Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

MEMORANDUM

Arnold Schwarzenegger
Governor

TO: Randy Segawa, Senior Environmental Research Scientist
Environmental Monitoring Branch

FROM: Bruce Johnson, Ph.D., Senior Environmental Research Scientist *Original signed by*
Terrell Barry, Ph.D., Senior Environmental Research Scientist *Original signed by*
Environmental Monitoring Branch
(916) 324-4140

DATE: October 3, 2005

SUBJECT: ESTIMATION OF METHYL BROMIDE FLUX FOR SIEMER STUDIES TC199.1 AND F1.1 AND USE OF STANDARD WEATHER CONDITIONS

Summary

Two field studies were utilized to establish permit conditions for methyl bromide (MeBr), which are protective at an acceptable 24 hour acute exposure of 815 µg/m^3 (210 ppb). The first field study was used to estimate an average flux for the 24 hour period showing the highest air concentrations. The result was a calibrated flux of 100µg/m^2-s. A buffer zone limit for 400 lb/acre application to a 20 acre field was established by simulating constant average wind conditions consisting of stability class C and speed of 1.4 meters per second. The resulting buffer zone was 180 meters or 591 feet. The adequacy of this buffer zone limit was tested by comparison to field monitoring results from the second field study. It was found to be adequate.

Introduction

The Department of Pesticide Regulation's preliminary risk characterization of MeBr indicates that an inadequate margin of safety exists for agricultural field fumigations (Nelson 1992). Field monitoring and computer simulation are being used to develop permit conditions that increase the margin of safety for off-site exposure. This memorandum discusses the derivation of the permit conditions for soil fumigations where MeBr is shanked-in and covered with a tarp. This analysis was originally conducted in 1992. This memorandum finalizes that analysis as it was originally conducted.

Two field studies (Siemer studies TC199.1 and F1.1) and a computer simulation model Industrial Source Complex, Short Term model (ISCST) version 90346, were used to develop the permit conditions. ISCST model is an atmospheric dispersion model capable of simulating area sources, including agricultural fields (Wagner 1987). The monitoring and ISCST data were used to derive an estimate of the width of a required buffer zone from the edge of an agricultural field that has been fumigated with MeBr. The buffer zone would be used to assure that persons off-site not be exposed to excessive concentrations of MeBr.

Part I: Evaluation of flux rate based on field studies

Methods Field 1 (TC199.1)

The procedure for estimating buffer zones consisted of estimating the highest 24 hour period flux by fitting the ISCST model to the measured off-site air concentrations. After estimating the highest 24 hour flux, screening level constant meteorological conditions were then simulated to determine the buffer zone distance.

Description of field measurements. MeBr was applied under the following conditions:

Application Rate: 400 lbs AI/ac (44.8g/m^2)
Area Treated: 20 ac
Injection Depth: 10 in
Injection Type: Noble Plow
Tarp Type: Dow High Barrier
Location: Wasco, California
Application Date: June 30, 1992

The field was square and air samplers were located at 50ft, 150ft, 300ft, 600ft, and 1000ft in 4 cardinal directions from the field (Figure 1). Meteorological data consisted of 4 to 6 hour periods of average wind speed with a percentage of the time that the wind blew in each direction (Table 1). Charcoal tube samplers measured MeBr concentrations for 6 days following application. Time weighted average air concentrations for 24 hour periods are summarized in Table 2.

The highest air concentrations were recorded on the first day following application, sampling periods 1-6 in Table 1 (6/30/92 and 7/1/92). Therefore this period of time was simulated with the ISCST model. The field was represented in the model as a 20 acre square (285m x 285m). In order to model it properly, the field was divided into 25 57m x 57m units, each of which was a source. Modeled receptors were located offsite at 50, 150, 300, 600, and 1000 feet (15, 46, 91, 182, and 304 m) from the field edge in four cardinal directions, corresponding to the actual field monitoring locations.

