

Natural Variations in the Decay and Oxidation of Parathion Foliar Residues

William J. Pependorf* and John T. Leffingwell

Results of foliar decay studies in 17 central California orange groves are reported. Data are analyzed using a first-order kinetic decay model for both parathion and paraoxon. Exponential decay rate coefficients for parathion were $0.72 \pm 40\%$ per day (for 3 days) and $0.076 \pm 30\%$ thereafter; paraoxon was $0.080 \pm 30\%$. Paraoxon yield from parathion decay ranged widely around 4% for the first 3 days, then dropped near 0.7% thereafter. Oxidation during the early phase was increased when zinc sulfate was included in the application. Residue oxidation and decay were found to correlate strongly with dry, stable weather conditions, implying that recent worker poisoning incidents (1975) may have been associated with foliar dust and airborne oxidants.

In our earlier research with parathion residues on orange trees (Spear et al., 1975), we reported finding various quantities of paraoxon in foliar residues following applications of parathion. This finding was in sharp contrast to early parathion residue research in which no paraoxon was reported on such fruits and foliage as apples (Fahey et al., 1952), peaches (Bobb, 1954; Brunson and Koblitsky, 1952), and citrus (Carman et al., 1952; Atkins et al., 1961). These paraoxon residues were also much higher than the 5 to 25% paraoxon more recently reported on tobacco and cotton. Our residues, collected from 32 groves 16 days postapplication, contained a median paraoxon content of 45% or 8.2 ng/cm^2 ; the maximum content observed was 88% paraoxon at a level of 18 ng/cm^2 . These levels of paraoxon all fell below the "no-effect" level as determined in later field experiments (Spear et al., 1977a). This knowledge of the greater production and persistence of highly toxic paraoxon may have proved academic; however, the apparent variability of the decay rates ($\pm 38\%$ of median values) suggested that "hot fields" with unusually high, hazardous levels of paraoxon might still occur, albeit infrequently, as exemplified by the most recent poisoning incident in which paraoxon in the range of 100–200 ng/cm^2 comprised 95% of the residue more than 20 and even 30 days postapplication (Spear et al., 1977b). Whether these rare events occur because of identifiable factors associated with application or environmental conditions or because of strict laws of probability is yet unknown.

Our first attempt to associate an application or environmental variable with high rates of parathion oxidation (Spear et al., 1975) was not productive. However, a later analysis of the estimated residue decay coefficients from matched "available" residue (Popendorf et al., 1975) samples [cf. "dislodgeable" residues (Gunther et al., 1974) in our first report] collected in these same 32 groves, revealed that a residue containing a larger proportion of paraoxon typically resulted following applications containing zinc sulfate (ZnSO_4) as a nutrient additive (neutral zinc such as zinc oxide (ZnO) did not produce a similar effect); also slower rates of residue decay were observed when kelthane was included in the formulation or when liquid parathion was used (cf. wettable powder). These same factors only weakly influenced decay coefficients estimated from "dislodgeable" residue results (Spear et al., 1975). The studies which follow were therefore undertaken to investigate further the effect of certain of these factors, including weather, on paraoxon production.

Department of Biomedical and Environmental Health Sciences, School of Public Health, University of California, Berkeley, California 94720.

EXPERIMENTAL METHODS

A total of 17 plots in 11 central California orange groves was included in these studies. Application variables for each plot are listed in Table I. Plots 1–8 received commercial applications which varied in their quality and formulation additives; plots 9–11 received controlled applications as part of our picker exposure study (Spear et al., 1977a); the final six plots were also controlled, each of three groves receiving paired applications of powder and liquid parathion formulations. Plots 3 and 8 were also within a single grove.

Serial foliar residue samples were taken from a designated group of trees in each plot using two methods. The vacuum method as described by Popendorf et al. in 1975 ("available" residue) was modified to recover the light deposit of particles which collect on the nozzle interior during each run; hexane from a wash bottle was used to rinse particles from the open bell-mouth of the nozzle, through its tip, and into the filter container, a 100-mm glass petri dish. In the laboratory, the $5.0\text{-}\mu$ pore-size Millipore filter was extracted by shaking with 100 mL of benzene for 30 min and again with 25 mL for 30 s. Recoveries of parathion and paraoxon from these filters have been quantitative.

