MONITORING A 1,3-DICHLOROPROPENE/METAM SODIUM APPLICATION IN DEL NORTE COUNTY

By

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ABSTRACT

Over 95% of all Easter lily bulbs are produced in a narrow coastal region along the Northern California/Oregon border from Smith River, California to Brookings, Oregon. Fumigants such as methyl bromide, 1,3-dichloropropene (Telone ®), and metam sodium are used in bulb production to control nematodes and fungi. The Department of Pesticide Regulation monitored air concentrations around an 8-acre application of metam sodium and 1,3-dichloropropene (1,3-D) in the Smith River Valley for a total of 144 hours following the start of application. The application was made on July 21st at an application rate of 310 lbs/acre (349 kilograms per hectare) of metam sodium active ingredient (a.i.) and 320 lbs/acre (359 kilograms per hectare) of 1,3-D a.i. The 1,3-D application was made through 5 shanks at a depth of injection of 18 – 20 inches. A ring roller was attached behind the shanks. The metam sodium application rig was equipped with a spray boom just behind the tractor wheels positioned just above the soil surface. The spray boom was followed by a rototiller and then a flat roller. The entire application took approximately eight hours.

For MITC, the breakdown product of metam sodium, maximum air concentrations were measured during the first day of monitoring. The highest individual sample (920 µg/m^3) was collected 20-24 hours after the start of application 33 feet (ft) from the edge of application. The highest 24-hour time-weighted average measured during the first day was 236 µg/m^3 at a sampler located 50 ft from the edge of the application area. The highest 24-hour "back-calculated" flux of 22.0 µg/m^2-s was observed during the first day of monitoring. The highest sampling interval flux of 49.4 µg/m^2-s was estimated 4-8 hours after the start of application. Flux rates showed a general decline over time, with higher emissions during daytime hours for the first three days and nighttime hours during the second three-day period. The total amount of MITC released from the application area during the 6-day monitoring study was approximately 14.1% of the MITC equivalent amount applied.

For 1,3-D, the maximum air concentrations occurred during the last day of monitoring, with the highest individual sample concentration of 186 µg/m^3 collected 132-144 hrs following application during the last night of monitoring 33 ft from the application. The highest 24-hour TWA measured on the last day was 9.04 µg/m^3 at a sampler located 59 ft from the application area. Since the concentrations were increasing up to day 6 it is possible that sampling did not capture the highest concentrations following the application. The highest 24-hour "back-calculated" flux of 9.00 µg/m^2-s was observed during the last day of monitoring. The highest flux for a single sampling interval of 10.8 µg/m^2-s was estimated during the last night of monitoring. 1,3-D flux rates were higher during daytime hours for the first three days and higher during nighttime hours for the second three-day period. The total amount of 1,3-D released from the application area during the monitoring study was approximately 7.24% of the amount applied.

ACKNOWLEDGMENTS

DISCLAIMER

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INTRODUCTION

Over 95% of all Easter lily bulbs are produced in a narrow coastal region along the Northern California/Oregon borders from Smith River, California to Brookings, Oregon. In 2003, 179 hectares (ha) in Del Norte County were planted for Easter lily bulb production, with a value of approximately $6.9 million dollars (Annual Crop Report for Del Norte County for 2003). Bulbs are sold to greenhouse operations to produce flowering plants. Soil fumigants are commonly used to control nematodes and fungi which are a serious threat to Easter lily production. The soil fumigants are applied in mid-July through mid-August just prior to planting. Fumigants used include methyl bromide, 1,3-dichloropropene (Telone ®), and metam sodium. In 2003 between July 21st through August 7th, 54,975 kilograms (kg) of 1,3-dicloropropene (1,3-D) active ingredient (a.i.) were applied to 178.3 hectares (ha) and 67,446 kg a.i. of metam sodium were applied to 190 ha of transplant/propagation fields in Del Norte County (DPR 2003).

A common method used in the Smith River Valley is to inject 1,3-D at a depth of 45.7 centimeters (cm) and follow immediately with a surface metam sodium application incorporated with a rototiller and roller. Both chemicals are applied at a rate of approximately 336–370 kg/ha a.i. The method utilizes a separate application rig for each chemical. The Department of Pesticide Regulation (DPR) does not have any previous monitoring data for this method. The purpose of this study was to determine back-calculated fluxes for fumigants not monitored previously and/or fumigations using more than one fumigant (Segawa 2004). This fumigation was monitored to measure air concentrations and back-calculate emission rates for both MITC, the breakdown product of metam sodium, and 1,3-D using an application method that has not been previously monitored.

METHODS AND MATERIALS

Pesticides Monitored

The metam sodium product monitored was Vapam®HL, which contains 42.0 percent (%) sodium methyldithiocarbamate (anhydrous) or 0.511 kg/L a.i. (4.26 lbs. a.i. per gallon). The other product monitored was Telone ™ II which is 97.5 percent 1,3-D. One liter (L) of Telone ™ II weighs 1.21 kg at 21 °C (1 gallon weighs 10.1 lb at 70 °F).

Sodium methyldithiocarbamate (metam-sodium) breaks down primarily into methyl isothiocyanate (MITC) which functions as the principal pesticidal agent. MITC is the biologically active product for soil fumigations. Field research has demonstrated that 87% to 95% of the applied metam-sodium degrades to MITC in various soils (Smelt et al. 1989; Gerstl et al. 1977; Leistra et al. 1974; Leistra 1974; Smelt and Leistra 1974; Turner and Corden 1963). These studies show that the conversion exhibits a half-life of less than 30 minutes to seven hours, and varies with soil conditions. Depending on various factors, the degradation of metam-sodium may also result in release of methyl isocyanate, methylamine, carbon disulfide, sulfur, and hydrogen sulfide.

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The technical product of 1,3-D is a mixture of approximately equal quantities of trans(E)- and cis(Z)- isomers. In aerobic soils the transformation of 1,3-D is initially by hydrolysis to 3-chloroallyl alcohol and then by microbial transformation to 3-chloro-acrolein and 3-chloroacrylic acid, all of which are highly mobile. The overall half-lives in soil have been estimated from about 6 days in one study to more than 50 days in another (NRA 2001). The persistence of 1,3-D in soil is influenced by volatilization, chemical and biological transformation, photochemical transformation, and organism uptake. Volatilization and diffusion in the vapor phase are the most significant mechanisms for environmental dispersion and dilution. Some physical and chemical properties for both MITC and 1,3-D are listed in Table 1.

Table 1. Some physical-chemical properties of MITC and 1,3-D. All data are from the DPR's Pesticide Chemistry Database, except where indicated.

	MITC	(EZ)-1,3-dichloropropene
Molecular formula	C_2H_3NS	$C_3H_4Cl_2$
Molecular weight	73.12	110.98
Solubility in water (ppm)	8.61E+03, 25 ℃	2.18E+03(Z), 2.32E+03(E), 25 ℃
Vapor Pressure (mm Hg)	16.0, 25 ℃	23.0 – 35.0, 25 ℃
Hydrolysis Half-life (days)	20.4, pH 7, 25 ℃	11.3, pH 7, 20 ℃
Aerobic Soil Half-life (days)	0.5 – 50[a], 25 ℃	11.5 – 53.9, 25 ℃
Henry's Law Constant (atm-m^3/mole)	1.79E-04, 25 ℃	1.43E-03 – 2.29E-03, 25 ℃

[a] Smelt et al., 1989

Application Description

1,3-D and metam sodium were applied in a broadcast application. The 1,3-D application rig was equipped with 5 shanks spaced 50.8 cm apart at an injection depth of 45.7 – 50.8 cm. A ring roller was attached behind the shanks. The metam sodium application rig was equipped with a spray boom just behind the tractor wheels with openings every 7.62 cm positioned just above the soil surface. The spray boom was followed by a rototiller and then a flat roller. The 1,3-D application started at approximately 7:35 AM and was followed with the start of the metam sodium application approximately 20 minutes later. The field application ended at approximately 4:00 PM. A total of 1003 L of Telone™ II (1162 kg a.i) and 2214 L of Vapam® HL (1130 kg a.i.) was applied to the field. The effective broadcast application rate for metam sodium and 1,3-D was 349.2 and 358.6 kg/ha, respectively.

Field Description

The field monitored was located in the Smith River area of northern California (Del Norte County) on July 21, 2004. The field was approximately 3.24 ha of tilled pasture. The field was surrounded by open pasture on three sides and lined by a creek and some tall trees and vegetation on the east side.

Monitoring

Sixteen samplers were set up around the field in two concentric circles at distance of approximately 15 and 46 meters (m) from the edge of the field (Table 2 and Figure 1). The sampler pumps were equipped with 200/400 mg coconut charcoal tubes (SKC Inc., #226-09) set at an air flow rate of 1.5 liters per minute (L/min). One set of background samples was collected for a 14-hour interval prior to the start of application to measure any background ambient air concentrations. Application monitoring began with the start of the 1,3-D application. Samples were collected every four hours for the first 24 hours, every 6 hours for the following 24 hours, and every 12 hours for the following four days, for a total of eighteen sampling intervals (Table 3). The use, operation, calibration and maintenance of air sampling pumps are described in DPR's SOP EQAI001.00 (Wofford 2001). The flow rate for each sampler was measured and recorded before and after each sampling interval. Flows were measured with DryCal® Primary Flowmeters. All equipment was checked and initially calibrated in the laboratory.

Table 2. Sampler identification and distances from the closest edge of application area.

