DEGRADATION OF AZINPHOS-METHYL RESIDUE ON PLUM FOLIAGE, 1987

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SUMMARY

Six plum orchards in Tulare County, California, were monitored for dislodgeable foliar residues of azinphos-methyl. The data was employed to assess the current one-day reentry interval. Replicate leaf disk samples were collected from each orchard at selected intervals over 28 days and analyzed for residues of azinphos-methyl and its oxygen analog. The mean concentrations of dislodgeable azinphos-methyl residues for all six orchards were above the calculated safe level of 1.6 ug/cm^2 at the expiration of the one-day reentry interval. The mean concentrations at one day after application ranged from 1.62 to 2.59 ug/cm^2. No oxon-analog residues were detected. The current reentry interval for azinphos-methyl on plums appears inadequate. The Department has proposed regulations to extend the reentry interval to 14 days.

INTRODUCTION

This study was conducted to evaluate the adequacy of the one-day reentry interval for azinphos-methyl (AZM) when applied to plums. AZM, a category 1 pesticide, has an oral LD_{50} of 11-13 mg/kg and a dermal LD_{50} of 220 mg/kg (1). The study was initiated as a portion of the Department's effort to determine if peach/nectarine reentry intervals should be applied to all stonefruit. The reentry interval for azinphos-methyl when applied to peaches and nectarines is 14 days. The calculated safe level of AZM foliar residue for reentry into treated fields is 1.6 ug/cm^2 leaf surface (2). Sampling technqiues were according to the methods of Iwata et al, (3).

Samples were analyzed for the parent compound and oxygen analog; the oxon was not detected in any sample. Analysis of the results indicates that residues can be expected to persist above the calculated safe level of 1.6 ug/cm^2 until approximately fourteen days after application.

MATERIALS AND METHODS

With the assistance of the Tulare County Agricultural Commissioner, six orchards, were selected and monitored for a 4-week period during April and May, 1987, to estimate the decay rate of AZM dislodgeable foliar residues. AZM was applied by conventional air blast sprayers (80-100 gallons water/acre) and at the rate of 1.5 pounds active ingredient per acre.

Sampling Techniques

Orchards were evaluated for a sampling strategy adapted from the following scheme:

Each orchard was divided into three sections with one row selected from each section. Eight trees, four trees on each side of the selected row, were chosen to approximate a diagonal across the orchard. The first and last tree in each sampling area were marked with flagging tape prior to the first azinphos-methyl application.

Two foliage samples were collected from each tree using a 2.54 cm (1 inch) Birkestrand leaf punch fitted with a four-ounce jar. Foliage punches were selected to represent all four "sides" of the tree. For example, two punches were collected from the north and west "sides" of four consecutive trees, and two punches were collected from the south and east "sides" of the four adjacent trees. All leaf punches were collected from a height of approximately two meters. One complete sample consisted of 16 foliage punches form each of the three sampling areas for a total of 48 foliage punches per orchard.

Three replicate samples were collected from each orchard. The jar containing each sample was sealed with aluminum foil, capped, sealed in a Zip-loc^R bag, and stored immediately on wet ice. Samples were shipped to Chemistry Services in Sacramento for residue extraction within 24 hours.

Sampling Schedule

Pre-application samples were collected on the day of application. Post-

application samples were collected after the spray had dried (within two hours), and at four hours, eight hours, one day, two days, four days, seven days after application, and every seven days therafter until 28 days. Three replicate samples were collected at each interval.

Analysis of Samples

Each sample was analyzed by Chemistry Services for dislodgeable residues of AZM and its oxon. 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.

Quality Assurance

For five of the six orchards, a sample of known concentration was drawn from the day's first tank mix. These tank mix samples were stored immediately on dry ice and shipped to Chemistry Services for analysis.

Statistical Methods (4) (5) (6)

Linear and nonlinear iterative least square regression techniques were employed to examine both initial deposition and decay rates in the study. Initial analysis will assume a first-order exponential decay model which takes the following functional form:

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

where Bo = initial deposition

B_1 = decay rate

and t = time since application

Comparisons of decay rate and initial deposition estimates were made by t-tests using the weighted asymptotic estimates of the standard deviation. Parallel analyses using the logarithmic transformed linearized regression were also conducted.

