Department of Pesticide Regulation





Mary-Ann Warmerdam Director

MEMORANDUM



Arnold Schwarzenegger Governor

Name: Pam Wofford Senior Environmental Scientist, Supervisor Environmental Monitoring Branch

Original signed by Bruce Johnson for

- FROM: Tamara Roush, Ph.D. Environmental Research Scientist Environmental Monitoring Branch (916) 324-4279
- DATE: June 20, 2007

SUBJECT: FLUX ESTIMATION AND EMISSION OF METHYL ISOTHIOCYANATE RESULTING FROM A SMALL PLOT APPLICATION OF DAZOMET IN WATSONVILLE, CALIFORNIA

In October 2006, the Department of Pesticide Regulation conducted a small plot study in conjunction with Plant Sciences, Inc. to monitor methyl isothiocyanate (MITC) emissions from an application of dazomet. In total, 452 pounds (205 kg) BasamidG[®] were applied by granular spreader to a fallow, 1.0175 acre (0.4118 ha) plot at Plant Sciences, Inc., Nakano Complex, Watsonville, California. Application began October 18, 2006 at 08:45. It took 2 hours 15 minutes to complete, and a sprinkler system was activated approximately 30 minutes after the application finished to incorporate the pesticide into the soil. This first irrigation session lasted 3 hours 15 minutes; intermittent watering continued over the next few days. Air monitoring with 8 receptors (numbered 1 through 8) began 12 hours before application for a background sample and continued for 6 consecutive days and a total of 16 sampling periods. Air monitoring for period 1 began at about 8:45, coincident with the application. Data for the 17th and 18th sampling periods were collected 5 days after the 16th period. Parakrama (Gura) Gurusinghe will report on this study and its results in greater detail.

Tammy Roush conducted modeling and back-calculation of the flux rates following methods established by Johnson et al. (1999). The Industrial Source Complex Short Term (ISCST3) (U.S. EPA 1995) was used to model the application. Pam Wofford and Tammy used WEATH6 to convert data recorded by the Department of Pesticide Regulation's (DPR's) weather station into the format required by ISCST3. The wind direction was calculated from magnetic north, which matched the orientation of the test plot. The receptor coordinates were input into the control file in the following order: 7, 8, 1, 2, 3, 4, 5, and 6. Appendix A shows an example of the control file for sampling period 1 and its resulting output data.

Modeled and measured MITC concentrations were compared by regression analysis for each period. Concentration data for all periods are listed in Appendix B. Only periods 6, 12, and 18 had significant r^2 values at alpha = 0.05. Additionally, period 2 showed an unusually high measured concentration of 1058 µg MITC/m³ at receptor 2. After consultation between Tammy, Pam, Gura, and Bruce Johnson, it was determined that this measurement corresponded to a small

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spill of BasamidG[®] at that receptor during application. Based on the recorded wind directions during this time period, this receptor was upwind from the plot.

Therefore, the high concentrations would not have come from the plot. We decided to remove measured and modeled data for receptor two from all analyses and re-run the regressions. Although this improved the fit of the data for all periods, 6, 12, and 18 were still the only 3 periods with significant r^2 values (Table 1). Consequently, measured and modeled concentrations for the 15 nonsignificant periods were sorted from lowest to highest and reanalyzed. After sorting, 14 of these 15 periods were significant at the 0.05 level; period 4 had a p-value equal to 0.07 (Table 1). Additionally, the intercepts for periods 3, 4, 5, 7, 8, 9, 10, 15, and 17 were significantly different from zero. We chose not to force them through the origin.

PERIOD	Bef	ore sorti	ng		After sorting				
_	R ²		Intercept (ug/m ³)		R ²		Intercept (ug/m ³)		
	Value	Р	Value	Р	Value	Р	Value	Р	
1	0.18	0.336	21.99	0.552	0.75	0.012	-5.55	0.784	
2	0.21	0.359	56.16	0.16	0.93	0.002	6.56	0.615	
3	0.38	0.142	181.19	0.086	0.72	0.016	148.31	0.049	
4	0.10	0.487	239.18	0.024	0.51	0.07	151.11	0.041	
5	0.26	0.24	92.39	0.009	0.89	0.001	73.04	0.0004	
6	0.80	0.007	30.53	0.108	not sorted;	no chang	je		
7	0.14	0.401	138.84	0.003	0.88	0.002	115.13	<0.0001	
8	0.41	0.119	97.97	0.009	0.77	0.01	88.97	0.002	
9	0.37	0.144	46.87	0.017	0.69	0.021	40.78	0.008	
10	0.49	0.08	6.61	0.651	0.62	0.036	4.17	0.741	
11	0.03	0.694	82.45	0.031	0.71	0.017	55.13	0.015	
12	0.60	0.04	10.25	0.152	not sorted;	no chang	je		
13	0.38	0.139	13.41	0.383	0.77	0.009	5.29	0.564	
14	0.35	0.162	1.96	0.835	0.50	0.06	-0.55	0.947	
15	0.04	0.602	42.99	0.098	0.76	0.011	9.08	0.011	
16	0.42	0.116	3.15	0.502	0.91	0.001	0.01	0.997	
17	0.08	0.547	4.92	0.032	0.84	0.004	3.05	0.007	
18	0.64	0.03	0.21	0.671	not sorted;	no chang	je		

