MONITORING AN UNTARPED BEDDED DRIP APPLICATION OF METAM SODIUM IN MERCED COUNTY

March 2005

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Abstract

The California Department of Pesticide Regulation (CDPR) collected air samples at an application of metam-sodium near Atwater, California in April of 2004. The application was an untarped, bedded drip chemigation of Sectagon 42® applied to a 9.13 acre field divided into five treatments. Two of the five treatments were monitored; treatment 1 had an application rate of 39.1 pounds metam sodium per acre and treatment 2 had an application rate of 48.5 pounds per acre with additional watering-in applied for one hour at sunset and one hour at midnight the evening of the treatment and the following evening at an irrigation rate of 0.3 acre-inches per hour. Samples were collected for 72 hours (14 sampling intervals) after the start of application. The objective of this study was to obtain a MITC flux estimate for this chemical/application method, characterize the flux profile during the monitoring period, and estimate the fractional mass loss during the first 24 and 48 hours.

The second sampling interval for both treatments produced the highest detections of MITC: 13.3 parts per billion (ppb) and 16.5 ppb for treatment 1 and treatment 2, respectively. For the first treatment, concentrations followed a diurnal pattern with concentrations decreasing during the day intervals and then increasing slightly during the night sampling intervals. The second treatment generally had decreasing concentrations from interval to interval. No samples exceeded the DPR exposure target level of 220 ppb 8-hr time weighted average (TWA).

Air dispersion modeling with the Industrial Source Complex Short Term Dispersion Model (ISCST3) together with the standard back calculation procedure was used to obtain MITC flux estimates. For both treatments the second sampling intervals had the highest fluxes of 0.116 and 0.0626 pounds per acre per hour for treatment 1 and treatment 2, respectively. For both treatments, in interval 4 the flux dropped significantly and was relatively low for the rest of the sampling time except for a slight increase during interval eight.

Calculations were done to estimate the percent of total MITC applied that was released (fractional mass loss) during monitoring. The emissions from treatment 2 were about half of that of treatment one with 3.62% and 1.76% of MITC being released during the first 24 hours for treatment 1 and treatment 2, respectively. This coincides with the difference in maximum fluxes for the two treatments despite there being a higher effective application rate for treatment 2. The data indicates that the intermittent watering done during the second treatment did not have an effect on emissions since the emissions were driven by the flux of the second sampling interval, which occurred prior to the watering-in.

4-hour emission percentages were compared for six application types: standard shank, standard sprinkler, intermittent watering-in shank, intermittent watering-in sprinkler, untarped bedded drip chemigation, and intermittent watering-in untarped bedded drip chemigation. The emissions for the untarped bedded drip chemigation applications were less than half of those for the sprinkler and shank application methods. 12-hour emission percentages were compared for the tarped and untarped bedded drip chemigation methods. The tarped application had the smallest percent released of 1.22 % of total MITC applied when compared to the untarped applications which released 3.14 and 1.52 % for the standard and intermittent watering application methods, respectively.

Acknowledgements

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Introduction

Metam-sodium (sodiumN-methyldithiocarbamate) is a broad-spectrum soil fumigant that can be used to control nematodes, weeds, and fungi affecting a variety fruit and vegetable crops. It acts by decomposition to methyl isothiocyanate (MITC) which functions as the principle pesticidal agent. Metam-sodium has a 50% dissipation time to MITC of 23 minutes to 4 days when in contact with moist soil (Tomlin, 1997) and also produces low concentrations of hydrogen sulfide (H_2S) and carbon disulfide (CS_2). The MITC half-life ranges from 29 to 39 hours and results in the production of methyl isocyanide, methyl isocyanate (MIC), methylamine, N-methyl formamide, sulfur dioxide, hydrogen sulfide, and carbonyl sulfide. While metam-sodium is non-volatile, MITC has a relatively high vapor pressure (16.0 mmHg at 25°C) and leaves the soil primarily due to volatilization (Leistra and Crum, 1990). Factors affecting the volatilization rate of MITC from soil include: soil temperature, soil type, soil pH, and soil moisture content (Ashley *et al.*, 1963).

In the state of California, metam-sodium is a highly used chemical with 6,000,398 kilograms (kg), 5,710,075 kg, 7,459,601 kg, and 6,720,352 kg of metam-sodium active ingredient applied in 2000, 2001, 2002, and 2003 respectively (CDPR, 2000; CDPR, 2001; CDPR, 2002a; CDPR, 2003). In 2003, the five counties with the highest use were Kern, Fresno, Imperial, Los Angeles, and Riverside accounting for 73% percent of all use within the state. Metam- sodium can be applied via drip irrigation, metered into a sprinkler irrigation or flood irrigation system, or directly injected into the soil.

The high volatility of MITC coupled with the high use of metam-sodium in several counties of California results in a significant potential for drift of MITC into neighboring communities. The California Department of Pesticide Regulation (DPR) conducted prior monitoring of metam-sodium under conditions that would favor maximum emissions of MITC (Wofford, *et al*, 1994). This study 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). DPR began evaluating mitigation measures to reduce off-site movement of MITC under these worst-case conditions. DPR has decided on an 8-hour reference concentration of 660 $\mu g/m^3$ (220 ppb), which was identified in the DPR risk assessment as the no-observable effect level (NOEL) (CDPR, 2002b).

Drip-irrigation is a potential way of minimizing off-site exposure of metam-sodium. The application rate to the treated acre is the same as other application methods, but since only the soil directly around the drip tape is fumigated the broadcast application rate can be much lower than other methods. For example, in this study the application was divided into five treatments. Since each treatment was applying to one-fifth of the gross acreage, only one-fifth of the total product needed for the application was applied during any one treatment. The objective of this study was to estimate the flux associated with this chemical/application method, characterize the flux profile during the monitoring period, and estimate the fractional mass loss during the first 24 and 48 hours (CDPR, 2004).

Materials and Methods

Application Site

Air monitoring was conducted around a 3.69 hectare (9.13 acre) bedded field approximately 2.6 kilometers northwest of Atwater in Merced County. Sweet potatoes were scheduled for planting after the conclusion of all metam-sodium treatments. The field was surrounded to the north by train tracks (24 meters) and Highway 99, to the east by a vacant farm worker camp and a residence (6.3 meters to the edge of property), to the south by Westside Blvd (9 meters) and a peach orchard (25 meters), and to the west by 13 rows of sweet potato hot beds and then additional unplanted bedded fields. The residence was located at the southeast corner of the field; a 45.7 by 42.1 meter section of the field was left untreated as a buffer for the residence. The beds ran in a north-south direction and were 1.7 meters wide with a 0.3 meters wide furrow between them. Metam-sodium was applied to the field via drip tape originating from two main irrigation lines (Figure 1); the field was left untarped. The chemigation system was located along the west side of the field about 143 meters from the southern edge of the field. Five treatments were made with the drip tape being moved to a different position on the bed between treatments (Figure 2); air monitoring occurred during the second and fourth treatments. The distance between drip tape emitters was 0.3 meters (12 inches). The day prior to treatments, the irrigation system was moved to the correct position on the bed and water was run through the lines to check for leaks. Seven days separated previous treatments with the treatments monitored.

Weather Data

Wind speed, wind direction, ambient air temperature, solar radiation, and relative humidity were collected for the duration of the study using Met1® meteorological sensors on a weather station with a 10 meter (32.8 foot) mast. The weather station was located west of the field at the southwest corner of the sweet potato hot beds. The measurements were recorded onto a Campbell Scientific, Inc. CR 21X Datalogger as one-minute averages of one-second readings, except wind direction, which was collected as an instantaneous reading every minute. In addition to these readings, percent cloud cover was noted at each sample change.
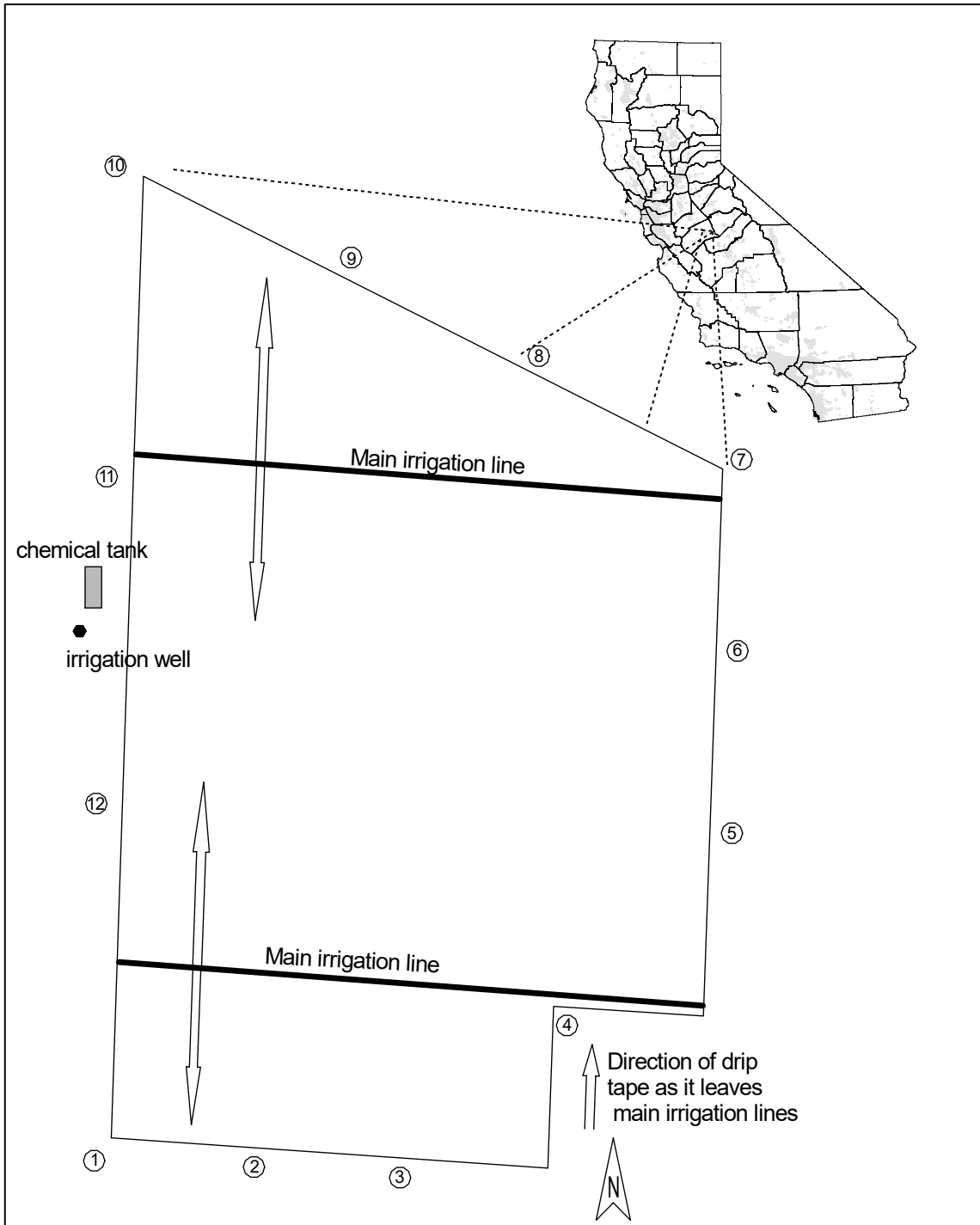
Figure 1. Field layout and air monitoring locations.
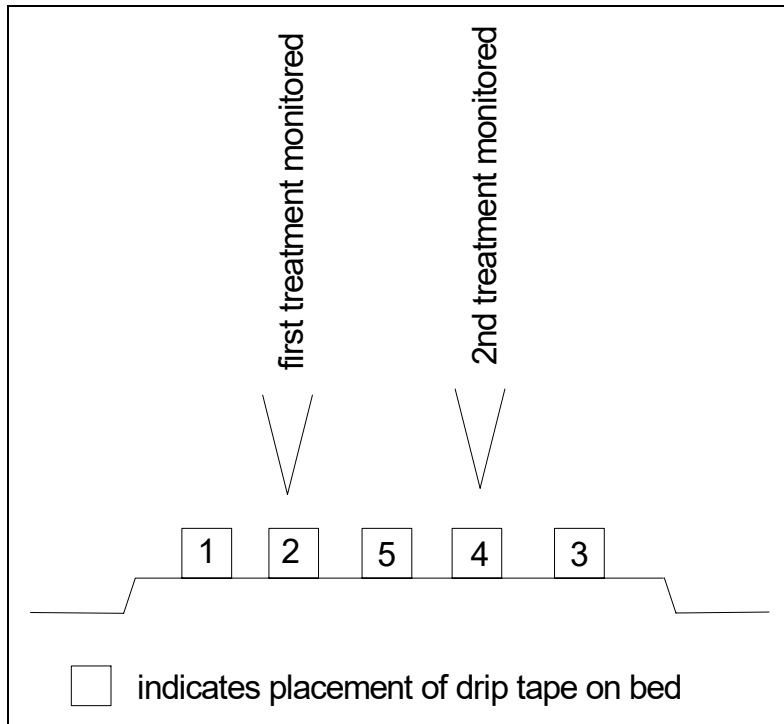
Figure 2. Drip tape placement and treatment sequence; sequence was mirror image of above for tape south of the southern irrigation line.

