DEGRADATION OF AZINPHOS-METHYL RESIDUE ON PEAR FOLIAGE, 1986

By

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HS-1402 September 28, 1987

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SUMMARY

This study was conducted to evaluate the 24-hour reentry interval for azinphos-methyl (AZM) when applied to pears. Six pear orchards in Lake and Sacramento Counties were monitored to estimate the decay rate of AZM dislodgeable foliar residues and to determine if residues accumulated after several cover sprays applied over the growing season of 1986. AZM was applied as low volume electrostatic and conventional sprays (25 - 100 gallons water/acre), and as high volume sprays (500-600 gallons water/acre) at the rates of 0.75 - 1.5 lbs. active ingredient/acre. Oil was applied during five of the 12 cover sprays monitored. Several leaf samples were collected within four days post application; additional samples were collected at least every seven days until the following cover spray or harvest. Samples were analyzed for the parent compound and oxygen analogue; the oxon was not detected in any sample. Initial depositions were greater for electrostatic sprays when compared with all airblast applications, but were similar when compared with all low volume applications. Initial depositions were greater in Sacramento County when compared with Lake County data; with the addition of oil to the tank mix, initial deposition was 20% greater in both counties. In comparison, AZM decayed at a slower rate in Sacramento County; within this county, airblast and electrostatic application decay rates were similar. Residue data does not indicate a cumulative effect after several applications. The mean concentration of foliar residues at each sample time never exceeded the (maximum) safe level of 1.6 ug/cm^2, therefore, the current reentry interval appears to provide

an adequate margin of safety when AZM is applied at the rates monitored and under the field conditions encountered during this study.

INTRODUCTION

During a routine "Day of Harvest" study in 1985, leaf samples were collected from pear orchards located in Sacramento and Yolo Counties. Several of these samples were found to contain azinphos-methyl (AZM) dislodgeable residues which were near or above the estimated safe (maximum) level of 1.6 micrograms per square centimeter (ug/cm^2) of leaf surface (2). Dislodgeable foliar residues should be below this safe level at the expiration of the 24-hour reentry interval to ensure workers are not exposed to hazardous levels of residue. In the above cases, AZM was applied at least seven to 14 days prior to sampling. Therefore, since AZM residues were near or over the safe level at harvest, they could have exceeded this level at the expiration of the reentry interval (1 day).

This degradation study was conducted to determine and characterize initial AZM deposition and decay rates when AZM was applied at several rates and under different field conditions. Further, the additive effects of subsequent cover sprays applied over the growing season were examined. The resulting data were used to assess the adequacy of the current 24-hour reentry interval for AZM when applied to pears.

MATERIALS AND METHODS

Several study sites were selected to represent different field conditions. Three orchards were located in Lake County and three orchards in the Sacramento River Valley (Sacramento County). Cooperating growers were contacted with assistance from the staff of the local County Agricultural Commissioners.

Application Information:

Each orchard was monitored starting with the first AZM cover spray of the growing season through subsequent AZM applications until harvest. Guthion^R (EPA #3125-301-AA) or Gowen Azinphos-M^R (EPA #10163-178-AA), both 50 percent wettable powder formulations, were applied using an electrostatic speed sprayer or a conventional orchard airblast sprayer.

The maximum label rate is 3.125 lbs active ingredient per acre (AI/A) applied as a high volume spray in 1,000 gallons of water per acre or as a low volume spray with the equivalent lbs AI/A. Pear growers usually apply AZM at the rate of 1 - 2 lbs AI/A, therefore these applications were monitored rather than applications at maximum label rates. Most cover sprays monitored included the addition of other materials such as other insecticides, oil, nutrients or sticker-spreaders. The application rates for AZM and other materials are listed by grower and cover spray in Table 1.

Sampling Techniques:

For sampling purposes, each orchard was divided into three sections with two adjacent rows selected from each section. Four trees from one row and four trees from the adjacent row were chosen as the sampling area. The location of each sampling area was selected to approximate a diagonal across the orchard. A total of 24 trees were chosen from each orchard. Trees in each sampling area were marked and used for sample collection throughout the study.

Foliage samples were collected using the methods similar to those described by Iwata, et al. (3). Two foliage samples were collected from each tree using a 2.54 centimeter (1 inch) Birkestrand leaf punch fitted with a four ounce jar. Foliage disks were selected from four areas of the tree which represented all four "sides" or quadrants of the tree. One complete sample consisted of 16 foliage disks from each sampling area for a total of 48 disks per orchard per sampling time. Leaf disks were collected from a height of approximately 1.5 meters. When possible, foliage free of excess moisture was collected. Older leaves were sampled to reduce the growth dilution factor. Samples collected from the first cover sprays consisted primarily of young leaf material since older leaves were not available at that time. After collection, samples were stored on wet ice and sent to the Department's Chemistry Laboratory Services in Sacramento for extraction within 24 hours.

Sampling Schedule:

Foliage samples were collected at the following intervals in relation to applications: pre-application (within one day prior to the application); and post-application samples at 0-2 hours, 4-7 hours, 20-26 hours, 3 days, 4 days, 7 days, and every 7 days until the next AZM application or harvest. Three replicate samples were collected at each interval. This sampling sequence varied slightly with each application.

Laboratory Analysis:

Each sample was analyzed for dislodgeable residues of the parent compound and the oxon. AZM residues were rinsed from the leaf surface using a water-surfactant solution then extracted from the aqueous solution with ethyl acetate. Analysis was by gas chromatography. Complete analytical methods are presented in Appendix I.

Variables Examined:

The following data was recorded for each application: orchard by county and grower, method of application (airblast or electrostatic), application rate (lbs AI/A) and dilution, number of previous AZM cover sprays, time of sample collection (expressed in hours or days post-application), and amount of residue detected in micrograms per square centimeter of leaf surface area (ug/cm^2).