The punch method of Gunther et al. (1974) ("dislodgeable" residue) was also used. Their extraction method was modified by partitioning all aqueous solutions into chloroform. This solvent was found to improve the recovery of paraoxon to $>95\%$ (cf. 22% using hexane) (MacLean et al., 1977). GLC procedures were as specified previously (Spear et al., 1977a).

The sampling schedule was expanded from our earlier work, and, although it varied among the selected plots, a typical schedule might be days 0, 2, 6, 13, 23, 33. As in our earlier work (Spear et al., 1975), the resulting serial residue values (ng/cm^2 of projected leaf area) were fitted to a first-order kinetic model, as expressed by eq 1 and 2,

$$dw/dt = dx/dt + dy/dt = -a_1x - b_1y \quad (1)$$

$$dr/dt = a_2x + b_2y - c_1r \quad (2)$$

in which the rate of each reaction is directly proportional to the amount of reacting material present at any time (t). It has recently been pointed out (Sutherland and Widmark, 1971) that the concept of exponential decay of pesticides on growth crops has "no basis in theory" and that their disappearance is "an accretion of a variety of causes"; nonetheless, the model can be justified not only by its empirical fit but also because it provides the conceptual facility of rate coefficients and their corresponding "half-lives" to aid in the interpretation of time series data. The exact form of the model thus has no intrinsic "truth"

Table I. Application Conditions and Additives for Each of the 17 Test Plots Included in This Study^a

Plot	Parathion		EC	ZnSO ₄	Neutral ZnO	Urea	Ethion	Applic. date
	AIA	Gal of H ₂ O						
1	2.0	250		x				17 May 74
2	5.0	1000		x				21 May 74
3	6.3	1200		x				23 May 74
4	2.5	500			x	x		29 May 74
5	2.5	500			x	x		20 May 74
6	3.0	1200			x		x	18 May 74
7	2.0	250						18 May 74
8	6.3	1200						23 May 74
9	2.0	500						10 June 74
10	4.0	1000						10 June 74
11	8.0	1500						14 June 74
12	7.5	1500						17 June 75
13	7.5	1500						18 June 75
14	7.5	1500						19 June 75
15	7.5	1500	x					17 June 75
16	7.5	1500	x					18 June 75
17	7.5	1500	x					19 June 75

^a Parathion formulations were wettable powders (WP) unless otherwise noted. All applications were by ground equipment.

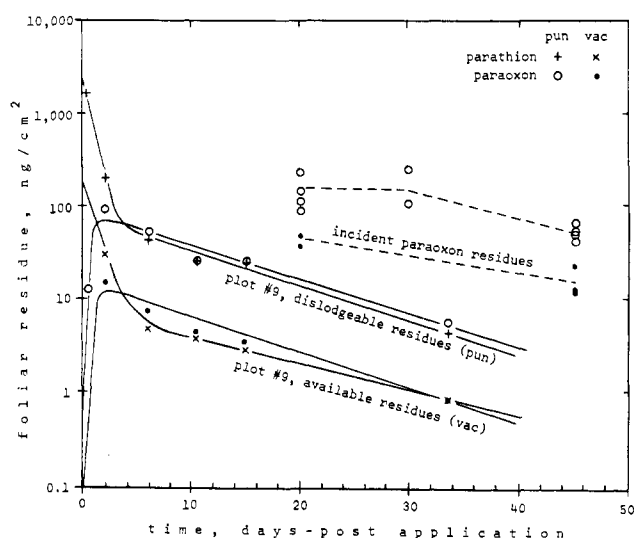


Figure 1. Comparisons of "typical" vs. "hot field" residue measurements from fields with similar application formulations. Replication tests for both methods indicate expected coefficients of variation for single samples of 10-15%.

but should be viewed only as a tool to further understanding.