The initial estimate for a flux from the field was calculated by assuming that 90% of the applied material volatilized from the field during the first 4 days. This assumption was based on an earlier study in which integrated off-site concentrations reached 90% after 4 days of the total integrated concentration (Seiber et al. 1987). The application rate of 400 lbs/acre was equivalent to 44.8 g/m^2. Dividing this rate by 4 days of time and multiplying by 0.9 yielded 117μgm^{-2}s^{-1}. This flux was used in the initial modeling.

To calibrate the flux in the initial modeling, model runs were made for six 4 hour periods, corresponding to the weather information (Table 1). A 24 hour average was composited from each of the six model estimates at each receptor. The model-predicted 24 hour averages were then regressed on the measured 24 hour averages and a correction factor derived for correcting the flux in order to match the measured air concentrations more closely. The north transect values were excluded from the regression because of sampling problems (Segawa, personal communication).

After calibrating the flux to the measured data, a final model run was made using 24 hour average wind speed 1.4 meters/s, an average wind direction of blowing toward the south east, and an average stability class of C. In addition, a receptor transect was placed diagonally, extending southeast from the field, in order to estimate the centerline downwind concentrations and establish a buffer zone. The results from these latter simulations were also compared to the measured values since the wind and stability information used were based on a 24 hour average, in contrast to the initial simulations which used six 4 hour periods of wind information. Modeling results for the centerline concentrations along the diagonal (ie with wind blowing towards the southeast) were nearly equal to modeling results for the centerline concentrations due south with wind blowing from the north, perpendicular to the field. Therefore, for simplicity, the centerline with wind to the south was used to determine the buffer zone.

Results Field 1

The initial modeling using $117\mu g m^{-2} s^{-1}$ flux resulted in generally higher air concentrations to the south and east than north and west (Table 3). These higher air concentrations reflected the dominance of the wind towards the south and the east (Table 1) and were also evidenced in the measured air concentration values (Table 2). The nearly even split between south and east in terms of wind direction distribution shown in Table 2 led us to hypothesize that wind direction was predominantly south east.

The results from the initial simulations were compared to the measured values (Table 3). The predicted concentrations were higher than the measured concentrations. To quantify this difference, the predicted values were regressed on the measured values (Figure 2a). The regression slope was 1, but the intercept was significantly different from 0. Thus the flux was reduced by 0.17/1.0 or 17% for the final run. This resulted in an estimated flux of $100\mu g m^{-2} s^{-1}$. The 17% adjustment was about the same as the 23% coefficient of variation of the replicated 24 hour averages shown in Table 2.

The final simulation for Siemer field TC199.1 resulted in a closer regression fit, providing confidence that the average flux was reasonably estimated, that using the 24 hour average wind direction, (towards the southeast), wind speed (1.4 m/s), and stability class (C) were reasonable for this particular 24 hour period data set, and that the resulting downwind transect air concentrations were reasonably approximated (Figure 2b).

While the model was calibrated to the monitoring transects, as shown in Table 4, these values were not used to determine a buffer zone because they represent values which do not lie along the downwind centerline wind direction. In the downwind centerline wind direction, the downwind air concentrations reach their maximum. Thus, we have used the calibration procedure to estimate a flux and to obtain general meteorological conditions for a typical application scenario. The next step in setting the buffer zone, requires simulation of downwind centerline concentrations under standard meteorological conditions.

To determine a preliminary buffer zone from field 1, the wind direction was set to blow towards the south at 1.4 meters/second with a stability class of C. The centerline concentrations were taken from the ISCST model at 10 m downwind increments to 320 m and at each downwind increment, averaged over 7 crosswind increments at 10 m apart. The crosswind averaging was done to smooth out model artifacts. These estimated downwind air concentrations were reduced to an equation by regressing the natural logarithm of air concentration on the square root of distance, shown in exponential form in equation 1 (Brown 1990). This equation will be useful later when other variables affecting the potential flux rate, and hence, buffer zone, will be considered.

$$C = e^{(7.7925787 - 0.079988757 * \sqrt{D})}$$

C is air concentration (μg/m^3) and D is distance from field in meters. To find the preliminary buffer zone, this equation was solved, setting C=815 μg/m^3 (210 ppb). The result using equation 1 is D=185 meters or 608 feet. The extra decimal digits in the estimated constants do not connote precision, but are carried along for consistency with the program which provided the estimates (Brown 1990).

