A Field Survey of Dislodgeable Zolone Residues in Twelve Commercially Treated Vineyards

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Interest in the course of the decay processes for that part of foliar insecticide residues which is available to fieldworkers has greatly increased in recent years because of growing political and regulatory pressure to control the occurrence of residue poisonings (SPEAR, et al., 1975). If any correlation is to be made between the toxicology data for a pesticide and potential hazards to fieldworkers operating in a treated crop, then basic information on the dynamics of the weathering of that pesticide and its alteration products is needed. The present study is designed to provide such information for phosalone (Zolone®) on grapes in one climatologically homogeneous region. The data reported include formulation, rate, the dislodgeable residue information and weather conditions throughout the study.

METHODS AND PROCEDURES

Vineyard Selection

The vineyards selected for the study are located in the vicinity of Stockton in the north-central San Joaquin Valley of California. This region was selected because there were a number of growers there who anticipated using phosalone during the 1974 growing season. Phosalone was applied with ground equipment during the months of July and August.

Sampling Procedure

Samples were collected for residue analyses using the dislodgeable residue procedure of GUNTHER, et al. (1973). Pre-treatment samples were collected as late as possible before the phosalone was applied — in most cases within one or two days before application. Post-treatment samples were collected on the following schedule: (1) one to three days after application, (2) seven to ten days after, (3) twenty to twenty-one days after, and (4) thirty-five days after application.

All sample sites were located no less than four rows from a road and no less than four vines from the edge of the vineyard. No two sample sites were less than ten rows apart and all were separated either geographically by roads or chronologically by one or more days between applications. The leaf punches were collected by punching one leaf from each vine from the right and left sides of the aisle alternately as the collector progressed

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down the aisle. When half the number of punches required for a composite sample were collected (30 punches for a composite of 60), the collector walked across three or four rows where the procedure was repeated in the opposite direction until the full composite was obtained. The leaf punches were then stored on dry ice for transportation to the laboratory for analysis.

A total of fourteen separate sample plots located in four vineyards were used in the study. Twelve of the plots were sampled through the 35th day after treatment. The sample data are given in Table I.

TABLE I

APPLICATION AND RESIDUE DATA FOR ZOLONE®

Plot #	Application Data		Residue Data ($ng\ cm^{-2}$)								
	AIA[a]		Days Post Application								
	pints	gallons	1	2	7	8	9	10	20	21	35
22	6	25	5930			3520			2500		2230
23	6	25	4990			3270			2030		1800
24	8	12	12700					3680		2790	2160
25	6	25	2290				2320		1160		495
26	6	25		7390		3680			2520		1750
27	5.5-6	50	3850			2656				1998	2220
28	5.5-6	50	4710			3290			2280		1400
29	5.5-6	50	4840			3950			2547		2060
30[b]	7		6610					668[c]			
31	5.5-6	50	4340		4120				3290		2130
32[b]	7		8000			3520					
33	8	20		15000			12500		9610		8170
34	8	20		9850			10500		9270		8080
35	8	20		10500			4200		9740		4620

In no case were pre-application levels above the limit of detectability.

a) In all cases Zolone 3EC was used.

b) These plots were irrigated with an overhead sprinkler system and sampling was discontinued.

c) This value comes from a sample taken after overhead irrigation.

Analytical Procedures

The frozen leaf-punch samples were brought to room temperature and then carefully transferred to one-pint, narrow-mouth Mason jars fitted with teflon cap inserts. Water (150 ml) plus six drops of surfactant (Sur Ten 1:50 dilution) were added, and the jars were shaken on a reciprocating shaker for one hour. The wash solution was decanted into a 500 ml separatory funnel. This wash procedure was repeated a second time but shaken for only 30 minutes. A third quick rinse was performed by adding 25 ml of water (no surfactant) and shaking by hand for 10 seconds. This was combined with the other rinses.

The pesticide was then extracted into organic solvent with three successive 50 ml aliquots of chloroform, shaken for 20 seconds each time. The chloroform was collected in a round-bottom flask, taken down on a rotor evaporator and replaced with 10 ml of benzene.

The samples were analyzed for Zolone® and zoloxon using a Tracor MT 222 Gas Chromatorgraph equipped with a flame photometric detector. A 77 x .35 cm ID glass column packed with 10% DC-200 on Chromosorb W, 80/100 mesh provided satisfactory separations. The gas flows were set at: hydrogen, 70 cc/min; air, 60 cc/min; oxygen, 5 cc/min; and the carrier gas, nitrogen, at 125 cc/min. With the oven temperature at 220°C, the retention times for zoloxon and Zolone® were 184 seconds and 260 seconds, respectively. An autolab Model 6300 Digital Integrator was used to quantitate peaks.

