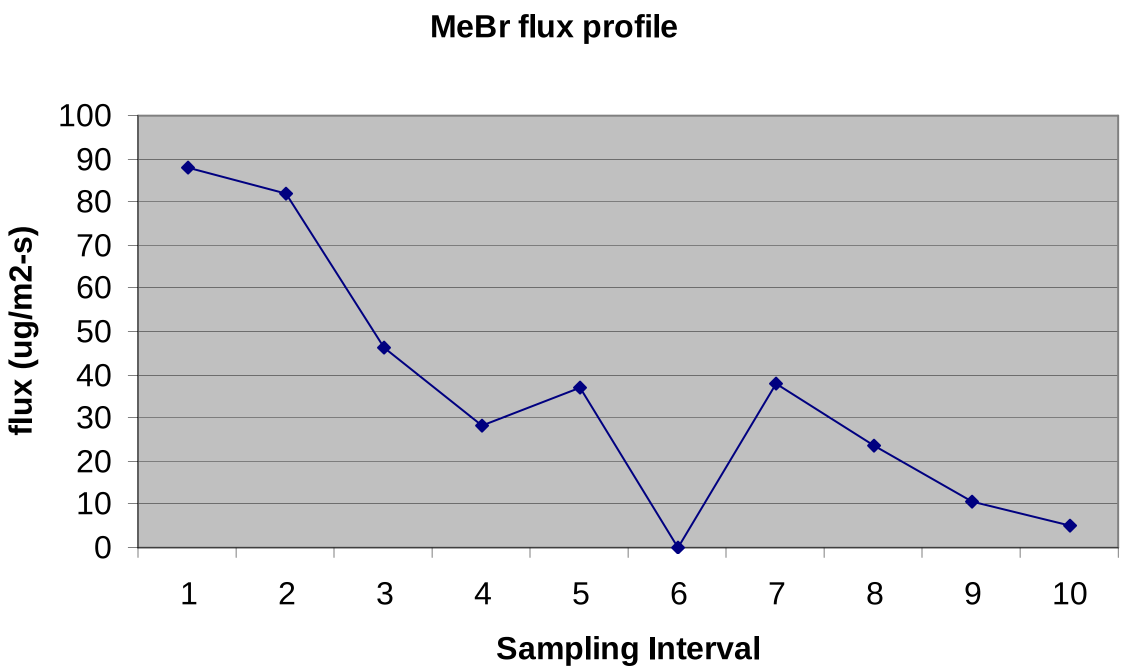
Sampling Interval	Duration (hrs)	Flux ($\mu g/m^2$-s)	R^2	F-test p-value	Time of Day
1	10	87.85	0.83	<0.001	Day
2	12	81.83	0.90	<0.001	Night
3	12	46.18*	0.83	**	Day
4	12	28.21	0.72	<0.001	Night
5	12	37.14*	0.78	**	Day
6	12	0	**	**	Night
7	12	37.90	0.68	<0.001	Day
8	12	23.68*	0.86	**	Night
9	12	10.45	0.42	0.02	Day
10	12	5.00***			Night

[1] No measurable amounts were detected during interval. Unable to calculate regression.
*Concentrations were sorted before regression analysis.
**p value cannot be calculated using conventional statistics.
***flux estimated by dividing sum of the measured concentrations by the sum of the modeled concentrations.

Table 4. 24-hour Time Weighted Average of flux calculation for methyl bromide.

Sampling Interval	Duration (hrs)	22-hr TWA flux ($\mu g/m^2$-s)
1	10	
2	12	84.6

Figure 2. Flux profile for methyl bromide at each sampling interval.



References:

Johnson, B., T. Barry, and P. Wofford. 1999. Workbook for Gaussian Modeling Analysis of Air Concentration Measurements. Report EH99-03. State of California. California Department of Pesticide Regulation.

