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Characterization of Methomyl Dissipation on Grape Foliage

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Dislodgeable foliar residues (DFRs) of the carbamate insecticide methomyl (Lannate(R)) on grapes were monitored during a six month period to help define safe worker reentry intervals. The study was conducted in response to two suspected (one confirmed) episodes of methomyl related illness during the summer of 1988 (O'Malley,1989). The confirmed incident occurred on May 25, 1988, and involved thirteen individuals in a grape girdling crew. Eleven of these workers displayed clinical symptoms typical of carbamate poisoning. Methomyl was implicated and later proven to be the causative agent. The data from a concurrent dislodgeable foliar residue study established 0.1 micrograms/cm^2 as the safe level for reentry into the field. A second potential illness episode which occurred on September 23, 1988 was evaluated and later discounted due to a lack of statistical and symptomatic evidence. However, the DFR data compiled as part of this second illness investigation were pivotal in characterizing the time dependent dissipation of methomyl.

Since DFRs are the principal determinant of harvester exposure (O'Malley 1990, Saunders 1987), a biphasic reentry program was developed. In late spring and early summer (through August 15th) the reentry interval is seven days. After August 15th, the interval is 21 days. The study included Fresno, Madera, Tulare and Kern Counties; prominent table grape growing regions in California. Samples were obtained from forty-two fields between the months of June and November. The principal finding was a one hundred percent increase in the length of DFR half-lives over the length of the study.

MATERIALS AND METHODS

The sampling scheme for this particular study followed a diagonal pattern within the designated fields. There were six (later reduced to four) randomly chosen rows per block, labelled A to D. A five row buffer was established on either side of the experimental plot to reduce the possibility of edge effects affecting data results. The location of sampling within rows was based on multiples of five vines. Row A included vines 5-44; row

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B, vines 10-49; row C, vines 15-54; row D, vines 20-59 etc..

One leaf disc was taken per vine, therefore one sample of forty leaf discs represented forty vines within a particular row. This same procedure was followed in subsequent sampling days as well. All sampled rows were identified by the presence of survey tape tied to the endpost and both margins of the forty vines. In order to provide an adequate representation of the overall degradation profile, north versus south facing rows were randomly assigned for each vineyard. A Birkestrand(R) leaf punch (2.5 cm diameter) and a four once glass jar were utilized for leaf disc collection. Once an entire sample was taken (40 leaf discs), the leaf punch was rinsed with Aerosol OT-75% (dioctyl sodium sulfosuccinate) solution in a plastic bag containing distilled water, and dried. This procedure was followed after every sample.

Leaf discs were triple rinsed in a 2% aqueous surfactant (dioctyl sodium sulfosuccinate) solution, and washings combined and extracted with dichloromethane. The extract was dehydrated with anhydrous sodium sulfate and filtered into a 250 ml boiling flask for rotary vacuum evaporation. Methomyl was determined by liquid chromatography using post-column derivatization and flourescence detection.

The quantity of methomyl in micrograms for each sample were divided by the surface area for 40 two-sided leaf discs (cm^2) in order to present the data in the units of micrograms/cm^2 (Iwata 1977, Gunther 1975). Half-lives were then determined using logarithmically transformed values of four to six sample replicates for each field as a function of time collected from date of application. The results were analyzed using a least squares fit regression of data. Regression correlation coefficients (r^2) value equal to or less than 0.2 were excluded from the analysis (n=5).

A number of fields in July were monitored until all of the replicates of the day were below the minimum level of detection (0.25 ug/sample). Only actual data were used for the regressions, therefore Minimum Detection Levels (MDLs) or estimates thereof were not considered. The same methodology was followed for the few MDLs present in June and August as well.

The criteria for categorizing half-life values were the date of application according to a monthly schedule and per field. The study was over a six month period, consequently there were six sets of half-life data. The high and low mensal estimates (half-life) were calculated using an analysis of variance and covariance procedure at the 0.95 level of confidence.

RESULTS AND DISCUSSION

In Figure 1, sampling site and weather station locations are given. The location, grape variety, application rate and method of irrigation for each of the fields monitored, are listed in Table 1. The coefficient of determination, standard error, half-life and date of application per field are included in Tables 2 and 3 for both the DuPont study and the CDFA study. Figure 2 displays a more qualitative view of month versus half-life values.

Table 1. Calculated half-lives for methomyl treated fields in 1989 (CDFA study).