Application

The Sectagon 42® product label, with a 42.2% active ingredient (4.22 pounds active ingredient per gallon or 1.91 kg active ingredient per 3.79 liters of water), specifies that the area of treatment (for a drip application) must be calculated in accordance with the size of the band treated at a rate of 40 gallons (151.5 liters) per broadcast acre (0.4 hectare) in one acre inch of water (102,276 liters; 27,000 gallons) (Tessenderlo Kerley, 2000 product label). Approximately 20% of the total acreage was treated during each treatment of this application. Soil temperatures at the time of fumigation should be in the range of 4° to 32°C, temperatures above 32°C are avoided to prevent rapid evaporation of the product from the soil. The label encourages applications in the early morning hours when soil temperature is the coolest. Soil moisture should be about 50-80% of field capacity. The field was bedded prior to any treatments to minimize any contamination from incorporated soils and the drip tape was left in the middle position after completion of all treatments for irrigation of the sweet potato crop after planting.

Treatment 1: untarped bed drip chemigation
Sectagon 42® was applied continuously at a broadcast rate of 9.3 gallons per acre (86.6 liters per hectare) or 39.1 pounds metam sodium per acre (43.8 kilograms per hectare) over 6.5 hours. An additional 38.6 kiloliters (10,200 gallons) of water was applied immediately following the application through the drip tape for approximately one hour to flush the drip system and cap the treatment. The treatment commenced at 6:50 on April 8, 2004 and ended at 13:20 the same day. The temperature during treatment ranged from 7.8 to 23.3°C (46 to 74° F) with a high wind speed of 4.3 meters per second (mps). The skies were clear and remained clear through the duration of sampling.

Treatment 2: intermittent watering-in untarped bed drip chemigation
Sectagon 42® was applied continuously at a broadcast rate of 11.5 gallons per acre (l07 liters per hectare) or 48.5 pounds per acre (54.4 kilograms per hectare) over 7.5 hours. An additional 27.5 kiloliters (7,267 gallons) of water was applied immediately following the application through the drip tape for approximately forty-five minutes to flush the drip system and cap the treatment. The treatment commenced at 7:08 on April 20, 2004 and ended at 14:30 the same day. Two additional intermittent waterings were applied for one hour at sunset and for one hour at midnight the evening of the treatment and the following evening at an irrigation rate of 31 cubic meters (0.3 acre-inches) per hour. The temperature during treatment ranged from 12.8 to 18.9°C (55 to 66° F) with a high wind speed of 5.6 mps. There was 100% cloud cover and a slight mist, no rain was detected at CIMIS station #148 (UC IPM, 2004), during the treatment; skies remained cloudy through that night. Subsequent days were clear with high winds occurring on April 22 during sampling interval 11.

Sampling
Air samples were collected using two-stage (200/400 mg) coconut charcoal resin tubes (SKC 226-09) mounted to SKC personal air sample pumps (SKC# 224-PCXR8) calibrated at a flow rate of approximately 1500 ml/minute. Samples were collected from twelve sites at a distance of 4.7 to 9.5 meters from the perimeter of the field; one at each corner and two equidistant along each side of the field (Figure 1, Table 1). Sample tubes were positioned approximately 1.2 meters above ground attached to metal stakes. Sample pumps were powered using external batteries that were changed frequently throughout the monitoring period.

Table 1. Distance of samplers from edge of field (meters).

Sampler location	Treatment 1	Treatment 2
1	7.6	7.6
2	4.7	4.7
3	4.8	4.8
4	6.2	6.2
5	6.5	5.8
6	6.3	5.6
7	5.9	5.9
8	5.0	5.0
9	5.9	5.9
10	8.8	9.5
11	7.5	8.2
12	7.3	8.0

Sample pumps were calibrated prior to setup at the Environmental Monitoring laboratory. Flow rates were checked and recorded at the beginning and end of each sampling interval using a DryCal® DC-Lite Primary Flow Meter (Bios International Corporation). Sample tubes were covered in foil during daytime sampling intervals to minimize loss of metam-sodium to photodegradation. Immediately following collection, sample tubes were tightly capped and individually sealed in plastic zip lock bags then stored on dry ice until delivery to the laboratory.

Two background samples were run for a minimum of 12 hours prior to the commencing of application. Samples were collected every four hours for the first 24 hours and then every 6 hours for the following 48 hours for a total of 14 sampling intervals. Table 2 displays the approximate timing of the sampling intervals.

Table 2. Approximate sample start times for the 14 sampling intervals.

Sampling interval	Duration (hrs)	Treatment 1	Treatment 2
1	4	6:55	7:00
2	4	10:55	11:00
3	4	14:55	15:00
4	4	18:55	19:00
5	4	22:55	23:00
6	4	2:55	3:00
7	6	6:55	7:00
8	6	12:55	13:00
9	6	18:55	19:00
10	6	0:55	1:00
11	6	6:55	7:00
12	6	12:55	13:00
13	6	18:55	19:00
14	6	0:55	1:00

Chemical Analysis/ Quality Control

The MITC samples were analyzed by the California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry. MITC was desorbed from the charcoal in 5ml of a 0.1% carbon disulfide in ethyl acetate solvent by occasionally agitating for 30 minutes. The first treatment extracts were analyzed on a 5890 GC-NPD; due to problems that arose with the NPD, the second treatment samples were analyzed with a Varian 3800 gas chromatograph equipped with TSD. The reporting limit on both instruments was 0.2 µg/sample. All raw data is found in Appendix A. In addition to the samples collected in the field, continuing quality control spikes were analyzed with each extraction set. Trip and field spikes were also collected and analyzed with each treatment (Appendix B).

Samples from the first treatment, third sampling interval were left off of dry ice overnight at the EM warehouse. The laboratory made five spikes at 12 µg to determine if this affected MITC recovery. Two of the spikes were analyzed at hour zero and the other three sat out at room temperature for 24-hours. Table 3 displays results from these spikes.

Table 3. Laboratory spikes (12 µg) to determine sample recovery after 24-hours at room
temperature.

Hours at room temperature	Result	Recovery
0	9.95	82.9
0	9.75	81.3
24	8.93	74.4
24	9.60	80.0
24	10.2	84.8

A two-sample t-test was conducted to determine if there was a significant difference in the
results of the samples analyzed at hour zero with those analyzed at hour 24. The test revealed no
significant difference with a p-value of 0.526.

Results and Discussion

Results

Tables 4 and 5 show the air sample results for treatments 1 and 2, respectively. Figure 3 displays
the maximum concentrations of MITC during each sampling interval for treatments 1 and 2. The
second sampling interval for both treatments produced the highest detections of MITC. For the
first treatment, the third interval concentrations decreased, with no MITC detected at six of the
sampling locations. The fourth and fifth intervals displayed increases in concentrations from the
third interval. Subsequent sampling intervals resulted in decreasing concentrations over time,
until the ninth and tenth intervals when concentrations increased. The increases in concentration
follow a diurnal pattern with concentration increasing slightly during the night sampling
intervals. The second treatment generally had decreasing concentrations from interval to
interval, except for the sixth interval where concentrations increased. It appears that the
watering-in during the night on day 1 and day 2 damped the nighttime concentrations. Table 6
displays the 8-hour TWA of maximum concentrations for the first 24 hours of monitoring along
with the DPR 8-hour exposure target level. The 8-hour TWA concentrations did not exceed the
DPR exposure target level of 660 µg/m^3.

Table 7 displays average wind speeds for each sampling interval. The overall wind speeds for
the second treatment were generally higher than the first treatment except for interval three. The
detected MITC concentrations trended similar to wind speeds for each interval. A decrease in
MITC concentrations correlates to the increase in wind speeds (Figures 4 and 5). For the first
treatment, the third interval concentrations decreased which correspond to the increase in wind
speeds during this interval; the ninth and tenth intervals wind speed decreases and the
concentration increases during these sampling intervals. With the exception of interval 2 during
the second half of the application, the wind speed/MITC concentration pattern generally follows
the diurnal pattern. At night wind speeds drop and atmospheric stability increases, leading to
increased air concentrations of MITC relative to the daylight intervals. For the second treatment,
wind speeds slowed during the sixth interval and there is a corresponding increase in MITC
concentrations. This treatment did not follow the same day/night pattern as the first treatment

due to two significant factors: 1) the intermittent watering in on the first and second nights following application, and 2) the rain/weather front that moved through the area caused much windier conditions for most of the sampling intervals.

Figures 6-9 and 10-13 are graphical displays of the wind data with the MITC concentrations for the first and second treatments, respectively. The wind roses depict the frequency distribution of wind direction as well as speed for each sampling interval. The spokes represent the direction of the wind, while the length represents the duration in that direction. The rings represent 20, 40, 60, 80, and 100 percent of time that the wind was blowing in a particular direction. The color represents the average speed in any given direction; refer to the figure legend for wind speed color correlation. Wind roses were created using WRPLOT View v. 3.5 (Lakes Environmental, 2000) and wind speed and direction data (one hour averages) collected using the Met1® weather station placed at the field. These wind roses illustrate the effect wind speed and direction on the location of the high detections. For the monitoring intervals with low wind speeds and a lack of decisive wind direction, monitoring results between samplers are fairly consistent. Whereas monitoring intervals with decisive wind directions and higher wind speeds the data is much more directional with high detections at the downwind sites.