Additional Data:

Irrigation schedules, type of irrigation, environmental conditions, and other pertinent observations were recorded for each study site. Minimum and maximum temperatures were recorded at the University of California Agriculture Extension Service weather stations located in Clear Lake in Lake County and Courtland in Sacramento County. Precipitation data were recorded from field observations and the National Weather Stations located in both counties. Temperature and precipitation data are presented in Appendices II and III.

STATISTICAL METHODS:

Non-linear iterative least square regression techniques were employed to examine both initial deposition and decay rates in this study (4)(5)(6). A first-order exponential decay model was used to describe decay and takes the following functional form:

$$y = f(t) = B_o e^{B_1 t},$$

where B_o = initial deposition

B_1 = decay rate

and t = time since application

Although the model may be viewed as intrinsically linear in the parameters to be estimated ($\ln y = \ln B_o + B_1 t$), the residuals from the non-linear regression model were smaller and better representative of a homoscedastic (randomness versus time) pattern.

Comparison of decay rates and initial deposition estimates were made by t-tests using the weighted asymptotic estimates of the standard errors. A parallel analyses using the logarithmic transformed linearized regression yielded similar conclusions.

RESULTS

Mean concentrations of dislodgeable residues were below the estimated safe level at the expiration of the reentry interval for every application monitored. The 24-hour post-application levels ranged from 0.47 to 1.55 ug/cm^2. The oxon-analog was not detected in any pre- or post-application samples. AZM levels following applications in Lake and Sacramento Counties are presented in Tables IV and V, respectively. Each application is designated by grower and cover spray; for example grower A, second cover spray is designated "A-2". Growers A - C, E and F used standard orchard airblast equipment and applied AZM as a low or high volume spray; Grower D used an electrostatic speed sprayer which applied a low volume spray.

Initial Deposition:

Analyses of the initial deposition estimates yielded several statistically significant results. Initial deposition was increased by approximately 20 percent when oil was added to the high volume airblast sprays both within Sacramento and Lake Counties ($P<.06$ and $P<.01$, respectively). No difference in initial deposition was observed between the low volume airblast and electrostatic sprays. However, when electrostatic applications were compared with all airblast applications, higher initial deposition estimates were noted (1.37 versus 1.08 ug/cm^2) following the electrostatic applications. Between geographical regions initial deposition was shown to be greater for Sacramento when compared with Lake County ($P<0.01$) (Figure 1). The average initial deposition for each application type in each county is represented graphically in Figure 2.

These results held for all as well as for first cover sprays only. In interpreting these results, it is important to remember that only high volume airblast applications were employed in Lake County. Therefore, a perceived county effect may in fact be related to differences in types of sprays. Greater detail with respect to initial deposition estimates is displayed in Table II.

Decay Rates:

Separate decay rates were estimated for each cover spray completed by each grower. Decay rates ranged from -0.027 to -0.244 per day with the most striking contrast of decay rates observed between Sacramento and Lake Counties. On the average, azinphos-methyl decayed 0.049 per day for all Sacramento County orchards compared with an average rate of decay of 0.173 ug/cm^2 per day for all Lake County orchards. This slower decay rate within Sacramento County was statistically less than the rate observed within Lake County ($P<0.001$). In the Sacramento County orchards, the decay rates between airblast and electrostatic application were not observed to be significantly different. The addition of oil to the high volume airblast application did not appear to affect decay rates in the Sacramento County orchards (-0.042 versus -0.041 ug/cm^2 per day). However, in Lake County orchards, azinphos-methyl decayed at a slower rate when oil was added ($P<0.01$). Decay rates between airblast and electrostatic applications were similiar when the Sacramento County data were examined. The estimated half-life for each application is presented graphically in Figure 3; the average half-life for each application type is presented in Figure 4. Greater detail for decay rates and half-lives is shown in Table III.

Cover Spray:

A secondary objective of this study was to examine the potential differences in decay and initial deposition between the first and subsequent ("cover") sprays. For most of the six growers, other confounding factors were present between the first and subsequent cover sprays. For example, Growers A and B added oil to the first cover spray and not the second. The first cover spray for Grower E was low volume airblast whereas the second cover spray was applied with high volume airblast. Consequently, the comparisons between the first and subsequent cover sprays were confined to Grower D (spray 1 versus spray 2) and Grower E (spray 1 versus spray 3). Analyses of these data revealed that both growers had higher initial depositions for the first cover spray ($P<0.06$) and the first cover spray decayed approximately twice as fast as the subsequent cover sprays ($P<0.06$). The reader is urged to interpret these results with caution since weather conditions with respect to both temperature and rainfall were not the same for both sprays. It rained approximately 0.01 inches on the day both first cover sprays were applied and trace amounts on the day following application.

DISCUSSION AND CONCLUSIONS

Azinphos-methyl is a broad spectrum phosphorodithioate organophosphate pesticide primarily used to control foliage feeding insects. Various application rates and dilutions are used for control of the coddling moth and other important pear pests. Data collected during this study indicate that application method and dilution rate may affect initial AZM deposition and subsequent dissipation of residues. Frequently materials such as other insecticides, fungicides, nutrients, and petroleum oils are added to cover sprays for complete pest control. In one case (application E-3), the use of a sticker-spreader appeared to slow AZM residue decay. Addition of petroleum oil to cover sprays increased the estimated initial AZM deposits on foliage. Kuhr and Lienk (7) found similar results after monitoring residues on the wood and foliage of plum trees. Other investigators found oil slightly decreased initial AZM deposition on apple leaves when applied as a concentrate spray (8).

The dissipation of dislodgeable foliar residues is dependent on many factors. Environmental conditions such as temperature, humidity, rainfall, sunlight, and wind may greatly affect pesticide decay. Decay rates differed substantially between geographical regions; AZM residues dissipated at a much slower rate in Sacramento when compared with Lake County. This difference may be a function of meteorological or other environmental conditions. Several investigators have found that rainfall occurring close to an application has a greater influence on the dissipation of foliar dislodgeable residue levels than rain occurring more than one week after an application. In addition, they found when AZM was applied as a wettable powder, residues were lost at a more rapid rate in wet weather as opposed to dry weather (9). Although rainfall patterns were similar between the two counties, total rainfall was considerably greater in Lake County. In Sacramento and Lake Counties, all rainfall occurred during the April 15 to May 12, 1986 monitoring period. Applications occurring during this rainy period were A-1, A-2, B-2 (Lake County) and D-1, E-1 (Sacramento County). Within Lake County, initial deposition and decay appeared to be unaffected by rain.

