

CHARACTERIZATION OF METHOMYL DISSIPATION
ON GRAPE FOLIAGE

By

Matthew Reeve, Environmental Hazard Scientist
Linda O'Connell, Associate Environmental Hazard Scientist

HS-1565 March 2, 1990

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection, and Worker Safety
Worker Health and Safety Branch
1220 N Street, Sacramento, California 95814

SUMMARY

The carbamate methomyl (Lannate(R)) was monitored over a six month period to evaluate the most recent regulatory policies concerning the biphasic reentry interval. This interval is 7 days up to July 1, followed by an increase to 21 days for the remainder of the growing season. The study included Fresno, Madera, and Kern counties; all of which are prominent table grape growing regions in California. Foliage sampling, using leaf punches, was the method of data collection. In all, 42 fields were sampled between the months of June and November, and the compiled results do show an increase in half-life values with the progression of summer months. However, the data does not conform with the deadline of July 1 as the establishment of the new reentry period. Instead, the 21 day interval does not seem justified until the middle of August.

INTRODUCTION

Methomyl (S-Methyl-N-((methylcarbamoyl)-thioacetimidate) is a broad spectrum insecticide registered for use on a large variety of crops. The carbamate is utilized throughout the growing season for quick and effective suppression of target insect populations. In the case of the table grape industry, methomyl is the chemical of choice for the control of the variegated leafhopper (Erythroneura elegantula), a serious pest. From a toxicological standpoint, the pesticide has a category I rating with an acute oral LD50 of 17 mg/kg and 23.5 mg/kg for male and female rats, respectively. When applied to the skin of rabbits at the maximal rate of 500 mg/kg, methomyl produced no sign of anticholinesterase effect or weight loss (8). It is available as a 90 percent water-soluble powder and as a 24 percent weight water-soluble liquid (8).

Two suspected (one confirmed) episodes of pesticide related illness during the summer of 1988 brought methomyl to the forefront of public scrutiny, and catalyzed a reassessment of the carbamate's behavior in the environment (1). 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 (DFR) study established 0.1 micrograms/cm² as the safe level for reentry into the field. A second potential illness episode on September 23, 1988 was evaluated, and later discounted due to a lack of statistical and symptomatic evidence (1). However, the DFR data compiled as part of this second investigation were pivotal in characterizing the seasonally related dissipative behavior of methomyl. The findings were incorporated into a regulatory policy which based the reentry interval on a seasonal parameter. In other words, prior to July 1, the interval was amended to seven days; after July 1 the interval was extended to 21 days. This was in marked contrast to the previous reentry period of two days.

In order to substantiate the newly proposed regulations, an investigative team was assigned to study the dissipative behavior of methomyl in grape vineyards located in three of the largest table grape producing counties in the state: Kern, Madera, and Fresno. Sampling was conducted over a six month period (June-November) to either validate or discount the current theory proposing a high correlation between the progression of summer months and a corresponding increase in half-life values.

METHODS AND MATERIALS

The sampling scheme for this particular study followed a diagonal pattern within the designated fields. There were six (later amended to four) randomly chosen rows per block, labelled A to F. A five row buffer was established on either side of the experimental plot to reduce the possibility of artifacts (edge effect) affecting data results. The location of sampling within rows was based on multiples of five vines, more specifically:

<u>Row</u>	<u>Sample Site Dimensions</u>
A	5-44
B	10-49
C	15-54
D	20-59
E	25-64
F	30-69

The leaves were randomly selected within close proximity to the ripening fruit to better estimate the extent of dermal exposure fieldworkers may be subjected to during harvesting activities. 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, so a number of leaves may have had more than one leaf punch. All sampled rows were identified by the presence of survey tape tied to the endpost and both margins of the forty vines.

Cultural activities such as cane turning, cane cutting, and harvesting are subject to the demands of a particular grape variety. As a result, it was difficult to determine which side of the vineyard row would eventually be harvested by the fieldworker. In order to provide an adequate representation of the overall degradation profile, north versus south facing rows were randomly assigned for each vineyard. For example, once the boundaries of the experimental plot were determined and the rows assigned, a decision was then made as to which side of the row (north versus south facing) would be sampled.

A Birkestrand leaf punch (2.523 cm in diameter) and a four ounce glass jar were utilized for the leaf disc collection. Once an entire sample was taken (40 leaf discs), the leaf punch was rinsed in a plastic bag containing distilled water, and dried; in the attempt to remove any residual pesticide present on the equipment. This procedure was followed after every sample. All of the sample collections were stored on ice and transported to Sacramento by the following morning to insure extraction within a 24 hour period.

Once at the laboratory, the leaf discs were triple rinsed in an aqueous surfactant solution, and the washings combined and extracted with dichloromethane. The extract was dehydrated by decanting through anhydrous sodium sulfate into a 250 ml boiling flask. The concentrations of methomyl were then determined by liquid chromatography (5). The dichloromethane was evaporated in vacuo and exchanged into methane to a final volume of 5 ml.

DATA ANALYSIS

The laboratory reported values of the methomyl concentration (ug/sample) for each sample (40 leaf discs) were divided by the surface area of 40 two-sided leaf discs in order to present the data in the units of micrograms/cm². Half-lives were then determined using logarithmically transformed mean values of sample replicates for each field. The results (mean values) were analyzed using a least squares fit regression of data. Regressions with an

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 sample were below the minimum level of detection (0.25 ug/sample). Only actual data were used for the regressions, therefore 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 was the date of application, according to a monthly schedule. 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

The results of our investigative study are provided in graphical and tabular form. Statistical results for half-lives each month are presented in Table 1. The location, grape variety, time of application, rate, irrigation method, and half-life for each of the fields monitored, are listed in Table 2. Monthly dewpoint data for May through October from 1983 to 1988, are presented in Table 3. Table 4 provides the monthly atmospheric pollutant concentrations for May through October in 1988 for the Bakersfield area (Oildale). Figures 1 and 2 display a more qualitative view of month versus half-life values. Figure 3 illustrates the inverse correlation of $1/\text{half-life}$ versus temperature for both years (1988-89) of the study. Figure 4 highlights the sampling site and weather station locations topographically. The dissipation curves for each month and location are provided in Figures 5 through 13 in 1989. This distinction (location) was provided to visually examine what importance geography may have on the degradative behavior of methomyl. Figures 14 through 16 exhibit temperature data for May to October. The bars denote the thirty year average, the solid lines represent 1988 data, and the corresponding dashed lines display 1989 temperatures. All of the data is reported on a daily basis, presenting both maximum and minimum temperatures for all three time frames. The filled in portions of the figure present the days in 1989 which have higher temperatures in comparison to 1988.

There was a noticeable increase in half-life values with the progression of summer months (Table 1, Figure 1). The upward trend was not linear, instead it appeared to follow a two stage pattern. June and July represented the lower level, followed by a substantial jump to the higher plateau of August, September, and October (Figure 1). A comparison with 1988 data tended to support this observation linking the environmental persistence of methomyl with the late growing season (Figures 1,2). The two year compilation of data also confirmed the importance of September from both the purely scientific and regulatory points of view. It represented the high point in half-life values, and the greatest potential health risk to fieldworkers. The month of October was equally important for these reasons, though it did not signal the onset of a substantially reduced dissipation rate as did September.

The sampling site was found to have a minimal effect on the degradation rate of methomyl according to Figures 6-11, and a comparison of half-life results in the months of July and August for Madera, Fresno, and Delano (Table 2).

The correlation between application rate and length of half-life for methomyl was also examined in Table 2, and there was no apparent trend. Several fields with rates of 0.5 lb/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.

DISCUSSION

The findings of the 1988 and 1989 studies emphasize the potential health risks to field personnel working in methomyl treated fields late in the growing season. The months of August through October are of particular interest since they signal the onset and continuation of a higher trend in half-lives (Figures 1,2). September is unique in having the highest mensal half-life for two consecutive years, according to dislodgeable foliar studies conducted in 1988 and 1989 (Table 1). Consequently, September has been established as the critical period for the implementation of the second phase of the reentry interval. This 21 day reentry interval is to be enacted to mitigate the greater health hazard associated with the continued presence of methomyl in the field.

The dissipative behavior of methomyl during the months of May through July (1988-89) follows a more predictable pattern, never exceeding a half-life of two days. From a regulatory standpoint, this reduces the window of reentry to seven days, the time correlated with a reduction of methomyl concentrations to levels equal to or less than 0.1 micrograms/cm².

Both phases of the regulation are significant in the respect that they are the result of a two year compilation of data. Rarely has a chemical been so closely monitored in an agricultural situation for one particular crop (grapes). The findings also raise several questions pertaining to the persistence of methomyl late in the growing season, a number of which will be addressed in the body of the discussion.

There are a number of factors in the environment which could explain the seasonally linked dissipative "behavior" of methomyl. In the table grape industry for example, the cultural practice of reducing or eliminating irrigation in the fields late in the growing season is followed to promote dormancy of the vines (6). This may also impede the rate of hydrolysis of methomyl by a reduction of available water in the environment, and provide some insight into explaining the extended half-life of methomyl later in the growing season. Conversely, the two fields monitored during the September precipitation (0.5 inch) had half-lives approaching two days (Table 2). It certainly seems plausible the rain may have just washed the chemical off the foliage, yet the instability of methomyl in the presence of water must also be considered. Recent studies tend to confirm the substantial role hydrolysis plays as a pathway of methomyl deactivation. The results of an experiment monitoring the residues of methomyl in mint hay and oil concluded such factors as location, application method, or plant species, were inconsequential in the carbamate's dissipation. Instead, vapor pressure and hydrolysis were believed to be the primary contributors to pesticide instability (2).

There are basically two types of irrigation practiced by the grape growers

in our study. Flood irrigation, which involves filling the furrows with water, via the use of a standpipe. The furrows are interrupted by a series of levies which contain the water to allow slow absorption into the soil, and evaporation into the atmosphere. The second practice utilizes more current technology and an efficient use of the irrigation water. Drip lines are laid adjacent to the base of the grapevine along the length of the row. Holes in the plastic tubing produce a steady drip of water within the root zone of the plant. One would suspect the levels of available water to be much higher in the case of flood irrigation. Higher levels of water, in turn, should increase the rate of hydrolysis of the pesticide. Five growers flood irrigate their vineyards. However, a comparison of these and other fields (using drip irrigation) monitored during the same period do not corroborate this line of thought. Instead, the rate of dissipation was well within the range of results for that particular month (Table 2). This inconsistency may be partially explained by the chemical properties of methomyl. The carbamate has a high water solubility (5.8 g/100 ml) which would retard its volatility in a humid environment (2). Therefore, the high humidity produced by flood irrigation may have a negligible effect on methomyl dissipation. Perhaps there is a specific level of water which corresponds with the maximum rate of hydrolysis for methomyl. Any increase in this level may not have any measurable effect on pesticide deactivation. It is certainly an area of study which warrants further investigation.