Methods and Results Field 2 (F1.1)

Field 2 was a triangular-shaped field (Figure 3) to which MeBr was applied under the following conditions:

Application Rate: 400 lbs AI/ac
Area Treated: 19 ac
Injection Depth: 10 in

Injection Type: Noble Plow
Tarp Type: Armin
Location: Wasco, California
Application Date: July 22, 1992

MeBr air concentrations were measured along two primary transects leading northwest and southeast off the field at 50, 150, 300, 600, and 1000 ft from the field. Application was at 400 lbs/acre injected to 10 inches and covered with a tarp. Weather data showed mean wind speed and a percentage of time in each cardinal direction (Table 4). Measured time weighted 24 hour air concentrations during the first 24 hours ranged from .064 ppm to 0.455 ppm along the transects (Table 5). Meteorology and MeBr were monitored in 3 eight hour periods during the first 24 hours.

The field was simulated by approximating its shape with a series of squares (Figure 3). As in the case of field 1 (TC199.1), simulations were performed for each cardinal direction during each of the first 3 eight hour time periods with wind speed and percentage in each direction as shown in Table 6 for sampling periods 1,2 and 3. The resulting concentrations for each monitor were composited with an average weighted by the percentage of time that the wind blew in that particular direction (Table 5).

These results were then regressed on the measured results to determine if the flux rate estimate was adequate (Table 6). The resulting regression was p = 0.0258 + 0.916*m with an r^2 of 72%, where p=model estimates and m=measured (24 hour time-weighted average). The slope was not significantly different from 1 and the intercept was not different from 0. Therefore, no adjustment to the flux was required. And the model appeared to adequately represent the measured data with the estimated average flux of 100µg/m^{2}s. Unlike the field 1 (TC1991.) measurements, the wind direction changed more in this field study. Therefore we did not attempt to model the 24 hour results with a single wind speed and direction. Since utilization of the same flux rate for both fields for the 24 hour period with maximum air concentrations gave reasonable model predictions compared to measured air concentrations, we have some confidence in the 100µg/m^{2}s average flux rate and in the ability of the model to estimate downwind air concentrations.

To evaluate the adequacy of the 608 foot buffer zone developed from field 1 data, the 24 hour time weighted averages along the north and south transects were compared to the buffer zone. These averages indicate that for both transects, the 608 foot buffer zone would have been adequate to keep 24 hour average concentrations below 0.210 ppm. For the south transect, the acceptable level of 210 ppb was reached between 150 and 300 feet and for the north transect the health limit was reached between 300 and 1000 feet and linear interpolation is well under the 608 foot buffer zone.

Field 2 was not used to establish a buffer zone because it was triangular shaped, there were fewer samplers and there were numerous missing data values.

References

Brown, Ron. 1990. TableCurve, Curve Fitting Software Version 2.1. Jandel Scientific, Corte Madera, California.

Nelson, Larry. 1992. Methyl Bromide Preliminary Risk Characterization. Memorandum to Jim Wells, Department of Pesticide Regulation. February 11, 1992.

Seiber, James N., M.M. McChesney, J.E. Woodrow, and T.S. Shibamoto. 1987. Final Report to the Air Resources Board Pilot Analysis of Methyl Bromide in Air. Contract #A5-169-43. Department of Environmental Toxicology, University of California, Davis

Wagner, Curtis P. 1987. Industrial source complex (ISC) dispersion model user's guide–second edition (revised -- Volume I). EPA-450/4-88-002a. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency

Table 1. Meteorological data for first field.