Absorption of AZM into the leaf may account for substantial loss of surface residues, particularly in Lake County. Dew or light rainfall, insufficiently heavy to cause foliar runoff, may enhance the absorption of foliar residues (10). Meteorological data and field observations available for April, May, and June indicates that morning dew was heavier and occurred more frequently in Lake County when compared with Sacramento County.

In the orchards monitored, there is insufficient evidence to conclude that AZM accumulates on treated foliage after several cover sprays. Dislodgeable foliar residue levels did not exceed the safe level at expiration of the reentry interval. Therefore, the current reentry interval appears to be adequate when AZM is applied to pears at the rates and under the field conditions encountered during this study.

TABLE I

Rates for Each Application in Lake County and the Sacramento River Valley

Grower-Cover Spray	Application Date	Azinphos-methyl Pound Active Ingredient/Gallons Water/Acre	Oil	Other Chemicals in Mix Tank
LAKE COUNTY:				
A-1	4/11/86	1.5 lbs/500 gal	3 gal/A	Streptomycin
A-2	4/21/86	1.0 lbs/500 gal	No	Streptomycin
B-1	4/28/86	1.0 lbs/500 gal	3 gal/A	Streptomycin; Terramycin
B-2	5/27/86	1.0 lbs/500 gal	No	No other materials
C-1	5/29/86	1.0 lbs/500 gal	3 gal/A	No other materials
SACRAMENTO COUNTY:				
D-1	4/15/86	0.75 lbs/25 gal	No	Cyhexatin (Plictran 50WP) Formetanate hydrochloride (Carzol 92% SP) Streptomycin
D-2	5/17/86	0.75 lbs/25 gal	No	Ethion Endosulfan Microshield (spreader-sticker)
D-3	6/23/86	0.75 lbs/25 gal	No	Cyhexatin (Plictran 50 WP), Naphthylacetic acid (NAA-800)
E-1	4/16/86	1.0 lbs/100 gal	No	Fenbutatin-oxide (Vendex 4L), Cyhexatin (Plictran 50 WP), Streptomycin, Triton B 1956 (spreader-sticker)
E-2	5/17/86	1.5 lbs/500 gal	1 gal/A	Copper 53
E-3	6/28/86	1.0 lbs/100 gal	No	Fenbutatin-oxide (Vendex 4L), Naphthylacetic acid (NAA 800)
F-1	NOT MONITORED; RATES UNKNOWN			
F-2	5/19/86	1.2 lbs/600 gal	5 gal/A	Copper

Table I (Continued)

Summary of Applications:

Number of Applications	Application Rate
3	0.75 lbs AI/25 gal. water (electrostatic applications)
2	1.0 lbs AI/100 gal. water
7	1.0-1.5 AI/500-600 gal. water

TABLE II

Estimation of Initial Deposition (ug/cm^2) for Azinphos-methyl on Pear Foliage

County	Grower	Spray Number	Application Type	Oil	Estimated Deposition	Adjusted Estimated Deposition[1]	95% Confidence Interval for Initial Deposition
Lake	A	1	Airblast-High	Yes	1.2770	1.2700	(1.1784, 1.3763)
Lake	A	2	Airblast-High	No	0.7707	0.3607	(0.6788, 0.8625)
Lake	B	1	Airblast-High	Yes	0.5765	0.5765	(0.5231, 0.6299)
Lake	B	2	Airblast-High	No	0.7528	0.6628	(0.6415, 0.8641)
Lake	C	1	Airblast-High	No	0.5255	0.1355	(0.4671, 0.5839)
Sacto.	D	1	Electrostatic	No	1.4768	1.4768	(1.3308, 1.6228)
Sacto.	D	2	Electrostatic	No	1.2257	0.9357	(1.0953, 1.3561)
Sacto.	D	3	Electrostatic	No	1.3799	N/A[2]	(1.2453, 1.5145)
Sacto.	E	1	Airblast-Low	No	1.4544	1.4544	(1.3400, 1.5689)
Sacto.	E	2	Airblast-High	Yes	0.9023	0.6523	(0.7979, 1.0067)
Sacto.	E	3	Airblast-Low	No	1.2508	1.0908	(1.2041, 1.2976)
Sacto.	F	2	Airblast-High	No	0.7187	N/A	(0.6322, 0.8052)

[1]Values adjusted for pre-application sampling average.
[2]Not available

TABLE III

Decay Rates and Half-Life Estimation for Azinphos-methyl on Pear Foliage

County	Grower	Spray Number	Application Type	Oil	Estimated Decay Rate	Half Life (Days)	95% Confidence Interval for Decay Rate
Lake	A	1	Airblast-High	Yes	-0.1289	5.4	(-0.1644, -0.0934)
Lake	A	2	Airblast-High	No	-0.1200	5.8	(-0.1697, -0.0702)
Lake	B	1	Airblast-High	Yes	-0.1777	3.9	(-0.2130, -0.1423)
Lake	B	2	Airblast-High	No	-0.2444	2.8	(-0.3440, -0.1448)
Lake	C	1	Airblast-High	No	-0.1951	3.6	(-0.2522, -0.1380)
Sacto.	D	1	Electrostatic	No	-0.0489	14.2	(-0.0623, -0.0354)
Sacto.	D	2	Electrostatic	No	-0.0261	26.6	(-0.0370, -0.0150)
Sacto.	D	3	Electrostatic	No	-0.0892	7.8	(-0.1211, -0.0572)
Sacto.	E	1	Airblast-Low	No	-0.0652	10.6	(-0.0806, -0.0497)
Sacto.	E	2	Airblast-High	Yes	-0.0416	16.7	(-0.0561, -0.0270)
Sacto.	E	3	Airblast-Low	No	-0.0303	22.9	(-0.0356, -0.0250)
Sacto.	F	2	Airblast-High	No	-0.0407	17.0	(-0.0574, -0.0240)

TABLE IV

Azinphos-methyl Dislodgeable Foliar Residues[1/] (micrograms/square centimeter) Following Applications to Orchards in Lake County.