RESULTS

Mean concentrations of dislodgeable residues were above the calculated safe level for all six orchards at the expiration of the one-day reentry interval. The mean concentration levels of AZM at 24-hour post-application ranged from 1.62 to 2.59 ug/cm^2. The oxon-analog was not detected in any pre- or post-application samples. AZM levels for all fields sampled are presented in Tables I and II. For two fields, the mean concentration levels of AZM dropped below the calculated safe level at four days post-application. For the remaining four fields sampled, the mean concentration of dislodgeable residues of AZM did not fall below the calculated safe level until 14 days post-application. The levels of AZM at 14 days ranged from 1.02 to 1.80 ug/cm^2 leaf surface. All applications were by conventional airblast sprayers and all applications were made at the nominal rate of 1.5 pounds active ingredient per acre of AZM. The measured concentrations of

AZM from tank mix analyses ranged from 1.67 to 2.66 pounds active ingredient per acre. Five of the six fields applied the spray at a delivery rate of 100 gal/A. Field five was sprayed at a delivery rate of 80 gal/A. (See Table III)

Decay Rates

Decay rates were estimated for each field. The estimated decay rates ranged from -0.029 to -0.043 for the linear model and from -0.019 to -0.050 for the non-linear model. The estimated days to attain the calculated safe level for each field ranged from one to 21 days for the linear model and from one to 19 days for the non-linear model. The summary of regression analyses is presented in Table IV. The graphical presentation of AZM foliar degradiation for each field is presented in Tables V through IX.

DISCUSSION AND CONCLUSIONS

Azinphos-methyl is a broad spectrum phosphorodithioate organophosphate pesticide used primarily to control foliage feeding insects. Various application rates and dilutions are used to control the coddling moth and other important stonefruit pests. AZM is used extensively on hand harvested stonefruit, including peaches, apricots, nectarines and plums. These crops are all propagated from the same rootstock and cultivation, irrigation and harvest practices are very similar for these crops. The reentry interval for peaches and nectarines after an AZM application is 14 days. For all other stonefruit, the reentry interval is one day. The Department initiated this study to determine the validity of the current one-day reentry interval for AZM on plums, given the basically similar cultivation and harvest practices for peaches, apricots, nectarines and plums. The calculated safe level for dislodgeable foliar residues for AZM is 1.60 ug/cm^2 leaf surface (2). Analysis of the one-day post-application residues from the six orchards monitored in this study showed that, for all fields, the residues were higher than the calculated safe level of 1.60 ug/cm^2.

Dislodgeable residues during the first 24 hours following application appeared to behave erratically. While this phenomenon has been noted in other studies, it has not been fully characterized. The erratic changes in the "dislodgeability" of residues during the first day post-application may be due to interaction of AZM with rapidly volatilizing inert ingredients, spray adjuvants, diluent and materials on the leaf surfaces. In addition, the time elapsed between sampling and analysis is relatively long in comparison with the time elapsed between application and sampling.

Two of the fields had residue levels below the safe level after three to four days. The residue levels for the remaining four fields did not fall below the calculated safe level until 13-14 days after the AZM application. There appears to be no correlation between the results of the tank mix analyses and the estimated days to reach the calculated safe level of 1.6 ug. The tank mix analysis for Field 5 shows a concnentration of AZM that is intermediate in the range of the five samples measured, yet Field 5 has the longest estimated dissipation rate (see Table II and III). The current one-day reentry interval for AZM on plums appears inadequate based on this study. The Department has proposed regulations to extend the reentry interval for azinphos-methyl on plums to 14 days.

Table I

Foliar Dislodgeable Residues for Azinphos-methyl
Data From Samples Taken April Through May 1987
All Residues Shown in Micrograms Per Square Centimeters