As Figure 1 demonstrates, parathion follows a traditional biphasal decay pattern. To account for the change in the rate of parathion decay from the early "X" phase to the slower "Y" phase of decay, the measured parathion residue (w) was partitioned into two components, one short-term (x) and one long-term (y) component, viz. $w = x + y$. The proportion of w initially allocated or partitioned into each component was determined by a computer optimization technique to be described later. The paraoxon residue was found to be adequately characterized by only one component, r . This model requires eight coefficients: three initial values (a_0 and b_0 for parathion and c_0 for paraoxon), plus five kinetic coefficients: two for parathion decay (a_1 for x , b_1 for y), two for conversion to paraoxon (a_2 for x , b_2 for y), and one for paraoxon decay (c_1). Units of all kinetic coefficients are "per day".

The values for all coefficients within each plot were estimated using a constrained optimization procedure as in our earlier work (Spear et al., 1975), except that the desired optimum was redefined to be the minimum sum of the ratios of the predicted value to observed value or

observed to predicted, whichever was larger, for all samples within each plot. This optimum was found to more equitably balance both rapid increases and decreases for first-order systems. The model always assumed the initial paraoxon coefficient (c_0) to be very much less than the initial parathion ($c_0 \ll a_0 + b_0$) even when significantly large values of paraoxon were measured in day 0 samples collected after the leaves had dried. In no case to date have levels of paraoxon in packaged formulations been found in excess of 0.01%.

RESULTS

The actual residue results, those used to estimate the kinetic coefficients, are included in the supplementary material (see Supplementary Material Available paragraph at the end of the paper). Certain of these data were deleted from further analysis either when residues became so low as to approach background levels or when it appeared that the samples were mishandled in the field. Furthermore, zero-day vacuum samples were always deleted because this sampling method is affected by the wetting of the leaf and foliar dust at the time of application which reduces the residue's "relative availability" (see plots 12-17); however, the available dust and pesticide will generally restabilize by day 1 and thereafter decay in a typical manner.

The model indicated in eq 1 and 2 above results in exponential solutions of the form:

$$w = a_0 e^{-a_1 t} + b_0 e^{-b_1 t} \quad (3)$$

$$r = \frac{a_2 a_0}{c_1 - a_1} e^{-a_1 t} + \frac{b_2 b_0}{c_1 - b_1} e^{-b_1 t} + \left(c_0 - \frac{a_2 a_0}{c_1 - a_1} - \frac{b_2 b_0}{c_1 - b_1} \right) e^{-c_1 t} \quad (4)$$

Values of each coefficient are shown in Tables II and III for punch and vacuum samples, respectively. The ratio of a_2/a_1 and b_2/b_1 , or yield of paraoxon produced from a given amount of parathion, is also listed under each parathion component. The mean error (absolute value [predicted - observed]/observed) of the model to the measured data is also included for general comparisons. Those comparisons indicated that this model fits the parathion decay pattern somewhat better than it fits that of paraoxon; and for paraoxon, the model fits dislodgeable values somewhat better than it does available values, with median mean errors ranging from 15 to 25%. All further discussions pertain to these model coefficients.

Table II. Coefficients for Equations 3 and 4 Estimated from Dislodgeable Residues