Post-Application Sample Time	APPLICATION RATE (Pounds Active Ingredient/Gallons Water/Acre): 1.0 lbs/500 gal			1.0 lb/500 gal with OIL	1.5 lbs/500 gal with OIL
Grower-Cover Spray	A-2	B-2	C-1	B-1	A-1
PRE-APPLIC	0.41 ±0.34	0.09 ±0.01	0.39 ±0.06	ND[2/]	ND
2 HR	0.94 ±0.08	0.76 ±0.19	0.43 ±0.03	-	1.16 ±0.04
6 HR	0.72 ±0.10	-	-	-	1.14 ±0.01
7 HR	-	-	0.47 ±0.06	-	-
20 HR	0.72 ±0.30	-	0.62 ±0.06	-	1.18 ±0.05
24 HR	0.71 ±0.07	-	-	0.47 ±0.02	1.14 ±0.24
30 HR	-	0.77 ±0.21	-	-	-
2 DAY	0.63 ±0.05	0.41 ±0.17	-	0.42 ±0.05	1.13 ±0.16
3 DAY	0.64 ±0.16	0.33 ±0.03	0.22 ±0.03	0.35 ±0.01	1.08 ±0.01
4 DAY	-	-	0.21 ±0.01	-	-
6 DAY	-	0.10 ±0.02	-	-	0.51 ±0.02
7 DAY	0.34 ±0.06	-	0.14 ±0.01	-	
8 DAY	-	-	-	0.10 ±0.01	
11 DAY	-	-	0.07 ±0	-	
13 DAY	-	0.05 ±0	-	-	
14 DAY	0.07 ±0.01	-	-	0.09 ±0.01	
19 DAY	-	-	0.05 ±0.01		
20 DAY	0.04 ±0.01	-	-		
21 DAY	-	0.05 ±0.01	-		
26 DAY	-	-	0.02 ±0.01		
28 DAY	-	0.01 ±0	-		
29 DAY	ND		-		
33 DAY			ND		

1/ Mean and standard deviation of three replicate samples

2/ None detected; minimum detectable level = 0.005 ug/cm^2.

- Indicates no samples collected.

TABLE V
Azinphos-methyl Dislodgeable Foliar Residues1/ (micrograms/square centimeter)
Following Applications to Orchards in Sacramento County

APPLICATION RATE
(Pounds Active Ingredient/Gallons Water/Acre)

Post-Application Sample Time	0.75 lbs/25 gal2/			1 lb/100 gal		1.2 lbs/ 600 gal	1.5 lbs/500 gal with OIL
Grower - Cover Spray	D-1	D-2	D-3	E-1	E-3	F-2	E-2
PRE-APPLIC	ND3/	0.29 ±0.05	0.49 ±0.02	ND	0.16 ±0.07	0.37 ±0.02	0.25 ±0.02
2 HOURS	1.38 ±0.02	1.06 ±0.40	1.54 ±0.29	1.33 ±0.12	1.29 ±0.04	0.80 ±0.09	0.70 ±0.12
5 HOURS	-	-	-	1.60 ±0.40	-	0.66 ±0.20	-
7 HOURS	-	-	-	-	1.18 ±0.14	-	0.79 ±0.29
15 HOURS	-	-	1.30 ±0.05	-	-	-	-
24 HOURS	1.38 ±0.002	1.31 ±0.05	1.12 ±0.12	1.55 ±0.16	1.27 ±0.08*	0.57 ±0.01	0.82 ±0.19
2 DAYS	1.36 ±0.003	1.45 ±0.24	1.09 ±0.05	1.29 ±0.18	1.17 ±0.01	0.90 ±0.17	0.96 ±0.23
3 DAYS	1.22 ±0.09	1.09 ±0.21	1.08 ±0.14	0.99 ±0.07	1.11 ±0.07	-	0.80 ±0.21
5 DAYS	-	-	-	-	-	0.46 ±0.02	-
6 DAYS	-	1.25 ±0.09	-	-	-	-	0.82 ±0.07
7 DAYS	1.28 ±0.15	-	-	0.82 ±0.09	-	-	-
8 DAYS	-	-	-	-	-	0.51 ±0.05	-
9 DAYS	-	-	0.77 ±0.33	-	0.29 ±0.02	-	-
13 DAYS	-	0.91 ±0.25	-	-	-	-	0.80 ±0.18
14 DAYS	1.13 ±0.05	-	0.31 ±0.31	0.49 ±0.04	-	-	-
16 DAYS	-	-	-	-	-	0.34 ±0.07	-
19 DAYS	-	0.75 ±0.07	-	-	-	-	0.26 ±0.06
21 DAYS	-	-	-	0.51 ±0.01	-	0.36 ±0.30	-
22 DAYS	0.28 ±0.05	-	-	-	-	-	-
27 DAYS	-	0.52 ±0.08	-	0.33 ±0.07	-	-	0.18 ±0.03

(Continued)

TABLE V (Continued)

Post-Application Sample Time	0.75 lbs/25 gal2/			1 lb/100 gal		1.2 lbs/ 600 gal	1.5 lbs/500 gal with OIL
Grower - Cover Spray	D-1	D-2	D-3	E-1	E-3	F-2	E-2
28 DAYS	0.14 ±0.05	-		-	-	0.24 ±0.01	-
30 DAYS	0.29 ±0.05	-		0.25 ±0.02			-
32 DAYS		0.49 ±0.02					0.20 ±0.01
39 DAYS							0.16 ±0.01

1/ Mean and standard deviation of three replicate samples.
2/ Electrostatic applications.
3/ None detected; minimum detectable level = 0.005 ug/cm^2

\- Indicates no samples collected.

