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SUBJECT: DAZOMET FLUX ANALYSIS AND RECOMMENDATIONS FOR FUTURE STUDY

Summary

Three studies were analyzed for estimating methyl isothiocyanate (MITC) flux from the application of dazomet. Two studies were conducted by BASF on commercial-sized acreages. A third study was a small-plot study primarily designed to test efficacy for a variety of soil fumigants including dazomet. The Department of Pesticide Regulation (DPR) monitored the latter. We confirmed our flux estimates for DPR study through independent calculations. In addition, we confirmed in detail the flux calculations for one BASF study. We are satisfied that both studies were analyzed for flux properly. DPR-monitored small-plot study yielded substantially higher flux estimates than the two BASF studies. In addition, stable conditions during a BASF study precluded straight-ahead regression analysis to determine flux. Based on these considerations, the divergence of flux estimates and stable meteorological conditions, we recommend that DPR conduct one or two further monitoring studies for dazomet on a commercial-size application.

This memorandum is organized into three sections: (1) Detailed parallel analysis of DPR Study 212 period 1 (the highest flux estimate), (2) Confirmation of BASF calculations, and (3) Summary and recommendations.

Detailed parallel analysis of DPR study 212, period 1

Background

The purpose of this section is to analyze in parallel the flux estimates for DPR study in order to confirm them. Study details will be described more fully in Fan (in preparation). Four plots, roughly 30x7m, were treated with 233 lbs/acre dazomet (equivalent to 104.9 lbs/acre MITC). Initial back-calculations showed a higher than expected flux during the first period.

Methods

First period calculations were conducted independently by Bruce Johnson and Pam Wofford. Plot and receptor locations were transcribed into Autodesk by Pam. Pam performed the initial modeling. Plot and receptor geometry was confirmed by Bruce using the Industrial Source Complex Short Term Version 3 (ISCST3) control file from Pam, plotting those points in Sigmaplot (Figure 1) and comparing the Sigmaplot figure to the original, hand drawn chart. Meteorological data was independently analyzed by Pam and Bruce using WEATH6.EXE and using the raw data file, downloaded from the CR21x.

Wind directions were fairly consistent during the 6 hours of period 1, largely blowing from west to east. Because there was some evidence that the two easternmost plots may have had a higher flux than the two westernmost plots and because of the consistent wind direction, the following strategy was utilized for an analysis which separately estimated the two fluxes:

1. Initial simulation used only sources A and B and receptors 1-6, 11,12 (Figure 1). Flux was estimated. Modeled concentrations were estimated for receptors 7-10.
2. The estimated contributions to receptors 7-10 were subtracted from the measured concentrations for 7-10. Then a second simulation, using only sources C and D was conducted and the flux estimated, now using the modified measured concentrations for 7-10.

The results of the above analysis by Bruce and Pam were compared. Further analysis was conducted consisting of concentration isopleths based on the best estimates of flux for both east and west sources. A sensitivity analysis was conducted to determine how sensitive the flux estimate was with 5 and 10 degree wind shifts.

Results

The plot geometry encoded into ISCST3 control files by Pam was extracted and entered into Sigmaplot graphing software (Figure 1). The resulting drawing was visually compared to the hand drawn figure. The two figures were consistent. Note, that the orientation of the plots was true North-South and East-West and this was confirmed using Google Earth first to locate the field and second to overlay a latitude and longitude grid. Meteorological data used for period 1 by Pam and Bruce was compared (Table 1). The difference occurred between the directions, where Pam used 14.5 degrees and Bruce used 14.0 degrees to correct for declination. Because the wind direction was basically from west to east during period 1 and because there was some initial indication that sources A and B on the west were fluxing at a lower rate than C and D on the east, an attempt was made to separately estimate those fluxes. Using only A and B as sources, and basing the back-calculation regression on receptors 1-6, 11, 12 resulted in an estimate of 44 ug/m2s ($p<.05$, $r2=61\%$) for A and B only. Using 44ug/m2s as input, we estimated A and B source contributions to receptors 7-10 at 0, 5, 9, 20 ug/m3. These modeled contributions were

Table 1. Comparison of period 1 meteorological modeling files used by Pam (top) and Bruce (bottom). Variables are year, month, day, hour, 'to' wind direction (degrees), speed (m/s), temperature (K), stability class and mixing heights (m).