Temperature is another important consideration potentially affecting the persistence of methomyl in the field. The average temperatures for the six month period indicate a correlation with the half-life trend of the chemical (Figures 1-3). That is, lower temperatures tend to prolong its presence in the field. Under cold extremes the carbamate is quite stable. Methomyl fortified corn fodder and silage could be stored four months at -15 degrees C with no measurable loss of insecticide (3). Similarly, corn and tomato samples stored at -17 degrees C and -36 degrees C showed no loss of the insecticide after 111 days of storage (3). This represents extremes of temperature which would never be encountered in an agricultural situation, yet it is a viable example of methomyl's stability at lower temperatures.

The inverse correlation of temperature versus one over half-life was examined for 1988 and 1989 in Figure 3. Except for the month of June in the 1989 study, there does appear to be a trend of higher half-lives with cooler temperatures. The same pattern is evident with 1988 data, the anomalous results evident in the early season half-life data (May). Apparently, temperature alone does not account for the transitory behavior of methomyl early in the growing season. This certainly does not suggest the data collected during these two months (May 1988, June 1989) are aberrant; rather, there may be other factors such as dew formation, or atmospheric oxidants which may adversely affect methomyl stability.

Dew point is defined as the temperature at which air reaches saturation, any further decrease in temperature will result in water condensation (10). In the case of methomyl, formation of water on the leaf surface would stimulate hydrolysis of the pesticide and reduce the half-life. This would seem to be a viable explanation for the lower $t_{1/2}$ values in May and June in Delano except for the discrepancy in mean monthly dewpoint results, and average temperatures. More specifically, the minimum temperatures were rarely low enough to reach dewpoint, therefore condensation of water on the grape foliage was seldom a factor (Table 3). The average monthly temperature in

May 1988 for the Delano area was 51.6 degrees F, the average monthly dewpoint was 47 degrees F (Table 3). The few instances where dewpoint was reached appear to have occurred early in the month; the study, however, was not initiated until late May (1). The same pattern was evident for June 1989, daily minimum temperatures never approached the mean monthly dewpoint of 47 degrees F (Figure 3).

The smog levels may be significantly lower during the early summer months. In Stanislaus county for example, the concentration of atmospheric oxidants were found to be much lower in June in comparison to July. Secondly, there was a highly significant correlation (one percent) between temperature and oxidant level (7). Air quality data for 1987 and 1988 tend to support these findings for ozone (O_3), which steadily increased from May through October, followed by a substantial decline to non-detectable levels in November and December. The atmospheric pollutant data for the summer of 1989 is not yet available, yet one would suspect the pattern (seasonal concentrations of ozone) to be quite similar to that of previous years.

The correlation of ozone levels with the methomyl dissipation rate over the six month period of the study is quite compelling (Tables 2,4). Perhaps the higher concentrations of O_3 late in the growing season induce plant foliar damage, in turn disrupting the metabolic activities of the grape leaves. Plant foliage damaged by ozone respond by closing their stomatal openings (10). This would reduce the transpiration rate and the amount of available water on the leaf surface. The most prevalent pathway of methomyl dissipation (hydrolysis) may as a consequence, significantly decrease. Other metabolic functions may be damaged as well, often resulting in leaf stippling (10). One can assume that this damage may alter the production of extracellular enzymes or other by-products of cellular activity which can potentially degrade methomyl. More sensitive plants show symptoms of ozone damage at concentrations as low as 0.05 to 0.10 ppm within a few hours of exposure. Readings from the Bakersfield area (Oildale) for the months of September and October (1988) exceeded 0.09 ppm for 16 and 17 days respectively (Table 4). Therefore, the potential does exist that atmospheric oxidants such as ozone may play a role in methomyl's environmental persistence in the late summer season.

The discussion would not be complete without some reference to the intimate association of methomyl with the plant surface. An understanding of the pesticide's chemical reactivity with the plant surface, and plant physiology (e.g., turgor pressure) are invaluable in assessing the carbamate's stability in the environment. When creating the commercial preparation for actual use, formulation chemists consider all of these aspects for best results. Different formulations tend to affect the rate of absorption of the pesticide into the plant. With water as a carrier, methomyl has demonstrated the ability to penetrate the leaf cuticle. Surface residues in one study were essentially depleted after 48 hours (4). Conversely, dust formulations tend to persist much longer in the environment and have very little translocative ability (4). This may be explained by the reduced contact of methomyl with the plant surface when in the presence of dust either as part of a formulation, or in the form of soil particles. It certainly seems plausible then, that methomyl applied in the presence of adjuvants such as spreaders, stickers, or buffers, would enhance leaf cuticle penetration of the pesticide, and rapidly decrease surface residue levels. Perhaps by altering the chemical formulation, growers can then

effectively deal with the persistence of methomyl later in the growing season. Sticker-spreaders were absent from all September and October applications, providing credence to this theory.

In this discussion, a few theorizations were provided on the salient physical and chemical properties of the environment which potentially affect the dissipative "behavior" of methomyl. Other factors such as soil type, microbial activity, and presence of other agricultural chemicals which may interact with methomyl, are also worthy of mention. Pinpointing which factor, and to what extent it contributed to the degradative pattern of methomyl in the field would be difficult, if not impossible. Several contributing elements acting in combination, would be the most likely explanation. Whatever the case, there is a clear cut trend; methomyl does persist in the field for extended periods later in the growing season. Consequently, a revised regulation will be implemented to prevent further illness incidents associated with the carbamate.

ACKNOWLEDGEMENTS

Special thanks to Stan Bissell for his help in the statistical analysis, to Muffet Wilkerson, Stacy Powell, and Jennifer Garland, for their work in producing Figures 14-16, and to Mercedita Del Valle, Marvin Roe, and Stella Taylor for their work in conducting the laboratory analyses.

TABLE 1

Methomyl Half-life Estimates (Days)

1989			
Month of Application	Estimate	Estimate ± Standard Error	Estimate ± 95% CI
June	2.07	1.99	2.24
		2.15	1.92
July	1.89	1.83	2.01
		1.95	1.78
August	3.52	3.33	3.95
		3.72	3.17
September	4.55	3.88	6.94
		5.50	3.38
October	4.39	4.20	4.81
		4.39	4.04
1988			
Month of Application	Estimate	Estimate ± Standard Error	Estimate ± 95% CI
May	1.11	1.08	0.98
		1.14	1.27
September	5.30	5.30	6.30
		5.30	4.60

TABLE 2

Calculated Half-Lives For Methomyl Treated Fields

Field	Days Post	# of MDLs	Replicates (ug/cm ²)										Half Life	Date of Appl'n	Rate Irrigation
			A	B	C	D	E	F	Mean	Log 10 Mean	Nat.log Mean				
University	1.00		0.131	0.037	0.214	0.216	0.221	0.281	0.183	-0.737	-1.697	2.21	June 3	0.50	D
	2.00		0.127	0.047	0.121	0.148	0.166	0.151	0.127	-0.898	-2.067				
	3.00		0.106	0.032	0.091	0.097	0.073	0.087	0.081	-1.091	-2.512				
	4.00		0.037	0.025	0.072	0.081	0.042	0.094	0.059	-1.232	-2.837				
	5.00		0.026	0.023	0.027	0.060	0.080	0.052	0.045	-1.350	-3.108				
	9.00		0.005	0.006	0.016	0.023	0.020	0.016	0.014	-1.839	-4.235				
16.00	x	0.001	0.000	0.002	0.005	0.002	0.004	0.002	-2.628	-6.051					
Christmas	1.00		0.158	0.139	0.219				0.172	-0.765	-1.761	2.41	June 3	0.50	D
	2.00		0.108	0.088	0.072				0.089	-1.048	-2.414				
	3.00		0.106	0.083	0.090				0.093	-1.031	-2.374				
	4.00		0.001	0.057	0.055				0.038	-1.423	-3.276				
	5.00		0.034	0.038	0.047				0.040	-1.402	-3.227				
	9.00		0.016	0.019	0.014				0.016	-1.785	-4.111				
Ribier	16.00		0.001	0.001	0.004				0.002	-2.746	-6.324				
	1.00		0.151	0.100	0.164	0.134	0.112	0.130	0.132	-0.880	-2.026	2.26	June 7	0.50	D
	2.00		0.205	0.103	0.149	0.138	0.128	0.180	0.150	-0.822	-1.894				
	5.00		0.048	0.060	0.035	0.026	0.031	0.054	0.042	-1.374	-3.164				
	12.00		0.011	0.003	0.007	0.003	0.003	0.005	0.005	-2.263	-5.210				
	1.00		0.480	0.742	0.125	0.000	0.119	0.411	0.313	-0.505	-1.162	1.38	June 9	0.50	D
Emperor	4.00		0.056	0.117	0.012	0.011	0.020	0.058	0.046	-1.341	-3.088				
	11.00		0.004	0.003	0.001	0.001	0.001	0.002	0.002	-2.727	-6.280				
	7.00		0.017	0.027	0.010	0.010	0.011	0.028	0.017	-1.765	-4.064	2.84	June 22	0.75	D
	8.00		0.017	0.017	0.015	0.006	0.025	0.010	0.015	-1.826	-4.205				
	11.00		0.008	0.008	0.002	0.003	0.004	0.003	0.005	-2.334	-5.374				
	14.00		0.002	0.008	0.003	0.001	0.003	0.005	0.004	-2.450	-5.641				

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm ²)										Half Life	Date of Appl'n	Rate Irrigation
			A	B	C	D	E	F	Mean	Log 10 Mean	Nat.log Mean				
5E	7.00		0.013	0.012	0.011	0.020	0.029	0.032	0.020	-1.710	-3.937	2.71	June 22	0.75	D
	8.00		0.022	0.028	0.012	0.021	0.028	0.009	0.020	-1.694	-3.901				
	11.00		0.010	0.008	0.006	0.010	0.010	0.010	0.009	-2.051	-4.723				
	14.00		0.003	0.005	0.003	0.002	0.005	0.003	0.004	-2.449	-5.638				
5G	8.00		0.027	0.012	0.054	0.080	0.014	0.023	0.035	-1.455	-3.351	1.72	June 22	0.75	D
	11.00		0.004	0.005	0.005	0.006	0.009	0.006	0.006	-2.238	-5.154				
	14.00		0.002	0.003	0.003	0.004	0.004	0.003	0.003	-2.504	-5.766				
FL1	0.13		1.099	1.056	1.106	0.978	1.059	1.235	1.089	0.037	0.085	1.83	June 29	1.00	D
	1.00		0.956	0.870	0.961	0.867	0.735	1.011	0.900	-0.046	-0.105				
FL2	4.00		0.388	0.507	0.441	0.220	0.321	0.275	0.358	-0.446	-1.026				
	7.00		0.080	0.084	0.094	0.043	0.127	0.049	0.080	-1.099	-2.531				
	0.13		1.261	1.148	1.036	1.068	1.209	0.945	1.111	0.046	0.105	2.14	June 29	1.00	D
	1.00		0.174	0.826	0.941	0.966	0.991	1.181	0.847	-0.072	-0.167				
DEblock	4.00		0.521	0.323	0.399	0.421	0.737	0.647	0.508	-0.294	-0.677				
	7.00		0.136	0.048	0.110	0.072	0.165	0.115	0.108	-0.967	-2.227				
	0.50		0.444	0.200	0.444	0.325	0.355	0.323	0.348	-0.458	-1.055	2.01	July 26	0.75	F
	1.00		0.288	0.231	0.338	0.447	0.338	0.360	0.334	-0.477	-1.098				
DWBblock	6.00		0.027	0.012	0.025	0.021	0.017	0.043	0.024	-1.614	-3.717				
	11.00		0.002	0.012	0.021	0.000	0.000	0.000	0.012	-1.927	-4.438				
	19.00	xx	0.001	0.001	0.000	0.000	0.000	0.000	0.001	-3.217	-7.408				
	26.00	xxx	0.000	0.000	0.000	0.001	0.000	0.000	0.000	-3.397	-7.823				
DWBblock	0.50		0.520	0.311	0.357	0.604	0.396	0.385	0.429	-0.368	-0.847	1.41	July 26	0.75	F
	1.00		0.075	0.283	0.283	0.348	0.385	0.225	0.267	-0.574	-1.322				
	6.00		0.022	0.008					0.015	-1.826	-4.206				
	11.00		0.001	0.004	0.002				0.002	-2.613	-6.016				
19.00	xxxx	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-3.505	-8.071					