FIGURE 1: AZINPHOS–METHYL INITIAL DEPOSITION IN PEAR ORCHARDS BY COUNTY
(INITIAL DEPOSITION: MICROGRAMS PER SQUARE CENTIMETER)

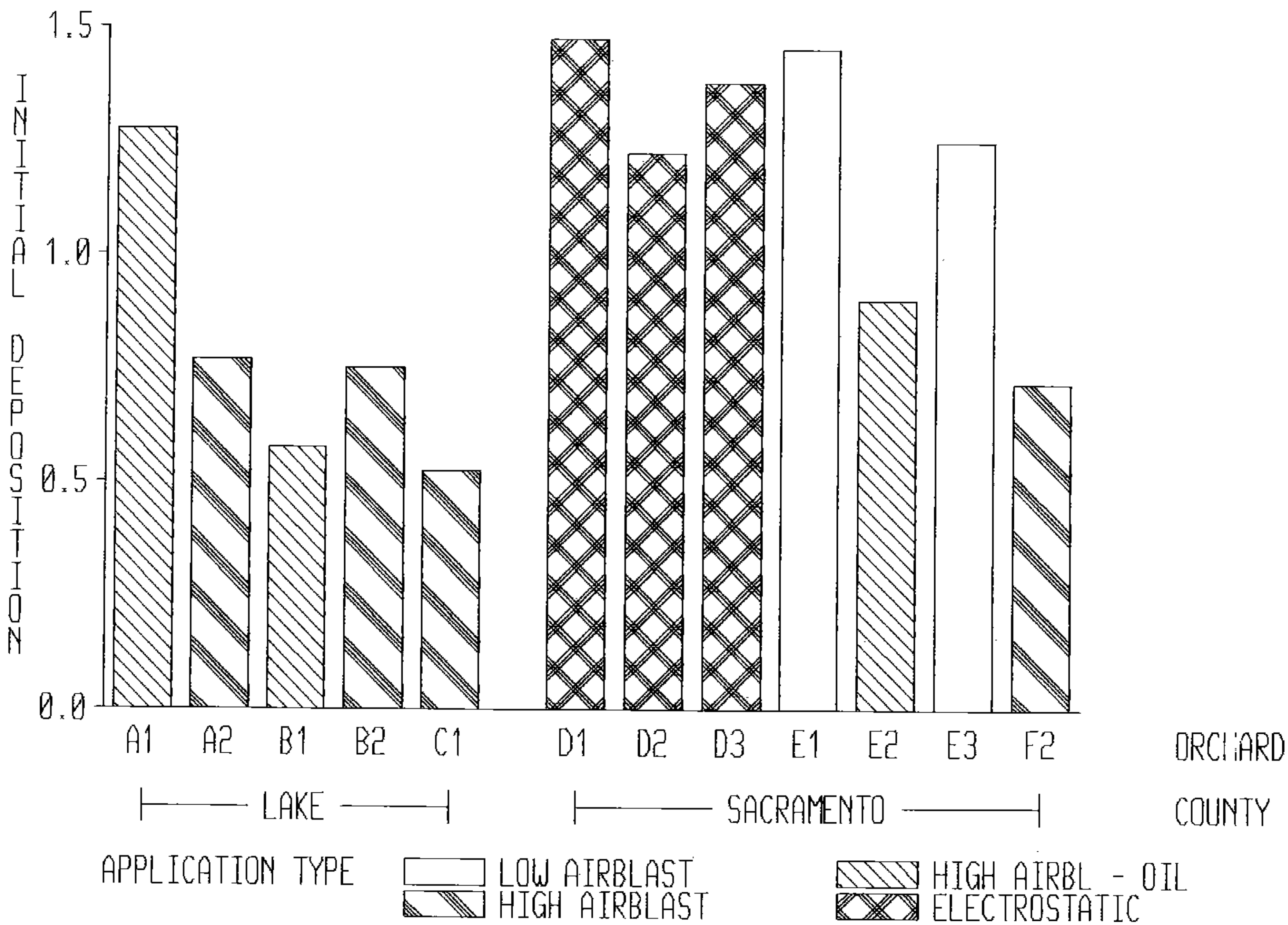


FIGURE 2: AZINPHOS–METHYL INITIAL DEPOSITION IN PEAR ORCHARDS BY COUNTY
(INITIAL DEPOSITION: MICROGRAMS PER SQUARE CENTIMETER)