Yr	M	D H	'To' dir	Speed	Temp	S	MH1	MH2
05	5	613	91.7095	2.1299	292.9	4	300.0	300.0
05	5	614	108.0577	2.1497	293.5	4	300.0	300.0
05	5	615	94.1602	1.7653	293.8	4	300.0	300.0
05	5	616	111.2572	3.9214	294.4	4	300.0	300.0
05	5	617	111.1207	5.5911	293.8	4	300.0	300.0
05	5	618	108.3021	5.9871	292.4	4	300.0	300.0
5	5	613	91.2095	2.1299	292.9	4	300.0	300.0
5	5	614	107.5577	2.1497	293.5	4	300.0	300.0
5	5	615	93.6602	1.7653	293.8	4	300.0	300.0
5	5	616	110.7572	3.9214	294.4	4	300.0	300.0
5	5	617	110.6207	5.5911	293.8	4	300.0	300.0
5	5	618	107.8021	5.9871	292.4	4	300.0	300.0

subtracted from the measured values for receptors 7-10, respectively, and the flux for sources C and D was estimated by running ISCST3 with the nominal flux (100 ug/m2s) and regressing the measured values (adjusted by subtraction as described above) on the modeled based on C and D only. The resulting flux was 58 ug/m2s ($p<.05$, $r2=93\%$). However, the 95th confidence interval for the A and B flux was 0.13 to 0.76 and for the C and D flux was 0.19 to 0.96. With this substantial overlap in confidence intervals, these values cannot be statistically different. The preceding calculations by Bruce were compared to the parallel calculations by Pam, which were 43 and 57 ug/m2s, respectively. Both analyses were in agreement.

A simulation was conducted using the two different fluxes on a grid of receptors, in order to generate a contour map of the air concentrations during period 1 (Figure 2). A notable feature in Figure 2 is that receptors 8, 9 and 1 (reference Figure 1 for numbering) appear to be located on the concentration surface where a steep gradient occurs. This implies that small errors in locating these receptors, errors resulting from using an hourly summary of wind direction, or errors resulting from measuring the wind direction, may have potentially larger consequences for flux estimate because each of those errors may be thought of as shifting the location of the receptor north or south, up or down a steep concentration gradient. This situation resulted because the wind direction was predominantly from west to east and the small plots were rectangular with the longest direction also running west to east. As a result, high localized concentrations resulted downwind from the long plot direction. Had the plots been more square and/or the wind direction more variable, these localized high concentrations would not have resulted to the same degree.

Table 2. Sensitivity of flux estimate to stepped-changes in hourly wind directions for the six hour period 1.

Wind direction adjustment (degrees added to hourly value)	Estimated Flux (ug/m2s)	Regression significance	Adjusted r2 for regression
-10	61	p<.01	80%
-5	56	p<.01	92%
0	54	p<.01	93%
5	48	p<.01	91%
10	44	p<.01	90%

In order to investigate the potential sensitivity to wind direction change, the back-calculation was redone using all four sources simultaneously. The resulting estimate was 54ug/m2s (p<.01, r2=93%). This calculation is also justified because the two separate (east vs. west sources) did not appear to have statistically separable flux estimates. The wind directions were then all changed by adding –10, -5, 0, 5, 10 degrees to each hourly value. For each set of directions, the flux was back-calculated. The result of these calculations is shown in Table 2.

The range of fluxes as the angular adjustment changed from –10 to +10 degrees was 61 to 44 ug/m2s. Adding –10 degrees was equivalent to shifting the hourly wind directions 10 degrees north. With reference to Figure 2 this places the key receptors 1, 8 and 9 lower on the concentration surface. Since lower concentration estimates result from the simulation, the flux must be increased in order to match up the modeled to measured concentrations. Conversely, adding 10 degrees was equivalent to shifting the receptors north because the wind direction was shifted 10 degrees to the south. This placed receptors 1, 8 and 9 on a higher part of the concentration surface, which lowered the flux estimate. These calculations indicate some sensitivity to errors either in location or measurement of wind direction. An angular change of 10 degrees resulted in +13% to –19% flux estimate sensitivity.

Another possible source of error in the calculation was the estimate for stability class. A ‘D’ stability class was assigned to all six hours based on field notes indicating mostly cloudy conditions and on nearby California Irrigation management Information System meteorological data which showed low solar radiation during this time period (implying cloudiness). Since it is daytime, the only other possibilities for assigned stability classes would be C, B, and A. Using any of these classes would result in higher flux estimates because these more unstable classes would estimate lower downwind air concentrations than using D stability. Another possible source of error could be the application rate. Due to the small plot size, material may have been applied outside of the defined plot perimeter. This could lead to higher apparent flux from the defined plot areas. The perimeter-to-area ratio is higher for this small plot than a commercial-sized plot.

Confirmation of BASF calculations

Using meteorological and geographical information provided from BASF, we reconstructed input files and meteorological data for the incorporated treatment application monitored by the registrant. The input data and met data were placed into the ISCST3 model and the results of the analysis confirmed the registrant modeling (Table 3).