Field Number	Sampling Interval	Replicate A	Replicate B	Replicate C	Field Number	Sampling Interval	Replicate A	Replicate B	Replicate C
1	1 Hour	2.2200	2.1500	2.0800	2	1 Hour	1.7700	1.9100	2.0000
	6 Hours	2.4500	2.8000	2.1500		6 Hours	2.2600	2.1600	2.2000
	Day 1	2.4700	2.4000	2.3300		Day 1	2.0400	2.4400	2.5300
	Day 3	1.9300	1.9900	1.9300		Day 3	1.9600	1.8800	2.0200
	Day 6	1.8700	2.0900	1.8800		Day 6	1.5700	1.6900	1.6100
	Day 13	LS	1.3300	1.8000		Day 14	1.4200	1.6500	1.4100
	Day 20	1.4400	1.2600	1.0800		Day 21	1.3400	1.6500	1.4500
	Day 28	1.0800	1.2400	1.1300		Day 28	1.1400	1.2600	1.2600
3	1 Hour	1.5700	1.5200	1.4700	4	1 Hour	1.2900	1.5900	1.7200
	6 Hours	1.4000	1.3700	1.4000		6 Hours	1.5700	1.3400	1.4200
	Day 1	1.4800	1.6900	1.6300		Day 1	1.9000	1.0700	1.9100
	Day 2	1.8400	1.5900	1.8000		Day 2	1.7300	1.7000	1.5600
	Day 4	1.4500	1.5100	1.5800		Day 4	1.3400	1.2800	1.1600
	Day 7	1.2700	1.5000	1.5300		Day 7	1.3400	1.3000	1.5300
	Day 14	1.0500	1.0000	1.0000		Day 14	0.7400	0.6100	0.7200
	Day 21	1.1500	0.9000	1.0700		Day 21	0.7400	0.6800	0.6600
	Day 27	1.0100	1.0300	0.9300		Day 27	0.5600	0.6300	0.6300
5	1 Hour	2.0800	1.9900	2.1100	6	1 Hour	1.8600	1.5500	1.6400
	6 Hours	2.4800	2.6300	2.6000		6 Hours	2.1000	2.1100	2.3300
	Day 1	2.4200	2.7900	2.5700		Day 3	1.6400	1.6500	1.4800
	Day 6	2.1600	2.0200	2.1300		Day 6	1.7400	1.5900	1.6600
	Day 28	1.6400	1.4400	1.5500		Day 28	0.7900	0.8400	0.7800

LS = Sample lost during extraction.

Table II
Application Information For Azinphos-methyl on Plums

	Formulation		Nominal		Results of
	Product	Rate	Rate	Delivery	Tank Mix Analysis
Field 1	50 WP	3#/A	1.5 #/A	100 gal/A	2.57 #/A
Field 2	50 WP	3#/A	1.5 #/A	100 gal/A	2.66 #/A
Field 3	50 WP	3#/A	1.5 #/A	100 gal/A	1.67 #/A
Field 4	50 WP	3#/A	1.5 #/A	100 gal/A	No sample
Field 5	50 WP	3#/A	1.5 #/A	80 gal/A	2.00 #/A
Field 6	50 WP	3#/A	1.5 #/A	100 gal/A	2.3 #/A

Table II: Summary of Regression Analyses for Azinphosmethyl on Plums

		INITIAL DEPOSIT-ION	DECAY RATE	R SQUARED	DAYS TO 1.6 UG
		estimate	estimate	estimate	estimate
FIELD	MODEL				
1	non-linear	2.3	0.027	0.99	13
	linear	2.2	0.043	0.85	15
2	MODEL				
	non-linear	2.1	0.021	0.73	14
	linear	2.1	0.033	0.70	15
3	MODEL				
	non-linear	1.7	0.024	0.81	2
	linear	1.6	0.029	0.78	2
4	MODEL				
	non-linear	1.7	0.050	0.79	1
	linear	1.6	0.042	0.75	1
5	MODEL				
	non-linear	2.3	0.019	0.64	19
	linear	2.3	0.032	0.60	21
6	MODEL				
	non-linear	1.8	0.031	0.89	4
	linear	1.7	0.035	0.86	3