Plot	Short-term thion				Long-term thion				Oxon, c_1	Mean percent error	
	a_1	a_2	a_2/a_1	a_0	b_1	b_2	b_2/b_1	b_0		Thion	Oxon
1	0.527	0.0258	4.9%	2170	0.0962	0.00116	1.2%	213	0.0889	13	13
2	0.592	0.116	20.0%	2720	0.132	0.00068	0.5%	106	0.256	6	20
3	0.930	0.103	11.0%	2920	0.0727	0.00033	0.5%	46	0.104	18	23
4	0.831	0.0067	0.8%	2290	0.121	0.00080	1.2%	222	0.0928	7	32
5	1.11	0.0107	1.0%	2160	0.0632	0.00452	7.1%	16	0.103	29	22
7	0.413	0.0162	3.9%	2180	0.109	0.00150	1.4%	119	0.108	27	21
8	1.11	0.0682	6.1%	3280	0.0689	0.00229	3.3%	81	0.0837	11	15
9	1.25	0.0532	4.3%	1800	0.0825	0.00272	3.3%	79	0.0786	8	20
10	1.37	0.0702	5.1%	3030	0.0830	0.00019	0.2%	105	0.0782	8	30
11	1.04	0.0490	4.7%	4120	0.0598	0.00508	8.5%	152	0.0429	15	19
12	0.644	0.0501	7.8%	2640	0.0861	0.00047	0.5%	160	0.0703	20	6
13	0.582	0.0379	6.5%	3230	0.0861	0.00044	0.5%	232	0.0678	38	40
14	0.602	0.0393	6.5%	3090	0.0590	0.00001	<0.1%	55	0.0868	20	19
15	0.537	0.0252	4.7%	2970	0.0714	0.00004	0.1%	126	0.0770	4	28
16	0.405	0.0215	5.3%	3140	0.0550	0.00241	4.4%	96	0.0673	11	36
17	0.494	0.0244	4.9%	2530	0.0529	0.00055	1.0%	84	0.0821	21	35

Table III. Coefficients for Equations 3 and 4 Estimated from Available Residues

Plot	Short-term thion				Long-term thion				Oxon, c_1	Mean percent error	
	a_1	a_2	a_2/a_1	a_0	b_1	b_2	b_2/b_1	b_0		Thion	Oxon
2	0.766	0.0587	7.7%	431	0.163	0.00004	<0.1%	39	0.182	24	8
4	0.666	0.0097	1.5%	497	0.0391	0.00021	0.5%	4	0.107	14	27
5	1.26	0.0121	1.0%	429	0.0945	0.00120	1.3%	13	0.114	7	23
6	0.503	0.0166	3.3%	158	0.0963	0.00045	0.5%	16	0.103	4	35
7	0.619	0.0064	1.0%	1018	0.0834	0.00040	0.5%	22	0.0962	19	30
9	0.906	0.0832	9.2%	175	0.0689	0.00020	0.3%	9	0.0924	6	23
10	0.872	0.0493	5.6%	583	0.0905	0.00114	1.3%	23	0.0782	12	16
11	0.860	0.0426	4.9%	1344	0.0944	0.00025	0.3%	140	0.0451	32	21
12	0.561	0.0238	4.2%	703	0.0908	0.00002	<0.1%	49	0.0862	11	20
13	0.523	0.0227	4.3%	732	0.0935	0.00014	0.1%	52	0.0817	25	36
14	0.438	0.0420	9.6%	507	0.0651	0.00016	0.3%	27	0.0786	12	23
15	0.827	0.0286	3.5%	366	0.0661	0.00534	8.1%	31	0.0696	16	41
16	0.593	0.0198	3.3%	596	0.0738	0.00145	2.0%	29	0.0787	41	47
17	0.866	0.0385	4.5%	250	0.0748	0.00574	7.7%	36	0.0685	40	41

First, for the initial deposits (a_0 and b_0), variations were expected and can largely be attributed to application conditions as well as certain other environmental conditions. Initial short-term deposits (a_0) of dislodgeable residues ranged from 2000–3500 ng/cm² and correlated quite strongly with pounds per acre (AIA), $r = 0.78$, $p < 0.005$; initial long-term deposits (b_0) range from 20–200 ng/cm² without significant correlations. Corresponding short-term available deposits ranged from 250–900 ng/cm², correlating with both application concentration (mass pesticide/volume of water), $r = 0.62$, $p < 0.05$ and available dust level, multiple $r = 0.74$, $p < 0.05$; long-term deposits were 25–50 ng/cm² and correlated with AIA, $r = 0.60$, $p < 0.05$. In general, parathion seemed to have a uniform decay pattern with from 92–98% of the initial deposit in the X-phase component. It was this component which appeared to generate most of the paraoxon due to both its greater magnitude and its greater yield.