Table 4. Monitoring results ($\mu g/m^3$) for treatment 1.

Sampling Interval	Sampling Location											
	1	2	3	4	5	6	7	8	9	10	11	12
1 (4)	3.57	11.6	11.3	11.5	9.34	10.9	7.91	6.08	6.05	ND*	2.93	3.52
2 (8)	ND	19.7	23.8	35.6	39.9	34.8	18.6	16.7	14.9	ND	0.996	1.15
3 (12)	ND	6.06	7.96	7.36	12.2	8.29	0.614	ND	ND	ND	ND	ND
4 (16)	2.25	4.71	8.51	15.7	20.8	20.1	8.88	10.1	12.0	6.08	8.56	7.27
5 (20)	19.5	4.85	5.02	10.1	9.26	13.6	7.79	9.20	**	11.8	14.0	8.53
6 (24)	**	3.82	3.71	4.60	6.99	6.00	4.81	4.86	3.87	1.10	2.89	2.44
7 (30)	0.656	1.22	1.16	1.48	2.19	1.86	0.923	0.942	1.06	ND	0.880	1.21
8 (36)	ND	0.921	1.23	1.25	1.91	1.37	ND	ND	0.372	ND	ND	ND
9 (42)	ND	0.628	1.31	2.40	3.57	2.56	0.670	1.50	1.69	1.11	1.58	0.960
10 (48)	1.58	1.87	1.68	1.94	2.65	4.08	3.72	3.11	2.84	**	2.98	2.33
11 (54)	ND	0.397	0.569	0.695	0.931	0.689	0.367	0.354	ND	ND	ND	ND
12 (60)	ND	0.360	0.489	0.541	0.820	0.549	ND	ND	ND	ND	ND	ND
13 (66)	ND	ND	ND	0.757	1.09	1.39	1.07	1.30	1.13	0.766	**	0.377
14 (72)	0.723	0.821	0.859	1.05	1.00	1.03	0.937	1.27	1.31	0.886	1.33	1.02

( ) = hours after start of application
* = ND- none detected at the minimum detection limit of 0.2 µg/sample
** = pump failure, equipment ran less than 70% of interval so no results are reported

Table 5. Monitoring results (µg/m^3) for treatment 2.

Sampling Interval	Sampling Location											
	1	2	3	4	5	6	7	8	9	10	11	12
1 (4)	2.75	7.15	7.69	13.7	20.9	16.2	13.5	19.6	19.9	9.90	14.5	13.6
2 (8)	ND*	1.06	1.32	26.8	37.0	49.4	49.3	45.0	45.6	2.73	4.74	3.56
3 (12)	ND	2.58	3.80	18.3	34.4	28.4	25.5	**	20.8	1.63	2.22	0.949
4 (16)	ND	4.47	5.06	7.20	13.1	7.50	3.05	1.47	1.35	ND	ND	ND
5 (20)	ND	3.26	3.25	3.72	4.58	2.43	ND	ND	ND	ND	ND	ND
6 (24)	0.586	3.59	4.36	6.82	10.3	5.80	3.04	2.17	1.12	ND	1.13	1.03
7 (30)	ND	1.68	1.89	2.83	4.40	2.60	1.01	0.955	0.542	ND	ND	ND
8 (36)	ND	1.88	**	2.56	3.85	2.18	0.596	0.440	0.387	ND	ND	ND
9 (42)	ND	1.41	1.30	1.23	1.39	0.955	ND	ND	ND	ND	ND	ND
10 (48)	**	0.796	**	0.882	1.09	0.721	ND	**	ND	ND	ND	ND
11 (54)	ND	0.448	0.490	0.630	0.848	0.530	ND	ND	ND	ND	ND	ND
12 (60)	ND	0.516	0.613	0.799	1.08	0.719	ND	ND	ND	ND	ND	ND
13 (66)	ND	0.722	0.795	0.844	1.01	0.608	ND	ND	ND	ND	0.416	0.443
14 (72)	1.78	2.33	1.83	2.25	1.16	**	0.436	0.485	0.425	ND	1.71	2.27

( ) = hours after start of application
* = ND- none detected at the minimum detection limit of 0.2 µg/sample
** = pump failure, equipment ran less than 70% of interval so no results are reported

Table 6. 8-hour TWA of maximum concentrations (µg/m^3) for the first 24 hours of monitoring.

Hours after start of application	Treatment 1	Treatment 2	DPR exposure target
8	25.7	35.1	660
16	16.5	17.7	660
24	13.2	7.43	660

Table 7. Average wind speed (meters per second) for each sampling interval.

	Average wind speed (m/s)	
Interval	Treatment 1	Treatment 2
1	1.28	1.71
2	2.69	2.90
3	4.13	2.24
4	1.62	3.44
5	1.10	3.59
6	1.51	2.16
7	2.24	3.57
8	3.19	4.52
9	1.74	3.99
10	1.31	4.08
11	2.63	7.52
12	3.86	6.48
13	2.07	4.24
14	1.43	1.62