Table 1. Comparisons of regression analyses before and after sorting data within each sampling period. Data from receptor two were excluded from all analyses.

Flux estimates from the regression analyses were used to calculate the percent emission of MITC for each period per the equation:

% emission =[((flux $\mu g / m^2 s^* 1 g / 1 x 10^6 \mu g) x$ (total seconds))/total MITC applied g/m²] x 100

where flux and total seconds are understood to be from the particular sampling period being estimated. Amount of MITC applied was calculated from the total amount of BasamidG[®] during the application as follows: Application rate of BasamidG[®] = 452 lb (205 kg)/ 1.0175 ac (0.4118 ha)= 444 lb/ac (498 kg/ha). The active ingredient, dazomet, comprises 99% of BasamidG[®], therefore application rate of dazomet = 447 lb (203 kg) / 1.0175 ac (0.4118 ha) = 440 lb/ac (493 kg/ha). Total dazomet applied = 447 lb x (453.6 g/lb) x (1 mol/162.3 g) (i.e. molecular weight of dazomet) = 1,250 mol. Whereas Gamliel et al. (2004) estimated that 98% of the dazomet in BasamidG[®] breaks down into MITC after incorporation into the soil, DPR assumes 100% degradation of dazomet into MITC. Thus, total amount of MITC applied = 1,250 mol x (73.1 g/mol) (i.e. molecular weight of MITC) = 91,405 g. The plot area measured 50.6m x 81.4m, or 4119 m², so the value used in the equation for percent emission for total MITC applied = 91,405g/4119m², or 22.2 g/m².

The 24-hour time-weighted average (TWA) flux rates were also calculated according to the equation: TWA = Σ (sampling hours * flux estimate) / total hours. Table 2 lists the flux estimates for each period, 24-hour TWA flux rates, percent emission, and cumulative emission. By the end of sampling period 18, 32% (29,250g) of the MITC applied was emitted from the plot. Ten percent of the MITC applied, or 9,140g, was released during the first 24-hr period. Twelve percent, 10,969 g, was released during the second 24-hr period; period 6 alone accounted for 8%. Emission of MITC declined over the remainder of the monitoring. During period 16, 127 hours after the application was completed, 1% MITC was emitted from the plot. The 24-hr time-weighted average flux during periods 17 and 18, which began 10 d, 8h after the application ended, was 0.75 µg/m²s. Essentially 0% MITC was emitted by this time.

Period	hours in period	Flux estimate (µg/m ² s)	% emission	TWA flux (µg/m²s)	Cumulative % emission
1	7	29	3		3
2	4	35	2		5
3	6	26	3		8
4	6	21	2	27.0	10
5	6	17	2		12
6	6	79	8		20
7	6	8	1		21
8	6	8	1	28.0	22
9	6	11	1		23
10	6	15	1		24
11	12	9	2	6.5	26
12	12	14	3		29
13	12	7	1	10.5	30
14	12	7	1		31
15	12	1	0	4.0	31
16	12	3	1		32
17	12	0.7	0		32
18	12	0.8	0	0.75	32

Table 2. MITC emissions calculated from flux estimates for each sampling period. Note that the flux estimate is 100x the multiplicative coefficient derived from the regression.

References:

Gamliel, Abraham, Miriam Austerweil, Yehudith Riben, Bracha Steiner, Marina Beniches, Victor Zilberg, Shachaf Triki, Eyal Klein, Moran Siti. 2004. Application of dazomet (Basamid[®]) as soil fumigant: generation, movement, and dissipation of MITC and pest controls. Available at: <www.agri.gov.il/AGEN/Reports/Gamli009.html>.

Johnson, Bruce, Terrell Barry, and Pamela Wofford. 1999. Workbook for Gaussian modeling analysis of air concentration measurements. Report EH-99-03. California Department of Pesticide Regulation.

U.S. EPA. 1995. User's Guide for the Industrial Source Complex Dispersion Models, Volume 1. User Instructions. U.S. EPA Office of Air Quality Planning and Standards; Emissions, Monitoring, and Analysis Division, Research Triangle Park, North Carolina.