The values of rate coefficients were then analyzed for associations and correlations. The distribution of values for each coefficient estimated from the various groves appears to be log-normal; geometric averages were therefore calculated (reported as medians) and used throughout this analysis. The effect of zinc sulfate on dislodgeable residues was tested using Student's t test and found to significantly increase the yield of paraoxon during the short-term phase of decay (a_2/a_1) from a mean of 4.0 to 10% ($p < 0.05$); this increase appears to have been primarily the result of an increase in paraoxon production rather than a decrease in parathion decay. The value of a_2 estimated from vacuum data also appears to have been higher than average although no significance can be at-

Table IV. Median Estimated Parathion Decay Rate Coefficient for Plots 4–17 (Those without ZnSO₄) and Their Equivalences or Analogies

	Punch	Vacuum	Equivalent to
a_1	0.735 ± 53%	0.700 ± 35%	1.0 day half-life
a_2	0.0297 ± 106%	0.0244 ± 105%	4.0 and 3.5% yields
b_1	0.0744 ± 29%	0.0773 ± 29%	9.1 day half-life
b_2	0.0006 ± 975%	0.0005 ± 400%	0.8 and 0.6% yields
c_1	0.0781 ± 26%	0.0832 ± 28%	8.6 day half-life

tributed to the one field with zinc sulfate which was sampled for its available residues. Zinc sulfate also appears to have increased the rate of paraoxon decay (c_1) in both dislodgeable and available residues ($p < 0.02$). The resultant effect was that peak paraoxon concentrations during the first 3 days postapplication in zinc sulfate treated plots were 1.5 to 2.5 times higher than in plots without zinc sulfate, while by 2 weeks the differences were negligible (cf. plots 3 and 8).

Removing these groves from further consideration results in median values and coefficients of variation for the estimated rate coefficients as shown in Table IV. The effect of pesticide formulation (EC vs. WP) was tested at this point by comparing the matched applications of plots 12–14 with those of 15–17. Dislodgeable residue coefficients a_2 and a_2/a_1 were both significantly reduced when EC formulations were applied ($p < 0.01$); for both dislodgeable and available residues predicted peak paraoxon levels as approximated by eq 7 were also reduced for EC plots ($p < 0.02$); while available residue coefficients b_2 and b_2/b_1 appeared to increase for EC plots ($p < 0.01$). Thus, for dislodgeable paraoxon levels the ratio between WP and