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm ²)										Half Life	Date of Appl'n	Rate Irrigation		
			A	B	C	D	E	F	Mean	Log 10 Mean	Nat.log Mean						
ThomS	1.50		0.922	1.022	1.329	0.752	1.229	0.835	1.015	0.006	0.015	0.015	0.006	0.015	July 26	0.75	F
	3.00		0.128	0.121	0.176		0.086		0.128	-0.893	-2.057	0.128	-0.893	-2.057			
	8.00		0.005	0.005	0.005	0.004	0.004	0.006	0.005	-2.314	-5.328	0.005	-2.314	-5.328			
	11.00		0.001	0.002					0.001	-2.825	-6.504	0.001	-2.825	-6.504			
	20.00	xx	0.001	0.000	0.000				0.001	-3.253	-7.491	0.001	-3.253	-7.491			
	27.00	xx	0.000	0.000	0.001	0.001			0.001	-3.253	-7.489	0.001	-3.253	-7.489			
ThomN	1.50		0.962	0.985	0.907	0.947	0.729	0.878	0.901	-0.045	-0.104	0.901	-0.045	-0.104	July 26	0.75	F
	3.00		0.126	0.019	0.081	0.104		0.105	0.087	-1.060	-2.441	0.087	-1.060	-2.441			
	8.00		0.006	0.007	0.007	0.006	0.004	0.007	0.006	-2.205	-5.078	0.006	-2.205	-5.078			
	11.00		0.015	0.001		0.002	0.022	0.003	0.009	-2.064	-4.752	0.009	-2.064	-4.752			
	20.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071	0.000	-3.505	-8.071			
	27.00	xxx	0.000	0.000	0.001	0.000			0.000	-3.325	-7.655	0.000	-3.325	-7.655			
ZerkerN	1.00		0.902	0.334	0.496	0.405	0.831	0.922	0.648	-0.188	-0.433	0.648	-0.188	-0.433	July 12	1.00	F
	5.00		0.093	0.086	0.243				0.141	-0.851	-1.960	0.141	-0.851	-1.960			
	11.00		0.010	0.005	0.017	0.004	0.023	0.004	0.011	-1.973	-4.543	0.011	-1.973	-4.543			
	20.00	xxx	0.001	0.000	0.000	0.000	0.001	0.000	0.001	-3.271	-7.531	0.001	-3.271	-7.531			
	1.00		1.580	1.054	1.266	0.588	1.003	0.831	1.054	0.023	0.052	1.054	0.023	0.052	July 13	1.00	F
	2.00		0.800	0.780	0.679				0.753	-0.123	-0.284	0.753	-0.123	-0.284			
ZerkerS	5.00		0.344	0.152	0.162				0.219	-0.659	-1.516	0.219	-0.659	-1.516			
	6.00		0.213	0.172	0.071	0.203	0.192	0.071	0.154	-0.814	-1.873	0.154	-0.814	-1.873			
	12.00		0.009	0.004	0.016	0.017	0.010	0.002	0.010	-2.011	-4.631	0.010	-2.011	-4.631			
	21.00		0.002	0.001	0.004	0.002	0.002	0.002	0.002	-2.627	-6.048	0.002	-2.627	-6.048			
	1.00		1.145	0.699	0.719	0.983	1.550	0.922	1.003	0.001	0.003	1.003	0.001	0.003	July 13	1.00	F
	4.00		0.628	0.436	0.405	0.314	0.476	0.284	0.424	-0.373	-0.859	0.424	-0.373	-0.859			
Ave24	5.00		0.203	0.243	0.233	0.294	0.284	0.003	0.210	-0.678	-1.562	0.210	-0.678	-1.562			
	11.00		0.053	0.008	0.025	0.018	0.021	0.005	0.022	-1.662	-3.827	0.022	-1.662	-3.827			

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm2)						Mean	Log 10 Mean	Nat.log Mean	Half Life	Date of Appl'n	Rate Irrigation	
			A	B	C	D	E	F							
DibMoE	0.50		0.901	1.369	1.066	1.491	1.939	2.060	1.471	0.168	0.386	1.53	July 25	0.75	F
	1.00		0.171	0.285	0.191	0.299	0.172	0.343	0.244	-0.613	-1.413				
	2.00		0.116	0.244	0.112	0.135	0.099		0.141	-0.850	-1.958				
	7.00		0.017	0.039	0.010	0.015	0.011	0.025	0.020	-1.708	-3.934				
	12.00		0.003	0.008	0.003	0.004	0.002	0.002	0.004	-2.448	-5.637				
	20.00	xxx	0.000	0.002	0.000	0.000			0.001	-3.089	-7.112				
	27.00	x	0.001	0.001	0.000	0.001			0.001	-3.105	-7.151				
	36.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				
	0.50		0.643	0.474	0.641	0.550	0.692	0.589	0.598	-0.223	-0.514	1.51	July 25	0.75	F
	1.00		0.240	0.255	0.333	0.235	0.311	0.192	0.261	-0.583	-1.343				
DibMoW	7.00		0.014	0.033	0.024	0.013	0.024	0.014	0.020	-1.690	-3.891				
	12.00		0.001	0.004	0.003	0.003	0.001	0.002	0.002	-2.623	-6.039				
	20.00	xx	0.001	0.000	0.001	0.000			0.001	-3.280	-7.552				
	36.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				
	0.50		0.664	0.575	0.408				0.970	-0.013	-0.031	1.97	July 27	0.50	F
	5.00		0.025	0.027	0.014	0.065	0.031	0.063	0.037	-1.427	-3.285				
	18.00		0.002	0.001	0.002	0.001			0.001	-2.892	-6.660				
	26.00	xxxx	0.000	0.000	0.000	0.001			0.000	-3.408	-7.848				
	33.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				
	0.50		0.392	0.299	0.409	0.389	0.525	0.523	0.423	-0.374	-0.861	1.85	July 27	0.50	F
LamEBloc	5.00		0.025	0.024	0.027	0.026	0.022	0.036	0.027	-1.574	-3.625				
	18.00	xx	0.001	0.000	0.000				0.000	-3.347	-7.706				
	26.00	xxx	0.000	0.000	0.000	0.001			0.000	-3.408	-7.848				
	33.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm ²)										Half Life	Date of Appl'n	Rate Irrigation
			A	B	C	D	E	F	Mean	Log 10 Mean	Nat.log Mean				
Malaga	4.00		0.191	0.147	0.153	0.128	0.097	0.075	0.132	-0.880	-2.027	3.38	July 22	1.00	F
	9.00		0.023	0.015	0.016	0.028	0.016	0.008	0.018	-1.750	-4.029				
	28.00		0.000	0.000	0.001	0.001			0.001	-3.157	-7.270				
	1.00		0.155	0.132	0.085	0.183	0.016	0.034	0.101	-0.996	-2.294	1.70	July 26	0.50	D
	2.00		0.115	0.064	0.041	0.117	0.008	0.014	0.060	-1.222	-2.813				
	6.00		0.038	0.003	0.010	0.017	0.006	0.002	0.013	-1.899	-4.373				
BCaN	15.00	xx	0.001	0.000	0.001	0.000			0.001	-3.280	-7.552				
	19.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				
	27.00	xxx	0.001	0.000	0.000	0.000			0.000	-3.388	-7.801				
	1.00		0.023	0.033	0.029	0.057	0.020	0.040	0.034	-1.471	-3.388	2.28	July 26	0.50	D
	2.00		0.027	0.040	0.028	0.033	0.037	0.034	0.033	-1.478	-3.404				
	6.00		0.003	0.014	0.007	0.012	0.009	0.004	0.008	-2.089	-4.809				
BCaS	15.00	xx	0.001	0.000	0.000	0.001			0.000	-3.329	-7.665				
	19.00	xxxx	0.000	0.000	0.000	0.000			0.000	-3.505	-8.071				
	27.00	xxxx	0.000	0.000	0.000	0.000			0.000						
	34.00	xxxx	0.000	0.000	0.000	0.000			0.000						
	0.50		0.424	0.900	0.609	1.030			0.740	-0.130	-0.300	3.54	Aug. 10	0.75	F
	5.00		0.111	0.178	0.146	0.092			0.132	-0.880	-2.027				
1 Gre	12.00		0.041	0.013	0.035	0.035			0.031	-1.506	-3.467				
	19.00		0.008	0.008	0.011	0.003			0.008	-2.121	-4.884				
	26.00		0.005	0.004	0.002	0.008			0.005	-2.315	-5.331				
	0.50		0.413	0.607	0.569	0.545			0.534	-0.273	-0.628	3.79	Aug. 10	0.75	F
	5.00		0.106	0.139	0.078	0.108			0.108	-0.967	-2.226				
	12.00		0.038	0.016	0.035	0.017			0.026	-1.579	-3.636				
2 Gre	19.00		0.016	0.020	0.008	0.025			0.017	-1.767	-4.069				