Sampler Identification	Distance (meters)
1	9.75
2	45.1
3	14.3
4	45.1
5	13.1
6	46.6
7	15.2
8	44.5
9	10.1
10	18.0
11	14.3
12	44.2
13	14.6
14	42.7
15	13.4
16	45.1

Prior to monitoring, sample labels with the study number and sample identification numbers were attached to the 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 on field measurements, sampler location, application data, and weather observations during the monitoring study.

Figure 1. Application area and sampler locations and approximate distances.
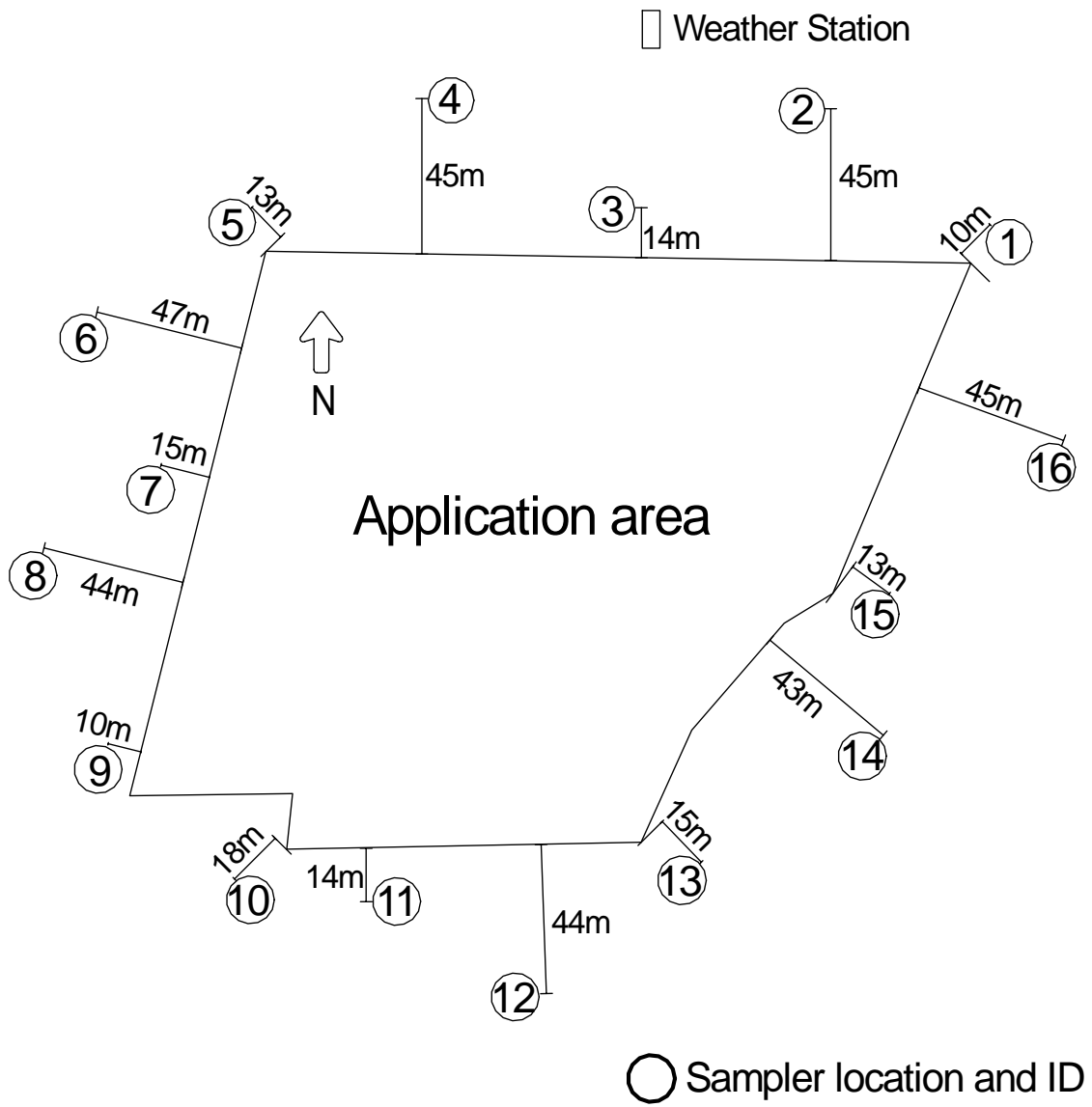
Table 3. Timing of the Sampling Intervals.

Sampling Interval	Date and Time On	Date and Time Off	Duration (hours)
background	20-Jul 16:15	21-Jul 6:35	10.2
1*	21-Jul 7:30	21-Jul 11:40	4
2	21-Jul 11:40	21-Jul 15:40	4
3**	21-Jul 15:40	21-Jul 19:40	4
4	21-Jul 19:40	21-Jul 23:40	4
5	21-Jul 23:40	22-Jul 3:40	4
6	22-Jul 3:40	22-Jul 7:40	4
7	22-Jul 7:40	22-Jul 13:40	6
8	22-Jul 13:40	22-Jul 19:40	6
9	22-Jul 19:40	23-Jul 1:40	6
10	23-Jul 1:40	23-Jul 7:40	6
11	23-Jul 7:40	23-Jul 19:40	12
12	23-Jul 19:40	24-Jul 7:40	12
13	24-Jul 7:40	24-Jul 19:40	12
14	24-Jul 19:40	25-Jul 7:40	12
15	25-Jul 7:40	25-Jul 19:40	12
16	25-Jul 19:40	26-Jul 7:40	12
17	26-Jul 7:40	26-Jul 19:40	12
18	26-Jul 19:40	27-Jul 7:40	12

*Application started at approximately 07:30.
**Application ended at approximately 16:00.

Soil sampling

Soil samples were collected at four locations across the field at a diagonal from the
northeast corner to the southwest corner. Samples were collected at a depth of 15.2 cm at
all of the locations and an additional sample was collected at 45.7 cm depth at two of the
locations. The samples were analyzed for bulk density, percent moisture, and texture.
Samples were collected and analyzed in accordance with DPR's SOP FSSO001.00 and
SOP FSSO002.0 (Garretson 1999a and 1999b).

Meteorological Measurements

In addition to air samples, a MetOne® meteorological station was located approximately
91.4 m north of the field (Figure 1). The MetOne® meteorological sensors were placed
on a trailer mast at a height of 10 m. The sensors measured wind direction, horizontal
wind speed, temperature, solar radiation and relative humidity every minute. The
meteorological data was recorded on a Campbell Scientific CR 21X Datalogger as a 5-
minute average except for wind direction which was an instantaneous measurement.

Sample Handling

Samples were collected, capped and immediately placed on dry ice. The 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 July 28, 2004. 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 SOP QAQC003.01 (Hoffman 1999).

QUALITY CONTROL METHODS

In addition to field samples collected, four collocated (duplicate) samples, two trip spikes, two field spikes (also known as sample spikes), and two trip blanks were also collected. Collocated samples are independent samples collected at the same time and place as a field sample. They provided an estimate of overall variation for the entire sampling system, including measurement, transportation and analysis.

The trip and field spikes were sample tubes with a known concentration of both MITC and 1,3-D added by the laboratory and stored on dry ice for shipment to the field. The two field spikes were placed on air samplers with air flowing through the sorbent tubes. Following the sampling interval they were treated like the other field samples, including storage and shipping conditions. The two trip spikes were placed on dry ice upon receipt from the laboratory, stored and transported until all samples were collected and returned for analysis. The field spike, in comparison with trip spikes and the respective field sample, gave information about any change in the ability to recover the analyte during air sampling.

The tubes used for trip blanks were taken from the same storage area where all other sampling tubes were kept prior to use. The trip blanks were sent with the field samples to the laboratory for analysis to detect any problems with contamination during the monitoring study.

Laboratory Methods

The MITC and 1,3-D samples were analyzed by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. MITC and 1,3-D were desorbed from the charcoal 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.

Method detection limits and limits of quantitation
The method detection limit (MDL) is the lowest concentration of an analyte that a method can reliably detect. The laboratory determined the MDLs by spiking seven charcoal tubes with known amounts of 1,3-D and MITC standards. The method detection limit is determined by calculating the 99 percent (%) confidence interval of the mean. The MDL for each analyte is given in the CDFA laboratory SOP in Appendix A.

The reporting limit (RL) is set at a certain factor above the method detection limit. The RL refers to the smallest amount of a chemical that can be reliably quantified. The RL was calculated as 5 times the MDL. The RL for the method was 0.1 µg/sample for both MITC and 1,3-D.

Method Validation
Previous to the field study, the laboratory determined the efficiency of the analytical method by analyzing five sets of tubes spiked at three concentration levels for both chemicals for a total of 15 samples. Recoveries ranged from 93 to 111% for MITC and 99 to 119% for 1,3-D. The results for all of the spiked samples can be found in Appendix A.

Continuing Quality Control
Continuing proficiency of analysis is demonstrated through ongoing analysis of laboratory spiked samples analyzed with each set of up to ten samples. Warning and control limits are determined by the method validation data and are used as a check on the results of the continuing quality control spikes. The exceedance of a warning limit could 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. The warning and control limits are located in Appendix D.