Attachment 1

Input File for dazomet application

```
CO STARTING
CO TITLEONE Basamid - Manteca 05/06/05
CO MODELOPT CONC   RURAL        NOSTD  NOBID  NOCALM
CO AVERTIME PERIOD
CO POLLUTID OTHER
CO DCAYCOEF    .000000
CO FLAGPOLE 1.2
CO RUNORNOT RUN
CO ERRORFIL ERRORS.OUT
CO FINISHED
SO STARTING
SO LOCATION APP01 AREA          0.0          0.0        .0000
SO SRCPARAM APP01 0.000100   0.00    30.78    6.86
SO LOCATION APP02 AREA          0.0         34.90       .0000
SO SRCPARAM APP02 0.000100   0.00    30.78    6.55
SO LOCATION APP03 AREA         63.10        23.78       .0000
SO SRCPARAM APP03 0.000100   0.00    31.08    7.62
SO LOCATION APP04 AREA         63.10        48.31       .0000
SO SRCPARAM APP04 0.000100   0.00    31.08    7.62
SO EMISUNIT    .100000E+07 (GRAMS/SEC)        (MICROGRAMS/CUBIC-METER)
SO SRCGROUP ALL
SO FINISHED
RE STARTING
RE DISCCART  46.33   -9.75 1.2
RE DISCCART  15.24  -10.06 1.2
RE DISCCART  -9.45   19.05 1.2
RE DISCCART  -8.84   44.65 1.2
RE DISCCART  15.85   73.15 1.2
RE DISCCART  45.87   72.45 1.2
RE DISCCART  78.33   74.98 1.2
RE DISCCART 103.63   45.42 1.2
RE DISCCART 103.33   21.18 1.2
RE DISCCART  76.50   -9.75 1.2
RE DISCCART  45.87   17.98 1.2
RE DISCCART  46.79   45.72 1.2
RE FINISHED
ME STARTING
ME INPUTFIL daz1.met          (4I2,2F9.4,F6.1,I2,2F7.1)
ME ANEMHGHT   10.000 METERS
ME SURFDATA  99999  2005          SURFNAME
ME UAIRDATA  99999  2005          UAIRNAME
ME WINDCATS    1.54    3.09    5.14    8.23   10.80
ME FINISHED
OU STARTING
OU PLOTFILE PERIOD ALL daz1.PLT
OU FINISHED
```

Attachment 2

Input File for methyl bromide application

```
CO STARTING
CO TITLEONE Methyl bromide - Manteca 05/06/05
CO MODELOPT CONC   RURAL        NOSTD  NOBID  NOCALM
CO AVERTIME PERIOD
CO POLLUTID OTHER
CO DCAYCOEF    .000000
CO FLAGPOLE 1.2
CO RUNORNOT RUN
```

```
CO ERRORFIL ERRORS.OUT
CO FINISHED
SO STARTING
SO LOCATION APP01 AREA          0.0          22.26        .0000
SO SRCPARAM APP01 0.000100   0.00     30.78     6.70
SO LOCATION APP02 AREA          0.0          46.80        .0000
SO SRCPARAM APP02 0.000100   0.00     30.78     6.71
SO LOCATION APP03 AREA         63.10          12.68        .0000
SO SRCPARAM APP03 0.000100   0.00     31.08     6.71
SO LOCATION APP04 AREA         63.10          37.03        .0000
SO SRCPARAM APP04 0.000100   0.00     31.08     6.71
SO EMISUNIT    .100000E+07 (GRAMS/SEC)         (MICROGRAMS/CUBIC-METER)
SO SRCGROUP ALL
SO FINISHED
RE STARTING
RE DISCCART  46.33   -9.75 1.2
RE DISCCART  15.24  -10.06 1.2
RE DISCCART  -9.45   19.05 1.2
RE DISCCART  -8.84   44.65 1.2
RE DISCCART  15.85   73.15 1.2
RE DISCCART  45.87   72.45 1.2
RE DISCCART  78.33   74.98 1.2
RE DISCCART 103.63   45.42 1.2
RE DISCCART 103.33   21.18 1.2
RE DISCCART  76.50   -9.75 1.2
RE DISCCART  45.87   17.98 1.2
RE DISCCART  46.79   45.72 1.2
RE FINISHED
ME STARTING
ME INPUTFIL  daz10.met           (4I2,2F9.4,F6.1,I2,2F7.1)
ME ANEMHGHT   10.000 METERS
ME SURFDATA  99999  2005           SURFNAME
ME UAIRDATA  99999  2005           UAIRNAME
ME WINDCATS    1.54    3.09    5.14    8.23   10.80
ME FINISHED
OU STARTING
```