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm ²)										Half Life	Date of Appl'n	Rate Irrigation			
			A	B	C	D	E	F	Mean	Log 10 Mean	Nat.log Mean							
3 Gre	0.50		0.327	0.899	0.610	0.787						0.656	-0.183	-0.422	4.66	Aug. 10	0.75	F
	5.00		0.090	0.200	0.180	0.142						0.153	-0.815	-1.877				
	12.00		0.028	0.224	0.108	0.025						0.096	-1.016	-2.340				
	19.00		0.025	0.034	0.033	0.037						0.032	-1.494	-3.440				
1 Pan	3.00		0.023	0.030	0.016	0.024						0.023	-1.634	-3.761	3.83	Aug. 11	0.50	D
	11.00		0.008	0.004	0.004	0.004						0.005	-2.294	-5.282				
	18.00		0.001	0.000	0.001	0.001						0.001	-3.197	-7.362				
	25.00		0.001	0.000	0.000							0.001	-3.240	-7.461				
25 Zino	3.00		0.167	0.207	0.280	0.257						0.228	-0.643	-1.480	2.27	Aug. 12	1.00	F
	11.00		0.010	0.008	0.023	0.070						0.028	-1.556	-3.583				
	18.00		0.002	0.001	0.003	0.002						0.002	-2.635	-6.067				
	4.00		0.189	0.188	0.142	0.847						0.341	-0.467	-1.074	1.59	Aug. 11	0.75	F
Mus	11.00		0.012	0.005	0.001	0.007						0.006	-2.210	-5.089				
	18.00		0.001	0.001	0.001	0.000						0.001	-3.122	-7.190				
	25.00	x	0.001	0.001	0.000	0.001						0.001	-3.211	-7.393				
	0.50		0.105	0.178	0.110	0.251						0.161	-0.793	-1.825	5.80	Aug. 29	0.50	D
Gs1	7.00		0.034	0.028	0.033							0.032	-1.500	-3.454				
	21.00		0.006	0.005	0.007	0.030						0.012	-1.918	-4.416				
	23.00		0.004	0.006	0.006	0.014						0.007	-2.125	-4.894				
	0.27		0.438			0.241						0.339	-0.469	-1.081	2.03	Sept. 18	0.50	D
Red Globe (rain)	1.00		0.046	0.088	0.142	0.038						0.079	-1.105	-2.544				
	7.00		0.015	0.042	0.015	0.011						0.021	-1.687	-3.886				
Thompson (rain)	1.00		0.063	0.085	0.034	0.016						0.050	-1.305	-3.004	2.34	Sept. 18	0.50	D or F
	7.00		0.033	0.013	0.002	0.005						0.013	-1.871	-4.309				
	14.00		0.003	0.000	0.000	0.000						0.001	-2.967	-6.833				

TABLE 2

Field	Days Post	# of MDLs	Replicates (ug/cm ²)						Mean	Log 10 Mean	Nat.log Mean	Half Life	Date of Appl'n	Rate Irrigation
			A	B	C	D	E	F						
Thompson	1.00		0.252	0.195	0.393	0.085		0.231	-0.636	-1.464	7.73	Sept. 26	0.50	D or F
	2.00		0.136	0.080	0.128	0.126		0.118	-0.929	-2.140				
	8.00		0.122	0.097	0.079	0.040		0.084	-1.075	-2.474				
	14.00		0.034	0.004	0.052	0.007		0.024	-1.620	-3.730				
	23.00		0.053	0.021	0.033	0.019		0.032	-1.500	-3.455				
Ribier	1.00		1.147	1.097	1.401	1.325		1.243	0.094	0.217	4.99	Oct. 3	1.00	D
	2.00		0.811	0.607	0.974	0.796		0.797	-0.099	-0.227				
	7.00		0.424	0.391	0.328	0.194		0.334	-0.476	-1.096				
Univ.	14.00		0.278	0.292	0.099	0.102		0.193	-0.715	-1.646				
	21.00		0.110	0.113	0.047	0.048		0.079	-1.101	-2.535				
	30.00		0.009	0.008	0.034	0.013		0.016	-1.804	-4.153				
	1.00		1.286	0.476	1.390	0.866		1.004	0.002	0.004	3.75	Oct. 10	1.00	D
	2.00		1.245	0.415	0.868	0.731		0.815	-0.089	-0.205				
	10.00		0.503	0.322	1.088	0.582		0.623	-0.205	-0.473				
	15.00		0.182	0.092	0.086	0.075		0.109	-0.965	-2.221				
Christmas	23.00		0.015	0.008	0.027	0.011		0.015	-1.821	-4.192				
	1.00		1.581	1.133	1.389	1.145		1.312	0.118	0.271	5.05	Oct. 10	1.00	D
	2.00		1.068	0.984	1.074	0.584		0.927	-0.033	-0.076				
	8.00		0.628	0.935	0.711	0.524		0.699	-0.155	-0.358				
	14.00		0.347	0.411	0.410	0.413		0.395	-0.403	-0.929				
Emperor	23.00		0.028	0.028	0.100	0.036		0.048	-1.318	-3.035				
	1.00		1.453	1.071	1.971	1.421		1.479	0.170	0.391	4.58	Oct. 10	1.00	D
	2.00		1.146	1.047	1.336	1.337		1.216	0.085	0.196				
	7.00		0.434	0.389	1.022	0.936		0.695	-0.158	-0.364				
	15.00		0.082	0.123	0.211	0.272		0.172	-0.764	-1.758				
23.00		0.013	0.011	0.093	0.098		0.054	-1.270	-2.924					

TABLE 3

Mean Monthly Dewpoint

McFarland

Year	May	June	July	August	September	October
1983	41	41	40	60	57	55
1984	52	50	58	57	53	46
1985	44	51	54	50	51	44
1986	47	52	51	57	51	47
1987	49	53	55	49	50	52
1988	47	53	60	56	50	50
1989	44	47	55	58	55	
Avg.	46.3	49.6	53.3	55.3	52.4	49.0

Visalia

Year	May	June	July	August	September	October
1983	25	48	55	63	60	54
1984	49	54	65	63	59	48
1985	46	56	59	58	56	50
1986	49	56	58	61	52	48
1987	51	55	53	58	55	53
1988	49	51	61	60	55	53
1989	43	46	54	57	56	
Avg.	44.6	52.3	57.9	60.0	56.1	51.0

TABLE 3

Mean Monthly Dewpoint

Fresno

Year	May	June	July	August	September	October
1983	48	48	48	56	54	51
1984	26	30	58	57	54	49
1985	47	55	56	55	55	45
1986	45	49	48	50	47	45
1987	44	44	43	47	45	51
1988	47	53	58	58	55	53
1989	51	52	58	59	57	
Avg.	44.0	47.3	52.7	54.6	52.4	49.0

(CIMIS, California Department of Water Resources)

TABLE 4

1988 Annual Statistics and Number of Occurrences of Daily Concentrations
Greater than 0.09 ppm

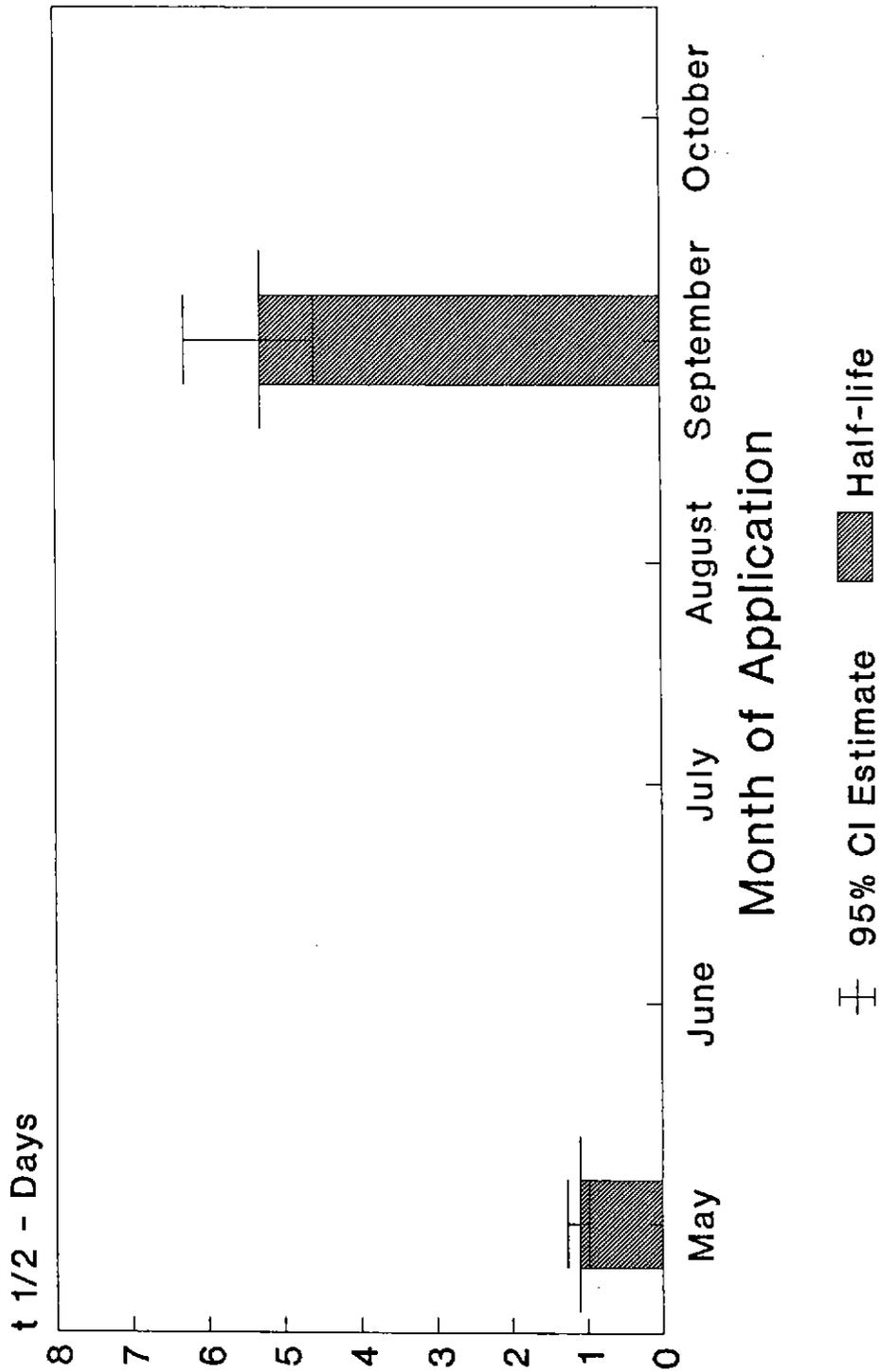
1988

	May	June	July	August	September	October
OZONE	2	8	13	13	16	17
CARBON MONOXIDE	0	0	0	0	0	0
NITROGEN DIOXIDE	0	0	0	0	0	0
SULFUR DIOXIDE	0	0	0	0	0	0

(California Air Quality Data, 1988, California Air Resources Board)