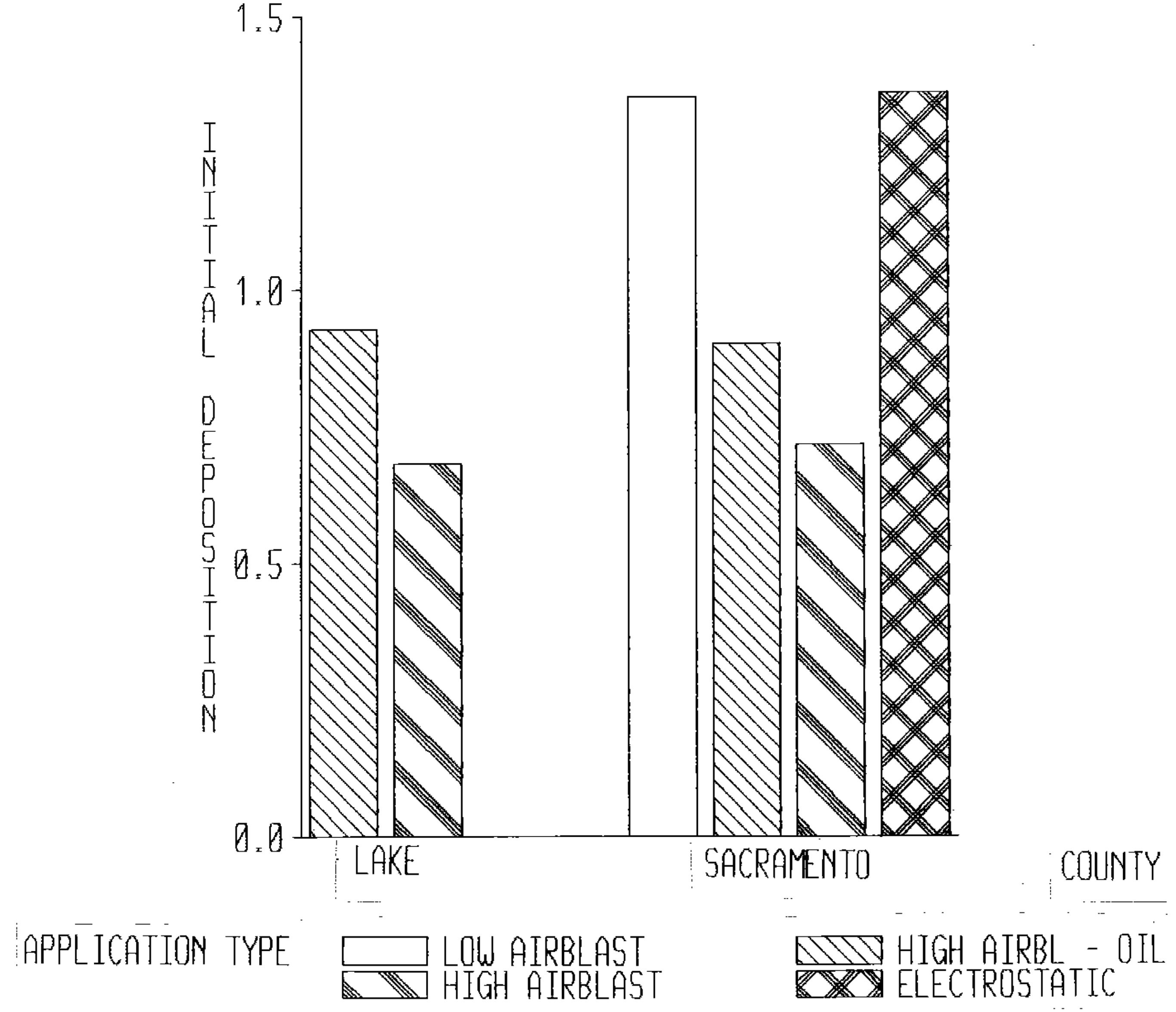


FIGURE 3: AZINPHOS–METHYL HALF LIVES IN PEAR ORCHARDS BY COUNTY
(HALF LIVES IN DAYS SINCE LAST APPLICATION)