Table 3. Regression analysis results of modeling by BASF and DPR on an incorporated application of dazomet.

Sampling		BASF			DPR	
Period	Slope	Intercept	Flux Rate	Slope	Intercept	Flux Rate
Day 1 8AM-2PM	0.020	1.73	1.97	0.019	1.85	1.86
Day 1 2PM-6PM	0.146	27.9	14.6	0.138	28.1	13.8
Day 1 6PM-10PM	0.011*	81.1	1.13	0.010*	81.5	1.00
Day 1 10PM-2AM	0.099*	414	9.88	0.088*	413	8.81

*not a significant regression

A comparison of the flux rates for the sampling periods with the highest estimated flux for the two BASF studies and DPR study are located in Table 3. The highest flux rates estimated for BASF studies were from sampling periods where the regressions were not significant so the measured and modeled concentrations were independently sorted within the sampling interval and compared through regression analysis. The line was not forced through the origin. Since the application rates differ for the three studies the rates can be standardized to make the comparison more meaningful. Using a standard shank application rate of 19.3 g/m^2 as a standard, the application rates of the three application types can be normalized to make them comparable to other MITC application methods monitored. The effective broadcast application rate of MITC determined for each application assumes the label rate percentage of dazomet in the product formulation (99%) and assumes a 1:1 molar stoichiometry and complete conversion of dazomet to MITC.

Table 4. A comparison of the standardized flux rates of the three studies.

	Sampling period	Duration (hours)	Flux estimate (ug/m^2-sec)	Effective broadcast application rate of MITC (g/m2)	Standarization multiplier[1]	Standardized TWA flux
BASF Surface	2	4	6.81	15.35	1.26	8.58
BASF Incorporated	4	4	24.1	30.15	0.633	15.3
DPR Surface	1	6	53.8	11.75	1.65	88.8

[1]used standard sprinkler application rate (19.3 g/m^2) as standard

The flux rate for DPR study is much higher than the applications monitored by BASF. The resulting standardized 6-hour time weighted average is higher for DPR study than any other 4-hour time weighted average flux of MITC application type monitored (Wofford, 2003).

Summary and recommendations

There appears to be a divergence in flux estimates between the small plot DPR study and the two BASF studies on commercial size fields. In DPR study, the small plot study design, coupled with the consistent wind direction lead to circumstances where the results were somewhat sensitive to various kinds of errors which would have placed the receptors higher or lower along a concentration gradient. The magnitude of this sensitivity, however, cannot account for the divergence in the flux estimates. BASF studies conducted on commercial size fields suffered from a high incidence of stable meteorological conditions, where ISCST3 may perform poorly. In addition, there are evidently some gaps in the qc aspects of BASF studies (Fan, personnel communication). For these reasons, we recommend one or two additional monitoring studies which would preferably be conducted by DPR and which would monitor commercial-size applications. The purpose of these studies would be to provide additional measurements of the MITC flux resulting from dazomet applications.

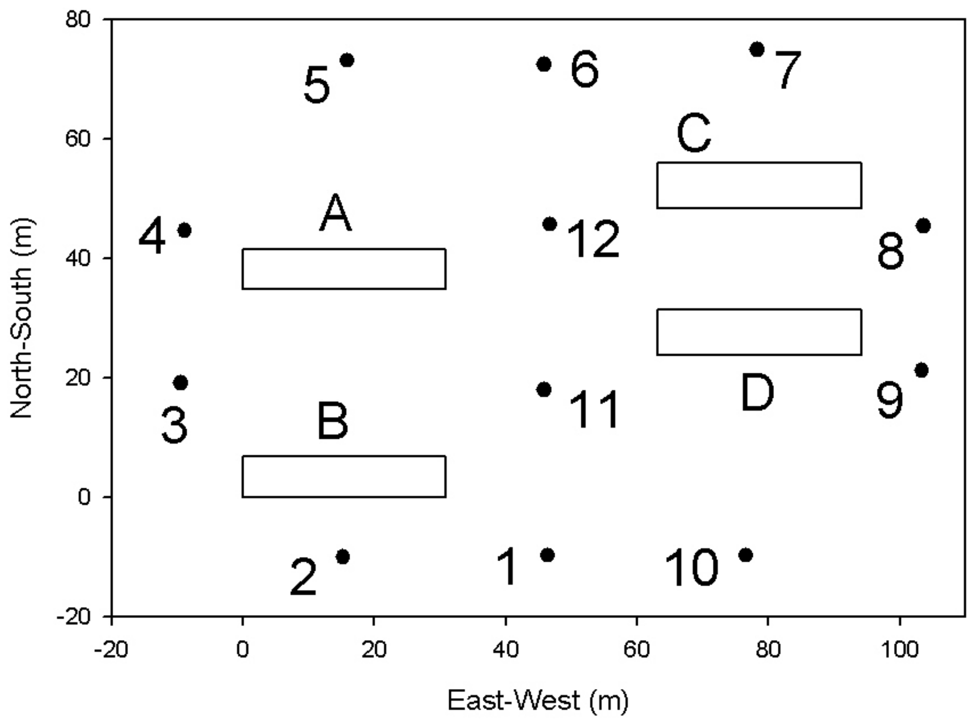

Figure 1. Source and receptor geometry.