FIGURE 1

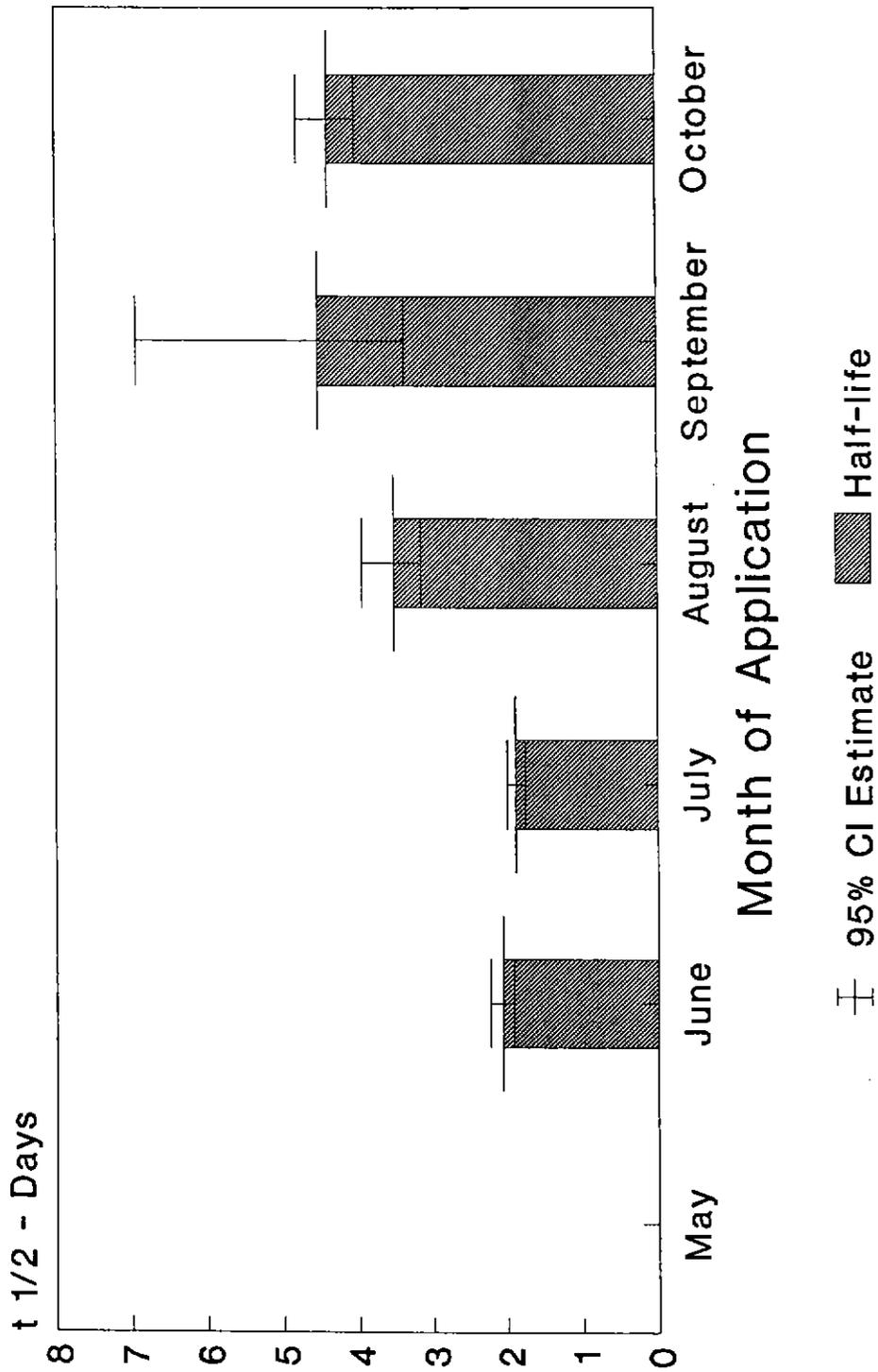
Methomyl Half-life Results 1988



95% Confidence Interval

FIGURE 2

Methomyl Half-life Results 1989



95% Confidence Interval

FIGURE 3

1/half-life vs. Temperature 1988-89

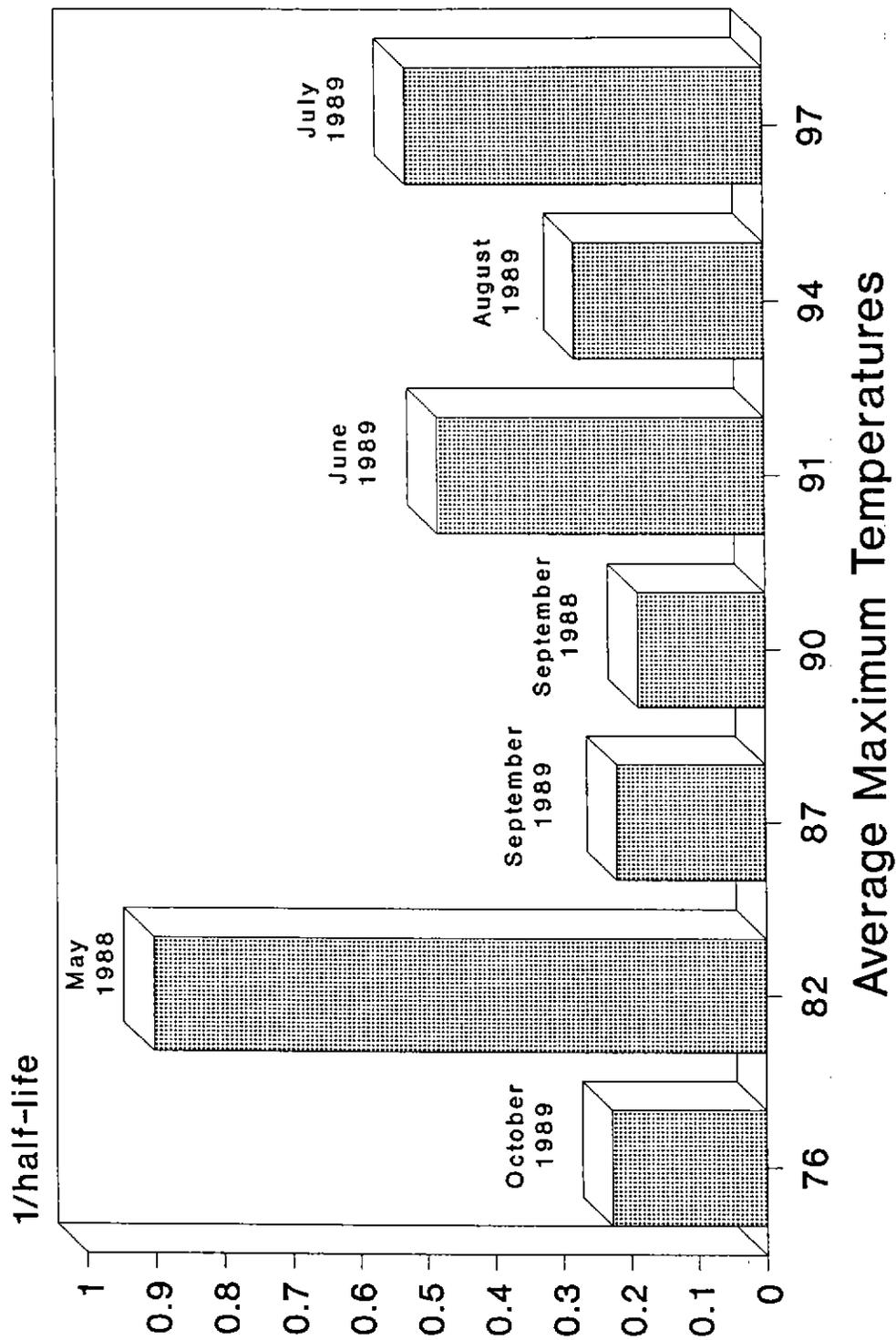


FIGURE 4 - Geographic Locations of Sampling Sites
and Weather Stations

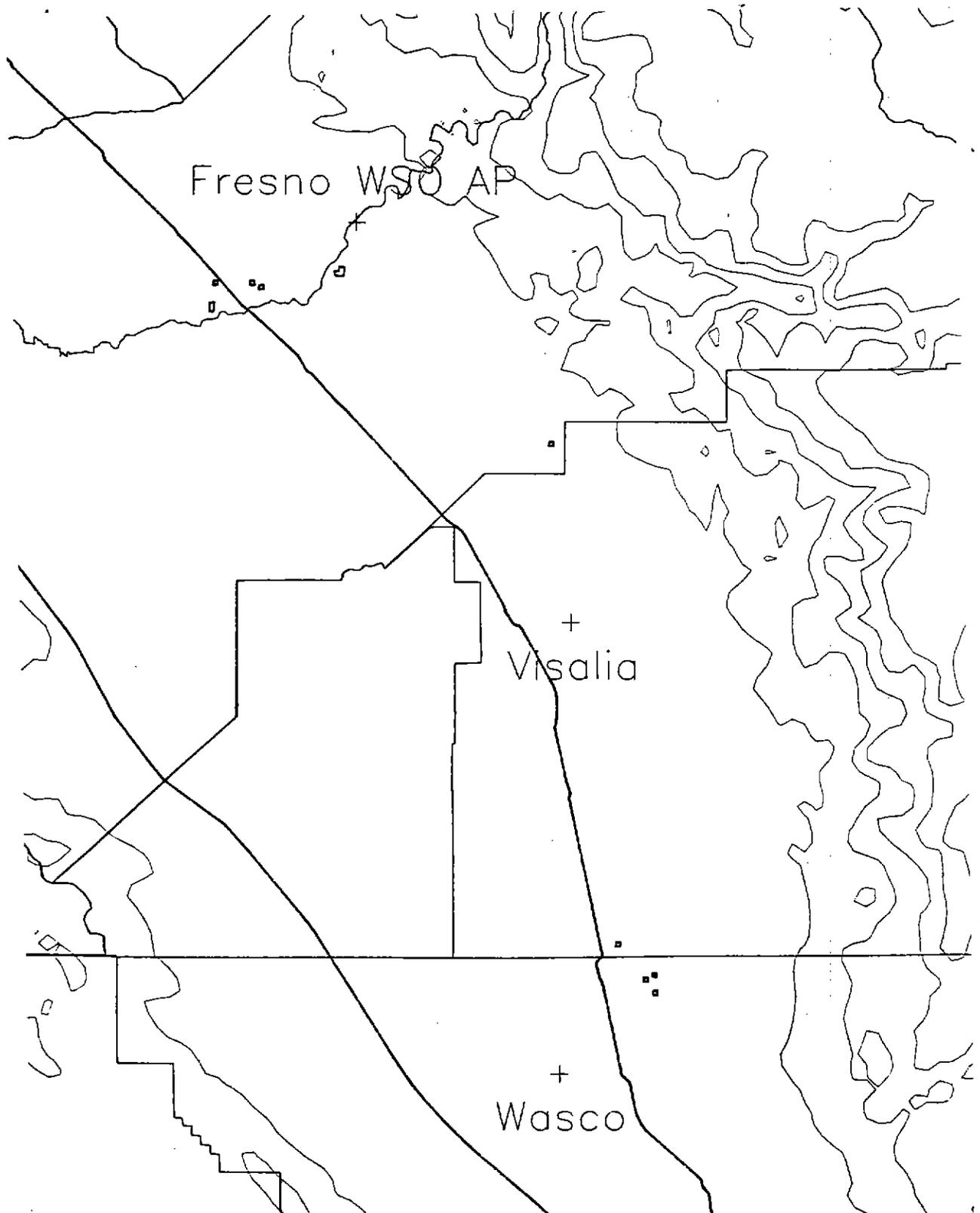
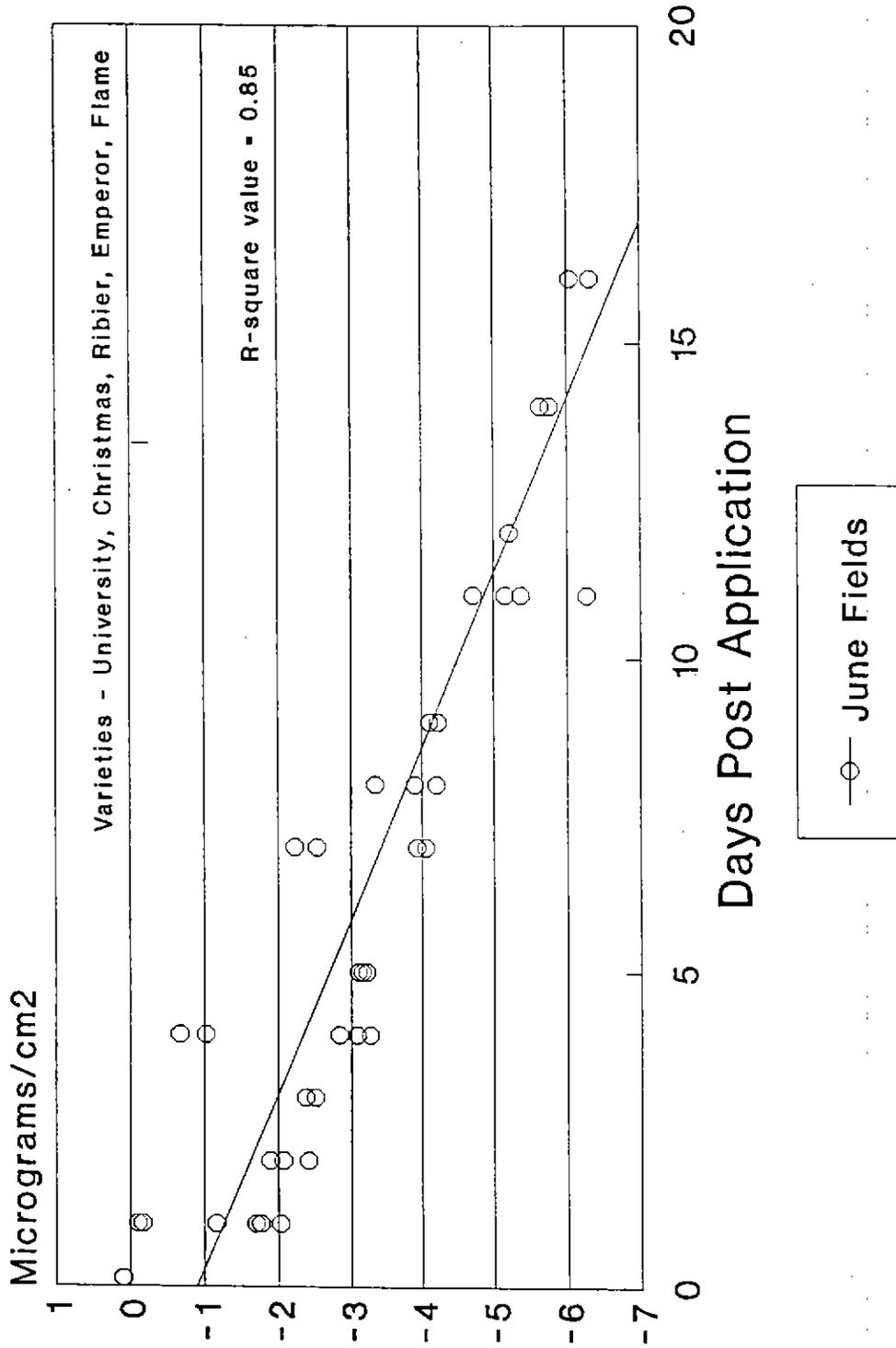