Field	r^2 value	Half-life Estimate		Standard Error	Application Date
1	0.99	2.2	±	0.04	6/3/89
2	0.98	2.4	±	0.11	6/3/89
3	0.98	2.3	±	0.10	6/7/89
4	0.99	1.4	±	0.13	6/9/89
5	0.93	2.8	±	0.13	6/22/89
6	0.97	2.7	±	0.07	6/22/89
7	0.92	1.7	±	0.21	6/22/89
8	0.98	1.8	±	0.09	6/29/89
9	0.94	2.1	±	0.14	6/29/89
10	0.99	1.7	±	0.04	7/12/89
11	0.96	2.2	±	0.24	7/13/89
12	0.99	1.8	±	0.08	7/13/89
13	0.96	3.4	±	0.31	7/22/89
14	0.91	1.5	±	0.35	7/25/89
15	0.99	1.5	±	0.13	7/25/89
16	0.93	2.0	±	0.24	7/26/89
17	0.98	1.4	±	0.16	7/26/89
18	0.97	1.0	±	0.29	7/26/89
19	0.82	1.5	±	0.52	7/26/89
20	0.99	1.7	±	0.04	7/26/89
21	0.97	2.3	±	0.09	7/26/89
22	0.93	1.9	±	0.53	7/27/89
23	0.95	3.5	±	0.24	8/10/89
24	0.91	3.8	±	0.25	8/10/89
25	0.93	4.7	±	0.18	8/10/89
26	0.92	3.8	±	0.27	8/11/89
27	0.97	1.6	±	0.34	8/11/89
28	0.99	2.3	±	0.12	8/12/89
29	0.92	5.8	±	0.19	8/29/89
30	0.81	2.0	±	0.37	9/18/89
31	0.98	2.3	±	0.16	9/18/89
32	0.76	7.7	±	0.22	9/26/89
33	0.98	5.9	±	0.10	10/3/89
34	0.91	3.8	±	0.27	10/10/89
35	0.92	5.1	±	0.18	10/10/89
36	0.99	4.6	±	0.03	10/10/89

There was an increase in methomyl half-life with the progression of summer months (Table 1, Figure 2). The upward trend was not linear during the six month period. In August there was a substantial increase ($t1/2$ > days) which persisted through September and October (Figure 2).

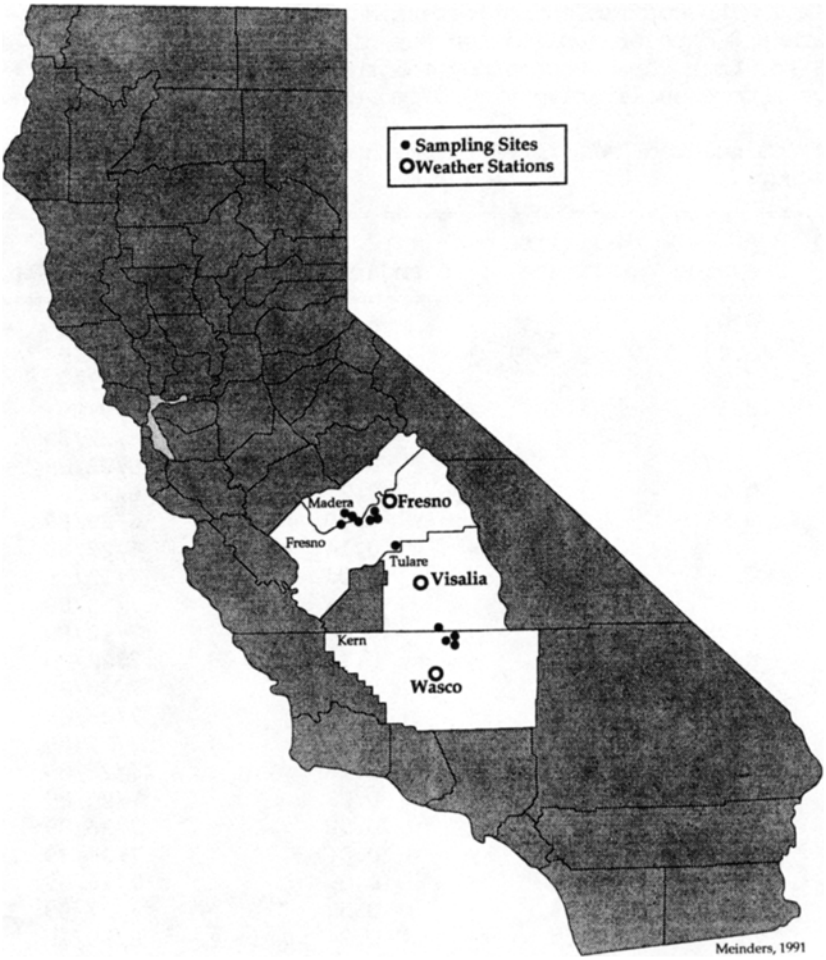

Figure 1. Geographic locations of sampling sites and weather stations.

The sampling site was found to have a minimal effect on the foliar dissipation of methomyl. The relationship between application rate and methomyl half-life was also examined (Tables 1 and 3). There was no apparent trend. Several fields with rates of 0.5 lbs./acre had half-lives equal to or exceeding other plots with application rates of 0.75 and 1.0 lbs./acre. Half-lives increased later in the growing season regardless of the initial deposition and or application rate.

Other parameters such as dew point, temperature, ozone concentration and method of irrigation (flood versus drip) were compared to the seasonal increases in methomyl half-lives. No clear contribution to the foliar degradation of methomyl was established.