Figure 3. Maximum MITC concentrations ($\mu g/m^3$) for treatment 1 and treatment 2.
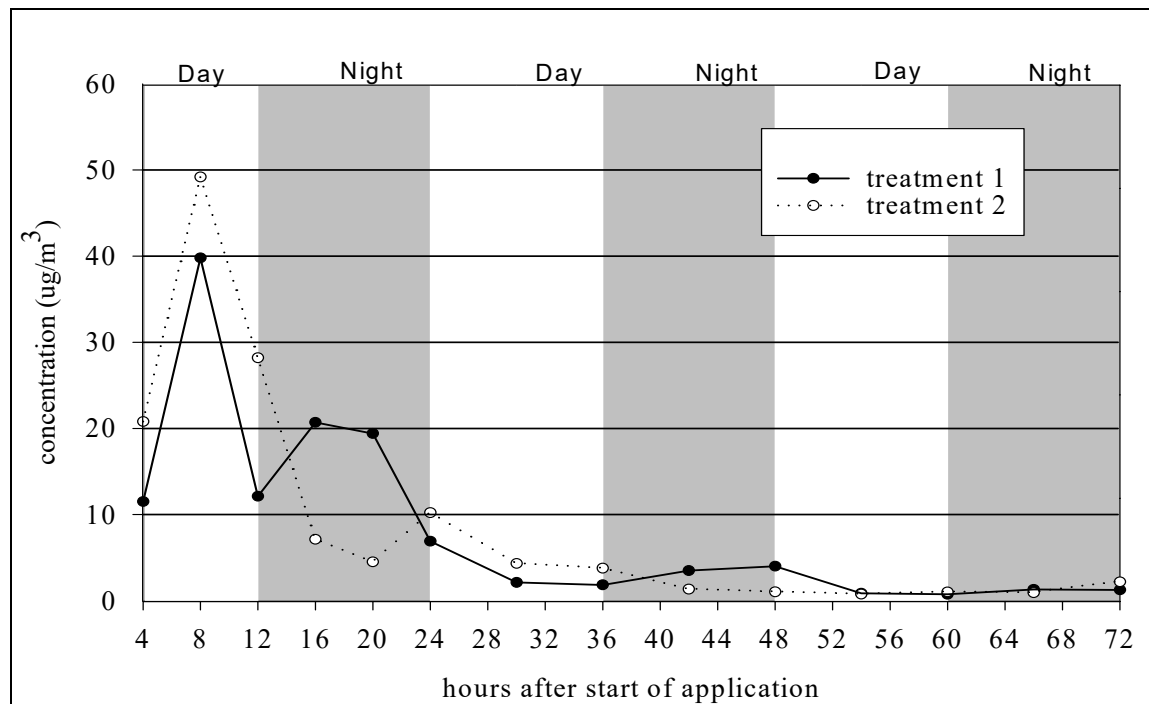
Figure 4. Maximum MITC concentration ($\mu g/m^3$) and wind speed (m/s) for treatment 1.
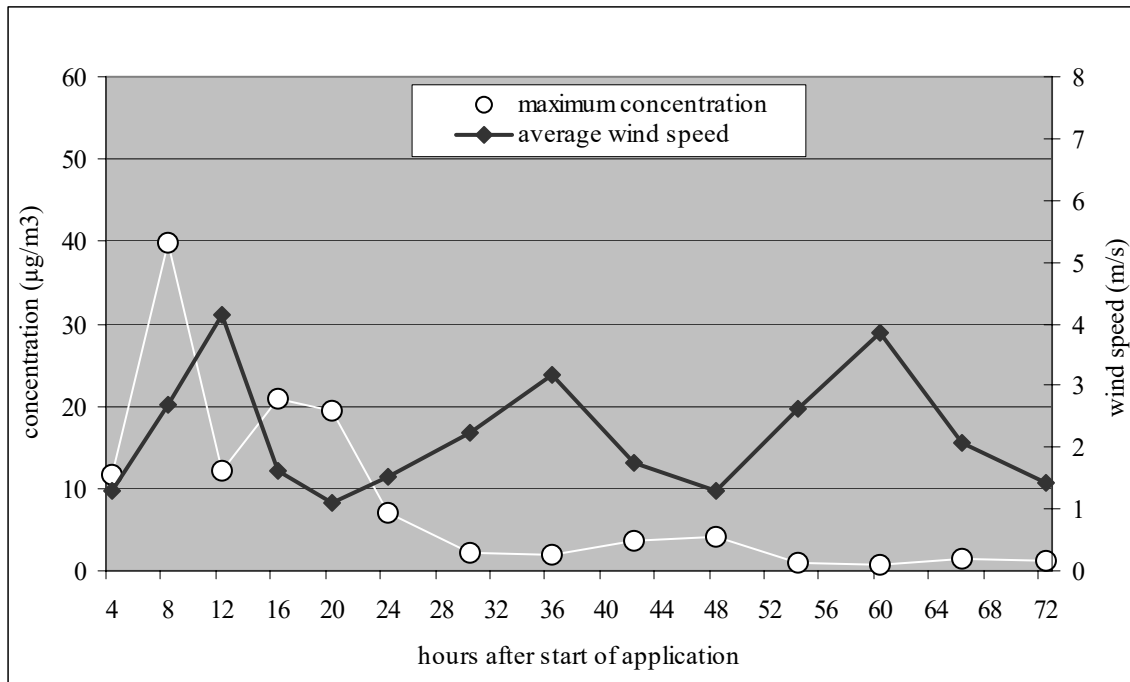
Figure 5. Maximum MITC concentration ($\mu g/m^3$) and wind speed (m/s) for treatment 2.
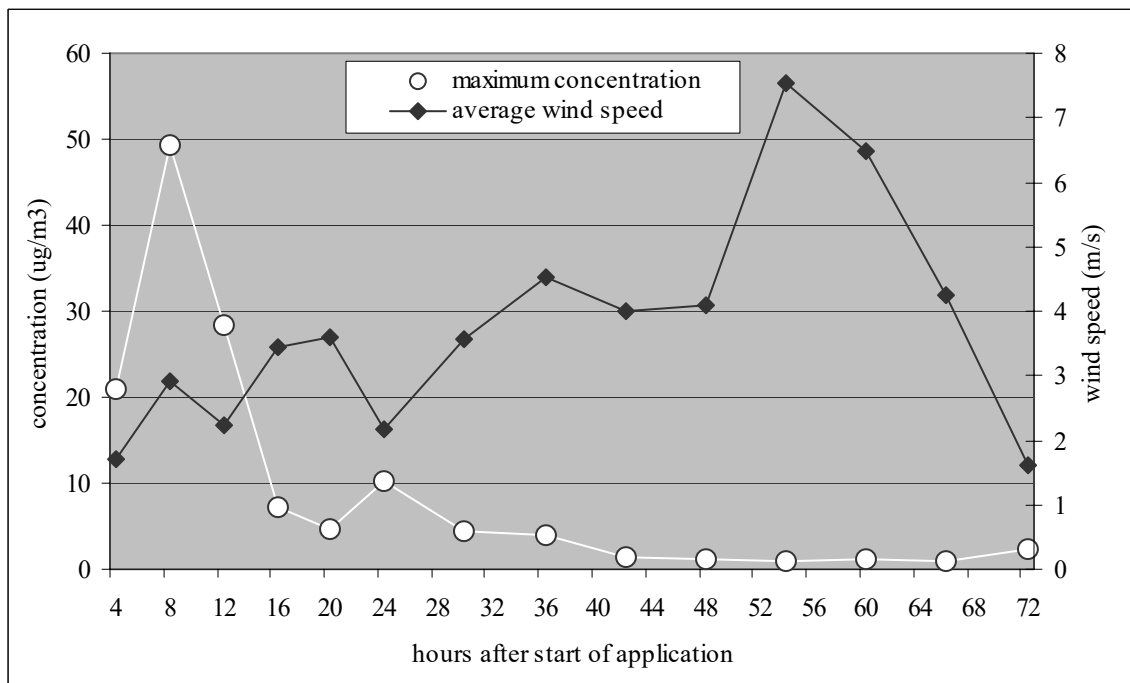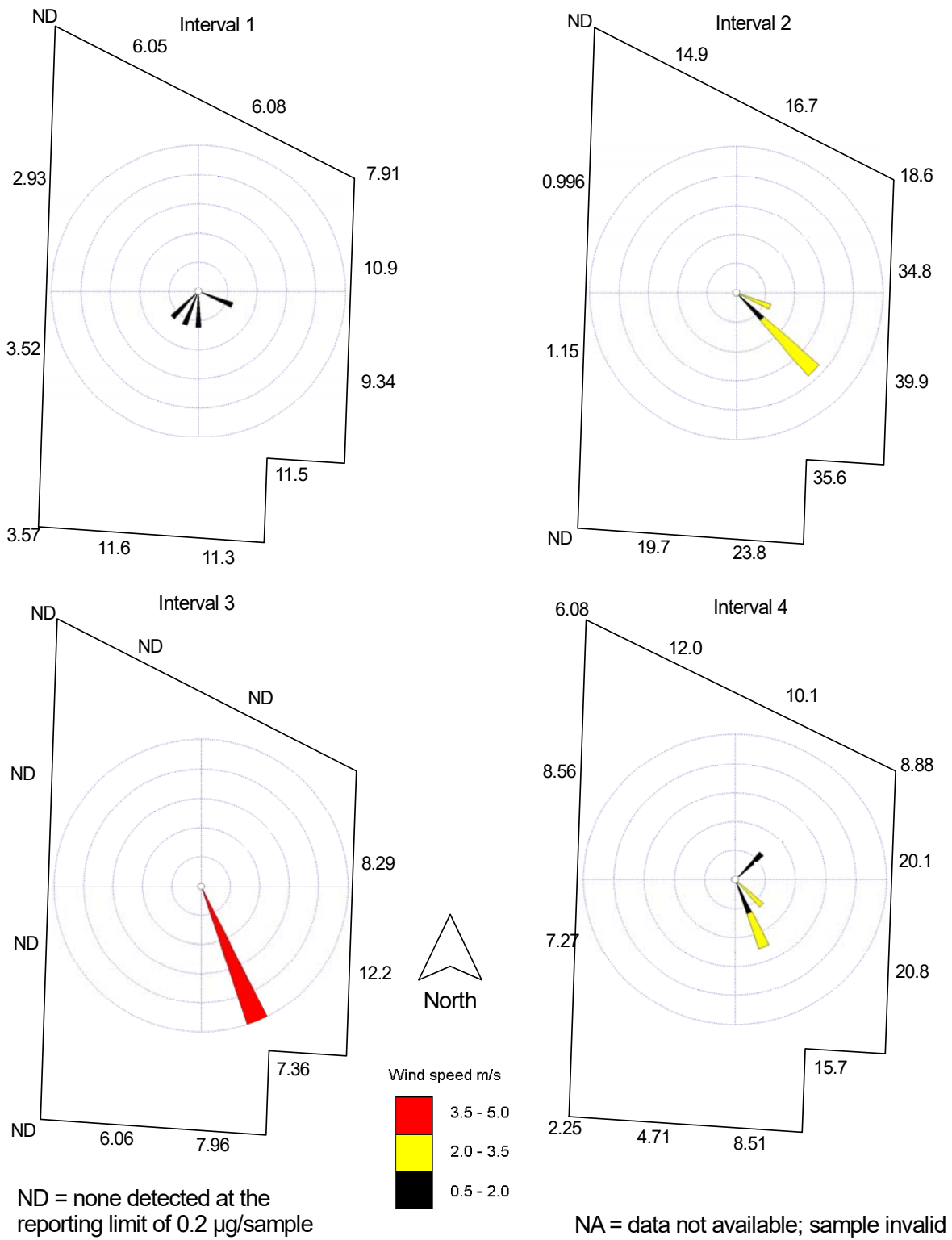
Figure 6. Wind rose and monitoring results (μg/m^3) for treatment 1, intervals 1-4.
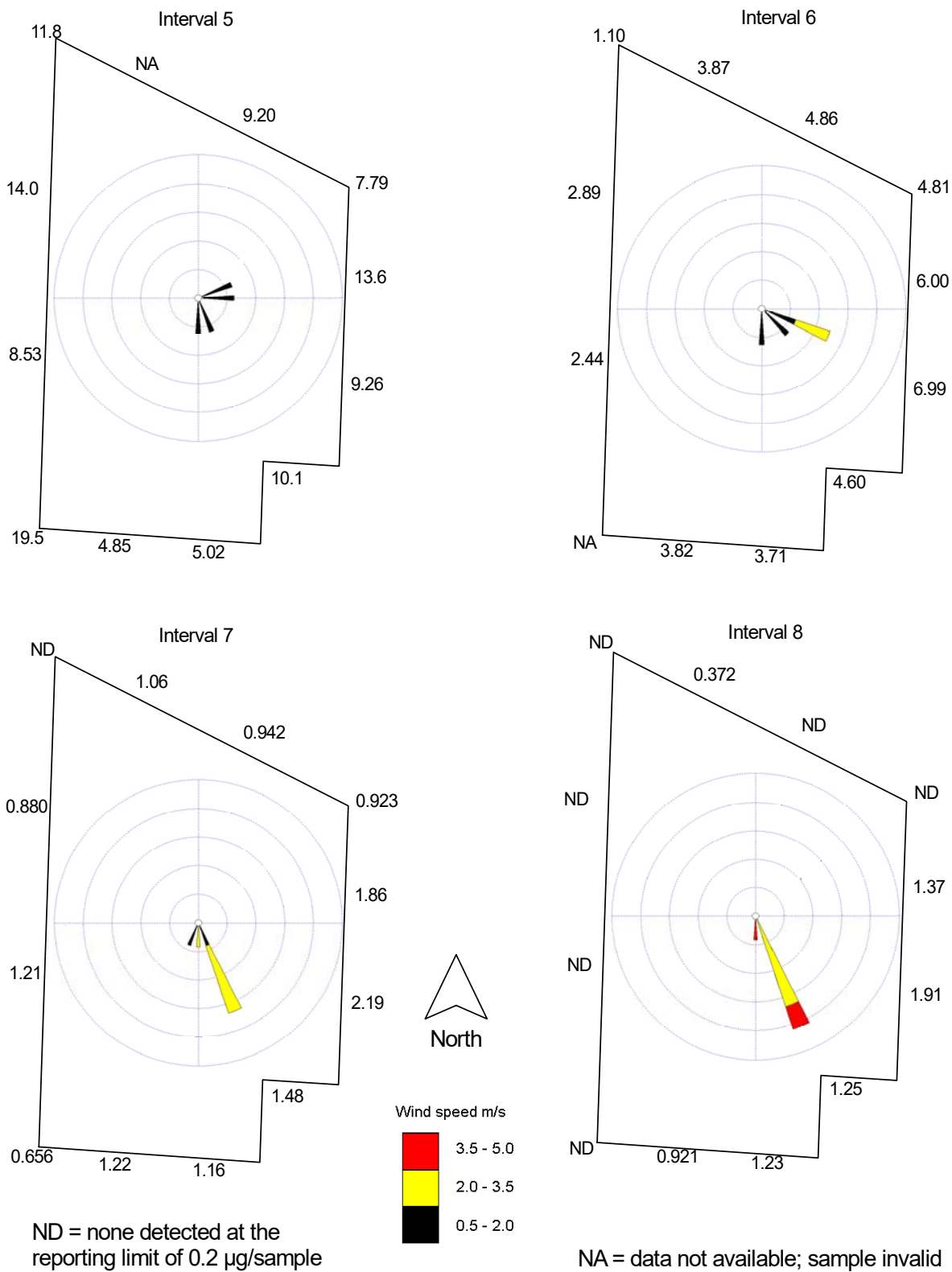
Figure 7. Wind rose and monitoring results ($\mu g/m^3$) for treatment 1, intervals 5-8.

Figure 8. Wind rose and monitoring results (μg/m^3) for treatment 1, intervals 9-12.

Interval 13

0.766
1.13
1.30
NA
1.07
1.39
0.377
1.09
ND   ND   ND
0.757

Interval 14

0.886
1.31
1.27
1.33
0.937
1.03
1.02
1.00
0.723   0.821   0.859
1.05

North

Wind speed m/s

3.5 - 5.0
2.0 - 3.5
0.5 - 2.0

ND = none detected at the
reporting limit of 0.2 μg/sample

NA = data not available; sample invalid

Figure 9. Wind rose and monitoring results (μg/m^3) for treatment 1, intervals 13-14.