Appendix A: Control file and the first page of output data from ISCST3 for sampling interval 1.

CO STARTING CO TITLEONE BASAMID TEST CO TITLETWO PERIOD 1 CO MODELOPT CONC RURAL CO AVERTIME PERIOD CO POLLUTID OTHER CO FLAGPOLE 1.20 CO RUNORNOT RUN CO ERRORFIL D:\Gaussian\P1newERR.OUT CO FINISHED SO STARTING SO LOCATION SRC0001 AREA 0.0 0.0 0.0 SO SRCPARAM SRC0001 1.e-4 0.00 50.0 81.4 SO EMISUNIT 0.100000E+07 (GRAMS/M**2/SEC) (MICROGRAMS/METER**3) SO SRCGROUP ALL SO FINISHED **RE STARTING** **receptor 7 RE DISCCART 62.2 -13.91 1.20 RE DISCCART 24.4 -12.3 1.20 **receptor 8 **receptor 1 RE DISCCART -13.1 -12.78 1.20 **receptor 2 RE DISCCART -12.2 40.5 1.20 **receptor 3 RE DISCCART -13.1 93.89 1.20 **receptor 4 RE DISCCART 25.3 93.0 1.20 RE DISCCART 62.2 94.87 1.20 **receptor 5 RE DISCCART 62.2 40.5 1.20 **receptor 6 **RE FINISHED ME STARTING** ME INPUTFIL D:\Gaussian\WP1.MET (4I2,2F9.4,F6.1,I2,2F7.1) ME ANEMHGHT 10.0 METERS ME SURFDATA 99999 2006 ME UAIRDATA 99999 2006 ME WINDCATS 2.00 3.09 5.14 8.23 10.80 ME FINISHED **OU STARTING** OU POSTFILE PERIOD ALL PLOT D:\Gaussian\P1.RAW **OU FINISHED**

* ISCST3 (02035): BASAMID TEST * MODELING OPTIONS USED: CONC RURAL FLAT FLGPOL POST/PLOT FILE OF PERIOD VALUES FOR SOURCE GROUP: ALL * FOR A TOTAL OF 8 RECEPTORS. FORMAT: (3(1X,F13.5),1X,F8.2,2X,A6,2X,A8,2X,I8.8,2X,A8) * AVERAGE CONC ZELEV AVE GRP NUM HRS NET ID Х Y -13.91000 25.05398 0.00 PERIOD ALL 0000007 62.20000 NA 24,40000 -12.300000.02400 0.00 PERIOD ALL 0000007 NA -13.10000 -12.78000 0.00000 0.00 PERIOD ALL 00000007 NA -12.20000 40.50000 101.03069 0.00 PERIOD ALL 0000007 NA -13.10000 93.89000 241.50749 0.00 PERIOD ALL 0000007 NA 25.30000 93.00000 360.79279 0.00 PERIOD ALL 0000007 NA 62.20000 94.87000 225.76189 0.00 PERIOD ALL 0000007 NA 00000007 62.20000 40.50000 453.03238 0.00 PERIOD ALL NA *** 02/22/07 *** *** PERIOD 1 10:44:22 **MODELOPTs: PAGE 6 CONC RURAL FLAT FLGPOL

*** THE FIRST 7 HOURS OF METEOROLOGICAL DATA ***

FILE: D:\Gaussian\WP1.MET FORMAT: (4I2,2F9.4,F6.1,I2,2F7.1) SURFACE STATION NO.: 99999 NAME: UNKNOWN YEAR: 2006

UPPER AIR STATION NO.: 99999 NAME: UNKNOWN YEAR: 2006

FLOW SPEED TEMP STAB MIXING HEIGHT (M) USTAR M-O LENGTH Z-0 IPCODE PRATE YR MN DY HR VECTOR (M/S) (K) CLASS RURAL URBAN (M/S) (M) (M) (mm/HR)

06 10 18 08 102.9 1.19 281.7 4 300.0 300.0 0.0000 0.0 0.0000 0 0.00 300.0 300.0 0.0000 0.0 0.0000 0 0.00 06 10 18 09 328.5 1.16 285.2 3 06 10 18 10 339.6 1.15 289.3 2 300.0 300.0 0.0000 0.0 0.0000 0 0.00 06 10 18 11 57.5 1.17 293.5 2 300.0 300.0 0.0000 $0.0 \ 0.0000 \ 0 \ 0.00$ 06 10 18 12 41.7 1.42 295.6 1 300.0 300.0 0.0000 $0.0 \ 0.0000 \ 0 \ 0.00$ 06 10 18 13 41.8 2.96 295.8 2 300.0 300.0 0.0000 0.0 0.0000 0 0.00 06 10 18 14 64.9 3.76 295.6 3 300.0 300.0 0.0000 0.0 0.0000 0 0.00

Appendix B. Measured and modeled MITC concentrations for all 18 periods.