Attachment 3

Meteorlogical input file:

```
   99999       5   99999       5
05 6 5 9  91.0511   3.2122 288.9 4  300.0  300.0
05 6 510  94.8942   4.0120 290.1 4  300.0  300.0
05 6 511  75.1881   3.4347 291.5 4  300.0  300.0
05 6 512  47.0260   2.2454 292.3 4  300.0  300.0
05 6 513  91.7095   2.1299 292.9 4  300.0  300.0
05 6 514 108.0577   2.1497 293.5 4  300.0  300.0
05 6 515  94.1602   1.7653 293.8 4  300.0  300.0
05 6 516 111.2572   3.9214 294.4 4  300.0  300.0
05 6 517 111.1207   5.5911 293.8 4  300.0  300.0
05 6 518 108.3021   5.9871 292.4 4  300.0  300.0
05 6 519 114.5228   4.9215 290.6 4  300.0  300.0
05 6 520 117.2739   3.8161 289.4 4  300.0  300.0
05 6 521 109.5444   4.5054 288.5 4  300.0  300.0
05 6 522 108.3232   4.3639 287.7 4  300.0  300.0
05 6 523 102.3582   3.7011 287.2 4  300.0  300.0
05 6 524 113.4667   3.1482 286.8 4  300.0  300.0
05 6 6 1 125.8235   2.9767 286.7 4  300.0  300.0
05 6 6 2 122.8956   2.7950 286.4 5  300.0  300.0
```

05 6 6 3 130.3528 2.5040 286.0 5 300.0 300.0
05 6 6 4 142.9283 2.1547 285.8 5 300.0 300.0
05 6 6 5 126.5963 2.5739 285.6 5 300.0 300.0
05 6 6 6 61.1877 1.2150 284.5 5 300.0 300.0
05 6 6 7 17.3273 0.6555 286.7 4 300.0 300.0
05 6 6 8 115.3709 2.4843 288.2 3 300.0 300.0
05 6 6 9 108.1740 2.6906 289.6 3 300.0 300.0
05 6 610 113.2157 2.0286 290.9 3 300.0 300.0
05 6 611 109.7282 2.0142 292.0 2 300.0 300.0
05 6 612 103.6144 2.4034 292.6 2 300.0 300.0
05 6 613 37.0655 2.1712 293.6 1 300.0 300.0
05 6 614 113.7080 2.2172 294.3 2 300.0 300.0
05 6 615 105.1325 2.0536 295.1 2 300.0 300.0
05 6 616 105.8527 2.1952 295.5 3 300.0 300.0
05 6 617 139.3742 2.7425 295.2 3 300.0 300.0
05 6 618 107.9633 4.6401 293.6 4 300.0 300.0
05 6 619 111.3758 4.7068 291.6 4 300.0 300.0
05 6 620 122.7063 4.9558 290.0 4 300.0 300.0
05 6 621 131.0031 4.8331 289.4 4 300.0 300.0
05 6 622 138.7460 4.3717 289.0 4 300.0 300.0
05 6 623 153.0309 3.6283 288.7 4 300.0 300.0
05 6 624 166.5282 3.1159 288.5 4 300.0 300.0
05 6 7 1 171.4298 2.6490 288.3 4 300.0 300.0
05 6 7 2 231.7104 1.9493 287.1 4 300.0 300.0
05 6 7 3 229.3420 1.5168 286.7 4 300.0 300.0
05 6 7 4 214.8470 0.8038 286.7 4 300.0 300.0
05 6 7 5 105.7584 0.9376 286.7 4 300.0 300.0
05 6 7 6 97.3807 1.2314 286.5 4 300.0 300.0
05 6 7 7 349.0522 0.5254 286.6 4 300.0 300.0
05 6 7 8 261.6951 2.3898 286.7 4 300.0 300.0
05 6 7 9 265.2965 3.0910 287.2 4 300.0 300.0
05 6 710 298.7889 2.6607 287.8 4 300.0 300.0
05 6 711 305.5848 3.0347 288.1 4 300.0 300.0
05 6 712 305.2000 3.3067 288.4 4 300.0 300.0
05 6 713 300.6305 3.6180 289.1 4 300.0 300.0
05 6 714 298.0908 3.8657 289.9 4 300.0 300.0
05 6 715 300.3234 3.8154 290.4 4 300.0 300.0
05 6 716 316.5858 3.9651 291.2 4 300.0 300.0
05 6 717 291.4960 2.9205 291.5 4 300.0 300.0
05 6 718 319.3613 2.9987 290.5 4 300.0 300.0
05 6 719 322.8036 3.1206 290.2 4 300.0 300.0
05 6 720 340.5055 4.0801 290.1 4 300.0 300.0
05 6 721 343.5382 4.7591 290.2 4 300.0 300.0
05 6 722 343.6806 4.8519 289.8 4 300.0 300.0
05 6 723 352.5138 3.9220 289.5 4 300.0 300.0
05 6 724 343.3477 3.1603 289.1 4 300.0 300.0
05 6 8 1 12.3060 3.1861 288.6 4 300.0 300.0
05 6 8 2 112.7206 1.2129 287.0 4 300.0 300.0
05 6 8 3 99.7960 2.1836 287.1 4 300.0 300.0
05 6 8 4 118.3741 3.5930 286.9 4 300.0 300.0
05 6 8 5 104.8716 3.4218 286.6 4 300.0 300.0
05 6 8 6 131.6665 2.8188 286.4 4 300.0 300.0
05 6 8 7 101.9187 2.6310 287.5 3 300.0 300.0
05 6 8 8 63.2040 2.8286 288.8 3 300.0 300.0
05 6 8 9 359.7307 1.8341 289.8 2 300.0 300.0
05 6 810 110.2787 3.0116 288.8 3 300.0 300.0

