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## Parathion Residues on Citrus Foliage. Decay and Composition as Related to Worker Hazard

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The decay of ethylparathion on citrus foliage was followed for 16 days post-application in 32 groves in central California. Paraoxon comprised a significant fraction of the foliar residue in all groves. In

31 fields paraoxon decayed more slowly than parathion. The combined residues of parathion and paraoxon degrade such that the hazard to workers decreases with time.

Foliar residues of organophosphate pesticides have been implicated in sporadic incidents of illness among agricultural fieldworkers in the western United States over the past 25 years (Quinby and Lemmon, 1958). It has been uncertain whether this problem is restricted to the semiarid agricultural regions of the U.S. or, given the world-wide pattern of organophosphate pesticide use, whether incidents occur and are not reported elsewhere. Recent information suggests that poisonings attributed to O-P residues have occurred in El Salvador within the last several years (Davies et al., 1975). In the United States, concern over this occupational health problem caused the establishment of regulations governing the entry of workers into treated fields (California Department of Food and Agriculture, 1971; *Fed. Regist.*, 1974). These regulations define the allowable time intervals between application of the pesticide and entry into the field or grove if work involves substantial foliar contact and appear to be a practical means of controlling exposures in conditions where medical surveillance is impractical.

The re-entry concept is based on an assumption that the potential for intoxication from foliar residues is a decreasing function of time. As the concept has been applied, it is further assumed that the decay process varies so little that a single re-entry interval can be equitably applied to a given pesticide-crop combination regardless of regional or climatological differences. However, the relative infrequency of reported organophosphate poisoning incidents suggests that an unusual combination of conditions must exist to cause overt intoxication. In the case of parathion such rare events may result from prolonged persistence of the pesticide residues or from the formation and persistence of a more toxic oxygen analog (Milby et al., 1964).

We have investigated the validity of the assumptions underlying the re-entry concept in a climatologically homogeneous region and attempted to discover a relationship between application variables and unusual persistence of residues. The focus of attention was on the degradation rate of the dislodgeable residues of parathion on citrus fo-

liage, since this pesticide-crop combination has been implicated in a number of poisoning incidents. Dislodgeable residues were determined using the technique of Gunther et al. (1973).

### EXPERIMENTAL SECTION

**Grove Selection and Sampling Procedure.** Sixteen Valencia orange groves and sixteen groves of navel oranges in Tulare County, Calif., were studied. All 32 groves received commercial applications of ethylparathion between May 15 and 24, 1973. Although 27 of the 32 applications were wettable powder formulations, the diversity of additive chemicals, irrigation practices, and rates of application otherwise reflected commercial practice in the region. The local weather during the study is summarized in Figure 1.

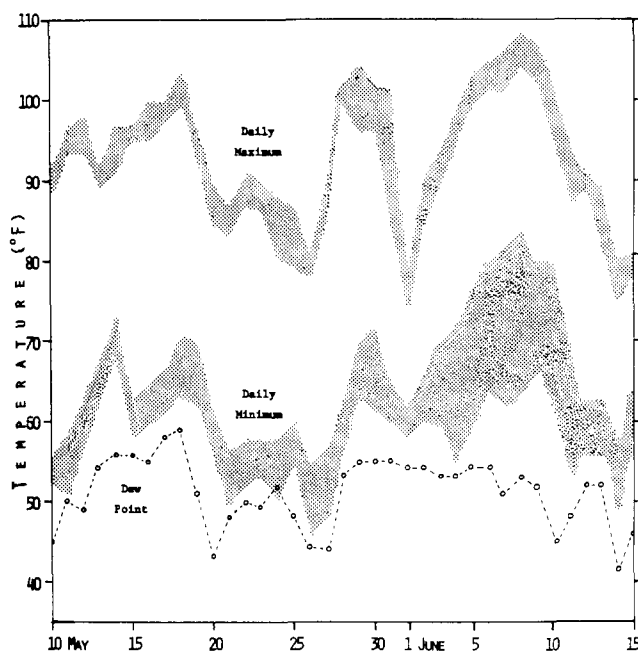
Sampling in each grove commenced 2 days after application in order to avoid the rapid initial loss of residue (Ebeling, 1963). A random sample of 15 trees was chosen from along a diagonal line through each grove. Subsequent samples were taken on days 9 and 16 post-application from the same trees in order to minimize tree-to-tree variability. Each sample consisted of a total of 60 leaf disks, each 3 cm in diameter, taken from the 15 trees according to the procedures of Gunther et al. (1973). The sample bottles were frozen immediately and returned to the laboratory for extraction and analysis for both parathion and paraoxon.