RESULTS AND DISCUSSION

Meteorological Data

A record of certain meteorological conditions, such as temperature, cloud cover, etc., which could affect the persistence of the phosalone or its metabolites was obtained from the U.S. Weather Bureau station at the Stockton Airport. A moderate amount of cloud cover was experienced in the area during the study period, July 18 to September 5, 1974. Approximately 13% of the sunrise to sunset sky was occluded, indicating that solar radiation was somewhat less than maximum possible. Figure 1 shows the temperature and dewpoint history of the region over the time of residue sampling. The daily maximum ranged from 84 to 107°F while the lows fell between 54 and 80°F. The average daily dewpoint was less than the daily low on all dates but one, indicating very little free moisture was available in the macroclimate. This does not mean, however, that in the microclimate of the leaf surface and the residues in question free moisture was not available since no foliar microclimate measurements were made.

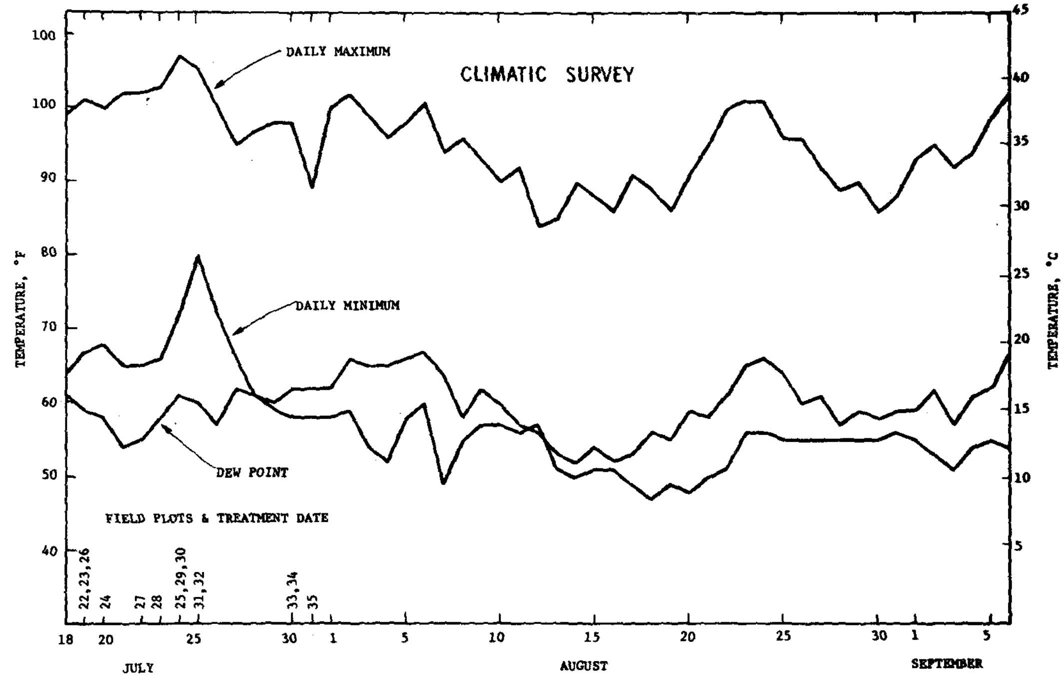

FIGURE 1. Temperature and Dewpoint History over the Study Period*

* (Taken from data for Stockton, California, provided by the National Weather Service, U.S. Department of Commerce, Ashville, North Carolina.)

Dislodgeable residue values for Zolone® as well as the application data are given in Table I. Table II contains the dislodgeable residue data for zoloxon. Figures 2, 3, and 4 show the residue decay curves for all plots sampled for the full 35 days post-application.

The residue decay process represented by this figure is remarkably similar to that observed in a previous study (LEFFINGWELL, et al., 1975) conducted in 1972 where replicated plots within one vineyard were treated with Zolone® at two different rates and gallonages. In both studies climatic conditions were quite similar, including cloud cover (estimated 12% for the 1972 study); in the study reported herein the dewpoint, however, ran somewhat higher than that of the earlier study. All the applications in the current study were of the "concentrate" type used in the 1972 study. The patterns of Zolone® disappearance and zoloxon formation are qualitatively identical. In some cases the initial deposits of the parent compound substantially exceed those of the 1972 study. In each of these cases, however, the gallonage of water per acre was less than that of the 1972 study.

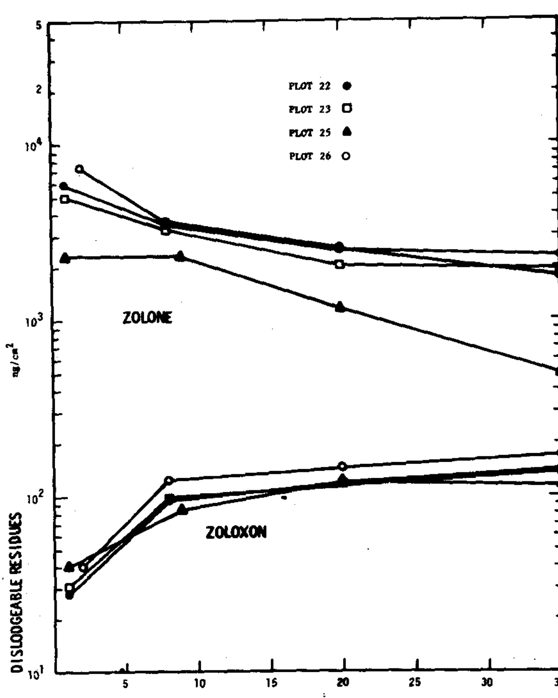

FIGURE 2. Dislodgeable Zolone® and Zoloxon Residues in Plots 22, 23, 25 and 26.