Period	Receptor	measured	modeled	Period	Recept	or measured	modeled	Period	Receptor	measured	modeled
1	1	8.18744211	0	7	1	155.158045	0	13	1	77.19149836	415.64706
	2		101.03069		2		0		2		529.11945
	3	31.07759763	241.50749		3	92.9366525	0		3	11.75762055	149.76237
	4	29.90193606	360.79279		4	128.2958504	242.74641		4	14.41416894	21.55596
	5	179.1055841	225.76189		5	97.56773311	191.67982		5	9.894170784	2.10798
	6	76.40621138	453.03238		6	199.4023076	1471.31104		6	26.09232003	601.07111
	7	7.041995903	25.05398		7	151.1326439	1137.81787		7	26.43337744	620.86011
	8	12.25969813	0.024		8	224.9308132	109.18357		8	63.61780871	808.83838
2	1	5.815352531	0	8	1	79.95066874	0	14	1	1.656074689	0
	2	52.78308595	186.59724		2		0		2		8.34322
	3	78.6072745	338.37653		3	62.62989067	0		3	4.597190297	49.79597
	4	94.01588869	405.66583		4	86.07463562	0		4	37.61416707	295.5051
	5	105.335334	172.11195		5	71.16299632	0		5	23.55421897	307.35385
	6	156.6968836	208.33745		6	166.4009496	1436.2334		6	21.57989633	357.77359
	7		0.00004		7	184.8208364	1222.19275		7	8.539364898	286.7222
	8		0		8	209.1917591	157.12614		8	4.791775571	312.61777
3	1	304.1726107	0	9	1	30.58384317	0.0026	15	1	24.06345519	28.83606
	2		0		2	•	126.42984		2		141.80403
	3	54.44667895	0		3	67.88253394	136.38155		3	6.1584162	0
	4	55.09113298	0		4	78.79648396	438.55887		4	8.095140386	128.36073
	5	66.63885619	0		5	20.90713902	77.5302		5	5.907500972	284.53262
	6	451.3949033	1496.75183		6	90.28555237	545.60242		6	20.70209683	1399.64685
	7	382.3556338	1379.20374		7	72.28752688	268.21353		7	15.03932576	929.67804
	8	559.9385082	322.83984		8	86.95911863	36.09587		8	25.82946404	232.72194
4	1	76.01112301	0	10	1	2.745325657	0.13137	16	1	1.793932576	62.47061
	2		0		2		80.14397		2		47.17303
	3	60.56447988	0		3	11.05492884	21.07357		3	14.00291152	59.3914
	4	417.9371815	0		4	21.54095946	366.61902		4	24.85406595	488.30502
	5	140.1123163	0		5	39.57516875	312.70602		5	8.370821865	100.50159
	6	50.42121796	1489.74109		6	99.77736971	331.05228		6	12.87993365	414.27103
	7	331.9312458	471.06015		7	5.10111576	3.96029		7	3.004996586	267.71478
	8	407.8094332	29.91035		8	7.817460588	0.01519		8	3.606120751	137.74352
5	1	85.54929003	20.10756	11	1	92.36103773	0	17	1	8.532716776	203.73401
	2		348.00464		2		0		2		451.27933
	3	80.86082425	244.49057		3	41.72874009	0		3	3.069722624	100.83681
	4	152.7911026	348.21597		4	59.58699828	190.33392		4	4.34117585	84.85691
	5	63.8390456	77.34594		5	44.06238384	172.17326		5	3.128993447	112.69553
	6	162.0107502	641.72162		6	102.3229511	1191.92224		6	9.032442856	794.77002
	7	108.8722033	421.95157		7	97.3534387	1056.29114		7	3.670667694	935.10028
	8	153.6374483	38.71024		8	192.6614425	193.83476		8	8.3124396	394.27292
6	1	5.03549612	28.28474	12	1	11.17821177	0.0532	18	1	0.342759212	73.12766
	2		1.05923		2		251.28008		2		368.19019
	3	44.67099972	0		3	9.722936327	141.92223		3	0.756000756	230.60695
	4	45.70651663	0.14836		4	18.72311715	130.46834		4	1.938845466	219.54231

5 98.79920961	14.27261	5	27.10183846	67.49207	5	2.577978742	215.2299
6 213.3764229	227.71033	6	56.23840445	329.23486	6	2.958579882	279.42398
7 13.80562802	1.01542	7	9.967734906	61.68396	7	0.269748041	0.48003
8 7.327825645	0.00097	8	21.26825016	2.18349	8	0.646983976	12.26311





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