Interval 1

9.90
19.9
19.6
14.5
13.5
16.2
13.6
20.9
13.7
2.75   7.15   7.69

Interval 2

2.73
45.6
45.0
4.74
49.3
49.4
3.56
37.0
26.8
ND   1.06   1.32

Interval 3

1.63
20.8
NA
2.22
25.5
28.4
0.949
34.4
18.3
ND   2.58   3.80

North

Wind speed m/s

3.5 - 5.0
2.0 - 3.5
0.5 - 2.0

Interval 4

ND
1.35
1.47
ND
3.05
7.50
ND
13.1
7.20
ND   4.47   5.06

ND = none detected at the
reporting limit of 0.2 µg/sample

NA = data not available; sample invalid

Figure 10. Wind rose and monitoring results (µg/m³) for treatment 2, intervals 1-4.
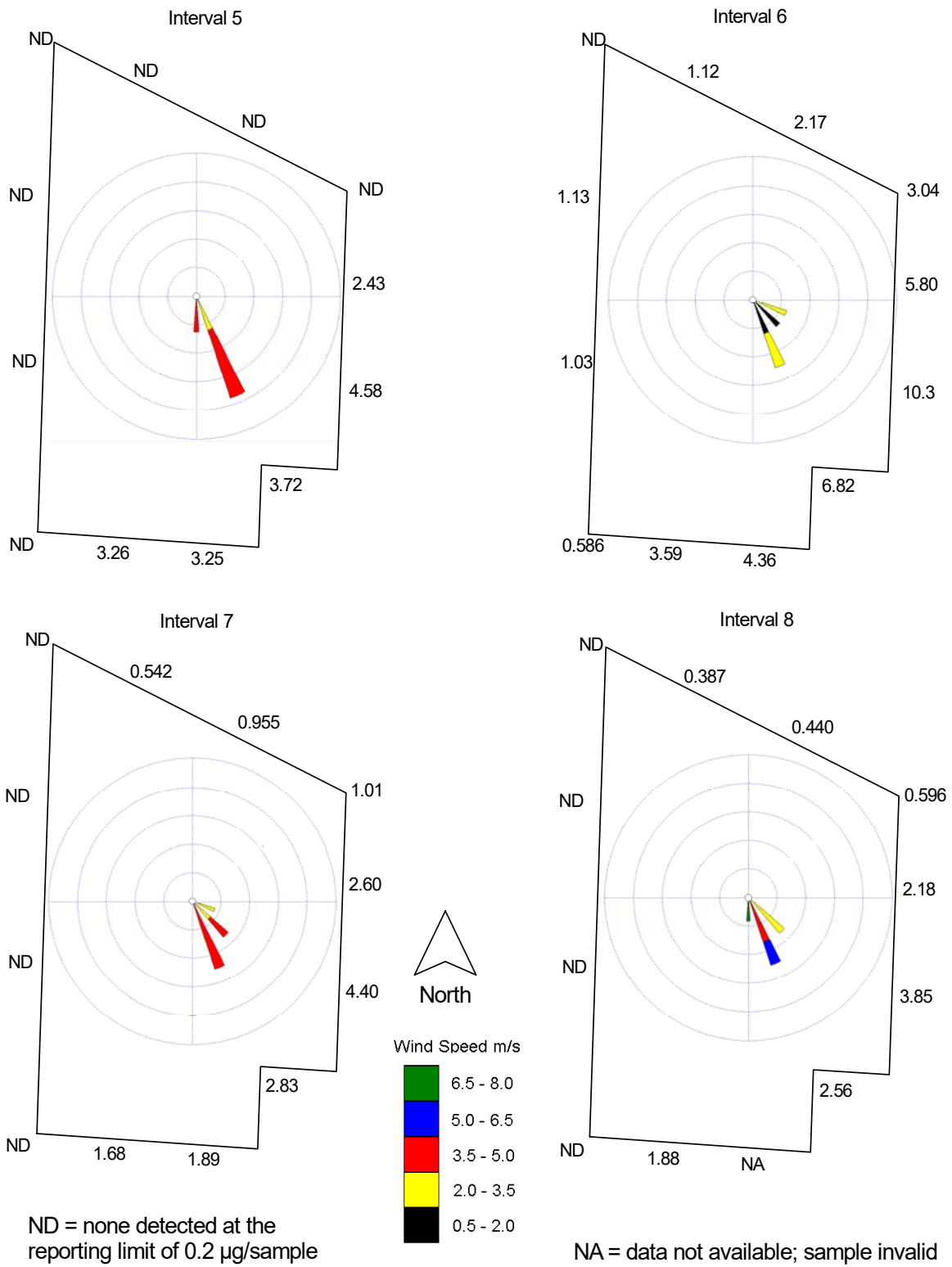
16

Figure 11. Wind rose and monitoring results (µg/m³) for treatment 2, intervals 5-8.

Interval 9

ND

ND

ND

ND

ND

ND

0.955

ND

1.39

1.23

ND

1.41

1.30

Interval 10

ND

ND

NA

ND

ND

0.721

ND

1.09

0.882

NA

0.796

NA

Interval 11

ND

ND

ND

ND

ND

0.530

ND

0.848

0.630

ND

0.448

0.490

ND = none detected at the
reporting limit of 0.2 µg/sample

Interval 12

ND

ND

ND

ND

ND

0.719

ND

1.08

0.799

ND

0.516

0.613

North

Wind Speed m/s

▮	> 8.0
▮	6.5 - 8.0
▮	5.0 - 6.5
▮	3.5 - 5.0
▮	2.0 - 3.5
▮	0.5- 2.0

NA = data not available; sample invalid
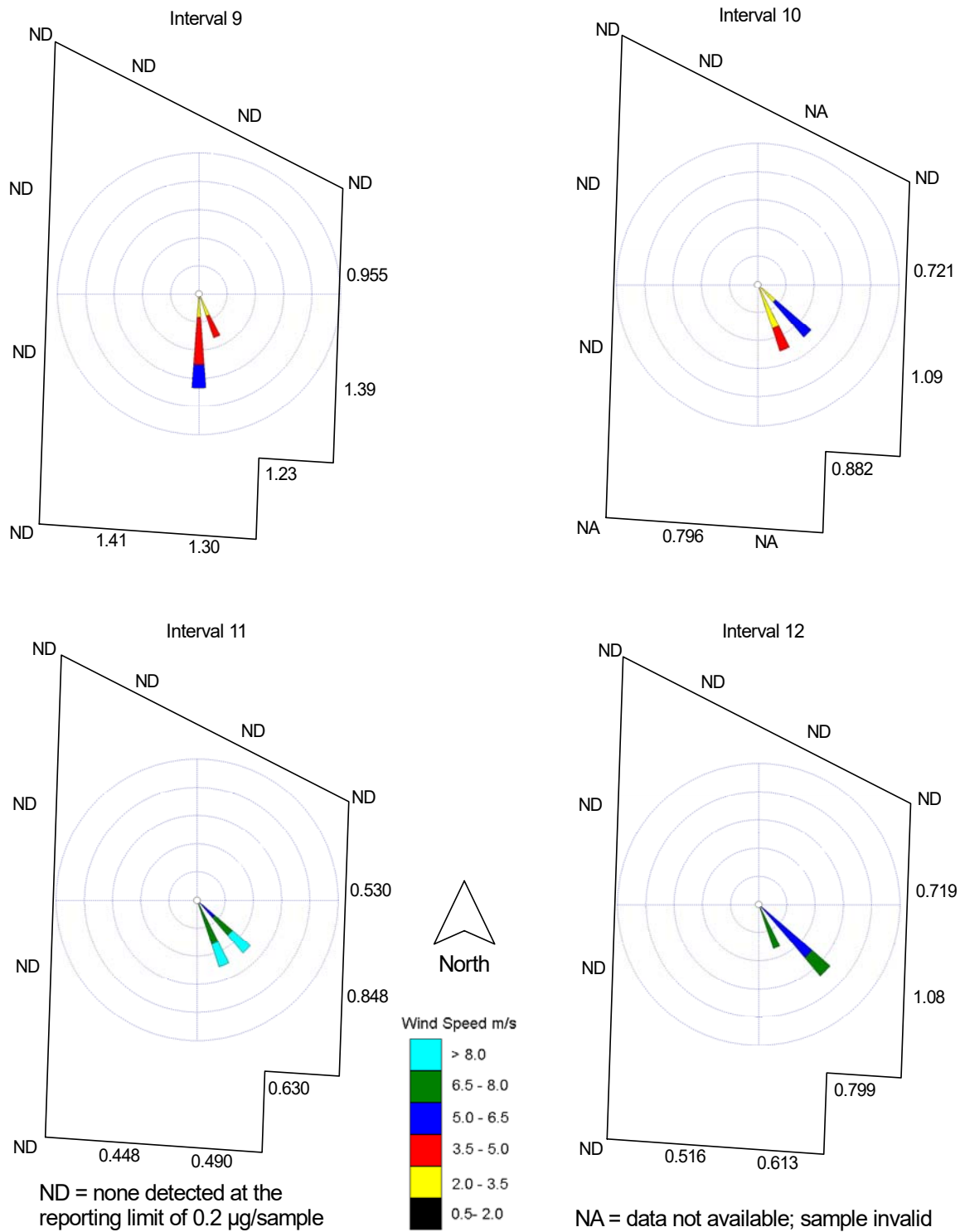
Figure 12. Wind rose and monitoring results ($\mu g/m^3$) for treatment 2, intervals 9-12.

Figure 13. Wind rose and monitoring results (µg/m³) for treatment 2, intervals 13-14.