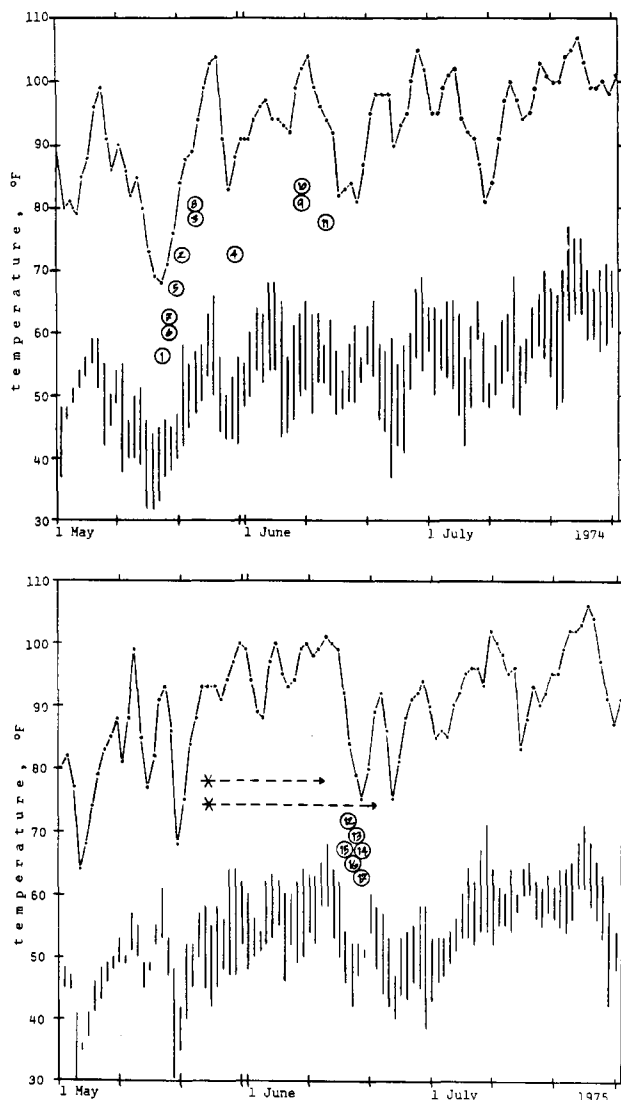


Figure 2. Reported weather data in Fresno, Calif. Upper line is daily maximum air temperatures; vertical lines represent daily spread between minimum air temperature (upper end of line) and dew point (lower end). Circled numbers indicate date of application for each plot; the incident groves are marked by an asterisk and an arrow for the corresponding reentry periods.

EC applications remained roughly 2:1 from day 3 through 14 DPA; whereas, this same ratio as measured by the available method increased from near 2:1 on day 2 to over 3.5:1 by day 14. Nonetheless, because all estimated parameters for these six plots were well within the range spanned by the other eight plots, none of these groves were excluded from further analyses.

The kinetic coefficients included in Table IV were tested for correlations with various environmental factors, including maximum and minimum temperatures, average dew points (U.S. DOC, 1974-1975), and airborne photochemical oxidant (Cal. ARB, 1974-1975) reported for the day of application and averaged for 3 days following application and 20 days thereafter. Temperature patterns are shown in Figures 2a and 2b. Air pollution values at Fresno and Parlier ranged from 5 to 25 pphm and should only be considered as indicators of conditions in the "orange belt" which lies near the foothills of the Sierra Nevada Mountains some 20-70 km downwind. No correlations of long-term coefficients (b_1 , b_2 , c_1) with weather were possible because the large fluctuations in the cyclic weather patterns shown in Figure 2 obscured any statistical significance between differences in average environmental

values taken over more than about 1 week. Nonetheless, long-term available residue conversion and yield seemed to correlate inversely with levels of available foliar dust $r = 0.59$, $p < 0.02$, and for both residues paraoxon decay correlated inversely with AIA $r = -0.81$, $p < 0.001$. These correlations suggest that foliar dust tends to further decrease the importance of Y-phase oxidation while heavy applications of parathion seem to retard oxon decay.

The converse problem of correlations exists for short-term coefficients: they tend to correlate with quite a variety of weather conditions, the result no doubt of strong intercorrelations between factors such as daily temperatures, short-term temperature variability, airborne oxidant, etc. Furthermore, coefficients from dislodgeable and available residue data did not always show similar correlations. For instance, short-term dislodgeable parathion decayed more rapidly under conditions of high minimum air temperatures, minimum air temperature vs. dew point spreads, and airborne oxidants ($p < 0.001$); short-term available decay was correlated with only the first two of these ($p < 0.02$ and 0.01 , respectively). On the other hand, the rate of conversion of available parathion to paraoxon was correlated with dew point temperatures and airborne oxidant ($p < 0.01$), while dislodgeable conversion correlated only with dew point ($p < 0.05$). The most important correlations were those for yield (a_2/a_1) and effective yield (eq 7). Only those yields for available residues showed significant correlations: $p < 0.01$ with dew point and an inverse correlation $p < 0.05$ with 3-day temperature variability. The many short-term correlations and their diversity suggest that while weather was a strong factor during this period, the primary agent may not have been adequately monitored.