**Materials and Apparatus.** Gas chromatographic analysis was performed on a Varian 1520 equipped with alkali flame ionization detectors. Columns were 6 ft × 2 mm glass packed with either 10% DC 200 or an equal mixture of 10% DC 200 and 15% QF-1 on 100-120 mesh Chromosorb W (HP) and were run at 220°. Detector and on-column injector temperatures were 245 and 235°, respectively. Carrier gas was nitrogen (20 ml/min) and flame parameters were 10 ml/min for hydrogen and 75 ml/min for air. The minimum detectable level for parathion ranged from 1-5 pg while for paraoxon it fell between 3 and 10 pg. The identity of paraoxon was confirmed by gas chromatography-mass spectrometry. The GC-MS was a Finnigan 1015D with a Systems Industries 150 control system and a chemical ionization source. Carrier gas was methane and the column was 6 ft × 4 mm glass packed with 3% OV-17 on 60-80 mesh Gas-Chrom Q, run at 205°. The parathion and paraoxon standards were obtained from Chem Service Inc., West Chester, Pa. Extractions were made with commercial pesticide grade solvents.

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**Table I. Application Rate (Active Ingredient per Acre), Decay Parameters, and Day 2 Residue Values for 32 Orange Groves in Tulare Co., California**

	AIA, lb/acre	$a_1$ , day <sup>-1</sup>	$a_2$ , day <sup>-1</sup>	$a_3$ , day <sup>-1</sup>	$x_1$ , ng/cm <sup>2</sup>	$x_2$ , ng/cm <sup>2</sup>
1	6.0	0.245	0.077	0.00113	264	18.6
2	5.0	0.181	0.126	<<10 <sup>-5</sup>	321	64.8
3	5.0	0.200	0.105	0.00387	398	32.1
4	5.0	0.156	0.076	<10 <sup>-5</sup>	413	29.7
5	2.3	0.179	0.109	0.00842	1430	109
6	2.0	0.229	0.183	0.00207	181	89.6
7	2.0	0.211	0.158	0.00049	171	71.4
8	2.0	0.430	0.171	<<10 <sup>-5</sup>	150	109
9	1.5	0.286	0.135	<<10 <sup>-5</sup>	191	10.5
10	1.5	0.265	0.165	<10 <sup>-5</sup>	49.7	6.30
11	1.3	0.233	0.096	0.00446	252	33.7
12	2.0	0.182	0.126	0.00002	187	52.8
13	3.1	0.182	0.076	<<10 <sup>-5</sup>	103	21.4
14	1.9	0.196	0.098	0.00124	175	35.1
15	2.5	0.115	0.091	0.00001	1.47	0.60
16	2.5	0.276	0.116	<10 <sup>-5</sup>	295	33.7
17	3.0	0.136	0.193	0.00268	89.1	23.1
18	2.0	0.251	0.090	0.00339	241	20.9
19	1.9	0.296	0.094	0.00028	688	25.5
20	1.9	0.214	0.115	0.00252	229	51.6
21	2.0	0.469	0.146	0.00009	483	166
22	7.5	0.247	0.174	0.00134	1300	227
23	2.0	0.264	0.200	0.00031	173	328
24	2.0	0.379	0.224	0.00006	439	396
25	1.9	0.374	0.134	<10 <sup>-5</sup>	153	15.6
26	2.5	0.345	0.129	0.00294	417	25.0
27	1.9	0.193	0.057	0.00221	13.2	1.65
28	2.0	0.263	0.197	0.00003	771	365
29	4.6	0.262	0.138	0.01160	387	11.4
30	7.5	0.237	0.137	0.01260	618	321
31	2.3	0.313	0.113	0.00144	363	32.1
32	1.9	0.224	0.172	0.00003	200	145

**Figure 1.** Regional weather conditions during the study period. Daily minimum and maximum temperatures indicate the range of the five local reporting stations: Orange Cove, Lemon Cove, Lindcove, Lindsay, and Porterville. Dew point is daily average recorded at Fresno.

## RESULTS AND DISCUSSION

**Decay Model.** To facilitate interpretation of the time

series data, a first-order decay process was assumed and the residue data were fitted to a model of the form:

$$dx_1/dt = -a_1x_1$$

$$dx_2/dt = a_3x_1 - a_2x_2$$

where  $x_1$  is the parathion residue in nanograms per square centimeter and  $x_2$  is the corresponding paraoxon residue. The parameters  $a_1$  and  $a_2$  are the decay rates of parathion and paraoxon, respectively, and  $a_3$  is the rate of conversion of parathion to paraoxon.

Separate parameters were estimated for the residue data from each grove using a constrained optimization procedure (Kuester and Mize, 1973). The parameter estimates were those values which minimized the sum of squares of observed minus predicted residue values. Table I shows the estimates for each grove together with the first set of observed residue values which were those taken 2 days after application. The process of locating treated fields made it impossible to obtain preapplication samples. However, during May, 1974, eight groves were sampled just prior to parathion application and the residue levels ranged from 0.35 to 8.8 ng/cm<sup>2</sup> for parathion and 0.15 to 3.8 ng/cm<sup>2</sup> for paraoxon.