Table IV

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 1

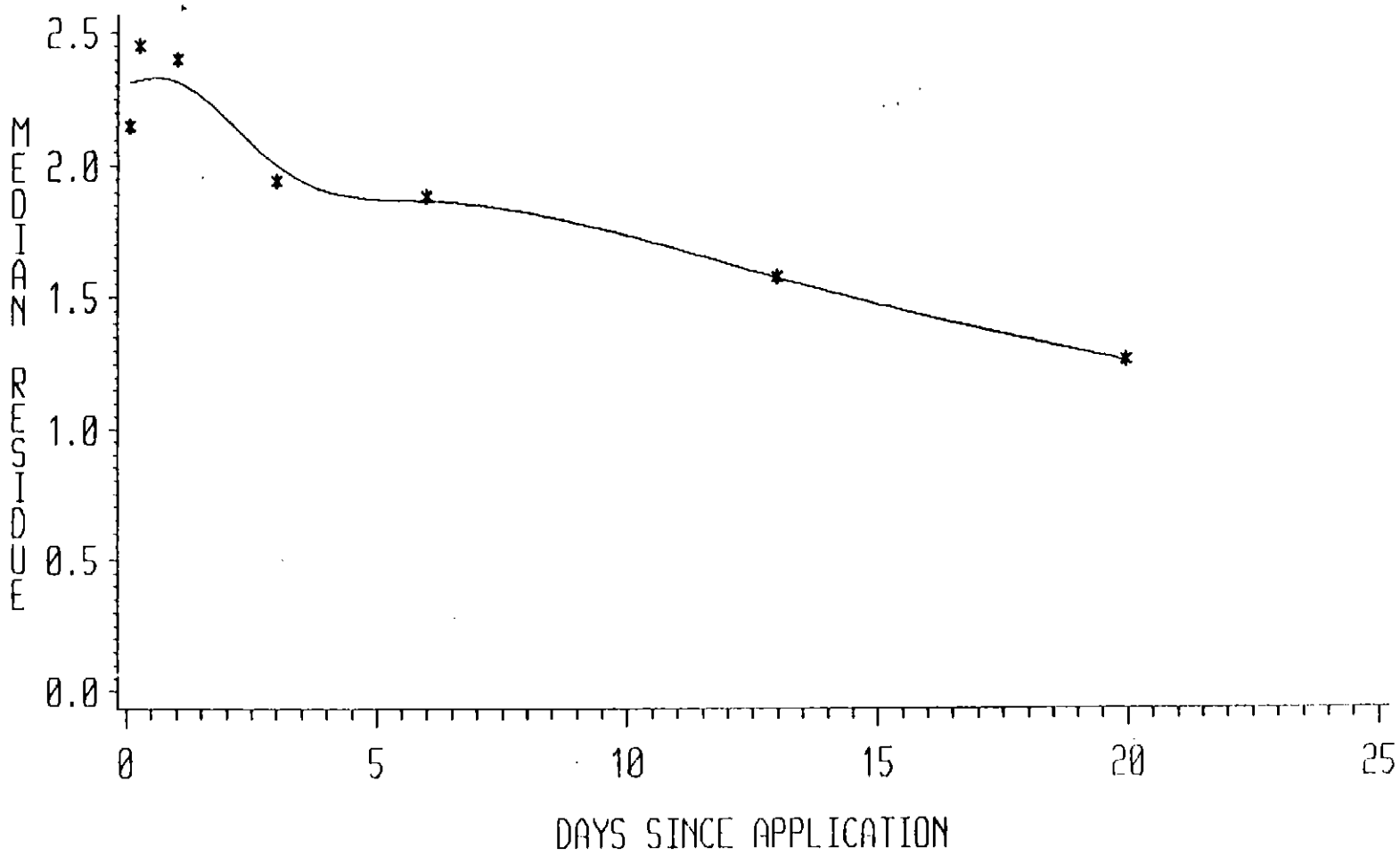

Table V

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 2