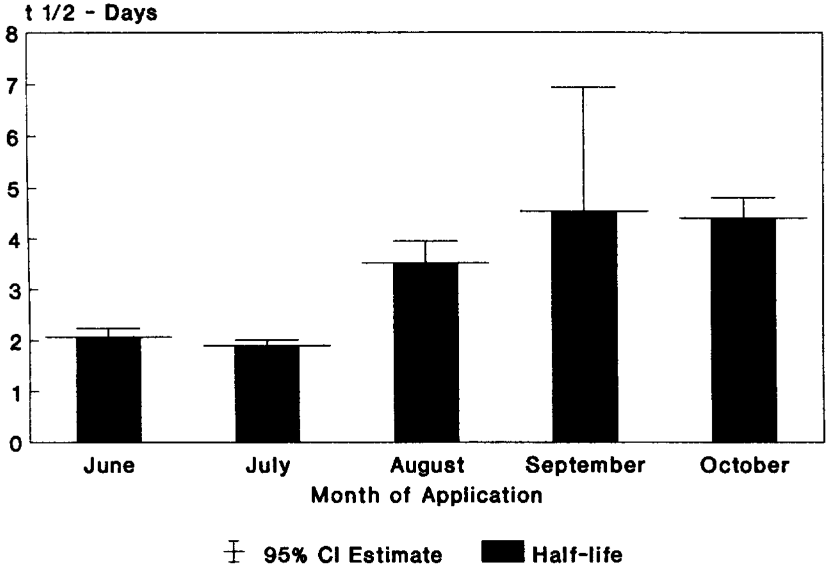

Figure 2. Methomyl half-life results according to a monthly schedule (CDFA study).

There are several factors in the environment which could explain the seasonal dissipation of methomyl. Previous studies suggested vapor pressure and hydrolysis play a contributory role (Bull,1974). The primary contributor to this phenomenon in our study has not been identified and is beyond the scope of this monitoring work. What is evident, however, is the consistent trend of methomyl degradation independent of location, temperature, method of irrigation and plant species. A comparison with the graphical results of the DuPont study data tended to support this observation linking the environmental persistance of methomyl with the late growing season (Table 2).

Table 2. Calculated half-lives for methomyl treated fields in 1989 (DuPont study).

Field	r^2 value	Half-life Estimate		Standard Error	Application Date
1	0.98	1.2	±	0.13	6/14/89
2	0.98	1.1	±	0.11	6/14/89
3	0.96	1.3	±	0.18	6/22/89
4	0.97	1.6	±	0.14	8/15/89
5	0.98	2.0	±	0.08	8/15/89
6	0.99	1.7	±	0.06	8/15/89
7	0.92	2.7	±	0.15	9/6/89
8	0.92	2.7	±	0.15	9/6/89
9	0.94	2.8	±	0.13	9/6/89

Consequently, a revised regulation has been implemented to address the increased health risks associated with methomyl applications late in the table grape growing season. The new regulation will be twofold: a seven day reentry interval from late spring to late summer (August 15th), followed by an increase to a twenty-one day reentry interval for the remainder of the

Table 3. Grape variety, application rate (lb/acre), method of irrigation and location of vineyards monitored by the CDFA in 1989.

Field	Grape Variety	Rate (lb/acre)	Type of Irrigation	Location
1	University	0.50	Drip	Delano
2	Christmas	0.50	Drip	Delano
3	Ribier	0.50	Drip	Delano
4	Emperor	0.50	Drip	Delano
5	Flame	0.75	Drip	Delano
6	Flame	0.75	Drip	Delano
7	Flame	0.75	Drip	Delano
8	Flame	1.00	Drip	Delano
9	Flame	1.00	Drip	Delano
10	Flame	1.00	Flood	Delano
11	Flame	1.00	Flood	Delano
12	Flame	1.00	Flood	Delano
13	Malaga	1.00	Flood	Madera
14	Flame	0.75	Flood	Madera
15	Flame	0.75	Flood	Madera
16	Flame	0.75	Flood	Madera
17	Flame	0.75	Flood	Madera
18	Thompson	0.75	Flood	Madera
19	Thompson	0.75	Flood	Madera
20	Calmeria	0.50	Drip	Madera
21	Thompson	0.50	Drip	Madera
22	Thompson	0.50	Flood	Fresno
23	Grenache	0.75	Flood	Fresno
24	Grenache	0.50	Flood	Fresno
25	Grenache	0.75	Flood	Fresno
26	Thompson	0.50	Drip	Delano
27	Muscat	0.75	Flood	Fresno
28	Flame	1.00	Flood	Delano
29	Flame	0.50	Drip	Madera
30	Red Globe	0.50	Drip	Delano
31	Thompson	0.50	Drip or Flood	Delano
32	Thompson	0.50	Drip or Flood	Delano
33	Ribier	1.00	Drip	Delano
34	University	1.00	Drip	Delano
35	Christmas	1.00	Drip	Delano
36	Emperor	1.00	Drip	Delano

growing season. The corresponding reduction in methomyl use, as a result of the longer reentry interval, should result in fewer fieldworker illnesses and lower populations of methomyl resistant insect pests.

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