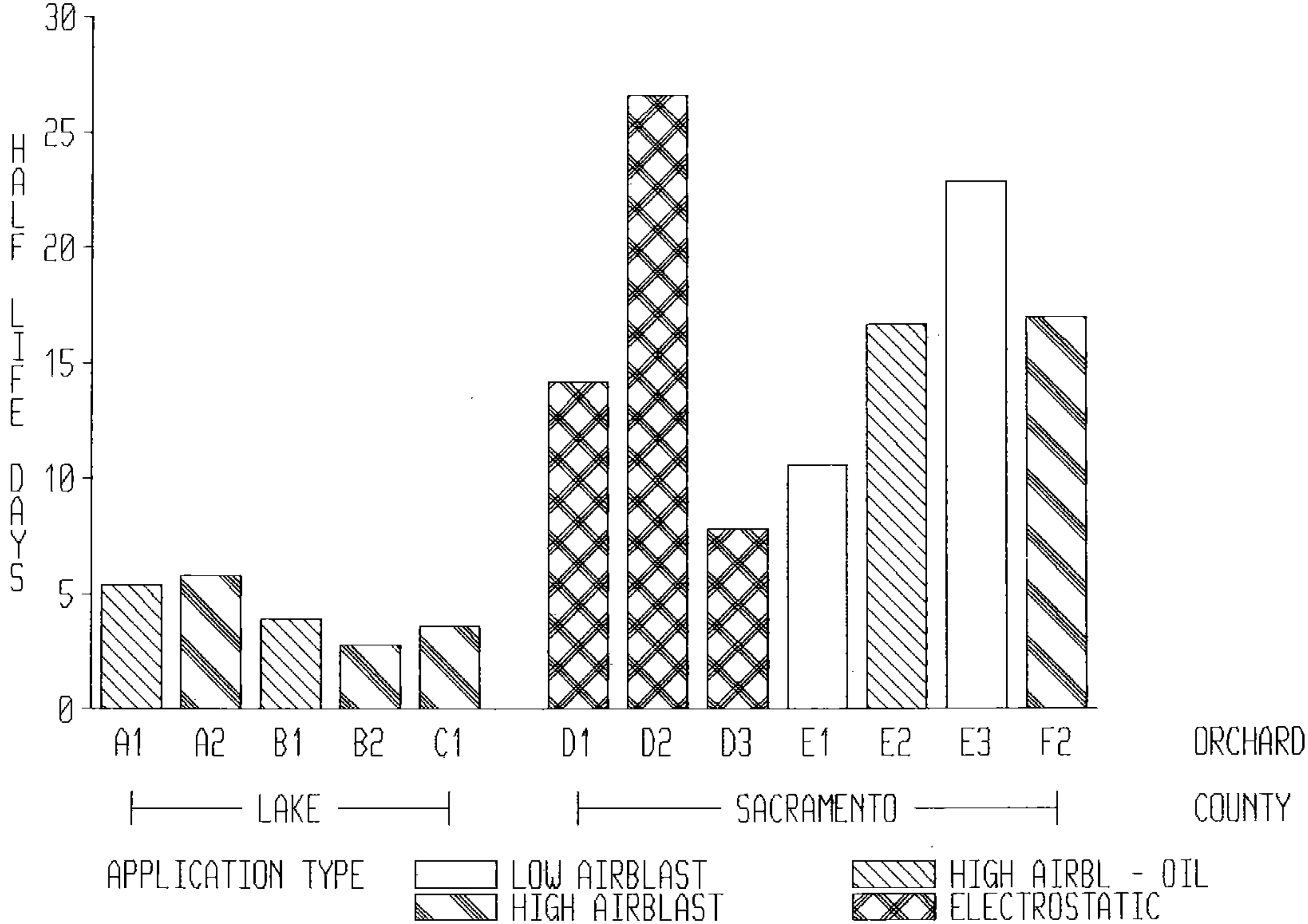
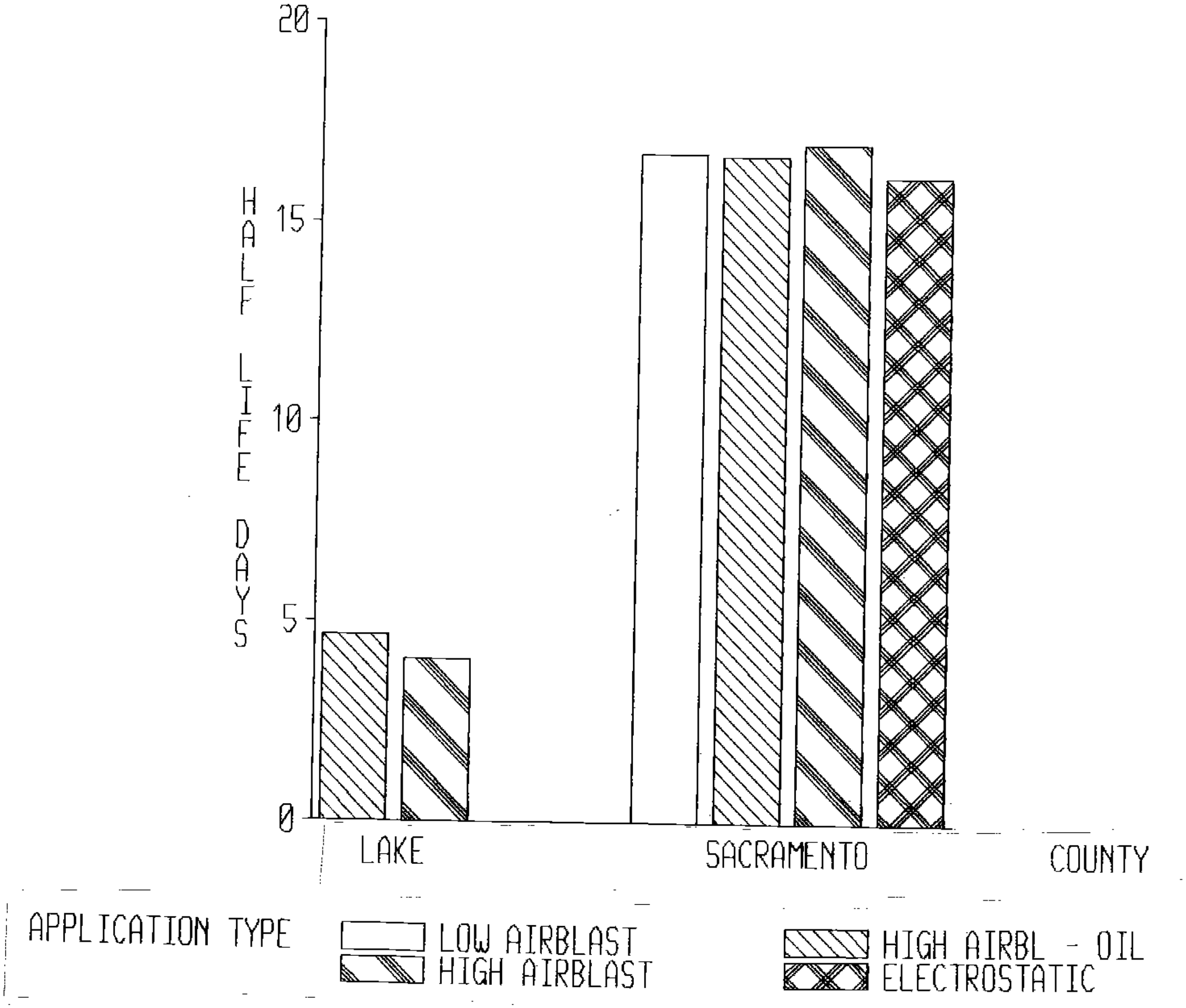


FIGURE 4: AZINPHOS-METHYL HALF LIVES IN PEAR ORCHARDS BY COUNTY
(HALF LIVES IN DAYS SINCE LAST APPLICATION)



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APPENDIX I

AZINPHOS-METHYL ANALYSIS

SCOPE:

This method is for the determination of dislodgeable residues of azinphos-methyl (AZM) and AZM Oxon Analogue (OA) leaf surfaces.

PRINCIPLE:

The surfaces of leaf discs are rinsed with a distilled water and surfactant solution to remove the pesticide. The aqueous solution is then extracted with ethyl acetate (EtAc). The extract is ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde. Check for interferences.
2. Distilled water.
3. Sur-ten solution, 2%.
4. NaCl.
5. Glass wool.
6. Na_2SO_4, anhydrous.
7. Separatory funnels, 500 ml capacity with glass stoppers and Teflon[R] stopcocks.
8. Glass filter funnels.
9. Graduated cylinders, 100 ml.
10. Analytical standards of AZM and AZM Oxygen Analogue.
    a) Stock standard - 1 mg/ml.
    b) Working standards - Dilute stock standards to several working standards covering the linear range of the gas chromatograph and detector used, e.g. 0.1 to 10 ng/ul AZM.
11. A gas chromatograph equipped with a Nitrogen-Phosphorus detector.
12. A 10m X 0.53 mm I.D. megabore column coated with 50% Phenyl Methyl Silicone.

ANALYSIS:

1. To the sample jar containing the leaf punches, add 50 mls of distilled water and two drops of 2% Sur-ten solution.
2. Rotate the sample jar for 20 minutes.
3. Decant the aqueous portion into a 500 ml separatory funnel.
4. Repeat step 1-3 twice more.
5. Add 40 grams of NaCl to the separatory funnel and shake to dissolve.
6. Extract the aqueous portion with 50 mls of EtAc, draining the solvent through glass wool and Na_2SO_4 into a 100 ml graduated cylinder.
7. Extract the aqueous portion twice more with 25 mls of EtAc, combining all extracts in the cylinder.