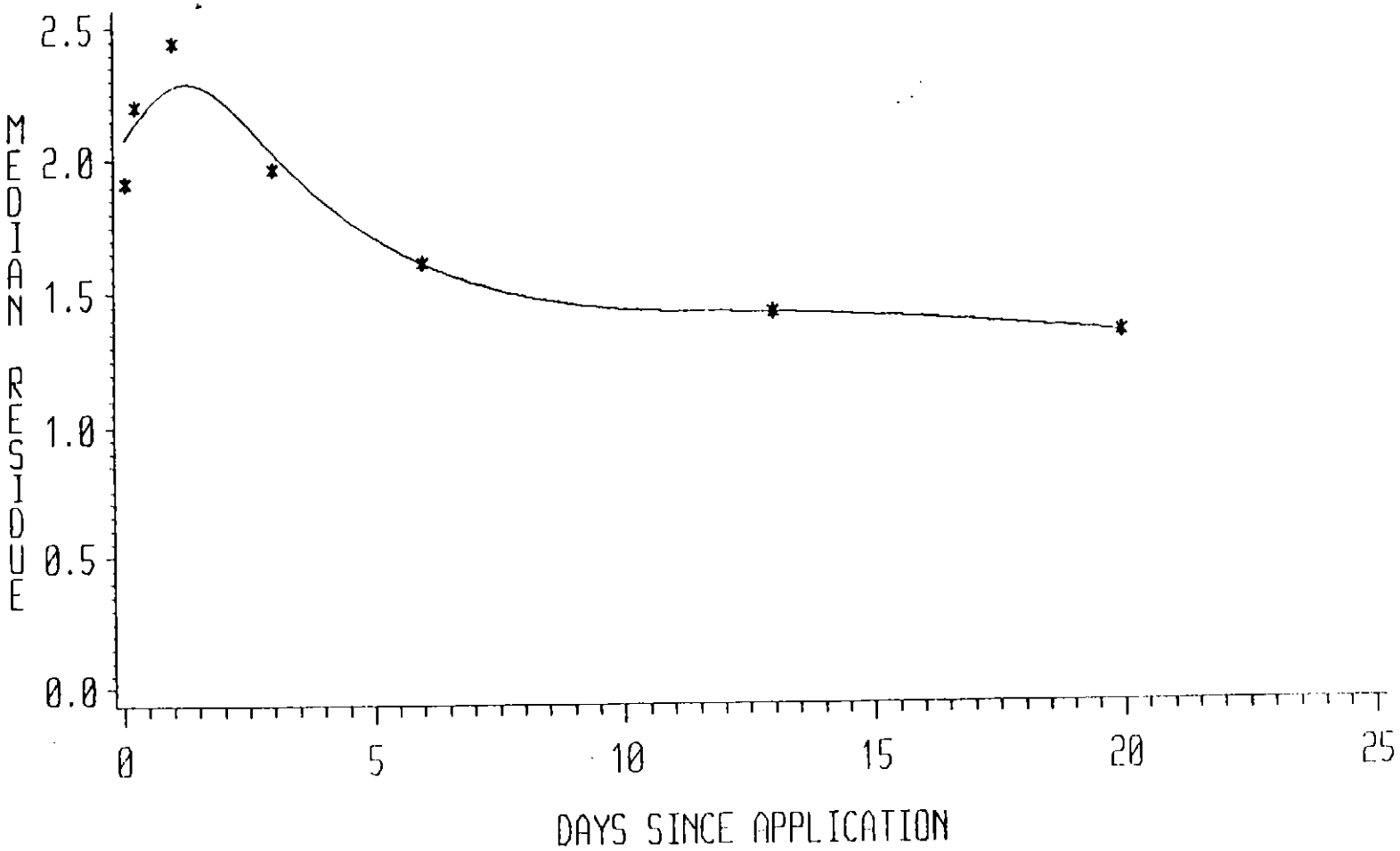

Table VI

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 3

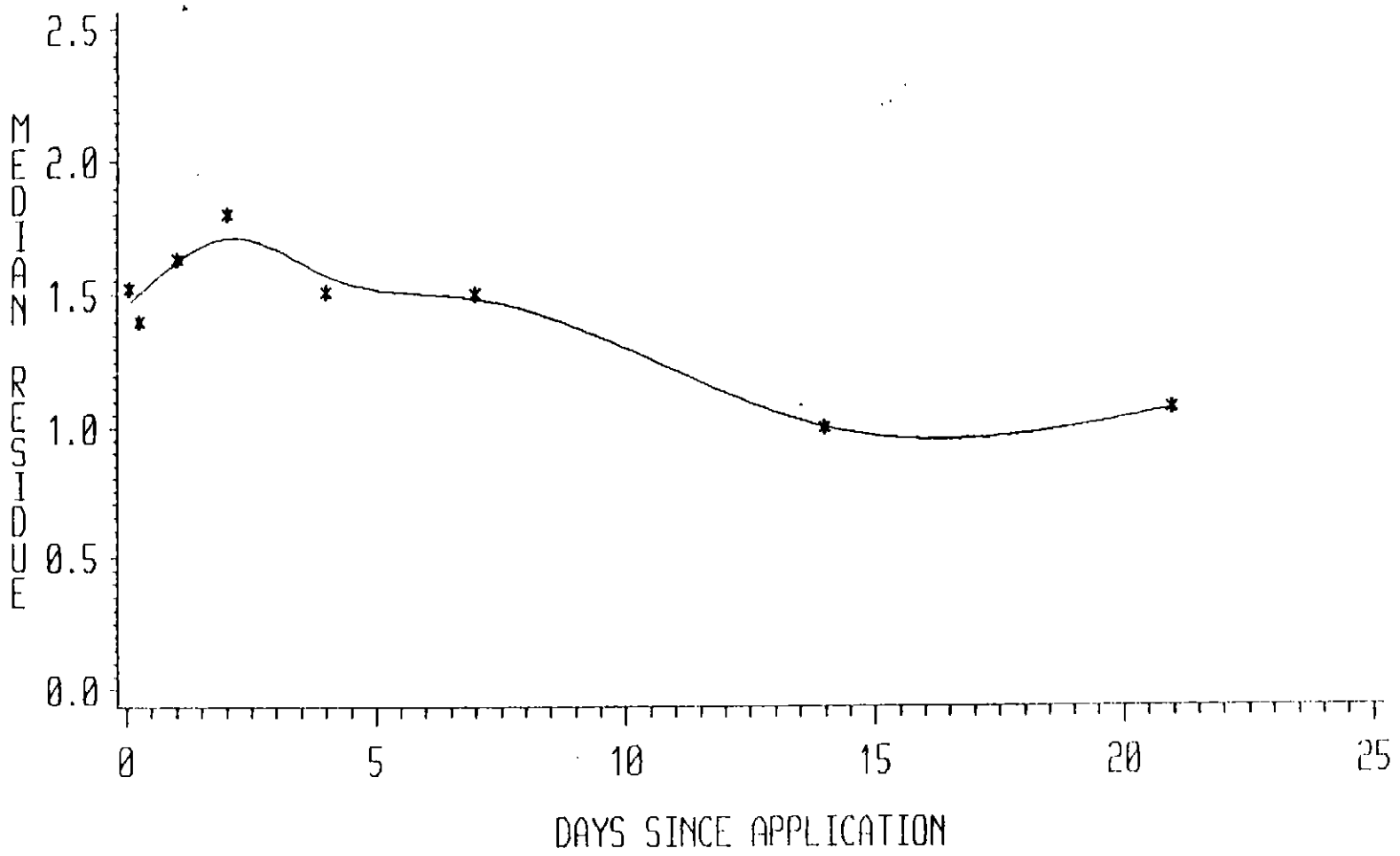

Table VII