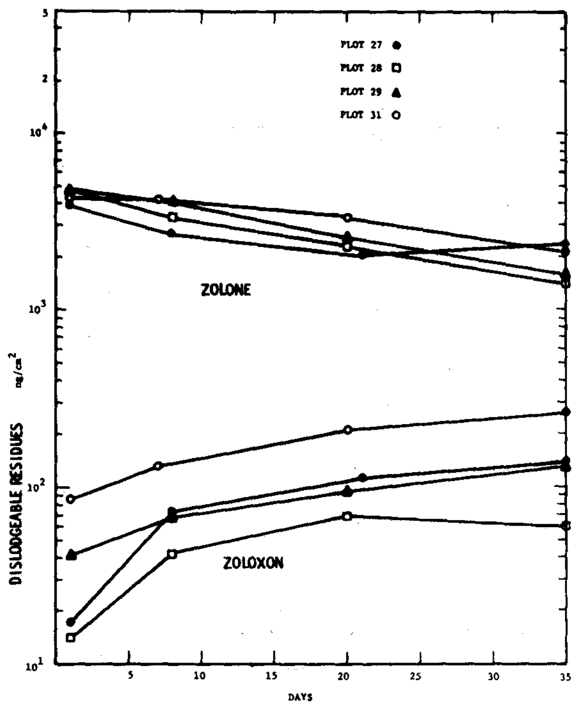

FIGURE 3. Dislodgeable Zolone® and Zoloxon Residues in Plots 27, 28, 29 and 30.

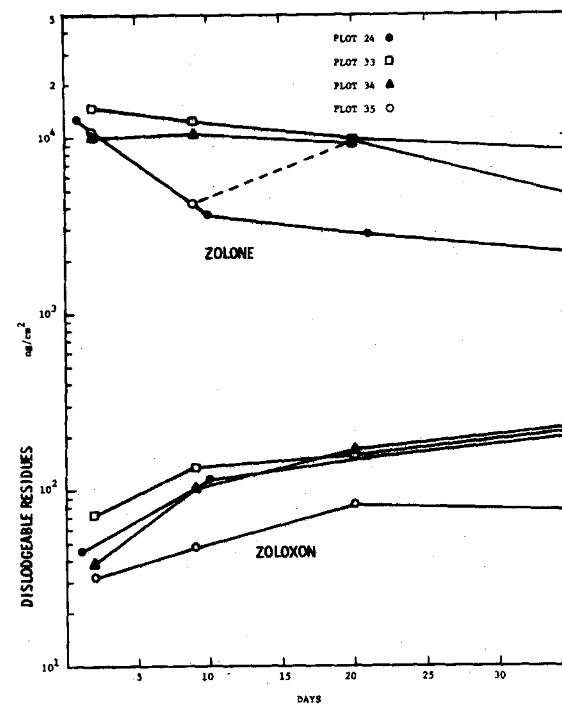

FIGURE 4. Dislodgeable Zolone® and Zoloxon Residues in Plots 24, 33, 34 and 35.

TABLE II

RESIDUE DATA FOR ZOLOXON

Plot #	Residue Data (ng cm^{-2})								
	Days Post Application								
	1	2	7	8	9	10	20	21	35
22	28			97			118		140
23	31			99		113	116		136
24	45				83			151	199
25	40						120		112
26		40		123			142		169
27	17			71				111	132
28	33			99			163		120
29	40			67			94		130
30[a)]	92					33b)			
31	85		130				208		261
32[a)]	99			177					
33		73			132		158		209
34		38			99		165		223
35		75			111		193		156

In no case were pre-application levels above the limit of detectability

a) These plots were irrigated with an overhead sprinkler system and sampling was discontinued.

b) This value comes from a sample taken after irrigation.

The foliar residues of zoloxon are remarkably similar among fields and between years regardless of application rate or gallonage. In the 1972 study the oxon levels were still increasing at the last sample date of 28 days post-application so in the current study the sampling period was extended to 35 days in anticipation that degradation of the oxon would have overtaken its formation from the parent. However, this was not the case, and the oxon levels showed little sign of diminishing at 35 days.

CONCLUSIONS

Again in a field study situation, it is difficult to distinguish the climatic factors which affect residue weathering. However, the strong similarities between the residue dynamics reported here and those observed in 1972 suggest that the pattern of Zolone® decay in central California in the summer months is relatively invariant.

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