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

$$\frac{sample\,results\,(ug) \times 1000\,L/m^3}{flow\,rate\,of\,sampler\,(L/\min) \times run\,time\,(\min)} = \mu g/m^3$$

Concentrations can be converted from µg/m³ to ppb with the following calculations at 25 ºC (298 ºK):

MITC:

$$\frac{\dfrac{ug\,MITC}{m^3} * \left[\dfrac{1\,mole\,MITC}{73.1g\,MITC}\right]}{\dfrac{40.93\,mole\,air}{m^3}} * \frac{1000\,ppb}{1\,ppm} * \frac{1\,ppm}{\dfrac{ug}{g}}$$

Therefore 1 µg/m³ MITC = 0.3342 ppb MITC

1,3-D:

$$\frac{\dfrac{ug\ 1,3D}{m^3} * \left[\dfrac{1\ mole\ 1,3D}{110.98g\ 1,3D}\right]}{\dfrac{40.93\ mole\ air}{m^3}} * \frac{1000\,ppb}{1\,ppm} * \frac{1\,ppm}{\dfrac{ug}{g}}$$

Therefore 1 µg/m^3 1,3-D = 0.2201 ppb 1,3-D

Results are presented as a 24-hour Time Weighted Average (TWA) which is calculated using the equation below where C is the sample concentration and T is the duration in time of sample. If a sample concentration was below the reporting limit, a value of ½ the reporting limit for that time period was used instead.

$$TWA = \frac{C_1T_1 + C_2T_2 + C_3T_3 + \ldots + C_nT_n}{T_1 + T_2 + T_3 + \ldots + T_n}$$

RESULTS AND DISCUSSION

Results of Air Monitoring

DPR collected 292 samples and analyzed each for both MITC and 1,3-D. Two of the samples were invalid due to sample pump failure and four were background samples collected to determine ambient levels prior to application. The four samples collected during the background interval did not contain any detectable amount of MITC but did contain low levels of 1,3-D. Since no previous applications of 1,3-D had been made in the area, it is possible that the concentrations detected were from the calibration of the application equipment the day before the application at a location approximately 2.4 – 3.2 kilometers (km) away.

MITC
The highest concentrations occurred during the first 24-hours of monitoring (Table 4, intervals 1 - 6). The highest individual sample measured (920 µg/m^3) was collected during a 4-hour interval of the first night following application (Table 4, interval 6) at sampler 9 located 10.1 m from the west side of the application. The highest 24-hour Time-Weighted Average (TWA) measured during the first 24-hour period (intervals 1-6) was 236 µg/m^3 at sampler 7 located 15.2 m from the west edge of the application area (Table 5). Generally, the concentrations declined following the first 24 hours with higher concentrations measured during nighttime hours (Figure 2). Other MITC studies have also reported highest concentrations measured around treated fields during the first 24-hour period following application (Wofford et al. 1994; ARB 1997, Saeed et al. 2000, Barry et al. 2004, Li 2004, Walters 2005). All raw data for sample results is located in Appendix B.

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<u>1,3-D</u>
The highest concentrations occurred during the last 24-hours of monitoring (Table 6, intervals 17 and 18). The highest individual sample measured (186 µg/m^3) was collected during a 12-hour interval of the sixth and last night of monitoring (Table 6, interval 18) at sampler 9 located 10.1 m from the west side of the application. The highest 24-hour TWA measured was during the last day at 94.6 µg/m^3 at sampler 9 located 10 m from the closest southern edge of the application area (Table 7). Since the concentrations were increasing up to day 6 it is possible that peak concentrations occurred after monitoring ceased (Figure 3). The study could not be extended further since all other applications in the area were being delayed so as not to interfere with this study. Albrecht and Chenchin (1985) found that air concentrations of 1,3-D at a height of 147 cm above an application peaked at day two and 10 and gradually declined through day 28. All raw data for sample results is located in Appendix B.

Table 4. Measured MITC concentrations ($\mu g/m^3$).

Sampling Interval	Sampler location																Average*	Maximum
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16		
1	321	27.6	104	4.39	3.26	NA	0.600	0.394	0.413	ND	0.315	ND	0.75	0.800	17.1	73.2	36.9	321
2	156	15.6	61.2	4.09	2.98	ND	0.775	ND	ND	ND	1.23	ND	39.0	80.1	314	154	51.8	314
3	91.1	80.8	219	123	80.3	7.49	41.2	ND	ND	0.442	4.36	ND	84.3	81.6	216	68.2	68.7	219
4	6.14	49.0	120	8.57	102	46.5	108	19.1	20.4	110	319	175	217	87.8	64.4	9.01	91.3	319
5	10.1	14.5	88.7	65.1	165	219	436	226	399	423	468	144	107	24.5	90.6	12.8	181	468
6	20.2	40.9	13.7	12.4	284	382	831	599	920	534	513	97.9	66.2	NA	68.6	ND	292	920
7	54.7	4.81	20.6	2.79	1.94	1.54	4.25	2.57	11.3	1.18	3.76	0.814	34.7	55.8	122	48.9	23.2	122
8	58.0	16.1	43.0	8.33	0.884	ND	0.336	ND	ND	ND	ND	ND	1.03	9.51	56.8	25.2	13.7	58.0
9	16.2	20.5	42.5	21.1	9.27	2.67	6.96	2.24	3.10	4.99	16.4	7.04	30.1	18.5	43.4	11.9	16.1	43.4
10	3.07	1.47	2.13	2.02	2.90	3.65	20.5	7.27	45.1	61.7	74.3	19.2	18.2	4.84	14.1	3.02	17.7	74.3
11	17.3	2.45	7.75	1.25	1.02	0.615	1.15	0.522	1.39	0.996	2.48	0.747	13.3	18.8	46.7	20.3	8.54	46.7
12	6.91	6.15	14.1	7.40	12.1	7.32	14.8	8.06	16.7	11.2	12.5	4.69	6.27	3.67	2.95	3.91	8.67	16.7
13	8.75	4.11	9.80	3.91	3.94	1.79	3.50	1.18	2.03	1.14	2.24	1.08	5.08	6.62	16.7	6.57	4.90	16.7
14	0.779	0.973	2.52	1.48	2.27	1.20	2.28	0.697	0.983	8.30	20.0	9.0	25.1	10.6	18.4	5.2	6.86	25.1
15	8.52	3.21	6.91	2.01	0.645	0.382	1.21	0.426	1.16	0.975	1.24	0.454	1.24	2.11	10.8	5.00	2.89	10.8
16	2.23	1.47	2.15	0.52	0.381	0.389	1.72	0.964	4.35	13.0	22.7	11.8	21.8	9.65	13.9	3.96	6.94	22.7
17	2.74	1.87	4.26	1.98	1.40	0.258	0.962	0.213	0.558	0.462	0.682	0.355	1.19	1.47	4.57	1.99	1.56	4.57
18	0.645	0.925	1.80	0.995	1.37	1.94	5.92	4.26	13.1	17.6	16.9	7.10	9.15	2.94	4.61	1.06	5.65	17.6

ND = No Detectable amount, reporting limit =0.1 µg/sample
*Average was calculated with ½ reporting limit for ND concentrations.

Table 5. 24-hour TWA MITC concentrations measured at each sampler location[1].

Sampler Location	MITC ($\mu g/m^3$)					
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
1	101	33.0	12.1	4.76	5.38	1.69
2	38.1	10.7	4.30	2.54	2.34	1.40
3	101	27.1	10.9	6.16	4.53	3.03
4	36.3	8.57	4.32	2.69	1.26	1.49
5	106	3.75	6.55	3.11	0.51	1.39
6	131	1.99	3.97	1.50	0.39	1.10
7	236	8.01	7.95	2.89	1.46	3.44
8	141	3.04	4.29	0.94	0.70	2.24
9	223	14.9	9.06	1.51	2.76	6.85
10	178	17.0	6.10	4.72	6.98	9.04
11	218	23.6	7.50	11.1	12.0	8.77
12	69.4	6.78	2.72	5.02	6.15	3.73
13	85.6	21.0	9.79	15.1	11.5	5.17
14	NA	22.1	11.2	8.60	5.88	2.20
15	128	59.0	24.8	17.5	12.4	4.59
16	52.9	22.3	12.1	5.9	4.48	1.52
maximum	236	59.0	24.8	17.5	12.4	9.04

[1]Non-detects used in calculation of the TWA were given a value of ½ the reporting limit.

Figure 2. Average MITC concentration of all samplers during each sampling interval and the highest concentration at any sampler during each sampling interval.

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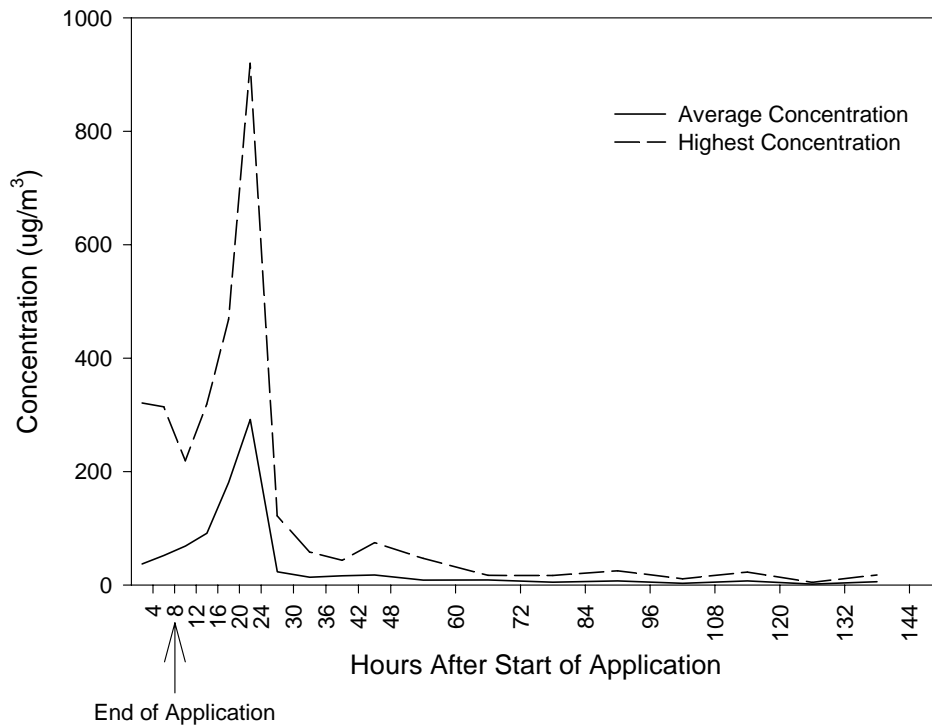
Table 6. Measured 1,3-D concentrations ($\mu g/m^3$).