FIGURE 5

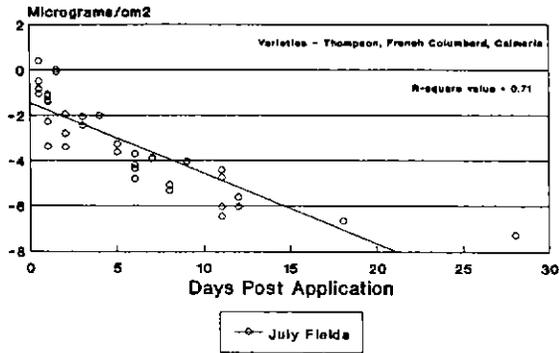
Methomyl Dissipation Curve Natural Log Values



Delano

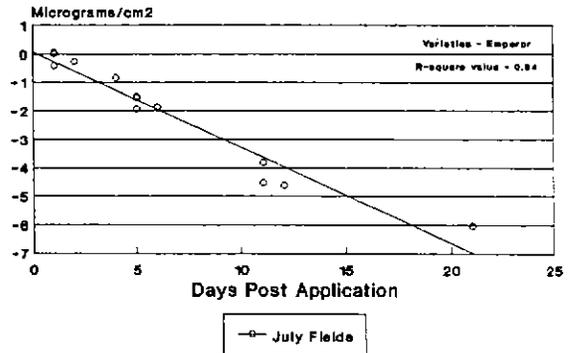
FIGURES 6-8

Methomyl Dissipation Curve
Natural Log Values



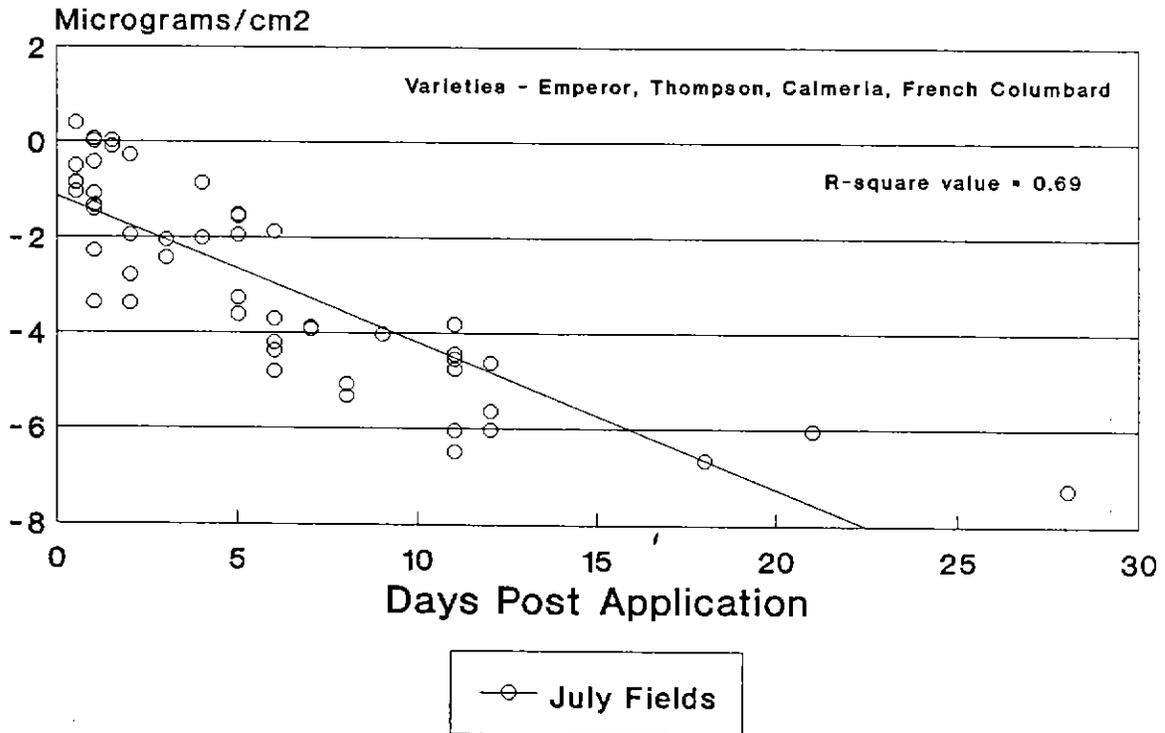
Madera and Fresno

Methomyl Dissipation Curve
Natural Log Values



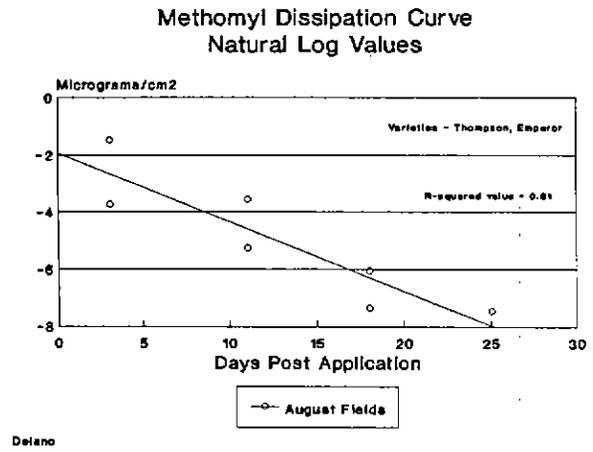
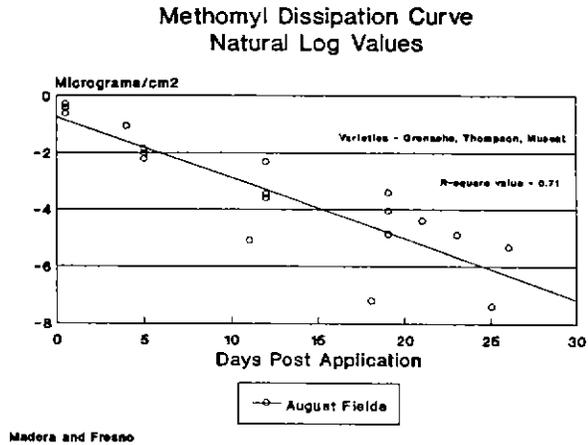
Delano