Interval	Date	Sampling Interval	Mean Wind Speed (mph)	Prevailing Wind Direction Determination* Downwind Transects East	South	West	North
29	7/6/92	6 hour	0.9	48%	50%	1%	1%
28	7/5/92	6 hour	0.7	46%	50%	2%	2%
27	7/5/92	6 hour	2.3	50%	50%	0%	0%
26	7/5/92	6 hour	2.1	49%	50%	0%	0%
25	7/5/92	6 hour	1.9	50%	50%	0%	0%
24	7/4/92	6 hour	1.1	50%	50%	0%	0%
23	7/4/92	6 hour	2.9	50%	50%	0%	0%
22	7/4/92	6 hour	4.0	50%	50%	0%	0%
21	7/4/92	6 hour	2.3	50%	50%	0%	0%
20	7/3/92	6 hour	3.3	50%	50%	0%	0%
19	7/3/92	6 hour	2.0	42%	50%	6%	3%
18	7/3/92	6 hour	2.9	50%	50%	0%	0%
17	7/3/92	6 hour	0.9	47%	50%	0%	2%
16	7/2/92	6 hour	0.4	37%	50%	1%	12%
15	7/2/92	4 hour	0.9	40%	50%	2%	8%
14	7/2/92	4 hour	3.4	50%	50%	0%	0%
13	7/2/92	4 hour	2.6	50%	50%	0%	0%
12	7/2/92	4 hour	1.2	44%	50%	0%	6%
11	7/2/92	4 hour	0.5	31%	50%	3%	16%
10	7/1/92	4 hour	0.2	19%	49%	9%	23%
9	7/1/92	4 hour	1.4	34%	50%	5%	11%
8	7/1/92	4 hour	3.0	50%	50%	0%	0%
7	7/1/92	4 hour	2.7	50%	50%	0%	0%
6	7/1/92	4 hour	1.0	38%	50%	2%	10%
5	7/1/92	4 hour	0.6	45%	50%	0%	5%
4	6/30/92	4 hour	3.8	50%	50%	0%	0%
3	6/30/92	4 hour	4.7	50%	50%	0%	0%
2	6/30/92	4 hour	3.2	50%	50%	0%	0%
1	6/30/92	4 hour	1.7	49%	50%	0%	1%
Control	6/30/92	4 hour	0.8	45%	50%	2%	3%

* Sample transects are considered downwind when the wind vector across the downwind edge is within 45 degrees of the transect.

Table 2. Summary of time weighted average (TWA - ppm in 24 hours) derived from drift data collected from a shallow tarp fumigation in Wasco, California, beginning on 6/30/92.

Transect Distance (ft)	24 hr. TWA by days after fumigation 1	2	3	4	5	6
South						
0	0.38	0.13	0.03	0.03	0.02	-
0	0.30	-	0.06	0.02	0.01	-
50	0.24	0.11	0.04	0.02	0.02	-
50	0.32	0.12	0.06	-	0.01	-
150	0.24	0.06	-	0.01	0.02	-
300	0.14	0.07	-	0.00	-	-
600	0.04	0.03	-	0.00	0.00	-
1000	0.04	-	-	0.00	-	-
East						
0	0.28	0.14	0.03	-	-	0.07
0	0.35	0.23	0.12	-	-	0.05
50	0.27	-	0.03	-	-	0.03
50	0.31	0.15	0.02	-	-	0.01
150	0.11	-	0.02	-	-	-
300	-	0.05	-	-	-	-
600	0.04	0.03	-	-	-	-
1000	0.03	0.03	-	-	-	-
North						
0	-	-	0.06	-	-	-
0	0.12	-	-	-	-	-
50	0.22	0.22	-	0.01	-	0.01
50	0.28	0.21	-	-	-	0.01
150	0.26	-	-	-	-	0.01
300	0.18	-	-	-	-	0.00
600	0.07	-	-	-	-	0.00
1000	0.11	-	-	-	-	0.01
West						
0	0.17	-	0.01	-	-	0.03
0	0.09	0.35	0.08	-	-	0.03
50	-	-	0.13	-	-	0.03
50	-	-	0.08	0.03	-	-
150	-	-	-	-	-	-
300	-	-	-	-	-	-
600	-	-	-	-	-	-
1000	-	-	-	-	-	-