Sampling Interval	Sampler location																Average*	Maximum
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16		
1	30.5	1.90	2.40	0.531	4.74	NA	0.323	0.264	0.294	ND	ND	ND	ND	0.294	1.34	12.9	3.74	30.5
2	3.89	ND	0.76	ND	ND	ND	ND	ND	ND	ND	0.64	ND	1.24	11.8	51.6	4.82	4.75	51.6
3	5.96	0.446	3.21	0.633	2.52	ND	1.36	ND	ND	ND	ND	ND	0.306	1.63	8.04	2.89	1.74	8.0
4	0.617	0.749	0.895	ND	2.39	1.13	2.87	0.523	0.831	1.79	2.92	1.69	4.28	2.82	3.06	0.60	1.71	4.3
5	1.31	1.03	3.08	1.94	4.13	5.95	13.4	7.23	15.3	10.2	9.48	4.06	2.99	1.23	2.39	0.78	5.3	15.3
6	1.56	2.78	8.67	7.10	15.2	20.9	45.4	27.9	34.3	19.2	23.65	4.98	4.03	NA	4.63	ND	14.7	45.4
7	10.8	0.449	1.50	0.267	0.547	ND	0.376	0.201	0.499	ND	ND	ND	1.09	3.93	15.3	5.30	2.54	15.3
8	27.5	3.64	9.76	3.09	0.336	ND	ND	ND	ND	ND	ND	ND	ND	2.01	17.9	6.83	4.49	27.5
9	19.1	11.93	21.5	11.8	5.50	1.47	3.66	1.09	1.31	2.02	5.07	3.01	17.7	17.6	21.4	9.85	9.62	21.5
10	6.30	1.66	2.25	2.41	3.55	3.56	24.9	9.35	46.0	29.1	36.4	15.3	14.8	4.91	9.06	3.81	13.3	46.0
11	40.5	3.57	9.76	1.97	1.49	0.840	1.52	0.669	1.24	0.79	1.30	0.662	8.24	18.1	58.5	27.7	11.1	58.5
12	24.7	12.76	32.1	16.1	31.1	18.0	43.9	20.0	31.4	16.5	18.7	6.60	10.7	5.70	17.0	6.51	19.5	43.9
13	45.8	14.9	33.4	15.0	15.7	5.64	11.6	2.61	3.46	1.48	2.80	1.62	9.01	14.5	48.8	20.4	15.4	48.8
14	5.10	4.87	12.1	6.81	10.4	4.15	8.43	2.10	3.97	30.9	53.1	31.6	89.4	65.7	75.4	32.0	27.3	89.4
15	74.2	18.2	38.6	12.8	3.76	1.86	7.43	2.13	4.57	2.52	3.45	1.25	3.59	6.30	45.5	20.9	15.4	74.2
16	29.9	11.5	18.9	4.47	2.79	3.62	19.2	10.8	26.3	81.4	110	72.2	144	91.6	106	39.4	48.3	144
17	37.4	18.3	43.3	19.5	13.4	1.41	6.45	1.17	3.00	1.94	2.83	1.52	4.63	6.43	30.9	14.6	12.9	43.3
18	7.16	8.79	20.4	9.68	18.6	31.9	119	72.1	186	183	152	66.0	78.8	31.2	48.7	10.8	65.3	186

ND = No Detectable amount, reporting limit =0.1 µg/sample
*Average was calculated with ½ reporting limit for ND concentrations.

Table 7. 24-hour TWA 1,3-D concentrations measured at each sampler location[1].

Sampling Location	1,3-D ($\mu g/m^3$)					
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
1	7.31	15.9	32.6	25.4	52.0	22.3
2	1.17	4.42	8.16	9.90	14.9	13.5
3	3.17	8.74	20.9	22.7	28.7	31.8
4	1.75	4.40	9.03	10.9	8.64	14.6
5	4.86	2.48	16.3	13.0	3.27	16.0
6	5.65	1.30	9.42	4.89	2.74	16.7
7	10.6	7.25	22.7	10.0	13.3	62.7
8	6.03	2.68	10.3	2.36	6.45	36.6
9	8.50	12.0	16.3	3.72	15.4	94.6
10	5.27	7.82	8.63	16.2	42.0	92.4
11	6.16	10.4	10.0	28.0	56.8	77.6
12	1.86	4.62	3.63	16.6	36.7	33.8
13	2.16	8.41	9.46	49.2	74.0	41.7
14	NA	7.12	11.9	40.1	48.9	18.8
15	11.8	15.9	37.8	62.1	76.0	39.8
16	3.69	6.45	17.1	26.2	30.1	12.7
maximum	11.8	15.9	37.8	62.1	76.0	94.6

[1]Any non-detect used in calculation was given a value of ½ the reporting limit.

Figure 3. Average 1,3-D concentrations of all samplers during each sampling interval and the highest concentration at any sampler during each sampling interval.


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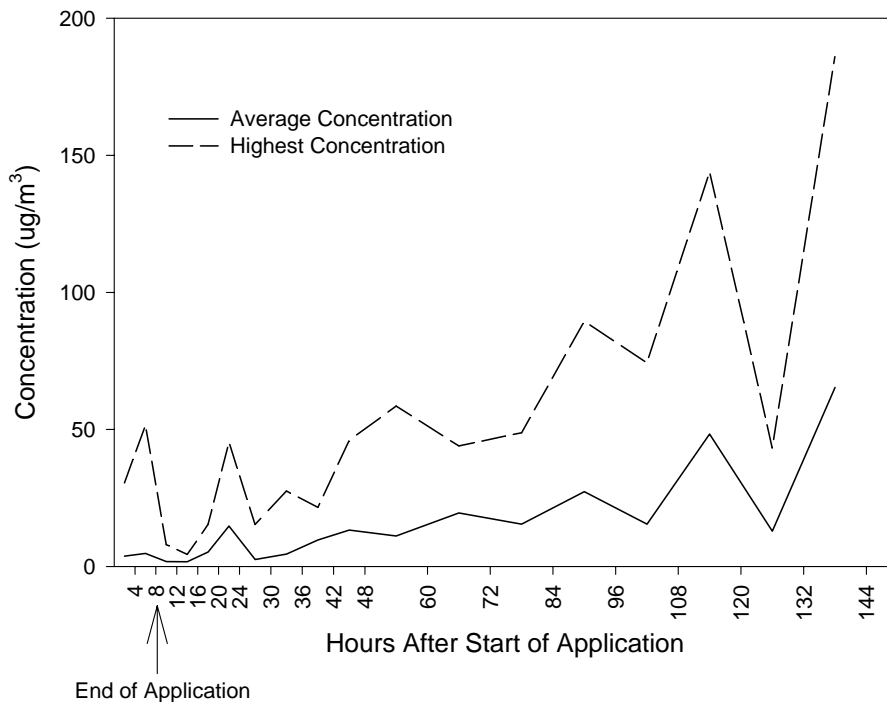
Weather summary

The application day was sunny with some light rolling fog and light winds and clear during the first night. The weather during the rest of the monitoring study was typical for the summer months on the North Coast of California with fog during the nights and mornings with clearing during the days. Wind speeds ranged from calm to 5.99 meters per second (m/s) and temperatures ranged from 10.6 to 20 ˚C.

Wind-rose diagrams were developed to graphically illustrate the relationship of meteorological data and concentrations measured around the applications. Wind-roses were created using WRPLOT View v. 3.5 (Lakes Environmental, 2000). The wind-rose diagrams are a frequency distribution of wind direction and speed measured during each sampling interval. The diagrams consist of spokes showing the direction the wind is blowing towards. The spoke length indicates the length of time the wind was blowing in that direction, and the color of the spoke indicates wind speed. The concentrations around the application area should be highest in the downwind area. Figure 4 presents the weather data and concentrations associated with the highest 24-hour TWA period for MITC (Day 1) and 1,3-D (Day 6). Wind-roses for all of the sampling intervals are available in Appendix C.