Methomyl Dissipation Curve
Natural Log Values



Madera, Fresno, and Delano

FIGURES 9-11



Methomyl Dissipation Curve Natural Log Values

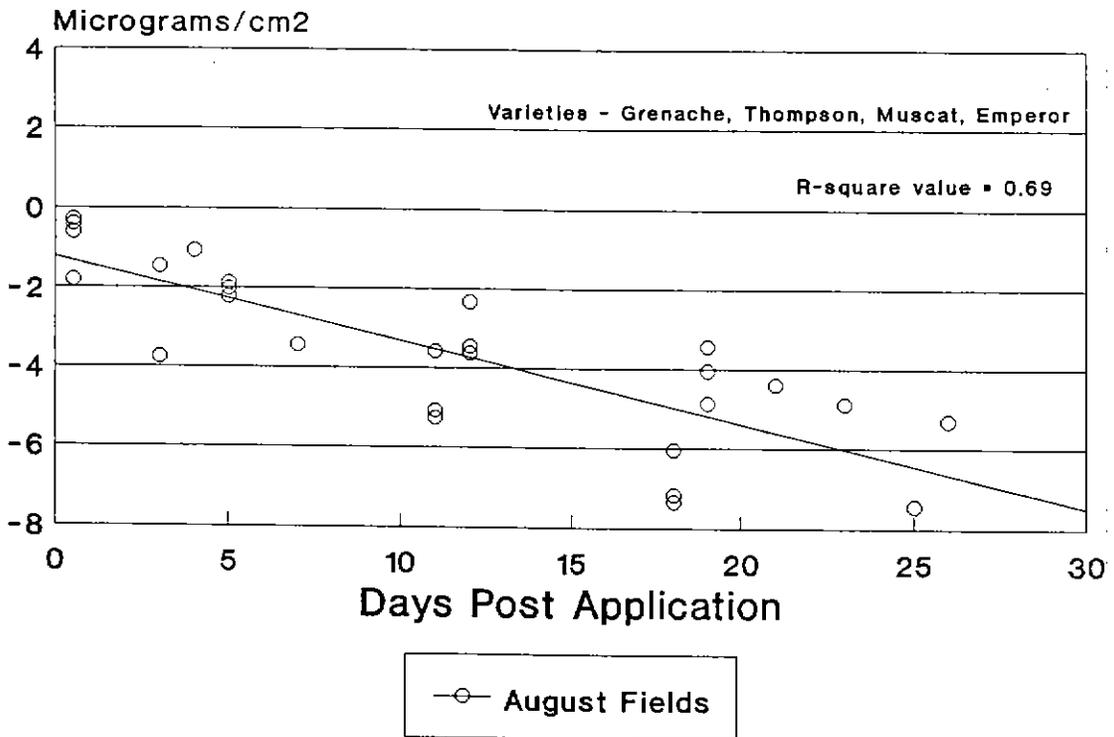
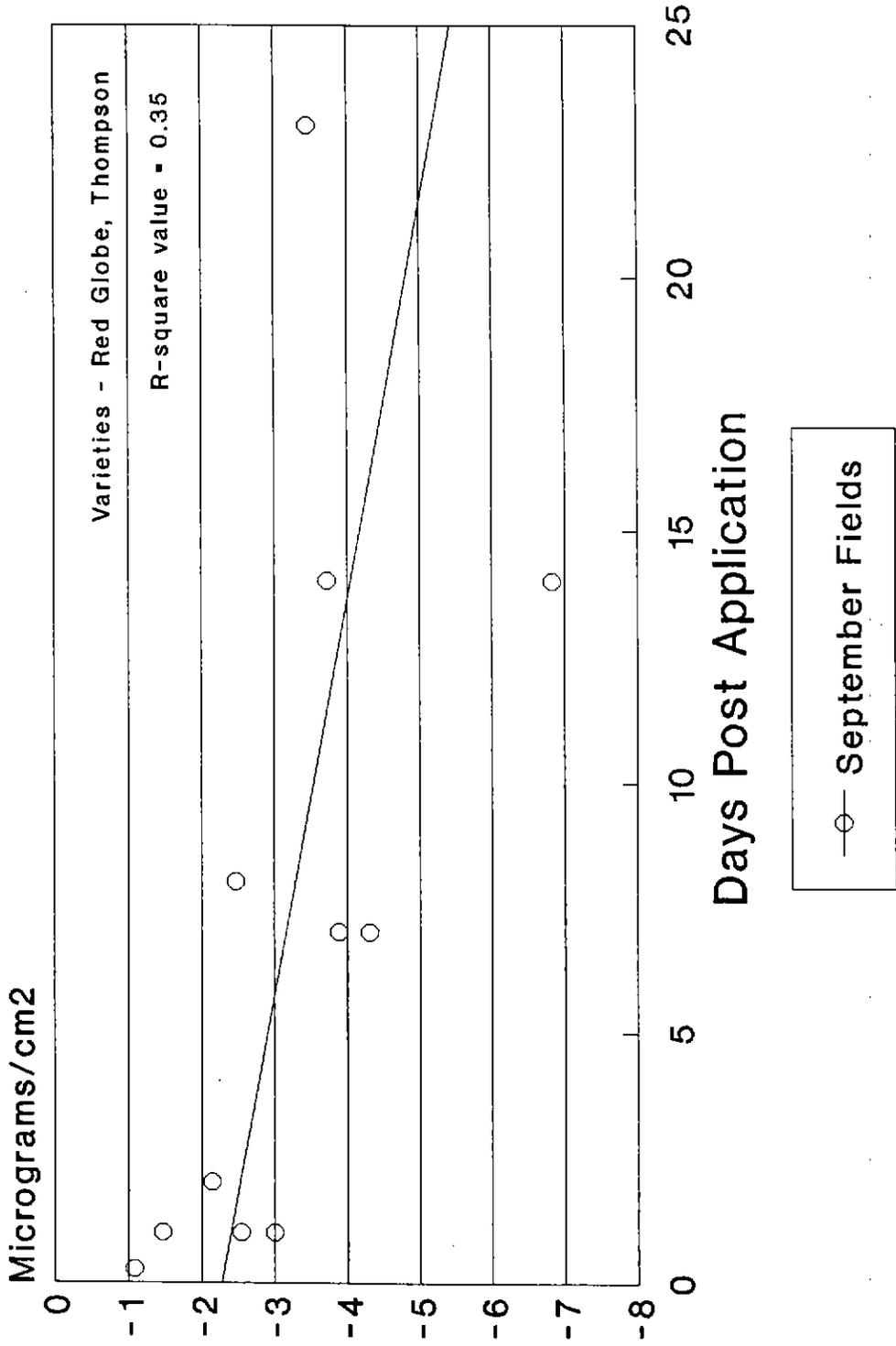


FIGURE 12

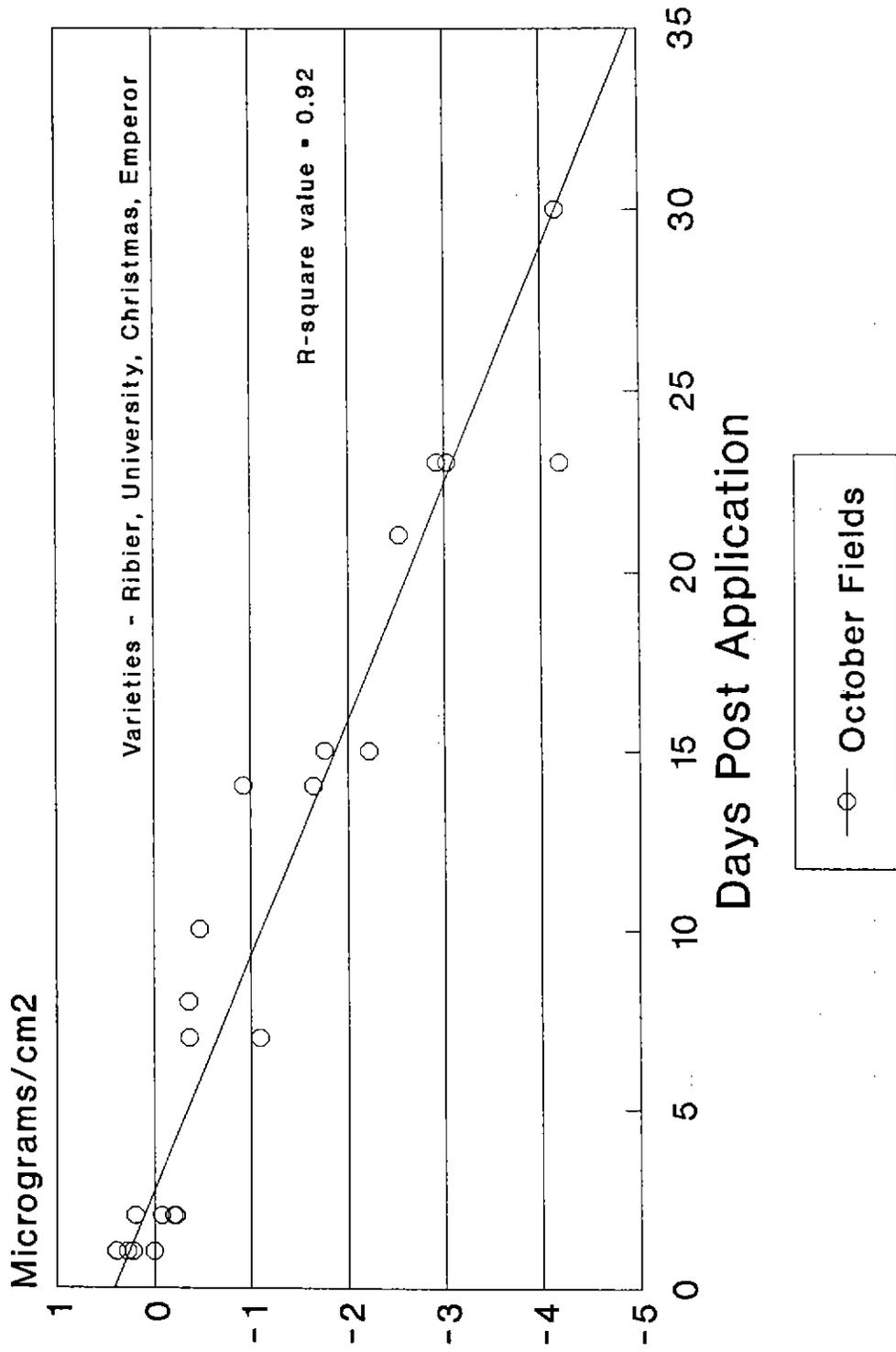
Methomyl Dissipation Curve Natural Log Values