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 4

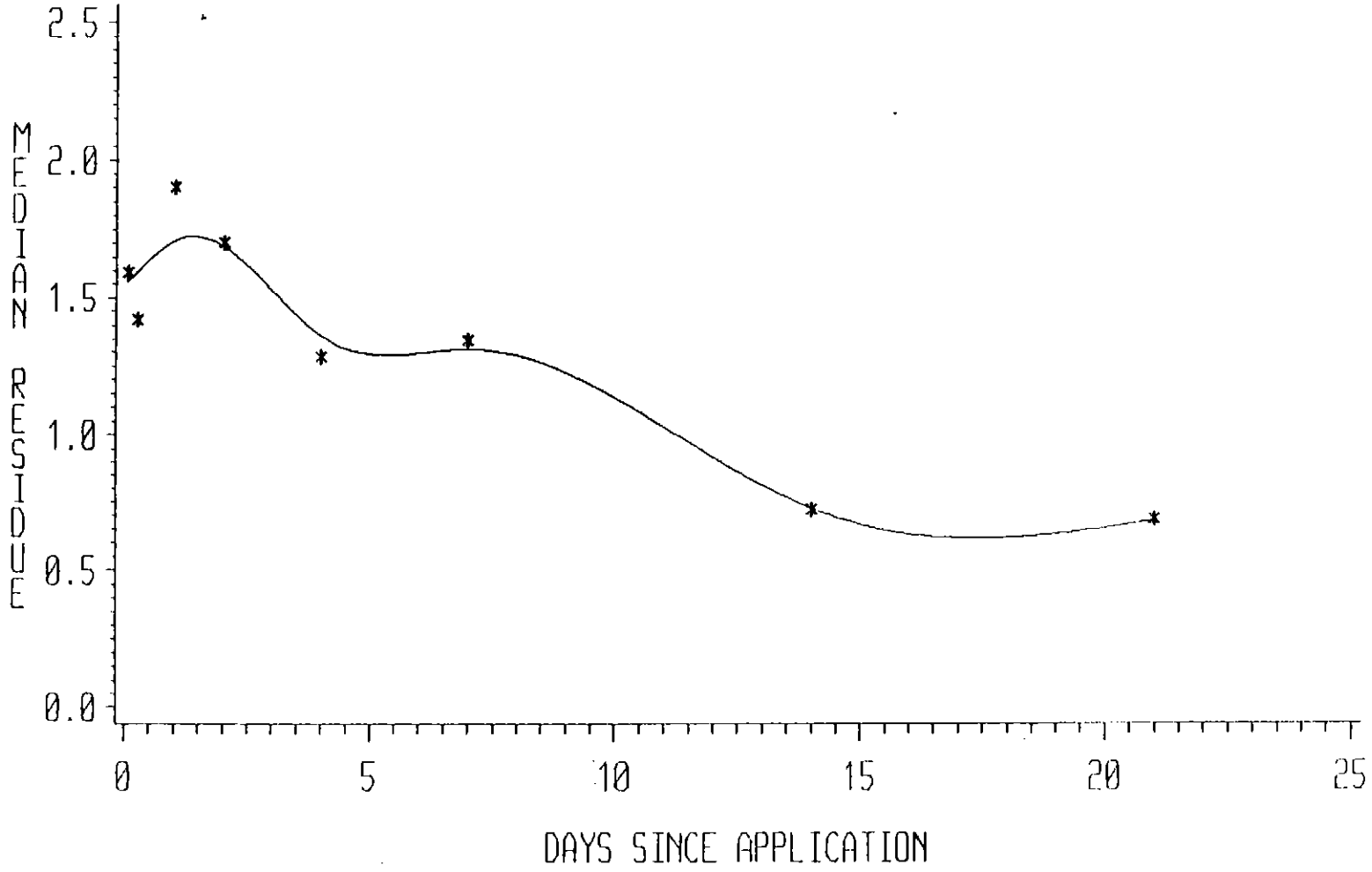

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Table VIII