Figure 4. Wind-roses and concentrations (μg/m^3) for highest 24-hour TWA period.
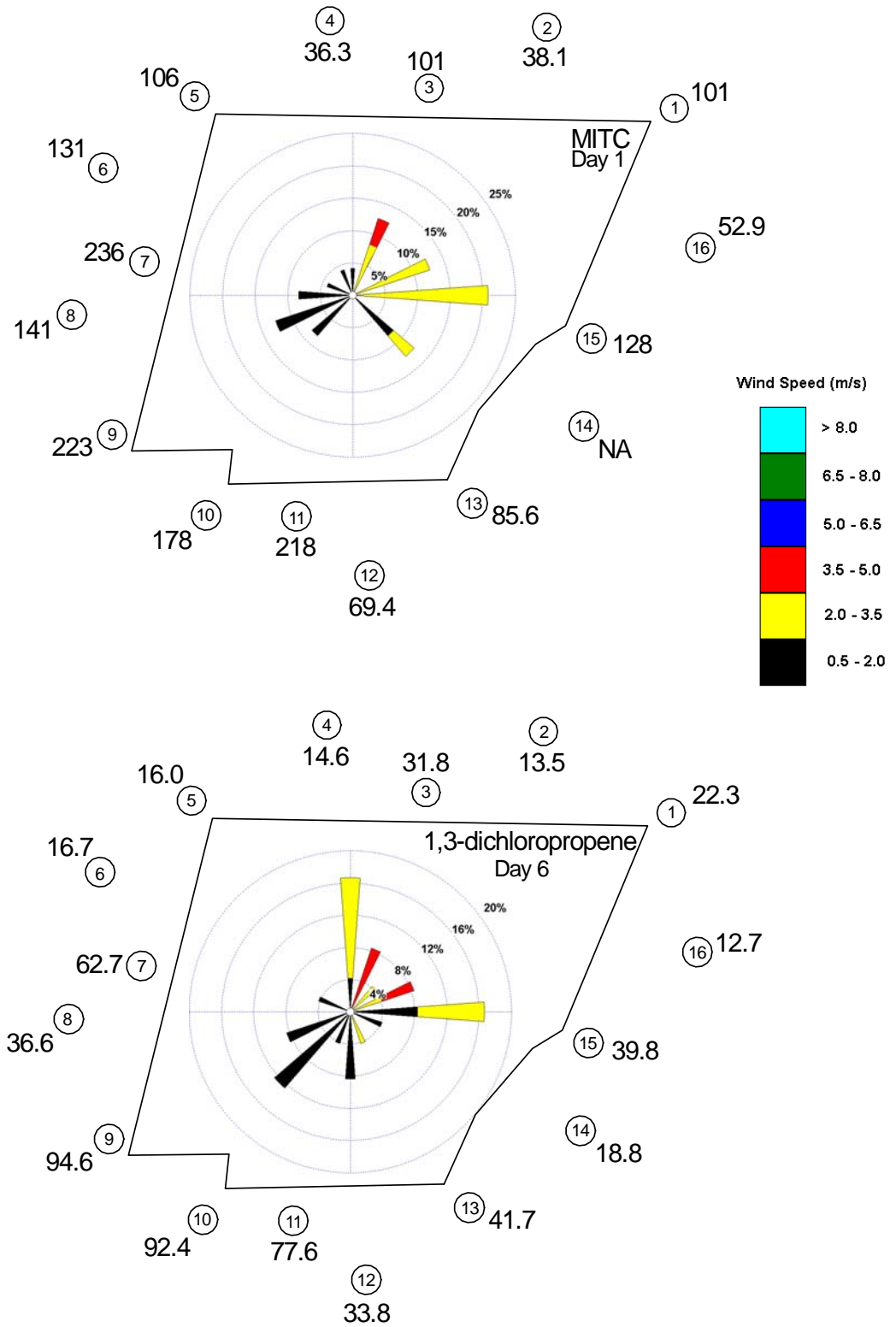
Soil sampling

The application area had previously been used as pasture for cattle and was recently tilled and plowed. The soil texture was determined to be clay loam near the surface and clay at a depth of 46 cm (Table 8). The soil moisture ranged from about 31% in the top 15 cm to 35% at the deeper depth. The soil organic carbon averaged 4.9 to 3.5% at 15 and 46 cm, respectively. A soil survey conducted by U.C. Davis in 1966 (McLaughlin and Harradine 1966) list the soil type in the area as a mixture of Rowdy gravelly clay loam and Rowdy clay loam. The applicator determined that the soil temperature just prior to the application was 19 - 20 ºC at a 15 cm depth and 21ºC at the 46 cm depth.

Table 8. Field soil characteristics.

Location	Depth (cm)	% moisture	Bulk Density (g/cm^3)	% Organic Carbon	% Sand	% Silt	% Clay	Texture Type
A	15	26.1	1.02	4.4	27	34	39	Clay loam
	46	32.6	1.02	3.0	24	33	43	Clay
B	15	29.9	0.93	4.6	27	33	40	Clay loam
C	15	30.3	0.96	4.9	26	35	39	Clay loam
	46	37.7	1.01	4.0	17	35	48	Clay
D	15	39.5	0.88	5.8	33	33	34	Clay loam
Average	15	31.5	0.95	4.9	28	34	38	Clay loam
	46	35.2	1.02	3.5	21	34	46	Clay

Quality Control Results

Four collocated samples were collected on samplers located adjacent to the primary samplers during the monitoring study. The average percent difference between collocated samples was less than 10% (Table 9).

Table 9. Comparison of collocated samples.

Sampling Interval	Sampling Location	MITC µg/m^3	MITC Average	MITC % difference*	1,3-D µg/m^3	1,3-D Average	1,3-D % difference*
8	1	58.0			27.5		
		57.9	57.9	0.173	28.2	27.9	2.51
12	3	12.0			28.0		
		14.1	13.0	16.1	32.1	30.1	13.6
14	7	2.28			8.43		
		2.14	2.21	6.33	8.40	8.42	0.357
16	1	1.89			26.4		
		2.23	2.06	16.5	29.9	28.2	12.4
Average % Difference				9.78			7.24

$$* \text{ % Difference} = \frac{|C1 - C2|}{(C1 + C2)/2} * 100$$

The trip and field spikes were prepared on July 19, 2004 and were transported and stored on dry ice during the monitoring study. The trip spikes were stored on dry ice during the entire study. The field spikes were stored on dry ice until being mounted on an air sampler and run adjacent to a field sampler. The spike level for the trip and field spikes for both MITC and 1,3-D was 100 µg/sample. The trip spike average recoveries for MITC and 1,3-D were 91.2 and 104%, respectively (Table 10). The field spike samplers were mounted alongside two of the four background samplers and run for 14 hours. The field spike average recoveries for MITC and 1,3-D were 94.9 and 109%, respectively (Table 11). The field spikes had to be adjusted for detections of low concentrations of 1,3-D in the background samples. The spike level for the laboratory spikes was 2 µg/sample. Laboratory spike recoveries averaged 98.3% for MITC and 106% for 1,3-D. The individual laboratory spikes are listed in Appendix D. There was no significant difference between the recoveries for the trip spike, the field spike, and laboratory spike indicating that analytical recoveries were unaffected by the field and transportation procedures.

Table 10. Trip spike results.

MITC			1,3-D		
	Spike Level	Percent		Spike Level	Percent
µg/sample	µg/sample	Recovery	µg/sample	µg/sample	Recovery
97.2	100	97.2	106	100	106
85.2	100	85.2	102	100	102
Average		91.2	Average		104
Standard deviation		8.5	Standard deviation		2.8

Table 11. Field spike results.

MITC			1,3-D			
	Spike Level	Percent Recovery		Minus colocated sample	Spike Level	Percent Recovery
µg/sample	µg/sample		µg/sample	µg/sample	µg/sample	
95.8	100	95.8	110	109.8	100	109.8
94.0	100	94.0	108	107.8	100	107.8
Average		94.9			Average	109
Standard deviation		1.3		Standard deviation		1.4

No MITC or 1,3-D was detected in either of the trip blanks.

<u>Continuing Quality Control</u>
The warning and control limits and continuing quality control sample results are located in Appendix D. There was one spiked sample that exceeded both the MITC and 1,3-D upper warning limit and one sample that surpassed the 1,3-D upper warning limit. No spiked samples exceeded the control limits for either MITC or 1,3-D.

Modeling Results

Emissions of applied chemicals from treated areas are described as the amount of residues that are offgassing from a unit area per unit time. Emissions quantified as such are referred to as flux, and are typically presented as microgram per square meter per second ($\mu g/m^2$-s). Flux rates are specific to the application method and conditions measured during the study. Flux rates can be back-calculated through a comparison of modeled concentrations and measured concentration by regression analysis.

The application was modeled with the U.S. EPA gaussian plume dispersion model, ISCST, Version 3 (U.S. EPA 1995, Version 02035). To estimate concentrations around an application the model requires locations of the application area and samplers, meteorological data and emission rate. The application area was represented as a polygon for purposes of modeling. The application area vertex and sampler location user-defined coordinates are located in Tables 12 and 13. The point of origin, SW1, was located at the most southwestern corner of the application area near sampling location 9. The measured meteorological data was averaged over one-hour periods for each sampling interval. Since the emission rate is unknown, a rate of 0.0001 g/m^2-s was used as a normative estimate. The modeled concentrations were then compared to the measured concentrations by regression analysis (Johnson et al. 1999, Ross et al. 1996) to back-calculate flux for the sampling intervals. A template control file and the meteorological input data are provided in Appendix E.

Stability classes were assigned to each hour based on field notes taken during the monitoring study, wind speed and solar radiation. The monitoring periods included many hours of foggy conditions. Approximate times of foggy periods were noted. In a memorandum to B. Johnson (Wofford 2005) two methods of selecting stability classes were compared: the conventional method of selecting stability classes from field notes on weather conditions versus use of solar radiation measurements from the meteorological station. No statistical difference was found between the two methods. The results from the conventional method were used for the simulations in this report.

Table 12. Vertices of the application area boundaries.

Location	X (meters)	Y (meters)
NE	248.4	157.6
NW	39.9	161.2
SW1	0.0	0.0
SW2	48.2	0.9
SW3	46.6	-15.5
SE	150.9	-13.4
E1	165.5	19.5
E2	193.2	50.9
E3	207.3	59.7
NE	248.4	157.6

Table 13. X and Y coordinates of air sampling locations.