Delano

FIGURE 13

Methomyl Dissipation Curve Natural Log Values



Delano

FIGURE 14

FRESNO

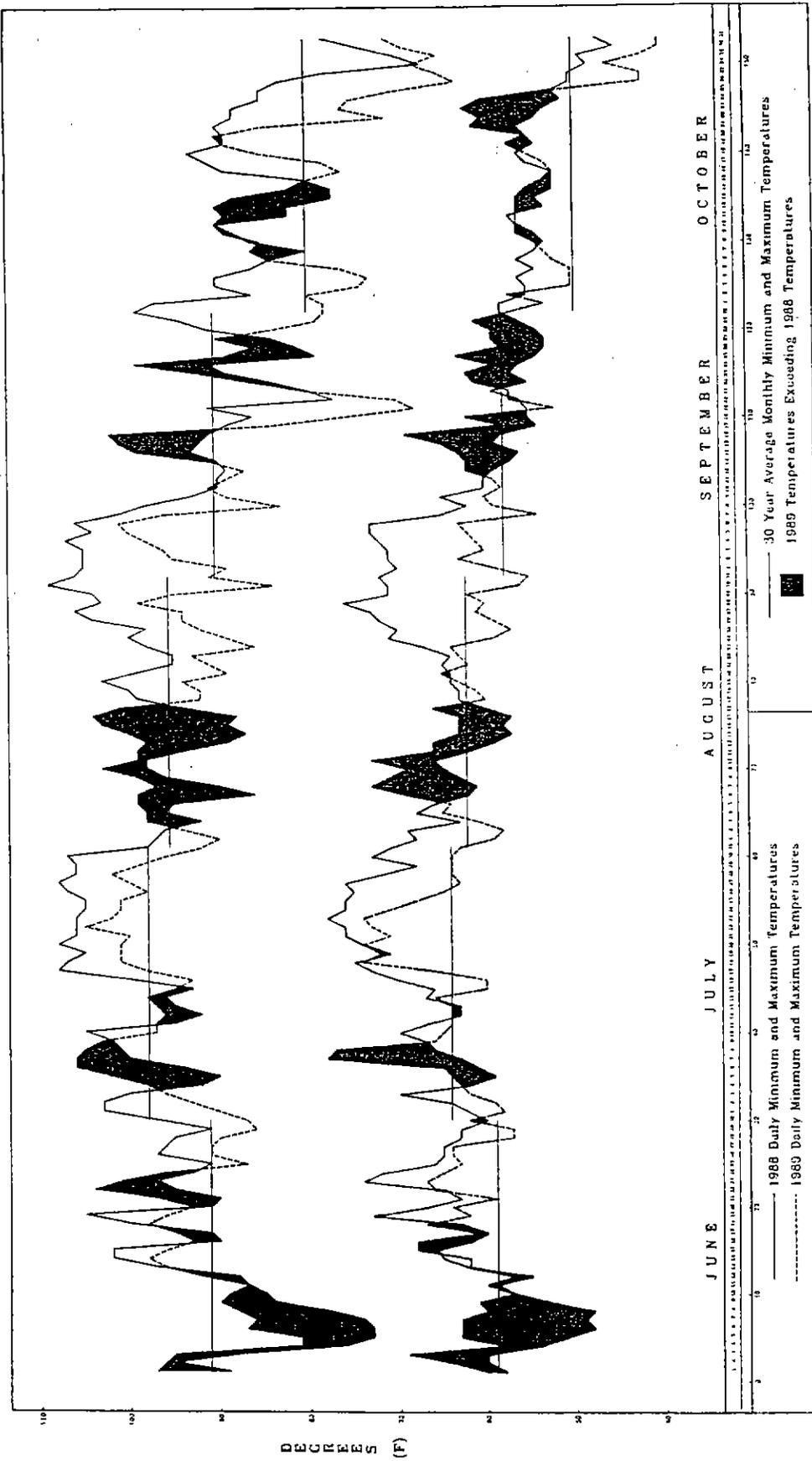


FIGURE 15

VISALIA

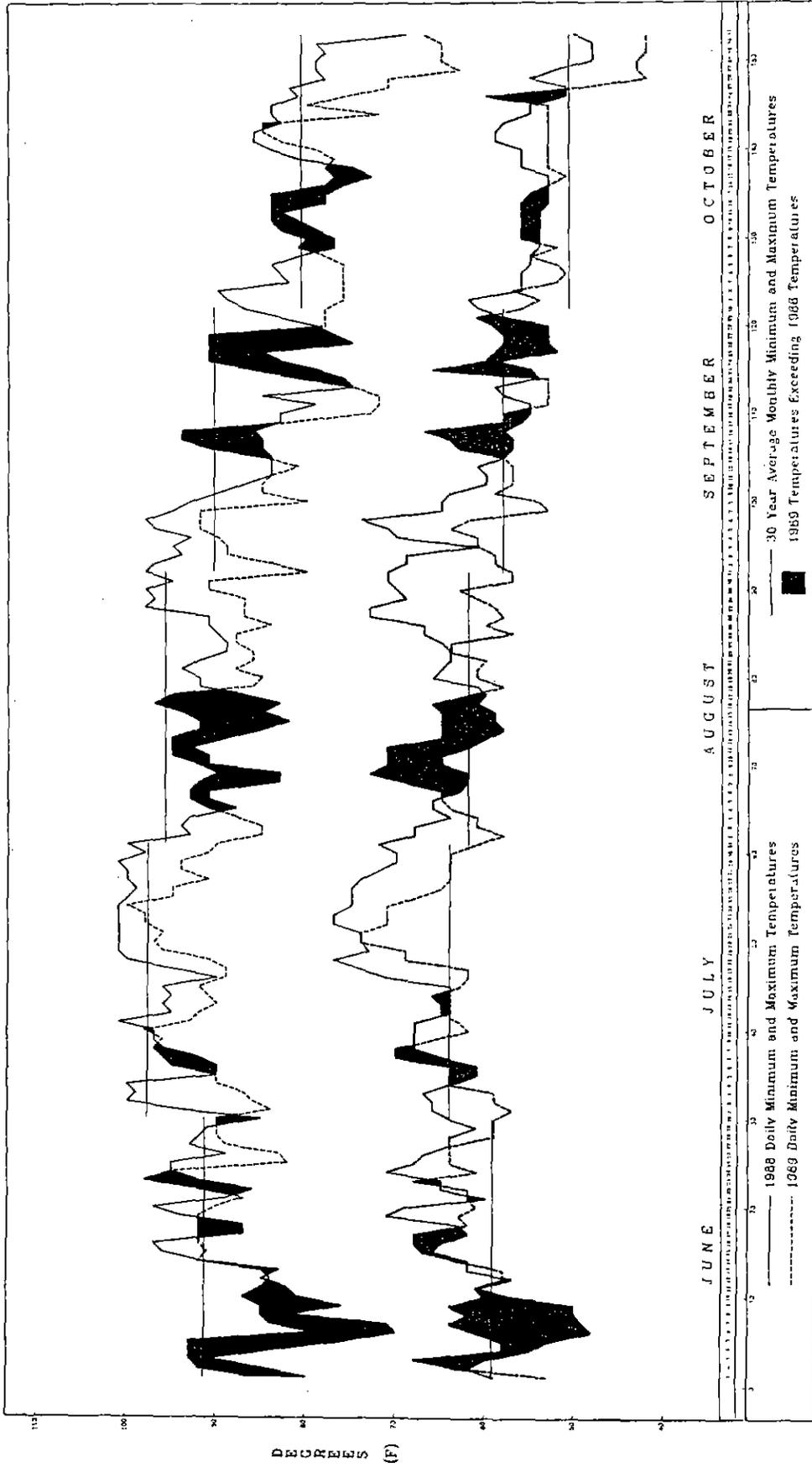
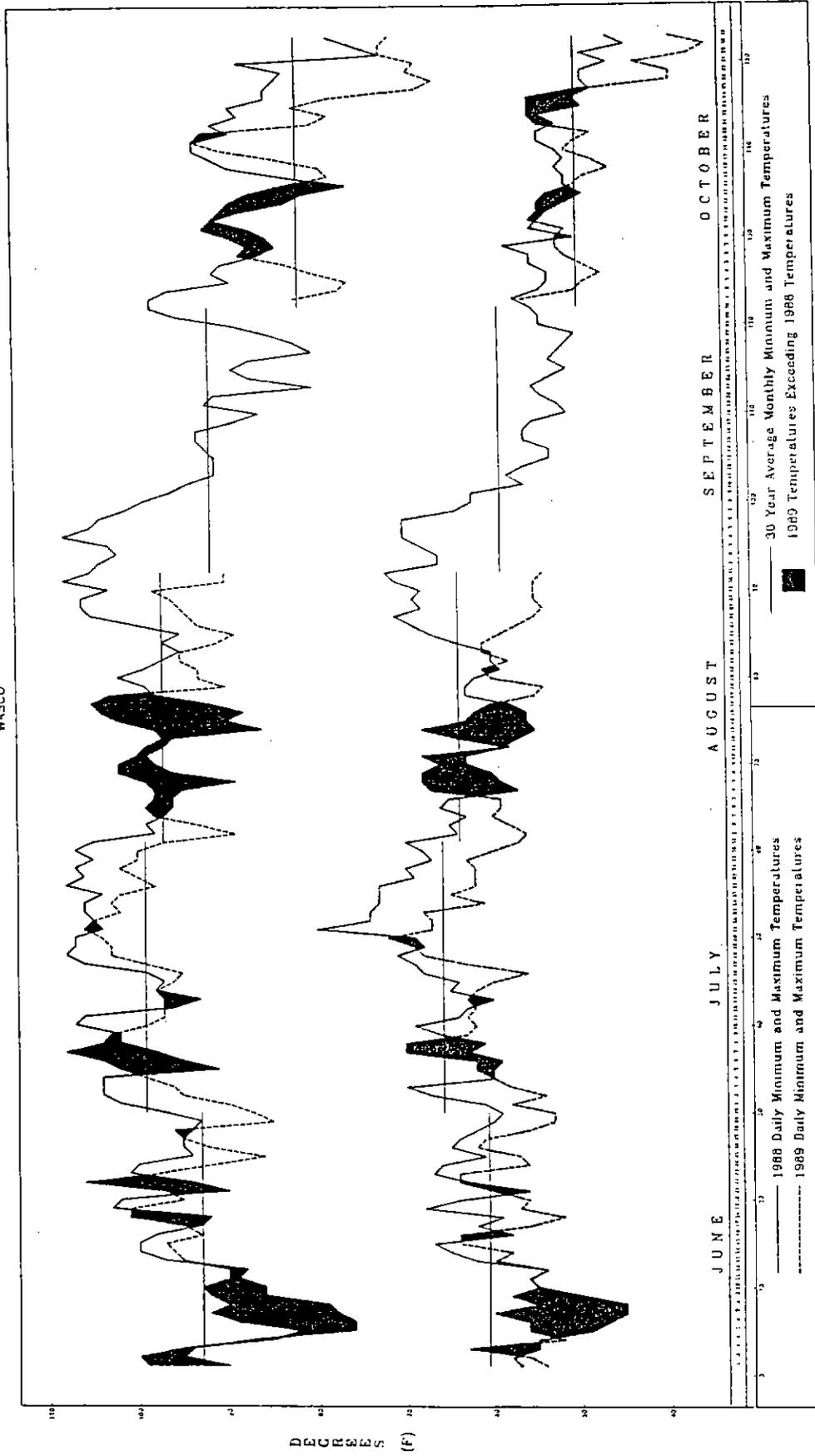


FIGURE 16

WASCO



REFERENCES

1. Michael O'Malley, Illnesses Associated with Exposure to Methomyl Among Grape Girdlers, Unpublished Memorandum, (1989)
2. Ulo Kiigemagi, Dennis Wellman, E.J. Cooley, and L.C. Terriere, Residues of the Insecticides Phorate and Methomyl in Mint Hay and Oil. Pesticide Science, Vol. 4, pp. 89-99, (1973)
3. Willis B. Wheeler, Neal P. Thompson, Robert L. Edelstein, and Richard T. Krause, Degradation of Methomyl Residues in Frozen Strawberries. Journal Association of Official Analytical Chemists, Inc., Vol. 64, pp. 1211-1220, (1981).
4. D.L. Bull, Fate of Methomyl on Cotton, Environmental Entomology, Vol. 3, pp. 723-724, (1974).
5. Chemistry Laboratory Services, Worker Health and Safety Section, California Department of Food and Agriculture.
6. The Kern County Agricultural Commissioner's Office.
7. Keith T. Maddy, Dana D. Meinders, Nirmal K. Saini, Vincent Quan, Degradation of Dislodgeable Azinphos-methyl (Guthion) Residue on Peach Foliage after Low-volume Application in Stanislaus County, California. Unpublished report. HS-1198, (1983)
8. Wayland J. Hayes, Jr., Pesticides Studied in Man. National Communicable Disease Center, U.S. Public Health Service, pp.455 (1982).
9. Stanley Bissell, Dislodgeable Foliar Residue Data Collected in 1988 for Methomyl on Table Grapes Grown in Kern County, Unpublished memorandum, (1988)
10. Samuel J. Williamson, Fundamentals of Air Pollution, Addison-Wesley Publishing Company. pp. 87. Copyright 1973.