1/ Value not calculated due to missing data.
The convention followed in calculating these 24 hr TWA's was deletion of any 24 hour interval that did <u>not</u> have a complete data set for the interval. For the purpose of this table, ND was presumed to be zero. Method sensitivy is 30 ppb.

Table 3. Measured and predicted 24 hour concentrations for the initial simulations for Siemer field #1 using $117 \mu g m^{-2} s^{-1}$ for flux, simulating six 4 hour periods with corresponding wind information and compositing the results for a 24 hour average.

		Measured (ppm)	Predicted (ppm)
South			
	0 ft	0.340	0.478
	50	0.280	0.502
	150	0.240	0.416
	300	0.140	0.340
	600	0.040	0.259
	1000	0.040	0.203
East			
	0	0.315	0.564
	50	0.290	0.398
	150	0.110	0.322
	600	0.040	0.196
	1000	0.030	0.153
West			
	0	0.130	0.238

Table 4. Meteorological data for second field.

Interval	Date	Time	to	Date	Time	Mean Wind Speed (mph)	Downwind Transects South	West	East	North
24	7/29	22:17		7/30	08:10	1.3	42%	30%	11%	17%
23	7/29	14:05		7/29	23:26	2.1	42%	45%	6%	7%
22	7/29	06:56		7/29	14:45	1.7	23%	41%	4%	32%
21	7/28	22:16		7/29	07:25	0.6	36%	27%	9%	27%
20	7/28	14:22		7/28	23:17	3.2	31%	29%	11%	29%
19	7/28	06:05		7/28	15:39	2.5	65%	16%	3%	16%
18	7/27	22:18		7/28	07:17	0.4	16%	42%	0%	42%
17	7/27	13:57		7/27	23:06	2.0	40%	27%	6%	27%
16	7/27	07:49		7/27	14:06	2.2	46%	26%	3%	26%
15	7/26	22:11		7/27	08:26	0.3	26%	34%	7%	34%
14	7/26	14:24		7/26	22:50	3.1	34%	30%	5%	30%
13	7/26	06:11		7/26	14:59	3.5	62%	15%	9%	15%
12	7/25	22:21		7/26	06:43	1.2	46%	24%	6%	24%
11	7/25	23:03		7/25	15:21	3.1	35%	30%	4%	30%
10	7/25	06:54		7/25	16:01	2.8	52%	23%	2%	23%
9	7/26	23:03		7/25	07:33	0.7	20%	39%	3%	39%
8	7/24	14:50		7/24	23:38	2.5	27%	36%	1%	36%
7	7/24	06:49		7/24	15:56	2.0	51%	12%	24%	12%
6	7/23	22:17		7/24	07:23	0.3	5%	31%	3%	61%
5	7/23	14:42		7/23	23:04	2.8	56%	15%	0%	29%
4	7/23	06:33		7/23	15:17	4.1	57%	40%	0%	3%
3	7/22	22:32		7/23	07:06	0.7	15%	35%	6%	44%
2	7/22	14:11		7/22	23:07	3.0	45%	50%	5%	1%
1	7/22	06:51		7/22	14:48	2.3	68%	19%	9%	4%

Table 5. Summary of methyl bromide data collected from the second tarped-shallow fumigation started at 6:20 AM on 7/22/92 in Wasco, California, applying ca. 400 lbs/A injected 10" deep, covered with a 1 mL tarpaulin. The data show 24 hour TWA expressed in ppm.