Fit to the model over a 2-week period of observation was reasonably good with normalized root-mean-square errors, calculated for each grove, on the order of 25% for parathion and 15% for paraoxon. Where large errors occurred, it appeared that the parathion had not completed the initial rapid decay phase by day 2. The estimated values of the decay parameters and all observed paraoxon-parathion residue levels are more nearly log normally distributed

than normally distributed. Therefore, estimated median values and logarithmic variances are quoted for these sample distributions.

The estimated median values for the decay parameters were  $a_1 = 0.239$  and  $a_2 = 0.125$ . In terms of "half-lives", the median parathion half-life was 2.90 days and the median oxon half-life, 5.55 days. The estimated variances of the logarithms of the decay parameters are 0.136 and 0.144. Since we chose to sample a large number of groves rather than to replicate samples in each grove, our data do not allow an estimate of the sampling error. Therefore, the variances given above are estimates of the upper bounds on the true variance of the decay parameters.

No significant correlation was found between the three model parameters. The highest simple correlation of +0.34 occurred for  $a_1$  vs.  $a_2$ . In only 1 of the 32 fields was  $a_2$  greater than  $a_1$ , indicating that paraoxon decays more slowly than parathion as suggested by the independent distributions of these decay rates.

The production of paraoxon was small when judged by the ratio of  $a_3/a_1$  which had a maximum estimated value of 0.054. (All parathion would be converted to paraoxon if  $a_3/a_1$  were unity, the upper bound imposed by mass balance considerations.) Based on a sample size of 32, approximately 90% of the population of all orange groves in this region will possess  $a_3/a_1$  ratios of less than 0.054 (Murphy, 1948). This result, coupled with the fact that parathion decays more rapidly than does paraoxon, suggests that paraoxon production occurs principally during the first few days after application when high levels of parathion are still present. Thereafter, paraoxon levels are largely independent of the decay of parathion.

Although the actual residue levels on day 2 are given in Table I, the paraoxon/parathion ratio was a more useful index of the relative importance of the oxon in the foliar residue. This ratio increased from 0.168 on day 2 to 0.610 and 0.825 on days 9 and 16, respectively; indeed, by day 16 30% of the groves showed greater foliar residues of paraoxon than of the parent compound, parathion, with the maximum observed ratio in excess of 4.0. By comparison the highest paraoxon/parathion ratios otherwise reported have been in the range of 20–50% on cotton and tobacco (Joiner and Baetcke, 1973; Ware et al., 1974; Sheets et al., 1974). Our data showed no clear association of high paraoxon/parathion ratios with application rate, irrigation practice, gallonage, or the variety of additives contained in the spray mixtures.

**Assessment of Occupational Hazard.** To relate the residue results to the occupational health hazard, we assumed that the intoxication potential,  $\psi$ , was proportionate to the combined dislodgeable residues of parathion and paraoxon as described by the expression:

$$\Psi = c_1x_1 + c_2x_2$$

where  $x_1$  and  $x_2$  are the residue values as defined above and  $c_1$  and  $c_2$  are unknown parameters reflecting the relative toxicity of parathion and paraoxon. A condition for the hazard to be a decreasing function of time, despite oxon production, was derived from the first-order decay model. This condition places an upper bound on the residue toxicity ratio,  $c_2/c_1$ . The values of the decay parameters and residues given in Table I yield an infinite upper bound on the toxicity ratio in 31 of the 32 groves. For these groves, therefore, the hazard was continuously decreasing after the second day regardless of the toxicity of paraoxon relative to that of parathion. In the remaining grove, the hazard was continuously decreasing if paraoxon is less than 34 times as toxic as parathion. If, on the other hand, paraoxon residues present a relative hazard  $c_2/c_1$  greater than 34 times those of

parathion, the combined residue hazard in this grove peaks sometime between the second and fifth day post-application, depending on the exact value of the ratio,  $c_2/c_1$ . Assuming that the principal exposure of fieldworkers is via the dermal route, limited animal data suggest that  $10 < c_2/c_1 < 55$  (Nabb et al., 1966).

Based on this analysis we have concluded that the re-entry concept is a valid strategy for protecting fieldworkers from parathion residues on citrus crops in the region studied. Although it appears reasonable to assume that the hazard will continue to decrease after day 16, the use of the model to quantitatively predict residue levels beyond that time is not warranted. Moreover, the possibility cannot be discounted that the hazard may increase beyond day 2 before beginning to decline in situations or for pesticides where a less rapid oxon buildup occurs (Leffingwell et al., 1975).

Preliminary results of coordinated studies designed to relate the exposure and response of volunteer workers harvesting oranges in parathion-treated fields indicate that blood cholinesterase depressions are highly correlated with dislodgeable residues of paraoxon at levels similar to those reported herein (Spear et al., 1974). These results coupled with our findings that substantial proportions of paraoxon in foliar residues commonly occur suggest that the establishment of re-entry intervals on a scientific basis should begin with the determination of the important parameters of the decay process. For the organophosphate pesticides, this determination must include data on the production and persistence of the oxygen analogs in the weathered residue.

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