Sampling Site Identification	X (meters)	Y (meters)
1	256.6	162.5
2	198.1	203.3
3	142.0	173.7
4	95.1	205.1
5	29.9	170.1
6	-14.6	135.9
7	6.7	91.1
8	-29.3	66.1
9	-8.2	8.5
10	35.7	-29.6
11	78.6	-29.3
12	113.7	-58.2
13	162.5	-22.6
14	216.7	13.1
15	219.8	54.9
16	272.2	97.8

MITC
The regressions of the measured and modeled concentrations were significant for most of the sampling intervals. Sampling intervals one, four and 15 did not result in a regression with a significant relationship so the concentrations were sorted from lowest to highest and regressed again. The resulting regression lines had improved r^2 values. Table 14

summarizes the MITC regression analyses. Graphical presentation of the regression results for each interval is found in Appendix F.

The highest flux for a single sampling interval was found during the four hours of the second half of the application (interval 2). The highest measured concentrations occurred during a 4-hour interval during the first night following application (Figure 5). Flux rates showed a general decline over time, with higher emissions during daytime hours for the first three days and nighttime hours during the second three-day period.

Table 14. Regression analysis summary for MITC.

Sampling Interval	Duration	r^2	F-test p-value	Flux ($\mu g/m^2$-s)	Day or Night
1	4	0.47*	**	18.31	Day
2	4	0.91	<0.001	49.37	Day
3	4	0.50	0.002	25.03	Day
4	4	0.87*	**	11.46	Night
5	4	0.70	<0.001	12.31	Night
6	4	0.94	<0.001	15.77	Night
7	6	0.39	0.010	5.230	Day
8	6	0.88	<0.001	6.741	Day
9	6	0.78	<0.001	2.289	Night
10	6	0.95	<0.001	2.320	Night
11	12	0.72	<0.001	4.182	Day
12	12	0.72	<0.001	0.9255	Night
13	12	0.77	<0.001	1.374	Day
14	12	0.91	<0.001	1.417	Night
15	12	0.81*	**	1.270	Day
16	12	0.84	<0.001	1.483	Night
17	12	0.86	<0.001	0.7698	Day
18	12	0.90	<0.001	0.9420	Night

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

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Figure 5. Fluxes and the highest measured concentration for MITC for any sampling site for each sampling interval.
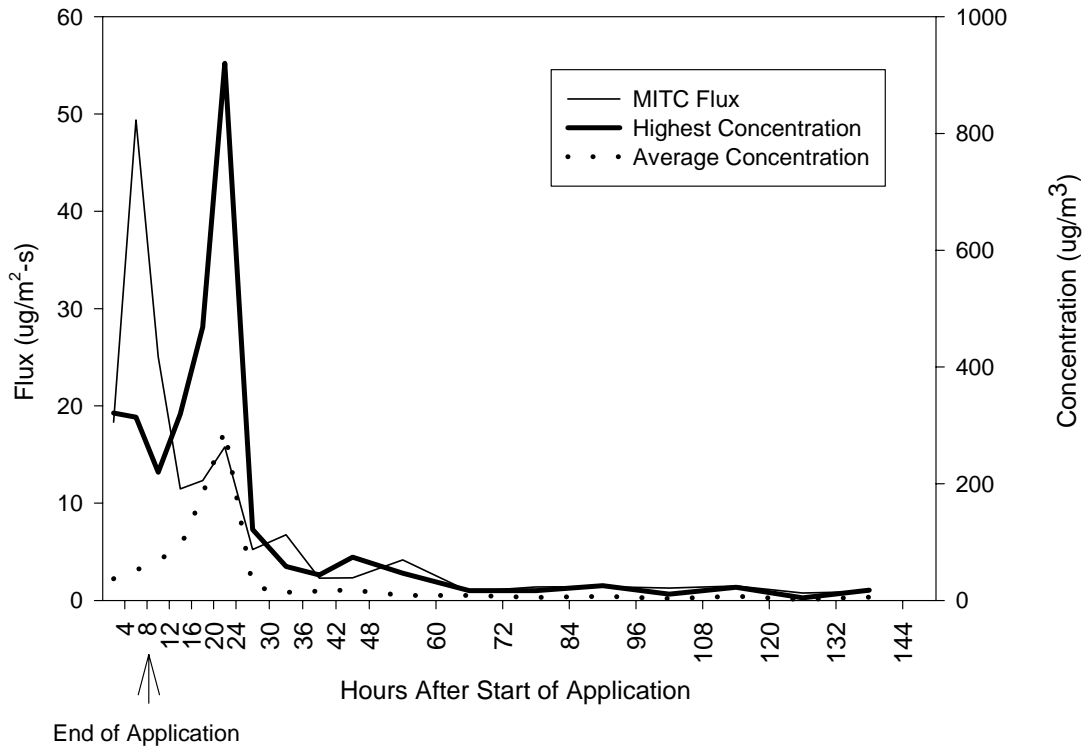
1,3-D

The regressions of the measured and modeled concentrations were significant for most of the sampling intervals. Sampling intervals one, three and 15 did not result in a regression with a significant relationship. The concentrations were sorted from lowest to highest and regressed again. The resulting regression lines had improved r^2 values. Regression results are summarized in Table 15. Graphical presentation of the regression results for each interval is located in Appendix F.

The highest flux for a single sampling interval was found during a 12-hour interval of the last night of monitoring (interval 18). The highest measured concentrations occurred during the same 12-hour (Figure 6). Similar to the MITC flux rates, 1,3-D showed higher flux rates during daytime hours for the first three days and during nighttime hours for the second three-day period.

Table 15. Regression analysis summary for 1,3-D.

Sampling Interval	Duration	r^2	F-test p-value	Flux ($\mu g/m^2$-s)	Day or Night
1	4	0.48*	**	1.772	Day
2	4	0.49	0.003	5.320	Day
3	4	0.94*	**	1.144	Day
4	4	0.41	0.008	0.1111	Night
5	4	0.81	<0.001	0.3712	Night
6	4	0.81	<0.001	0.6254	Night
7	6	0.56	<0.001	0.8435	Day
8	6	0.92	<0.001	2.612	Day
9	6	0.67	<0.001	1.245	Night
10	6	0.76	<0.001	1.249	Night
11	12	0.77	<0.001	5.946	Day
12	12	0.84	<0.001	2.489	Night
13	12	0.80	<0.001	5.117	Day
14	12	0.95	<0.001	5.311	Night
15	12	0.74*	**	7.780	Day
16	12	0.94	<0.001	9.432	Night
17	12	0.72	<0.001	7.208	Day
18	12	0.98	<0.001	10.79	Night

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

Figure 6. Fluxes and the highest measured concentration for 1,3-D over all monitors during each sampling interval.
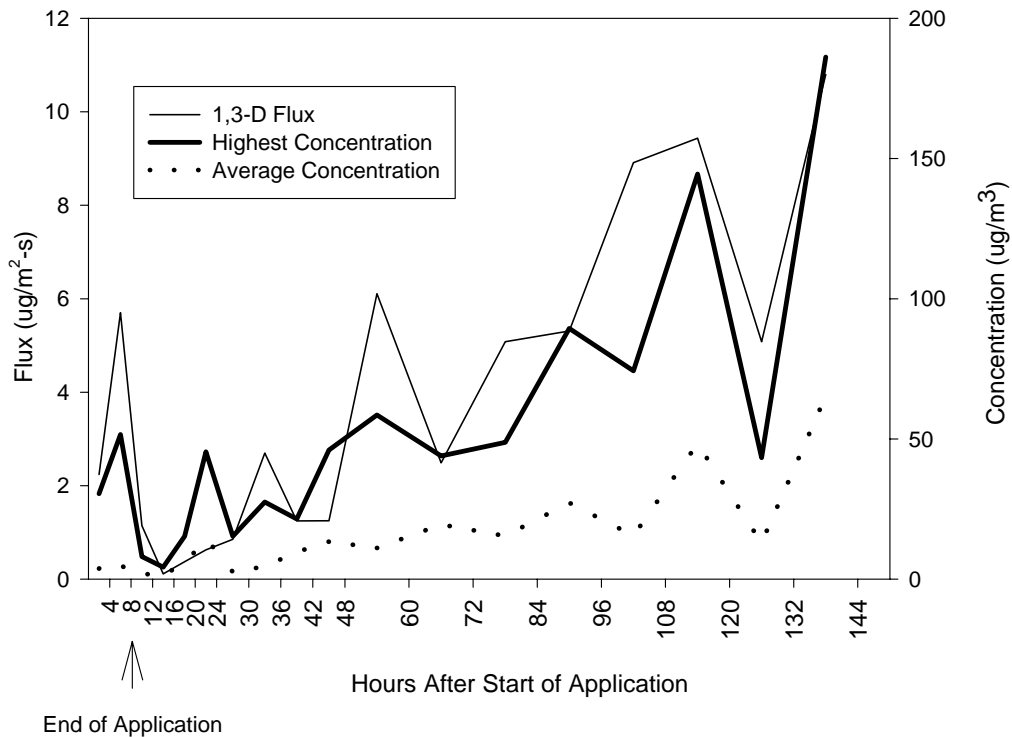
End of Application

Emission Calculations

The amount of a chemical offgassing (emission) from an application area can be calculated using the estimated fluxes. Emission can be calculated as a percent of the total amount of chemical applied to the application area. To determine the emission the total amount applied must first be calculated. The emission percentage is calculated as:

$$\text{Percent emission} = \frac{\left[flux \ (ug/m^2-s) \ \times \dfrac{1g}{1000000\,ug} \right] \times \left[\sec onds \right]}{amount \ applied \ (g/m^2)} \times 100$$

where the time is the period over which to calculated the emission percent.