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 5

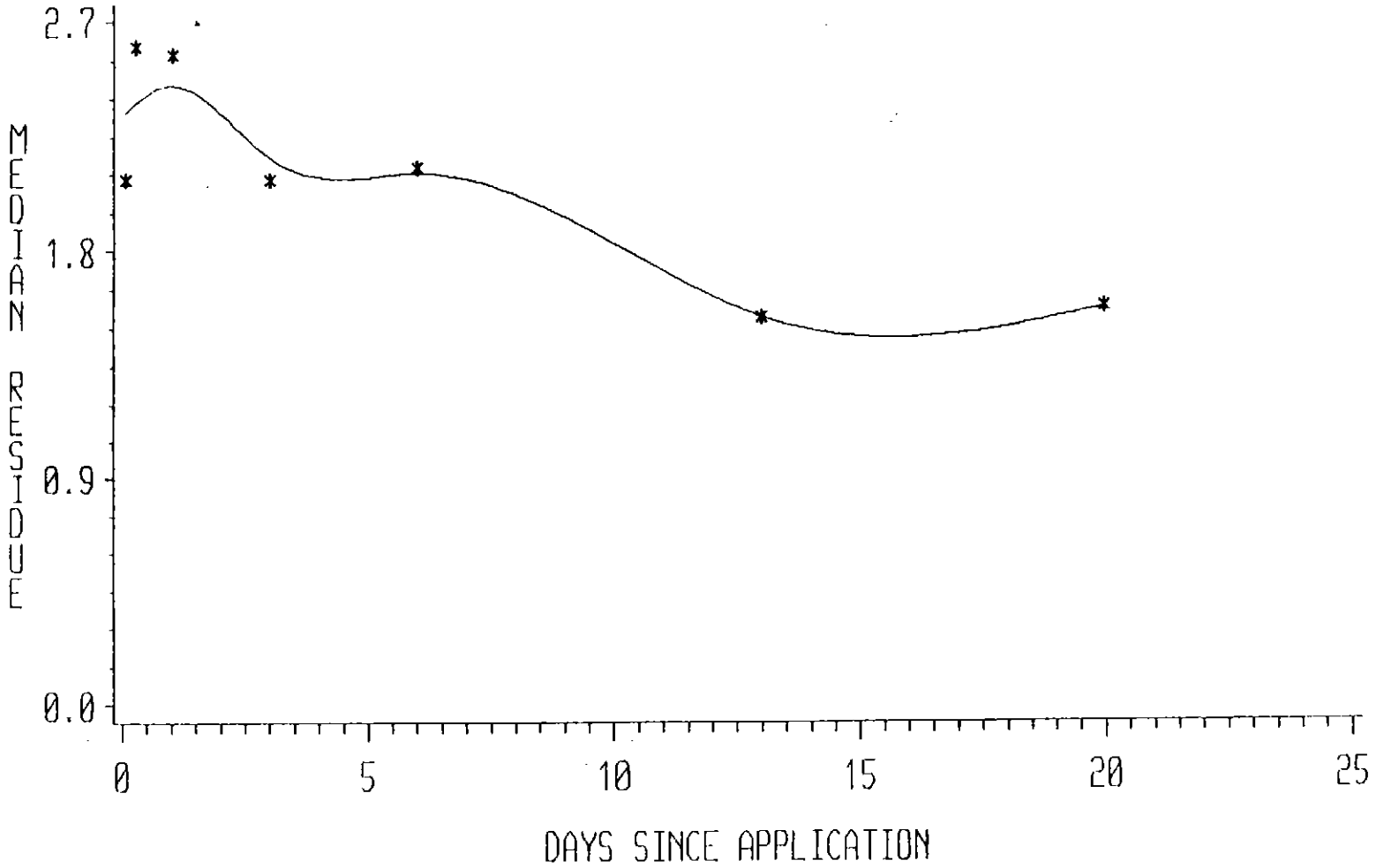
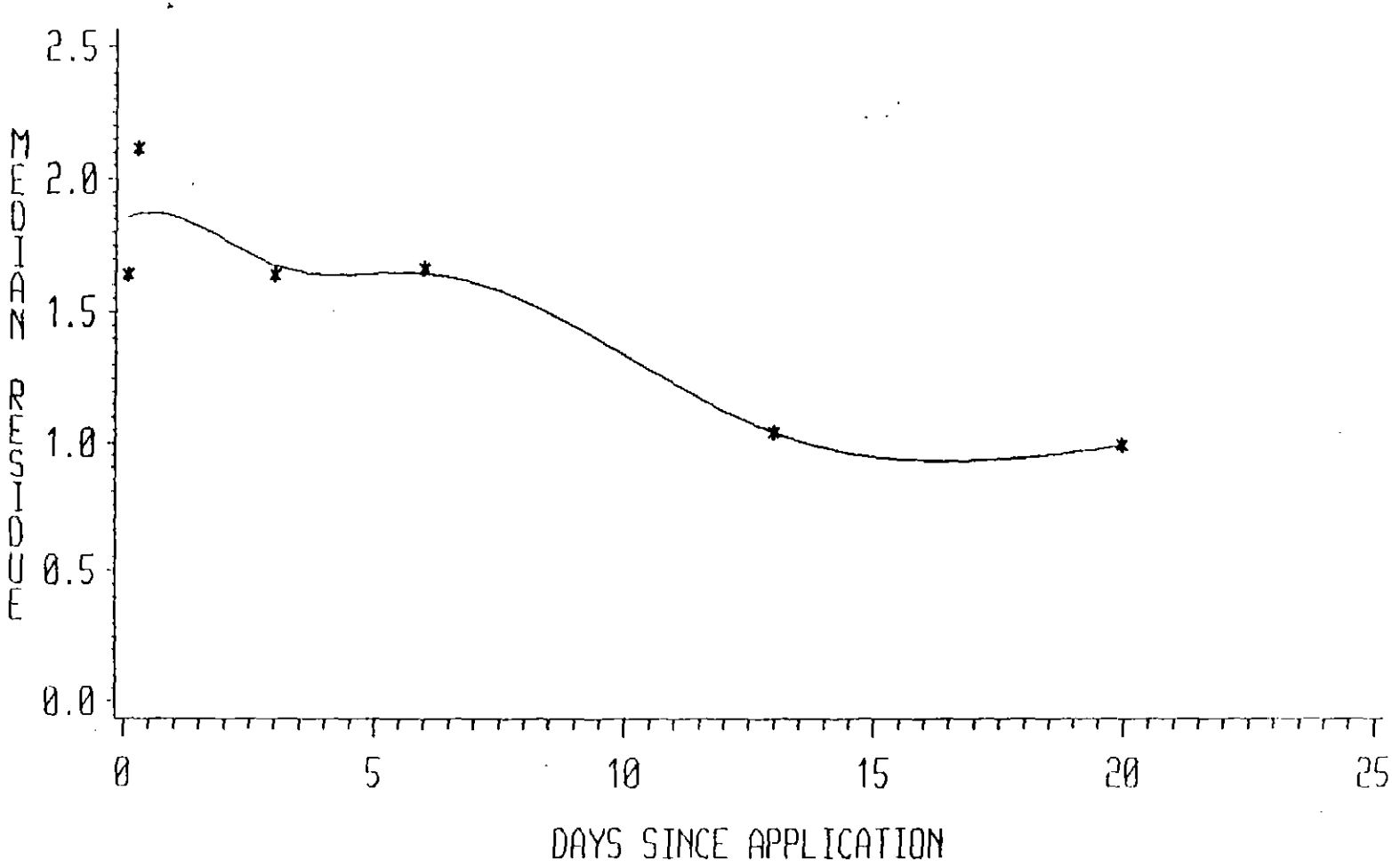


Table IX

AZINPHOSMETHYL FOLIAR DEGRADATION STUDY ON PLUMS

(RESIDUE: MICROGRAMS PER SQUARE CENTIMETER)

FIELD 6



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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%