8. Bring the volume in the cylinder up to 100 mls with EtAc.
9. Extract is ready for analysis.

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A.
   a) Oven temperature - 250°C.
   b) Injector temperature - 225°C.
   c) Detector temperature - 300°C.
   d) Helium carrier gas flow - 15 mls/min.
   e) Helium make-up gas flow (NPD detector) - 5 mls/min.

Using these conditions, AZM has a retention time of 4.19 minutes and AZM OA has a retention time of 3.44 minutes.

CALCUALTIONS:

Results are reported as micrograms per square centimeter.

DISCUSSION:

Recoveries: 10 ug AZM - 99%
10 ug AZM OA - 98%

APPENDIX II

Minimum and Maximum Daily Temperatures; and Daily Precipitation.
Recorded Clearlake, Lake County, California, 1986

Date		°F Minimum	°F Maximum	Precipitation (Inches)
APRIL	10	35	76	
	11	36	76	
	12	37	54	T
	13	31	64	
	14	38	67	T
	15	36	58	0.15
	16	38	51	0.14
	17	34	63	0.03
	18	33	73	
	19	37	79	
	20	39	85	
	21	40	85	
	22	39	76	
	23	36	67	
	24	34	62	
	25	39	63	
	26	32	69	
	27	46	75	
	28	43	69	
	29	35	69	
	30	32	73	
MAY	1	35	60	
	2	50	58	0.24
	3	44	59	0.01
	4	41	61	T
	5	35	56	0.06
	6	33	55	0.11
	7	32	69	
	8	34	75	
	9	37	80	
	10	40	66	
	11	34	70	
	12	33	80	T
	13	41	79	
	14	39	71	
	15	37	78	
	16	38	85	
	17	42	88	
	18	42	88	
	19	41	81	
	20	44	69	
	21	38	64	
	22	33	74	
	23	41	75	
	24	37	82	
	25	47	85	
MAY	26	48	82	
(cont)	27	50	84	
	28	46	89	
	29	50	92	
	30	52	90	
	31	54	88	
JUNE	1	53	91	
	2	51	84	
	3	43	79	
	4	43	75	
	5	51	71	
	6	52	73	
	7	48	78	
	8	41	86	
	9	43	91	
	10	45	95	
	11	51	87	
	12	52	87	
	13	53	86	
	14	51	74	
	15	49	77	
	16	43	79	
	17	48	70	
	18	42	74	
	19	39	79	
	20	46	83	
	21	46	92	
	22	50	95	
	23	53	95	
	24	50	95	
	25	47	92	
	26	52	79	
	27	49	85	
	28	53	79	
	29	46	80	
	30	49	88	
JULY	1	51	91	
	2	51	90	
	3	54	85	
	4	54	82	
	5	46	84	
	6	46	82	
	7	47	85	
	8	45	88	
	9	50	87	

(Conntinued)

APPENDIX II (Continued)

Date		F° Minimum	Maximum	Precipitation (Inches)
JULY	10	52	90	
(cont)	11	57	89	
	12	54	92	
	13	50	91	
	14	53	90	
	15	50	85	
	16	50	79	
	17	44	80	
	18	44	82	
	19	44	87	
	20	46	95	
	21	53	95	
	22	57	85	
	23	54	86	
	24	51	88	
	25	50	85	
	26	47	86	
	27	47	85	
	28	46	86	
	29	47	90	
	30	49	93	
	31	49	98	
AUGUST	1	52	97	
	2	50	98	
	3	52	99	
	4	52	99	
	5	52	97	
	6	53	95	
	7	48	95	
	8	47	97	
	9	49	97	
	10	51	94	

T = trace rainfall (field observations)

APPENDIX III (Continued)

Date	F^o Minimum	Maximum	Precipitation (Inches)
JULY 15	57	82	
(cont) 16	55	87	
17	53	83	
18	54	84	
19	48	94	
20	52	98	
21	61	97	
22	58	85	
23	63	89	
24	60	83	

T = trace rainfall
- = no precipitation data available

APPENDIX III

Maximum Daily Temperatures, and Daily Precipitation.
Recorded Courtland, Sacramento County, California, 1986

	F°		Precipitation
Date	Minimum	Maximum	(Inches)
APRIL 15	47	58	0.01
16	44	58	T
17	41	67	
18	45	76	
19	40	79	
20	44	86	
21	46	87	
22	51	68	
23	50	72	
24	48	70	
25	51	69	
26	42	72	
27	47	79	
28	53	76	
29	46	75	
30	38	77	
MAY 1	50	64	
2	47	74	T
3	47	65	T
4	48	66	0.06
5	46	64	-
6	39	63	0.01
7	33	75	
8	46	80	
9	55	85	
10	52	75	
11	41	78	
12	49	81	
13	48	85	
14	53	81	
15	50	84	
16	57	89	
17	53	93	
18	48	88	
19	53	80	
20	54	73	
21	47	74	
22	51	80	
23	53	74	
24	43	84	
25	51	92	
26	59	87	
27	58	84	
28	54	89	
29	55	94	
30	55	84	
MAY (cont) 31	55	77	
JUNE 1	56	74	
2	55	72	
3	55	79	
4	56	77	
5	57	72	
6	54	73	
7	54	85	
8	60	92	
9	59	95	
10	55	100	
11	58	74	
12	57	85	
13	56	76	
14	57	78	
15	56	79	
16	55	83	
17	59	81	
18	54	84	
19	55	88	
20	51	90	
21	56	96	
22	55	101	
23	60	96	
24	59	89	
25	57	87	
26	55	79	
27	55	82	
28	59	82	
29	55	89	
30	52	94	
JULY 1	56	98	
2	59	95	
3	57	85	
4	57	84	
5	57	85	
6	59	79	
7	55	88	
8	53	90	
9	53	88	
10	54	99	
11	63	99	
12	62	95	
13	58	86	
14	56	93	

(Continued)