Amount of MITC applied
Application rate: 684.01 L/ha (73.13 gals/ac)
Active ingredient: 0.511 kg/L (4.26 lbs/gal) of metam sodium
Therefore the application rate = 349.2 kg/ha (311.5 lbs/ac) of metam sodium
Application area: 3.24 ha (8 ac) = 32,376 m^2
Total applied amount: 2,214.23 L (585 gals) of metam sodium
Therefore total applied amount: 2,492.1 lbs metam sodium
Total metam sodium applied = 2,492.1 lbs metam sodium x 453.6 g/lb = 1,130,416.56 g
     1,130,416.56 g ÷ 128.2 molecular weight (m.w.) = 8,817.6 moles metam sodium
At a 1:1 conversion the total MITC applied = 8,817.6 moles x 73.1 m.w. = 644,566.56 g MITC.

Table 16 presents the 24-hour TWA flux rates, emission percentages, mass of MITC released and cumulative calculations during the monitoring study. The total amount of MITC released from the application area during the monitoring period (6 days) was approximately 90,540 g or 14.1% of the equivalent amount applied of MITC

Table 16. Emission of MITC calculated from estimated flux. Bolded rows are 24-hour TWA summations.

Hours after Application	Duration of TWA	TWA flux rate ($\mu g/m^2$-s)	TWA Emission (%)	Kilograms of MITC released	Cumulative Emission (%)
4	4	18.3	1.32	8.54	1.32
8	4	49.4	3.57	23.0	4.89
12	4	25.0	1.81	11.7	6.70
16	4	11.5	0.83	5.34	7.53
20	4	12.3	0.89	5.74	8.42
24	4	15.8	1.14	7.35	9.56
24[a]	**24**	**22.0**	**9.57**	**61.7**	**9.56**
30	6	5.23	0.57	3.66	10.1
36	6	6.74	0.73	4.71	10.9
42	6	2.29	0.25	1.60	11.1
48	6	2.32	0.25	1.62	11.4
48	**24**	**4.14**	**1.80**	**11.6**	**11.4**
60	12	4.18	0.908	5.85	12.3
72	12	0.926	0.201	1.29	12.5
72	**24**	**2.55**	**1.11**	**7.14**	**12.5**
84	12	1.37	0.298	1.92	12.8
96	12	1.42	0.307	1.98	13.1
96	**24**	**1.40**	**0.606**	**3.90**	**13.1**
108	12	1.27	0.276	1.78	13.4
120	12	1.48	0.322	2.07	13.7
120	**24**	**1.38**	**0.597**	**3.85**	**13.7**
132	12	0.770	0.167	1.08	13.8
144	12	0.942	0.204	1.32	14.0
144	**24**	**0.856**	**0.371**	**2.39**	**14.1**

Amount of 1,3-D applied
Active ingredient: 10.1 lbs/gal @ 70 ºF, 95.7 % 1,3-D
Total applied for 8 acres = 265 gals = 2,561.41 lbs a.i. 1,3-D
Application area: 8 acres = 32,376 m^2
Total 1,3-D applied = 2,561.41 lbs a.i. 1,3-D x 453.6 g/lb = 1,161,855.58 g 1,3-D

Table 17 presents the 24-hour TWA flux rates, emission percentages, mass of 1,3-D released and cumulative calculations during the monitoring study. The total amount of 1,3-D released from the 3.2 ha application area during the monitoring period (6 days) was approximately 84,150 g or 7.24% of the amount applied.

Table 17. Emission of 1,3-D calculated from estimated flux.

Hours after Application	24-hour TWA flux rate ($\mu g/m^2$-s)	24-hour TWA Emission (%)	24-hour Kilograms of 1,3-D released	Cumulative Emission (%)
24	1.56	0.375	4.36	0.37
48	1.49	0.358	4.16	0.73
72	4.22	1.02	11.8	1.75
96	5.21	1.26	14.6	3.00
120	8.61	2.07	24.1	5.08
144	9.00	2.17	25.2	7.24

Comparisons to Other Monitoring Results

MITC
Metam sodium can be applied by several methods, including; soil injected (shanked-in), sprinkler, flood and furrow, and drip irrigation, (with tarp and watering-in variations for many of them). Back-calculated flux estimates have been made for several of these methods (Barry et al. 2004; Li 2004). Table 18 displays 4-hour flux estimates for six application types: standard shank, standard sprinkler, intermittent watering-in shank, intermittent watering-in sprinkler, untarped bed drip chemigation, intermittent watering-in untarped bed drip chemigation, and the results of this current study (incorporated surface application). The flux estimates from the shank and sprinkler applications, including the intermittent watering-in applications, may not be the highest flux estimates for these applications. However, they are the critical flux estimates, which means that they represent flux estimates for the period associated with the highest measured air concentrations. Both the highest 4-hour flux and the critical 4-hour flux are listed for this current study. These critical periods are most often at night due to stable atmospheric conditions possibly accompanied by surface-based inversions (Barry et al. 2004). These nighttime atmospheric conditions can produce the highest air concentrations, even though flux is below the maximum.

The 4-hour critical flux estimated during this current study was lower than both the standard shank and intermittent watering-in shank studies which both were bed applications with lower a effective broadcast application rate. The highest flux estimates for the untarped bed drip chemigation and intermittent watering-in untarped bed drip chemigation are used for comparison since the critical periods for these applications have not been calculated. The 4-hour flux estimates for these applications are significantly smaller than the other application methods.

The flux rate is also influenced by various soil characteristics. Soil texture has an indirect influence on the diffusion of a fumigant since finer textured soils generally possess greater moisture-holding capacity, percent pore space, and number of binding sites for adsorption. Organic matter can also increase the soil holding capacity and binding sites.

Ashley et al. (1963) found that soil temperature, soil type, soil pH and soil moisture content, in order of importance, all influenced the rate of MITC loss from treated soils. Increasing the soil temperature from 10 °C to 15 °C can increase the loss of MITC as much as 50% (Ashley et al. 1963). In a laboratory study, Gan et al. (1999) found that as soil moisture content increased MITC degradation decreased. The soil organic matter content can also have an effect on volatilization. Gan et al. (1998) found that the addition of 5% of composted manure to a sandy loam soil with 1.08% organic matter almost completely eliminated the volatilization of MITC.

Table 18. 4-hour TWA flux ($\mu g/m^2$-s) for different metam sodium applications. The incorporated surface applied is this current study. The last column presents the fluxes adjusted to the same application rate of 19.9 g/m^2 of MITC.

Application type	4-hour TWA flux ($\mu g/m^2$-s)	Night or Day	Effective broadcast application rate of MITC (g/m^2)	Standardization Multiplier	Standardized 4-hour TWA flux ($\mu g/m^2$-s)
Standard shank*	34.0	night	9.64	2.06	70.0
Standard sprinkler*	74.0	night	19.3	1.03	76.2
Intermittent watering-in shank*	25.8	day	9.64	2.06	53.1
Intermittent watering-in sprinkler*	43.6	night	19.3	1.03	44.9
Incorporated surface applied**	15.8	night	19.9	1	15.8
Incorporated surface applied [1]	49.4	day	19.9	1	49.4
Untarped bed drip chemigation	3.94	day	2.50	7.96	31.4
Intermittent watering-in untarped bed drip chemigation	2.12	day	3.10	6.42	13.6

  * Data are critical period flux estimates from Barry et al., 2004.
  ** Critical 4-hour flux estimate from present study.
 [1] Highest 4-hour flux estimate.

1,3-D

1,3-D is applied by standard and deep soil shanked-in and drip irrigation (both tarped and untarped). Table 19 lists some fluxes determined during other monitoring studies (Johnson and Kollman 2002). The maximum flux rate found during this study (shown in bold) is similar to the other 45.7 cm (18in) deep shanked-in application maximum flux rates. Care should be taken when comparing the other application types since the maximum flux rates were determined for intervals approximately half as long. Wang et al. (2001) measured volatilization from a bedded shanked-in at 30.5 cm depth, tarped shallow drip, and deep drip at 20.3 cm depth and found a total emission loss of 93, 66 and 57%, respectively, over a 10-day study.

As with MITC, the flux rate of 1,3-D is influenced by application method and soil conditions. The high soil moisture could be a limiting factor in the diffusion of 1,3-D. McKenry and Thomason (1977) found that in a silty clay loam soil moisture content of 23% both lowered and delayed the peak diffusion of 1,3-D in the soil. In addition, an increase in soil organic matter content can reduce the maximum soil vapor concentration. Gan et al. (1999) found that unlike MITC, 1,3-D degradation accelerated with an increase in soil moisture content. Dungan et al. (2001) found that the addition of organic matter increased the rate of degradation of 1,3-D significantly, leaving less available for volatilization. However, they found that soil moisture had no effect on degradation.

Table 19. Flux from other 1,3-D application monitoring studies. The Shank-45.7 cm is this current study. The last column presents the fluxes adjusted to the same application rate of 35.9 g/m^2 of 1,3-D.