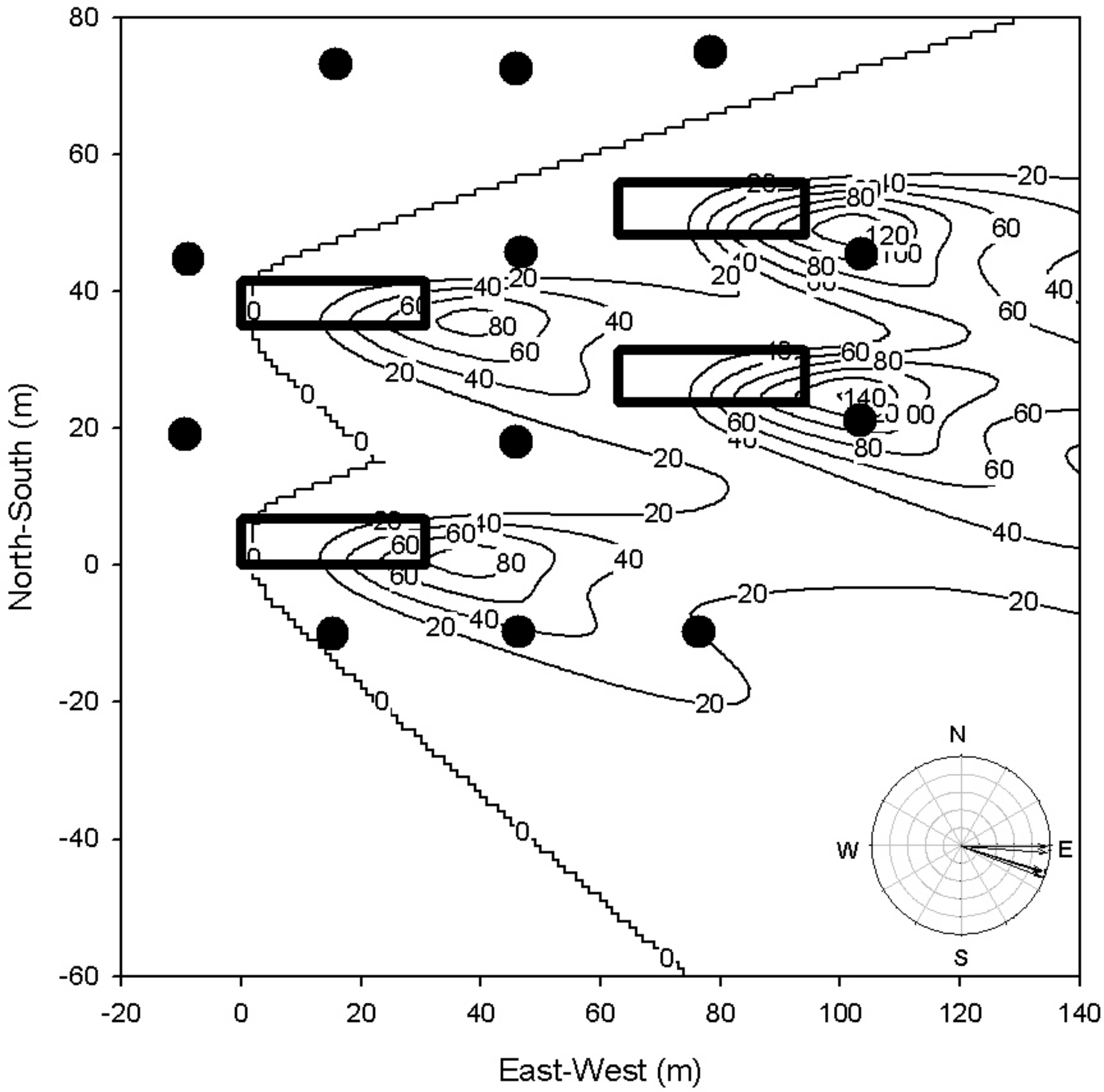

Figure 2. Dazomet small plot study, concentration (ug/m3) contours for period 1. Receptors are black dots, sources are rectangular shapes, hourly "to" wind directions are shown for this period.