Modeling

Modeling of air concentrations measured during the treatments was utilized to estimate the flux associated with this method of metam-sodium application. Modeling was done using the Industrial Source Complex Short Term Dispersion Model (ISCST3) (US EPA, 1995, 2002) together with the standard back calculation procedure (Johnson, *et al*, 1999). The application was represented as a polygon source (Table 8) with an initial emission rate of 100 ug/m²s at ground level. The weather data measured near the field with the Met1® weather station was processed for use in the ISCST3 model. The processed wea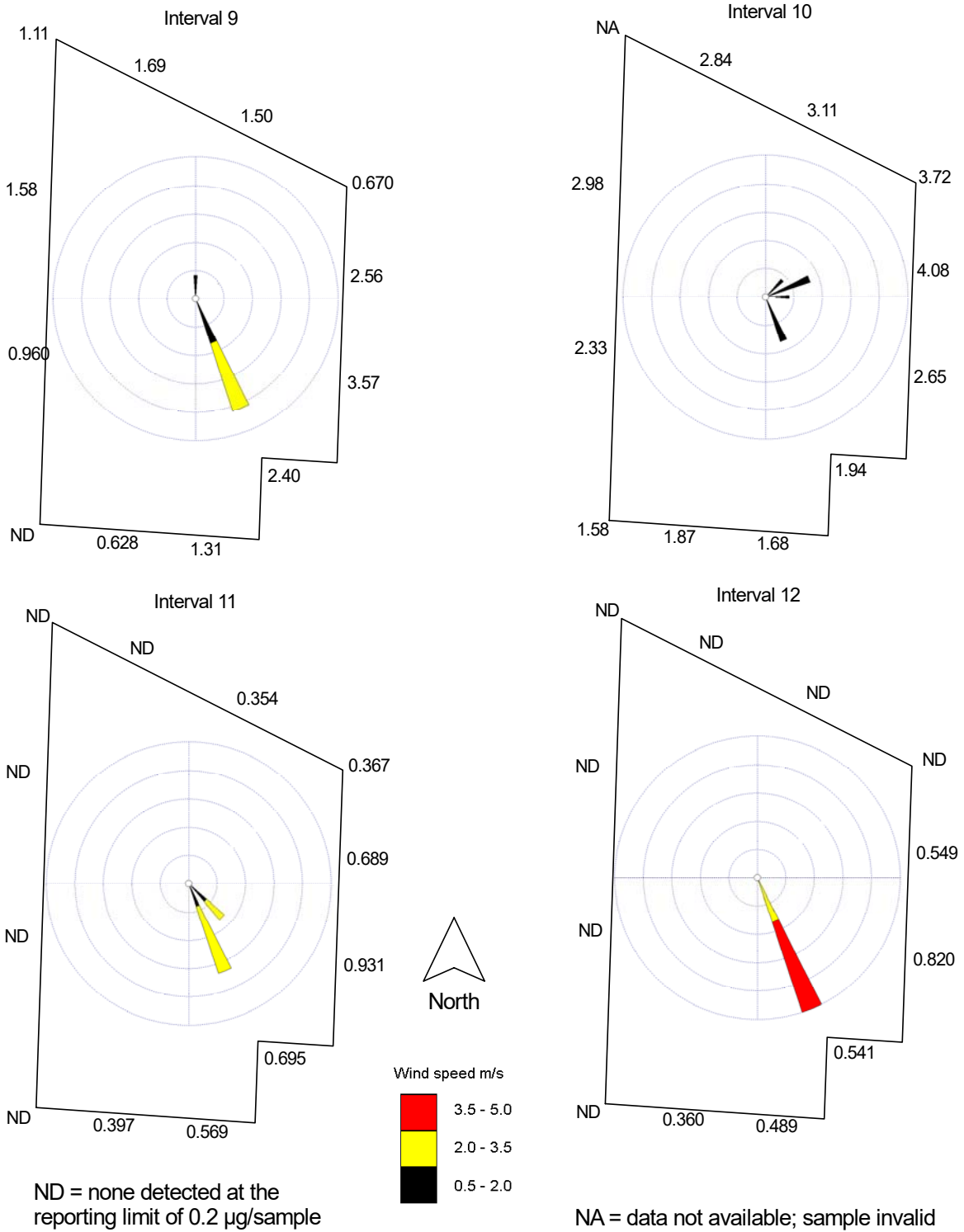ther data and examples of control files are found in Appendix C. Table 9 gives the x and y coordinates used for sampler locations in the model. Modeling was conducted for both treatments in similar fashion with sampler location coordinates and weather data adjusted for each treatment. Regression analysis was then performed on the modeled (x-axis) and measured (y-axis) values (Johnson, *et al*, 1999). The regression results for the monitored treatments are listed in Tables 10 and 12. For treatment 1, six of the 14 sampling intervals had significant regressions; for treatment 2 one interval was not significant. For those sampling intervals without significant regressions, the measured and modeled values were sorted and the regression was redone (sorted intervals are noted with an asterisk). 24-hour time weighted average (TWA) flux was determined using the following formula:

$$24\text{-hour TWA} = \sum_{i=1}^{n} \frac{(\text{flux index}_i)(\text{interval duration}_i)}{24}$$

where:
flux index = regression slope x 100 (the initial emission rate)
interval durations = hours
$i = 1,\ldots,n$ sampling intervals to obtain a full 24 hours

The interval fluxes, cumulative fluxes, and 24-hour TWA fluxes are listed in Tables 11 and 13. For both treatments the second sampling intervals had the highest flux, which correlates to the highest detected MITC concentrations (Table 4). The high flux for treatment 2 was about half of the high flux for treatment 1. For both treatments, at interval 4 the flux dropped significantly and was relatively low for the rest of the sampling time except for a slight increase during interval eight. Overall the 24-hour TWA flux for each treatment decreased over the three days that were monitored for each application. Figures 14 and 15 display the maximum and average MITC concentrations and flux for treatments 1 and 2, respectively. Figure 16 displays standardized interval fluxes for treatments 1 and 2. Standardization was conducted by multiplying the treatment 1 interval fluxes by a factor 1.24, the multiplier of the effective application rates for the two treatments. It is difficult to conclude what effect the intermittent watering in had on the flux of treatment 2 since, in addition to the application rate difference, the wind speeds for intervals 4 and 5 during treatment 2 were higher than during treatment 1. Higher wind speeds will decrease air concentrations for the same flux but can also increase flux due to removal of mass from the soil surface at a more rapid rate. Based on the maximum concentrations displayed Figures 14 and 15, it appears that the watering in has some damping effect on air concentrations.

Table 8. Polygon vertices of the field used for modeling both treatments.

vertices	x-coord	y-coord
1	0.0	0.0
2	122.2	-8.6
3	123.8	37.2
4	165.8	34.4
5	171.2	188.9
6	9.1	271.5

Table 9. X and Y coordinates of sampler locations used for modeling the first treatment monitored.

sampler	1st Treatment		2nd Treatment	
	x-coord	y-coord	x-coord	y-coord
1	-5.1	-5.7	-5.1	-5.7
2	39.9	-7.4	39.9	-7.4
3	80.9	-10.4	80.9	-10.4
4	127.7	32.3	127.7	32.3
5	174.1	86.3	173.4	86.3
6	175.6	137.5	174.9	137.5
7	176.4	191.6	176.5	191.6
8	119.7	220.7	119.7	220.7
9	67.2	248.5	67.2	248.5
10	0.4	273.2	-0.3	273.2
11	-1.3	186.7	-2.0	186.7
12	-4.2	94.4	-4.9	94.4

Table 10. Regression results for treatment 1.

Sampling interval	Duration	Slope	R^2	F test p-value
1*	4	0.00358	0.896	<0.001
2	4	0.0394	0.849	<0.001
3	4	0.0115	0.697	<0.001
4	4	0.00412	0.502	9.93E-03
5*	4	0.00316	0.883	<0.001
6*	4	0.00111	0.766	<0.001
7*	6	0.000593	0.764	<0.001
8	6	0.00165	0.542	6.30E-03
9*	6	0.00105	0.908	<0.001
10*	6	0.000596	0.929	<0.001
11	6	0.000391	0.661	1.31E-03
12	6	0.000693	0.645	1.65E-03
13*	6	0.000953	0.924	<0.001
14*	6	0.000163	0.868	<0.001

* indicates that values for slope, R^2, and F test p-value are from regressions on sorted modeled and measured values

Table 11. Interval flux, cumulative flux and 24-hour time weighted average flux for treatment 1.

Sampling Interval	Duration (hrs)	Time of day	Flux ($\mu g/m^2 s$)	Cumulative flux ($\mu g/m^2 s$)	24-hr TWA flux ($\mu g/m^2 s$)
1 (4)	4	day	0.358	0.358	
2 (8)	4	day	3.94	2.15	
3 (12)	4	day	1.15	1.82	
4 (16)	4	night	0.412	1.47	
5 (20)	4	night	0.316	1.24	
6 (24)	4	night	0.111	1.05	1.05
7 (30)	6	day	0.0593	0.851	
8 (36)	6	day	0.165	0.737	
9 (42)	6	night	0.105	0.647	
10 (48)	6	night	0.0596	0.573	0.0973
11 (54)	6	day	0.0391	0.514	
12 (60)	6	day	0.0693	0.469	
13 (66)	6	night	0.0953	0.435	
14 (72)	6	night	0.0163	0.400	0.0550

( ) = hours after start of application

Figure 14. Maximum and average MITC concentrations ($\mu g/m^3$) and flux ($\mu g/m^2 s$) for treatment 1.

Table 12. Regression results for treatment 2.
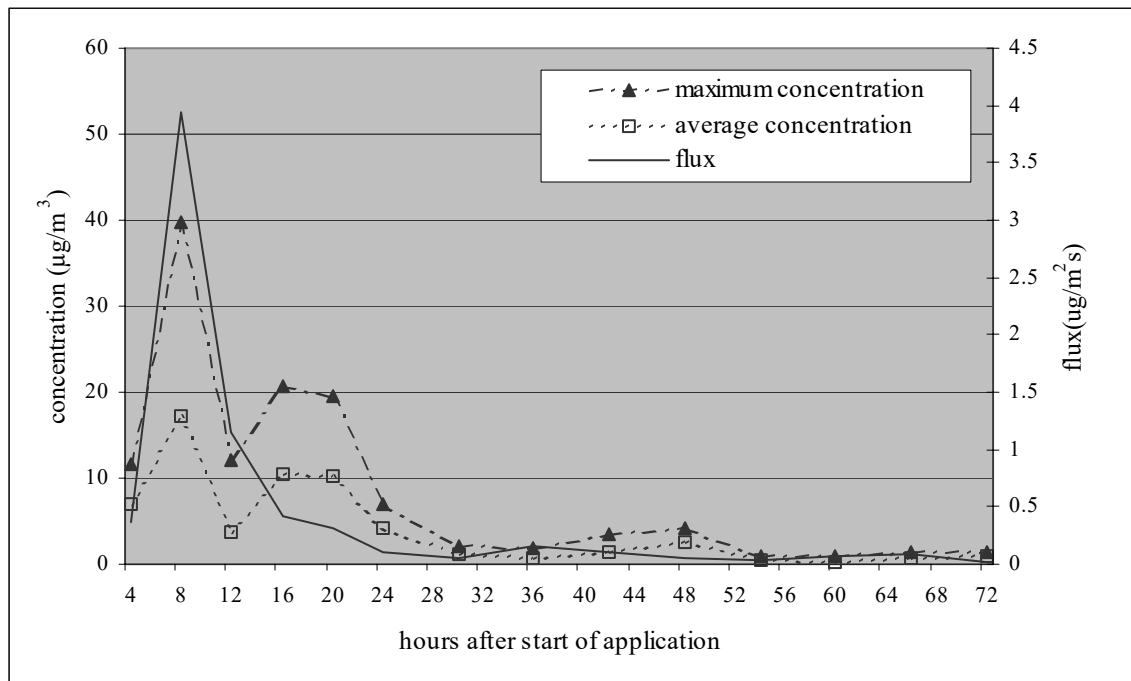
Sampling interval	Duration (hrs)	Slope	R^2	F test p-value
1*	4	0.00371	0.842	<0.001
2	4	0.0212	0.981	<0.001
3	4	0.00775	0.929	<0.001
4	4	0.00302	0.820	<0.001
5	4	0.00124	0.794	<0.001
6	4	0.00102	0.841	<0.001
7	6	0.00166	0.859	<0.001
8	6	0.00274	0.743	<0.001
9	6	0.000526	0.785	<0.001
10	6	0.000461	0.891	<0.001
11	6	0.000805	0.941	<0.001
12	6	0.000950	0.948	<0.001
13	6	0.000388	0.804	<0.001
14	6	0.000260	0.705	1.22E-03

* indicates that values for slope, R^2, and F test p-value are from regressions on sorted modeled and measures values

Table 13. Interval flux, cumulative flux and 24-hour time weighted average flux for treatment 2.