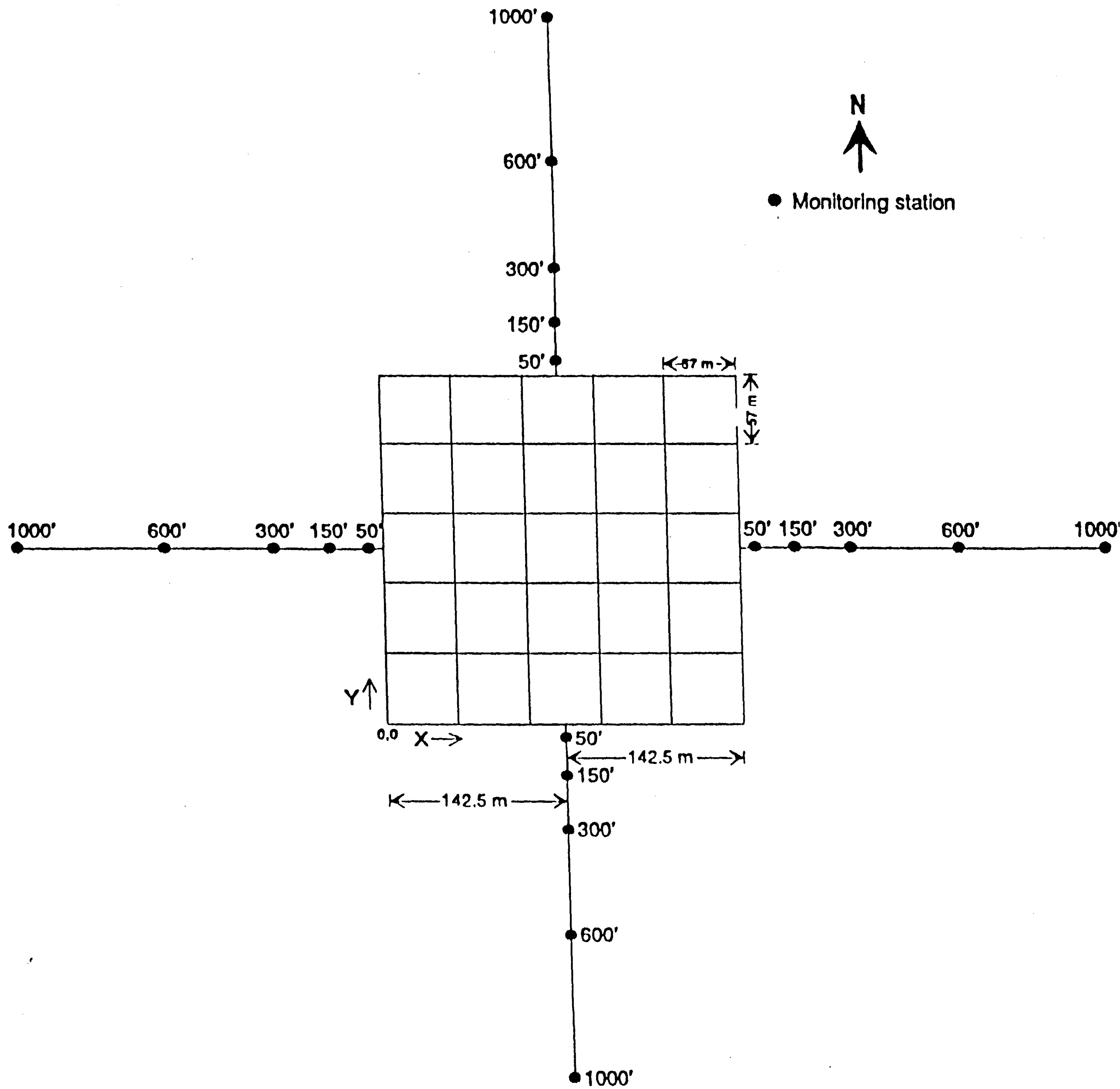
Transect Distance (ft)	24 hr. TWA by days after fumigation							
	1	2	3	4	5	6	7	8
South								
0	.455	.048	.052	.013	.000	.006	.034	.011
0	.204	.044	.040	- 1/	.000	.006	-	.022
50								
150	.178	.026	.034	.012	.000	.007	-	
150	.212	.034	.043	.011	.000	.007	-	
300	-	-	.185	.007	.000	.006	-	
600	-	-	.009	-	.000	.000	-	
1000	.078	.004	.000	.003	.000	.005	-	
East								
0								
0								
50	.166	.017	.010	.004	.000	.004		-
50	.170	.018	.011	-	.000	.004		-
150								
300								
600								
1000								
North								
0	.388	.170	.015	.005	.007	.045	-	
0	.389	.176	.038	.007	.007	.011	-	
50								
150	.231	.129	.022	.004	.005	.003	-	
150	.262	.126	.021	.004	.012	.013	.008	
300			.012	.002	.007	.013	.008	
600			.006	.001	.000	.011	.008	
1000	.064	.011	.003	.001	.000	.015	.013	
West								
0								
0								
50	-	.128	.044	.020	.006	.052	-	-
50	-	.136	.054	.020	.007	.035	-	-
150								
300								
600								
1000								