05 6 811 318.0869 1.8863 288.9 2 300.0 300.0
05 6 812 71.7856 4.9644 288.4 3 300.0 300.0
05 6 813 74.3132 3.8330 289.2 3 300.0 300.0
05 6 814 74.9043 5.0895 289.7 3 300.0 300.0
05 6 815 90.9281 5.6581 289.3 4 300.0 300.0
05 6 816 85.6816 5.6680 290.7 4 300.0 300.0
05 6 817 110.4580 7.0244 290.5 4 300.0 300.0
05 6 818 126.9091 5.8512 289.7 4 300.0 300.0
05 6 819 119.7442 4.4526 288.0 5 300.0 300.0
05 6 820 125.5132 2.0317 286.6 6 300.0 300.0
05 6 821 227.7687 1.5731 285.7 6 300.0 300.0
05 6 822 309.5893 1.1350 284.5 6 300.0 300.0
05 6 823 356.2125 0.8343 283.2 6 300.0 300.0
05 6 824 354.5291 1.0592 282.3 6 300.0 300.0
05 6 9 1 324.5452 0.7093 281.6 6 300.0 300.0
05 6 9 2 328.7172 1.5325 281.5 6 300.0 300.0
05 6 9 3 302.1661 0.9691 281.1 6 300.0 300.0
05 6 9 4 320.4964 0.9134 281.0 6 300.0 300.0
05 6 9 5 339.5101 0.8029 280.6 6 300.0 300.0
05 6 9 6 217.7966 0.5182 281.1 6 300.0 300.0
05 6 9 7 131.3373 2.1527 283.9 5 300.0 300.0
05 6 9 8 126.1575 4.7957 285.8 4 300.0 300.0
05 6 9 9 137.8247 5.4230 286.9 4 300.0 300.0
05 6 910 135.2999 5.0692 287.9 3 300.0 300.0
05 6 911 136.7464 5.1170 289.0 3 300.0 300.0
05 6 912 140.5245 5.1305 290.1 3 300.0 300.0
05 6 913 141.1274 4.8807 291.0 2 300.0 300.0
05 6 914 128.3776 5.2750 291.7 3 300.0 300.0
05 6 915 130.5610 5.6811 292.1 3 300.0 300.0
05 6 916 141.3949 5.6190 292.8 4 300.0 300.0
05 6 917 137.2824 5.2703 293.1 4 300.0 300.0
05 6 918 131.2940 5.1211 292.9 4 300.0 300.0
05 6 919 105.8941 5.1386 291.4 5 300.0 300.0
05 6 920 100.3560 4.4813 289.0 5 300.0 300.0
05 6 921 102.4340 3.8843 287.5 5 300.0 300.0
05 6 922 113.1499 2.5899 286.3 6 300.0 300.0
05 6 923 115.7665 2.3843 285.5 6 300.0 300.0
05 6 924 118.2909 2.5552 285.5 6 300.0 300.0
05 610 1 114.3802 2.5113 285.4 6 300.0 300.0
05 610 2 199.9969 1.4964 284.9 6 300.0 300.0
05 610 3 159.8008 1.3589 283.7 6 300.0 300.0
05 610 4 132.5950 2.7193 284.6 6 300.0 300.0
05 610 5 147.3305 2.6015 284.2 6 300.0 300.0
05 610 6 148.6459 2.2203 284.3 6 300.0 300.0