Application type	Study length (days)	Total emission (percent)	Maximum flux (µg/m^2-s)	Flux period length (hours)	Effective broadcast application rate of a.i. (g/m^2)	Standardization Multiplier	Standardized Maximum flux (µg/m^2-s)
Tarped-bed drip*	17	28.9	14.4	6	14.3	2.51	36.1
Tarped-bed drip*, **	9	29.2**	20.1	5	7.51	4.78	96.1
Shank – 35.6cm*	14	65	38.1	6	13.7	2.62	99.8
Bedded Shank-30.5cm*	14	65	31.9	5	7.66	4.69	150
Bedded Shank-51.8-55.9cm*	21	26.2	17.5	6	13.4	2.68	46.9
Shank – 45.7cm*	14	25	9.75	12	13.7	2.62	25.5
Shank – 45.7cm *, **	8	11.2**	5.67	12	13.6	2.64	15.0
Shank – 45.7cm **	**6**	**7.24****	**10.8**	**12**	**35.9**	**1**	**10.8**

*Studies compiled in Johnson and Kollman 2002
** These three studies were markedly shorted in duration than the others. Therefore, caution should be used in judging the total emission percent, which may be understated.
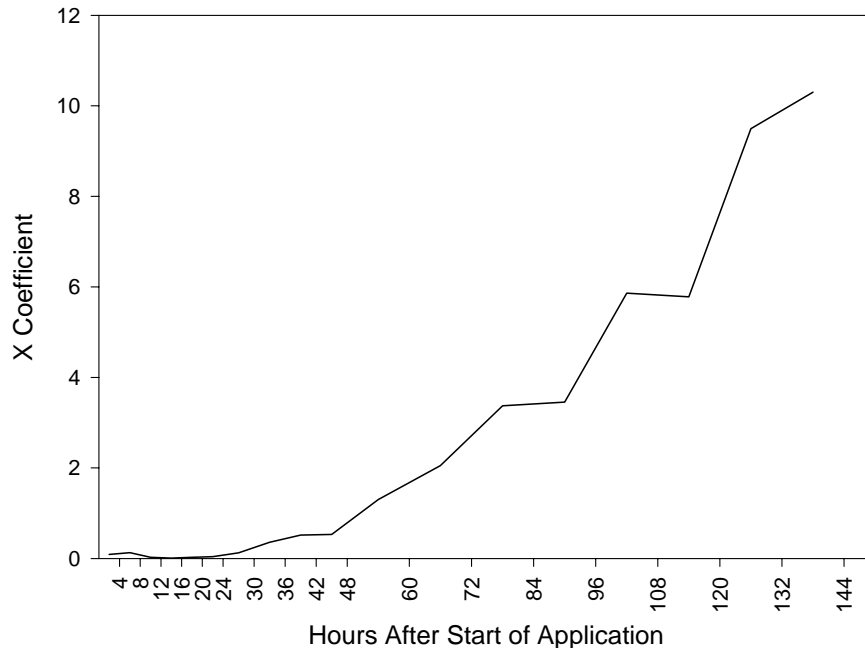
Correlation between MITC and 1,3-D concentrations
Each sampling tube was analyzed to determine both an MITC and 1,3-D concentration. A regression between these co-sampled concentrations over all sampling periods and locations was conducted. There was no relationship between these co-sampled concentrations (p>0.1, r2<0.001, n=284). There was no correlation between the estimated fluxes for MITC and 1,3-D (p> 0.1, r^2 = 0.06, n = 18).

When compared within sample intervals, the regression analysis results showed a strong correlation. The sampling locations with high concentrations of MITC were similar to the locations with high concentrations of 1,3-D indicating that the actual movement of the released chemicals was driven by physical conditions such as wind speed and direction and not dependant on the pesticide. Table 20 presents the regression analyses for the measured concentrations of MITC (x-axis) and 1, 3-D (y-axis). Figure 7 is a graph of the multiplicative coefficient from the regression analysis for each sampling interval. The increasing slope over time indicated that the 1,3-D concentrations were increasing in comparison to the MITC concentrations over time.

Table 20. Regression results for MITC concentrations (x) vs. 1,3-D concentrations (y).

Sampling Interval	r^2	p-value	coefficient	Sampling Interval	r^2	p-value	coefficient
1	0.88	<0.001	0.0903	10	0.79	<0.001	0.534
2	0.75	<0.001	0.127	11	0.90	<0.001	1.30
3	0.53	0.001	0.0241	12	0.68	<0.001	2.05
4	0.48	0.003	0.0098	13	0.86	<0.001	3.37
5	0.89	<0.001	0.0263	14	0.90	<0.001	3.46
6	0.92	<0.001	0.0409	15	0.84	<0.001	5.86
7	0.88	<0.001	0.125	16	0.92	<0.001	5.78
8	0.90	<0.001	0.359	17	0.86	<0.001	9.50
9	0.79	<0.001	0.521	18	0.88	<0.001	10.30

Figure 7. The multiplicative coefficient from the regression analysis of the measured air concentrations of 1,3-D (y) on MITC (x) and during each sampling interval.

Both Spearman rank correlation and Kendall's tau quantify the strength of the association between the concentrations of both chemicals. For both the Spearman and Kendall's tau, a correlation coefficient near +1 indicates a strong positive relationship between the concentrations. The statistically significant regressions and high r^2 values indicated that the locations with the high concentrations for both chemicals were similar during all sampling intervals (Table 21).

Table 21. Correlation coefficients of MITC versus 1,3-D concentrations for each interval**.**

Sampling Interval	Spearman's Correlation coefficient	Kendall's Correlation coefficient
1	0.89	0.81
2	0.86	0.88
3	0.82	0.70
4	0.77	0.55
5	0.95	0.83
6	0.86	0.75
7	0.90	0.82
8	0.94	0.97
9	0.92	0.78
10	0.97	0.88
11	0.92	0.78
12	0.82	0.67
13	0.91	0.75
14	0.95	0.83
15	0.92	0.78
16	0.98	0.90
17	0.97	0.87
18	0.97	0.88

Based on the positive correlation between sampled concentrations of MITC and 1,3-D within each sampling interval, there was reason to believe that success of the back-calculated regressions for the two pesticides might be correlated within each interval as well. To check this, the r^2 values within each sampling interval that resulted from the back-calculation for each pesticide were compared. The r^2 values represent a measure of success of the regression. Of the 18 sampling intervals, 5 were excluded (intervals 1-4 and 15) because either (1) they occurred during the application period, (2) the back-calculation was redone with sorted concentrations, or (3) both. The correlation between the r^2 values from the flux regressions was 0.64 (p<0.02). While this correlation was significant, it was not as high as expected given the high correlations between measured

concentrations within intervals between the two pesticides. This suggests that there is a common set of physical processes governing the flux within each monitoring interval and that the methodology that was used to model and related the concentrations in order to estimate flux is approximately the same for both pesticides. However, the lower than expected correlation of 0.64 implies that there were pesticide-specific effects, which caused differences in the success of the interval-by-interval regressions to estimate flux.

CONCLUSION

MITC

The highest concentrations occurred during the first day of monitoring, with a highest individual sample concentration of 920 $\mu g/m^3$ collected during a 4-hour interval of the first night following application at a sampler located 10.1 m from edge of application. The highest 24-hour TWA measured during the first day was 236 $\mu g/m^3$ at a sampler located 15.2 m from the edge of the application area. Generally, the concentrations declined following the first 24 hours with higher concentrations measured during nighttime hours.

Gaussian modeling of the application and comparison with the measured concentrations resulted in a highest flux of 49.4 $\mu g/m^2$-s for a single 4-hour sampling interval during the second half of application (interval 2). The flux for the first 24-hour monitoring period was 22.0 $\mu g/m^2$-s. Flux rates showed a general decline over time, with higher emissions during daytime hours for the first three days and nighttime hours during the second three-day period. The total amount of MITC released from the 8-acre application area during the 6-day monitoring study was approximately 90,540 g or 14.1% of the equivalent amount applied.

The flux rate estimated for the sampling interval which produced the highest concentrations furthest from the edge of application (critical flux rate) was lower than critical fluxes estimated for a standard shank and intermittent watering-in shank method. In addition, when adjusted for application rate the critical 4-hour TWA flux rate estimated for the current study was lower than the critical flux rates determined in 4 other studies (Table 18, first 5 rows). The high clay content (38 to 46%), organic carbon content (3.5 to 4.9%) and soil moisture (31.5 to 35.2%) may also have contributed to a lower flux.

1,3-D

The highest concentrations occurred during the last day of monitoring, with a highest individual sample concentration of 186 $\mu g/m^3$ collected during a 12-hour interval of the sixth and last night of monitoring at a sampler located 10.1 m from the edge of the application. The highest 24-hour TWA measured on the last day was 9.04 $\mu g/m^3$ at a sampler located 18 m from the edge of the application area. Since the concentrations were increasing up to day 6 it is likely that the highest concentrations occurred after monitoring ended.

Modeling of the application and comparison with the measured concentrations resulted in a highest flux for a single 12-hour sampling interval of 10.8 µg/m^2-s measured during the last night of monitoring. Similar to the MITC flux rates, 1,3-D showed higher flux rates during daytime hours for the first three days and higher flux at nighttime hours during the second three-day period. The total amount of 1,3-D released from the application area during the monitoring study was approximately 84,150 g or 7.24% of the amount applied. This amount likely understates the total atmospheric volatilization of 1,3-D from this application since the flux increased during the monitoring period.

The maximum flux rate found during this study was similar to the other deep shanked-in application study results. When standardized for application rate, the maximum flux rate was lower than other application method monitored, such as tarped-bed drip, 35.6 cm deep shanked-in and bedded shanked-in applications. As with MITC, the flux rate of 1,3-D is influenced by application method and soil conditions. The high soil moisture could be a limiting factor in the diffusion of 1,3-D and an increase in soil organic matter content can reduce the maximum soil vapor concentration available for offgassing.

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