1/ Value not calculated due to missing data.
Any 24 hour interval that did not have a complete data set for the interval was not used.
ND was presumed to be zero. Method sensitivity is 30 ppb.

Table 6. ISCST modeled and measured 24 hour time weighted average air concentrations from Siemer field 2 for initial flux estimate of 100ug/m2s and 3 composited sampling periods with meteorology as shown in Table 4.

Modeled (ppm)	Measured (ppm)
0.379	0.329
0.243	0.195
0.091	0.078
0.058	0.168
0.354	0.388
0.266	0.246
0.134	0.064

Figure 1. ISCST Representation of Field in Study TC199.1



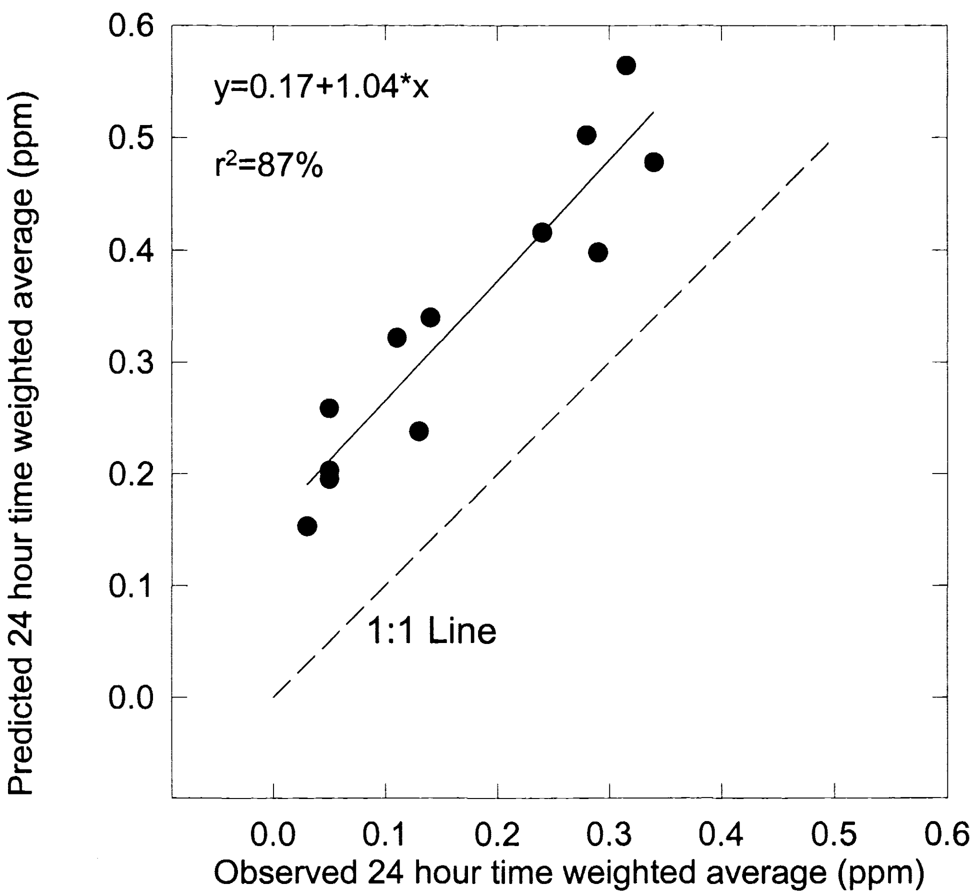


Figure 2a. Predicted versus observed based on initial estimate of 117ug/m^{2}s flux rate.

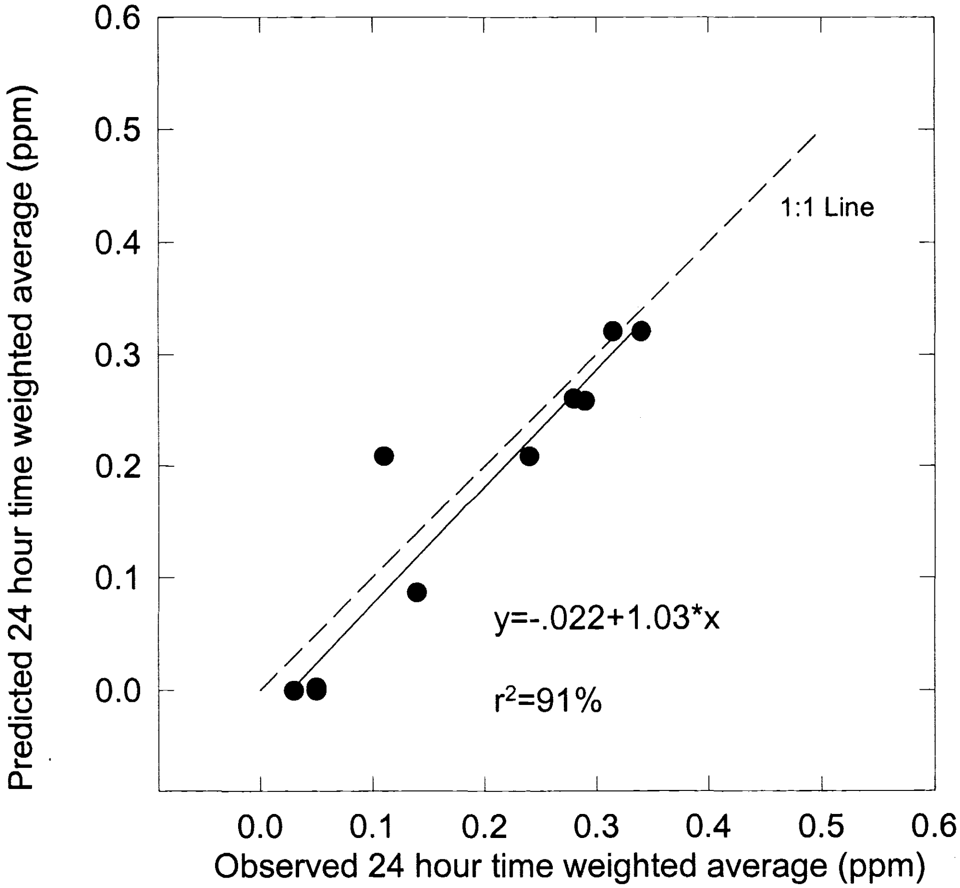


Figure 2b. Predicted vs observed after reducing flux from 117ug/m^{2}s to 100ug/m^{2}s and using constant wind direction of 135^o (to S.E.) and 1.4 m/s

Figure 3. ISCST Representation of Field for Study F1.1.