Sampling Interval	Duration (hrs)	Time of day	Flux ($\mu g/m^2 s$)	Cumulative Flux ($\mu g/m^2 s$)	24-hr TWA flux ($\mu g/m^2 s$)
1 (4)	4	day	0.371	0.371	
2 (8)	4	day	2.12	1.25	
3 (12)	4	day	0.775	1.09	
4 (16)	4	night	0.302	0.8924	
5 (20)	4	night	0.124	0.739	
6 (24)	4	night	0.102	0.633	0.633
7 (30)	6	day	0.166	0.539	
8 (36)	6	day	0.274	0.495	
9 (42)	6	night	0.0526	0.432	
10 (48)	6	night	0.0461	0.384	0.135
11 (54)	6	day	0.0805	0.350	
12 (60)	6	day	0.0950	0.324	
13 (66)	6	night	0.0388	0.298	
14 (72)	6	night	0.0260	0.276	0.0601

( ) = hours after start of application

Figure 15. Maximum and average MITC concentrations ($\mu g/m^3$) and flux ($\mu g/m^2 s$) for treatment 2.
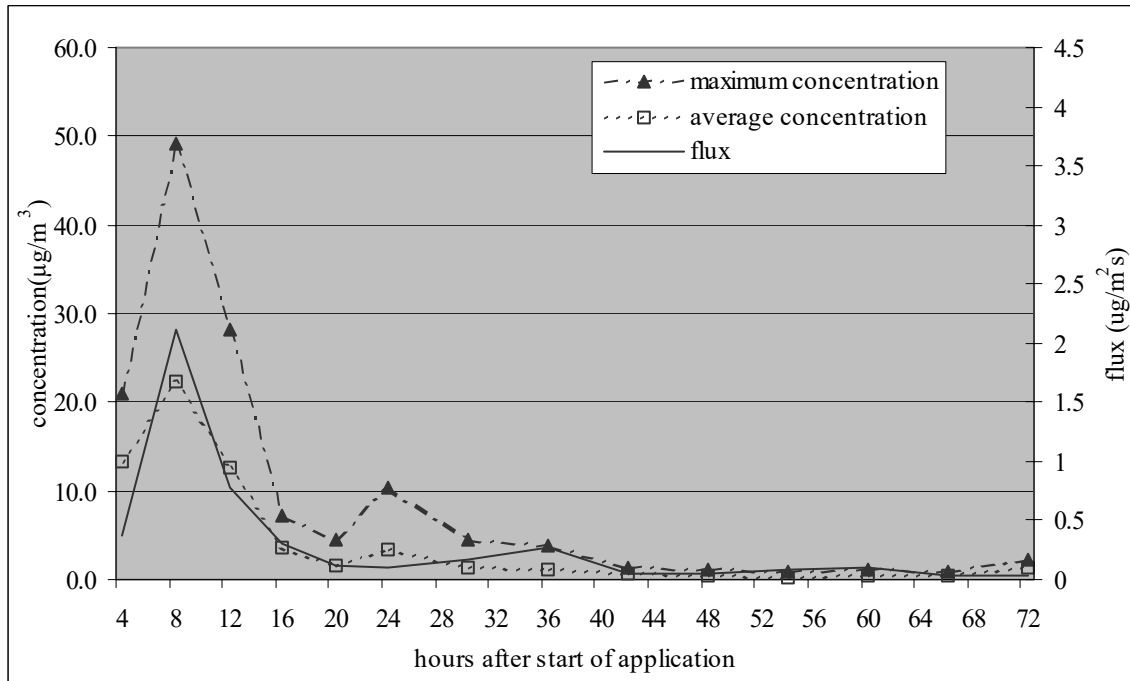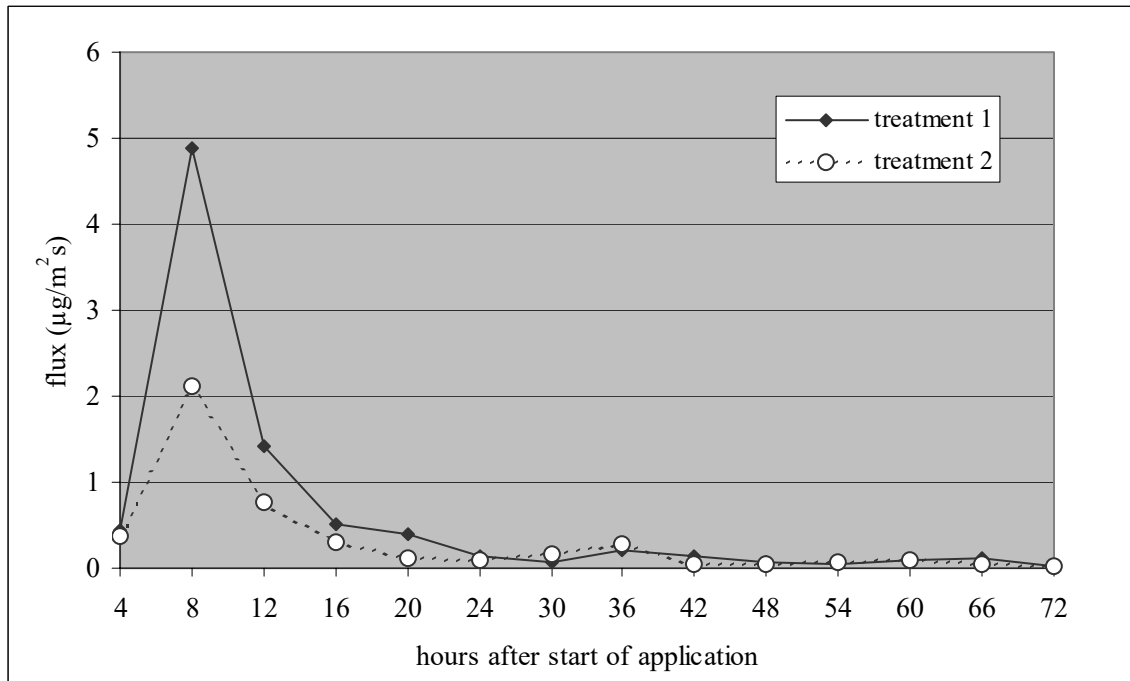

Figure 16. Interval fluxes ($\mu g/m^2 s$) for treatments 1 and 2 (treatment 1 flux standardized for application rate).

MITC Emission Calculations

Calculations were done based on the effective application rate of MITC and the flux from Tables 10 and 12 to determine the percentage of MITC that was released during each interval, cumulative, and for each 24-hour period (see calculation following). The emission percentage is calculated as:

$$= \frac{[\text{flux } (\mu g/m^2 s) \div 1000000] \times [\text{time}]}{\text{effective application rate } (g \text{ MITC}/m^2)} \times 100$$

where time is the duration (seconds) of the flux estimate interval.

Tables 14 and 15 display the sampling interval emissions, cumulative emissions, and 24-hour emissions for treatments 1 and 2, respectively, as a percent of total MITC applied. Figure 17 displays the cumulative emissions and 24-hour emissions (as percent of total MITC applied) for treatments 1 and 2. The emissions from treatment 2 were about half of that of treatment one, which coincides with the difference in maximum fluxes for the two treatments (see Figure 16), despite the higher effective application rate for treatment 2.

Treatment 1: untarped bed drip chemigation
Application rate: 84.5 gallons of product in 66,300 gallons of water
Active ingredient: 4.22 lbs/gal

Therefore: 84.5 gal x 4.22 lbs/gal= 356.6 lbs a.i.

Gross area: 9.13 acres = 36940.7 m^2

Molecular weight of metam-sodium = 128.2
Molecular weight of MITC = 73.1

Moles metam-sodium applied = 356.6 lbs x 453.6 g/lb = 161,749.2 g
                                      161,749.2 g ÷ 128.2 m.w. = 1262.3 moles

Total MITC applied = 1262.3 moles x 73.1 m.w. = 92,274.1 g MITC
Effective application rate = 92,274.1 g MITC ÷ 36940.7 m^2 = 2.50 g MITC/m^2

Table 14. Sampling interval emissions, cumulative emissions, and 24-hour emissions for Treatment 1 (% of MITC applied).

Sampling interval	Flux ($\mu g/m^2 s$)	Emission (%)	Cumulative emission (%)	Emission per 24-hours (%)
1 (4)	0.358	0.206	0.206	
2 (8)	3.94	2.27	2.48	
3 (12)	1.15	0.665	3.14	
4 (16)	0.412	0.237	3.38	
5 (20)	0.316	0.182	3.56	
6 (24)	0.111	0.0639	3.63	3.62
7 (30)	0.0593	0.0512	3.68	
8 (36)	0.165	0.143	3.82	
9 (42)	0.105	0.0906	3.91	
10 (48)	0.0596	0.0515	3.96	0.337
11 (54)	0.0391	0.0338	4.00	
12 (60)	0.0693	0.0599	4.06	
13 (66)	0.0953	0.0824	4.14	
14 (72)	0.0163	0.0141	4.15	0.190

( ) = hours after start of application

Treatment 2: intermittent watering-in untarped bed drip chemigation
Application rate: 105 gallons of product in 72,675 gallons of water
Active ingredient: 4.22 lbs/gal

Therefore: 105 gal x 4.22 lbs/gal= 443.1 lbs a.i.

Moles metam-sodium applied = 443.1 lbs x 453.6 g/lb = 200,990.2 g
$\qquad$ 200,990.2 g ÷ 128.2 m.w. = 1567.8 moles

Total MITC applied = 1567.8 moles x 73.1 m.w. = 114,605.2 g MITC
Effective application rate = 114,605.2 g MITC ÷ 36940.7 m^2 = 3.10 g MITC/m^2

Table 15. Sampling interval emissions, cumulative emissions, and 24-hour emissions for Treatment 2 (% of MITC applied).

Sampling interval	Flux ($\mu g/m^2 s$)	Emission (%)	Cumulative emission (%)	Emission per 24-hours (%)
1 (4)	0.371	0.172	0.172	
2 (8)	2.12	0.985	1.16	
3 (12)	0.775	0.360	1.52	
4 (16)	0.302	0.140	1.66	
5 (20)	0.124	0.0575	1.71	
6 (24)	0.102	0.0475	1.76	1.76
7 (30)	0.166	0.116	1.88	
8 (36)	0.274	0.191	2.07	
9 (42)	0.0526	0.0366	2.10	
10 (48)	0.0461	0.0321	2.14	0.375
11 (54)	0.0805	0.0560	2.19	
12 (60)	0.0950	0.0661	2.26	
13 (66)	0.0388	0.0270	2.29	
14 (72)	0.0260	0.0181	2.30	0.167

( ) = hours after start of application

Figure 17. Cumulative emissions and 24-hour emissions (as percent of total MITC applied) for treatments 1 and 2.
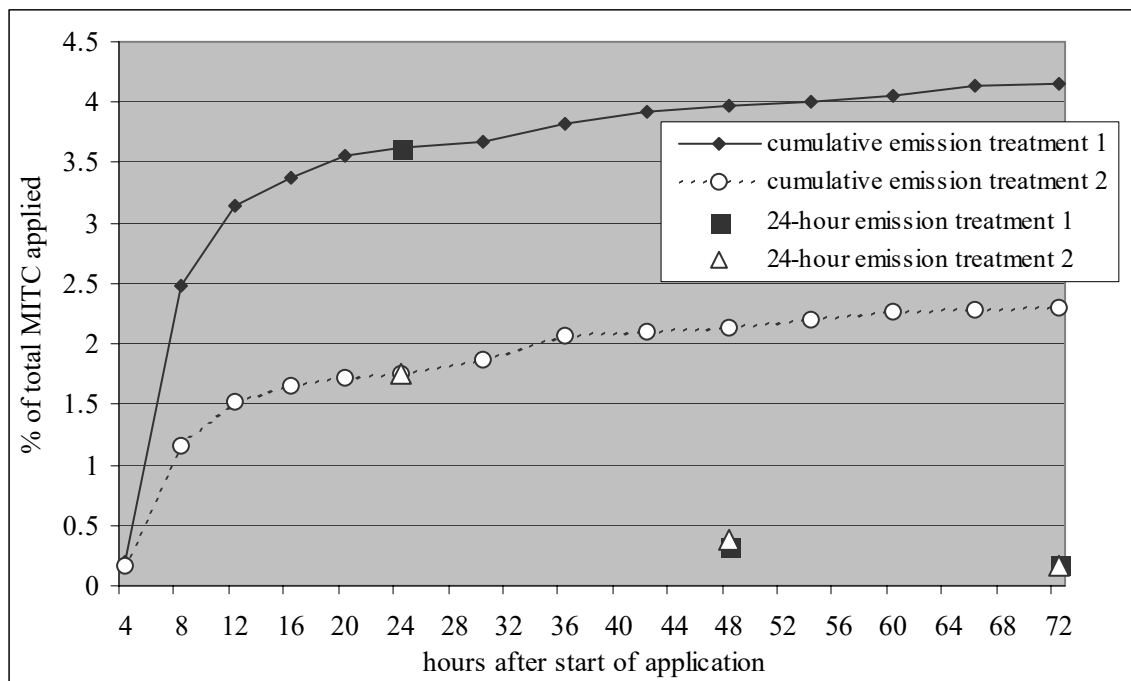
Comparison of MITC Flux rates for various application methods

The back calculation process has been used to determine the flux of several metam sodium application methods (Barry, 2004; Li, 2004). Table 16 displays standardized 4-hour flux estimates for six application types: standard shank, standard sprinkler, intermittent watering-in shank, intermittent watering-in sprinkler, untarped bed drip chemigation, and intermittent watering-in untarped bed drip chemigation. 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 but are the critical flux estimates, meaning that these represent the flux estimates for the period that would require the largest buffer zone. These critical periods are most often at night because of the tendency for stable atmospheric conditions accompanied with a surface based inversion condition (Barry, 2004). 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 standardized 4-hour flux estimates for the untarped bedded drip applications were substantially smaller than those for the shank and sprinkler applications. Figure 18 displays the emission percentage of total MITC applied for these application types. Although it appears that for the three application types emission percentages and flux estimates were reduced when intermittent watering-in was introduced, it cannot be certain for the untarped bed drip chemigation since the flux presented occurred prior to watering-in.

Table 17 displays the standardized 12-hour TWA flux estimates for the tarped and untarped drip chemigation applications. Only a 12-hour flux estimate is available for the tarped bed drip chemigation application so all comparisons must be done for this length of time. Since 12-hour TWA flux estimates are not available for the standard shank, standard sprinkler, intermittent watering-in shank, and intermittent watering-in sprinkler application methods, these flux estimates cannot be compared. The standardized 12-hour flux estimates for the tarped bed drip chemigation and intermittent watering-in untarped bed drip chemigation are comparable and are less than half of that of the untarped bed drip chemigation. Figure 19 displays a similar pattern in the emission percentages for these application types.

Table 16. Standardized 4-hour TWA flux ($\mu g/m^2 s$) for different metam sodium applications.

Application type	4-hour TWA flux ($\mu g/m^2 s$)	Time of day	Effective broadcast application rate of MITC (g/m^2)	Standardization multiplier	Standardized 4-hour TWA flux ($\mu g/m^2 s$)	Emission %
Standard shank*	34.0	night	9.64	2.002	68.1	5.08
Standard sprinkler*	74.0	night	19.3	1	74.0	3.85
Intermittent watering-in shank*	25.8	day	9.64	2.002	51.6	5.52
Intermittent watering-in sprinkler*	43.6	night	19.3	1	43.6	3.25
Untarped bed drip chemigation	3.94	day	2.50	7.72	30.4	2.27
Intermittent watering-in untarped bed drip chemigation	2.12	day	3.10	6.226	13.2	0.985

* Data are critical flux estimates from Barry, 2004.

Table 17. Standardized 12-hour TWA flux ($\mu g/m^2 s$) for different metam sodium applications.

Application type	12-hour TWA flux ($\mu g/m^2 s$)	Time of day	Effective broadcast application rate of MITC (g/m^2)	Standardization multiplier	Standardized 12-hour TWA flux ($\mu g/m^2 s$)	Emission %
Tarped bed drip chemigation*	4.30	day	15.2	1	4.30	1.22
Untarped bed drip chemigation	1.82	day	2.50	6.08	11.1	3.14
Intermittent watering-in untarped bed drip chemigation	1.09	day	3.10	4.903	5.34	1.52

* Data from Li, 2004.

Figure 18. Percent of total MITC applied emitted using the 4- hour TWA flux.
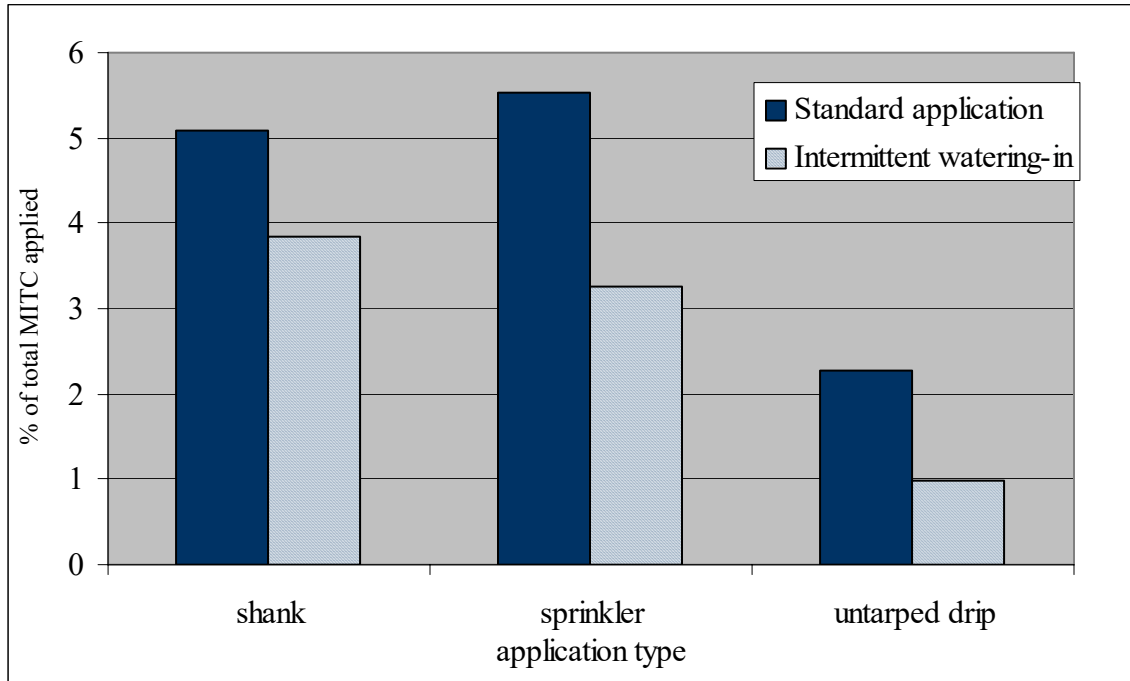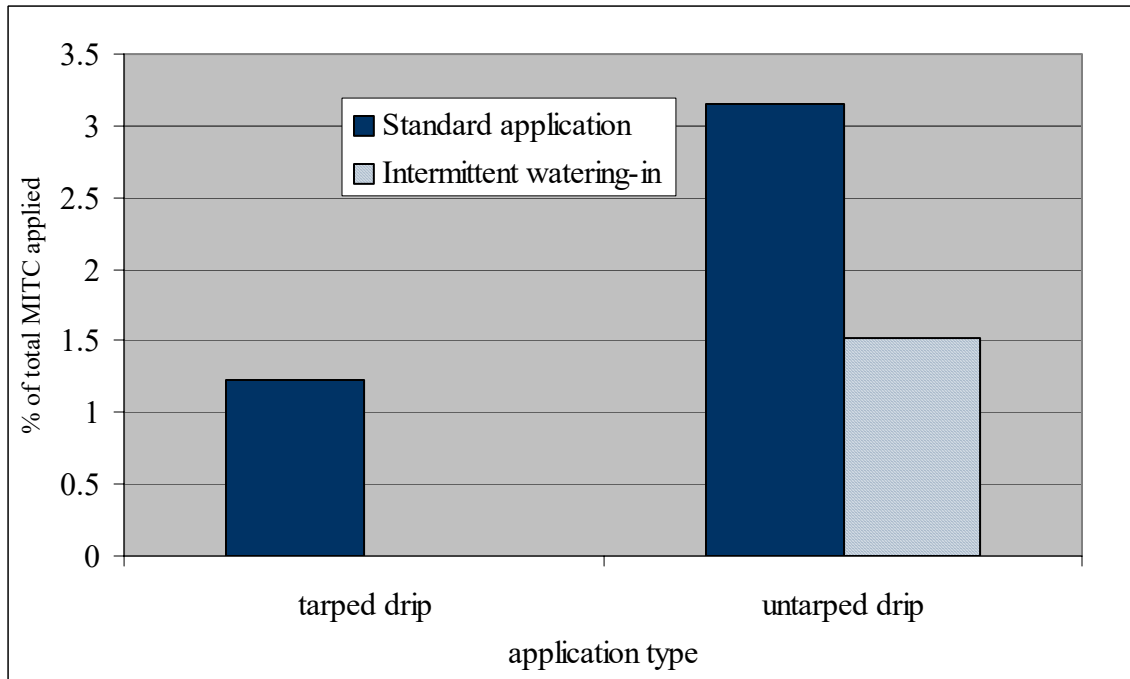

Figure 19. Percent of total MITC applied emitted using the 12-hour TWA flux; no intermittent watering-in information for the tarped drip application was examined for comparison.

Discussion

The objective of this study was to estimate the flux associated with the untarped bedded drip application without (treatment 1) and with (treatment 2) intermittent watering-in, characterize the flux profile during the monitoring period, and estimate the fractional mass loss during the first 24 and 48 hours. In general, the flux estimates for the second treatment were lower than those for the first treatment. It is difficult to compare the two treatments and conclude what effect the intermittent watering-in had on the flux of treatment 2 since, in addition to there being a higher application rate for treatment 2, the wind speeds for intervals 4 and 5 during treatment 2 were much higher than during treatment 1. Higher wind speeds will decrease air concentrations for the same flux but can also increase flux due to removal of mass from the soil surface at a more rapid rate. Based on the maximum concentrations it appears that the watering-in has some damping effect on air concentrations. When flux was standardized for application rate the flux profile for treatment 2 was about half of that for treatment 1 during the first 12 hours. The fractional mass loss was 3.62 and 0.337% for treatment 1 and 1.76 and 0.375% for treatment 2 for the first and second 24-hour periods following application, respectively.

When flux estimates standardized for application rates were compared with those for shank and sprinkler applications, the untarped bedded drip application flux estimates were substantially lower. Even though the flux estimates used for comparison were from a sampling interval prior to watering-in, the decrease in flux estimate and in the percent of MITC emitted followed a similar pattern to those seen for the shank and sprinkler applications with and without watering-in.

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