DISCUSSION

This study of pattern and variation in parathion decay by means of a multiple component kinetic model incorporating paraoxon is unique. Not only does this model isolate several parameters for individual study, but it also allows the calculation of various combinations of parameters such as "yield", discussed earlier, or the time for transition from the X to Y phase of decay:

$$t_{\text{transition}} = \ln(a_0/b_0)/a_1 - b_1 \quad (5)$$

To obtain some more interesting combinations of terms, rather complicated equations must be further simplified by neglecting less significant terms, assuming estimated coefficient values from Table IV. For example, the time at which peak paraoxon residues occur can be approximated by the expression

$$t_{\text{peak}} \approx \ln\left(\frac{a_1 - c_1}{c_1}\right)/a_1 - c_1 \quad (6)$$

and the levels of paraoxon at this peak by

$$r_{\text{max}} \approx a_2 a_0 / a_1 - c_1 \quad (7)$$

These estimates are specific for parathion or to compounds whose general decay patterns allow similar simplifications.

The above differences in the correlation of available and dislodgeable residue coefficients with environmental factors can be explained in part by the methods of residue collection. Since the vacuum collects only loosely adherent foliar dust, its measured levels will always be less than dislodgeable levels. The ratio of these two levels (we use the term "availability ratio"), while nearly constant within a grove, varies roughly from 0.1 to 0.3 between groves and is not always equal for both parathion and paraoxon; the availability ratio for inert foliar dust on citrus is also

consistent within each test plot, but varies more narrowly from 0.15 to 0.25 between groves; and in cases of some other compounds such as Guthion on citrus, we have found pesticide availability ratios in the range of 0.01 to 0.03. Thus it seems that with different foliar dust particles and with different compounds, pesticides partition themselves in quite different ways while on the leaf surface or during an aqueous extraction process. It has already been shown that different dusts can greatly affect the rates of parathion and paraoxon decay (Iwata et al., 1973; Adams et al., 1977). It follows that available residues in these different groves could be affected more or less strongly by environmental factors than are dislodgeable residues.

From a mechanistic if not statistical point of view, airborne oxidant is the most likely agent directly affecting paraoxon production on foliar dust. In addition to the above correlations, Gunther has shown ozone to be a strong oxon-producing agent in vitro (Gunther et al., 1970). The central valley of California, where most of the reported incidents of worker residue poisoning have occurred, is also an area of excessive air pollution (Popendorf et al., 1975; Cal. ARB, 1974-1975). Unfortunately, these reported air pollution data do not necessarily reflect the microclimate near the foothills. Had these data been recorded locally and other application conditions been constant, we feel that the association would have been more pronounced. That the production of available paraoxon was more strongly correlated with these environmental factors than was dislodgeable paraoxon suggests that decay and oxidation reactions on dust particles may be more strongly affected by weather than are reactions on other portions of the leaf surface.

These findings can be directly applied to the interpretation of the most recent case of citrus harvester poisonings (Spear et al., 1977b). Although the coefficients of Table IV indicate some variability in parathion decay rates, the general pattern in central California citrus groves is remarkably regular, as typified in plot 9, Figure 1. Superimposed on this diagram are residue samples from this latest incident. Given the existent combination of a concentrated application formulation, high levels of foliar dust, airborne oxidant at the time of application, and dry, stable conditions thereafter, it is now not hard to envision paraoxon yields in excess of 10 or 15% resulting in unusually hazardous levels coupled with relatively slower rates of residue decay. The conditions shown in Figure 2b suggest a sort of "environmental window" surrounding the reentry interval for this particular field: moderate temperatures but extremely stable weather at the time of application followed by abnormally invariant conditions for the next 20 or more days (variance < 0.5 normal, $p < 0.02$).

These findings generally confirm our earlier study on foliar parathion decay in terms of the levels of paraoxon obtained and the variability of rate coefficients. The new rate coefficients in Table IV reflect a more accurate characterization of the total decay pattern resulting from a more thorough residue sampling schedule. Insofar as

worker hazard is concerned, peak levels of paraoxon still generally occur within 1 to 3 days and then decay at rates nearly identical with parathion; however, the level at this peak and later in time is clearly dependent upon factors in addition to the dosage applied to the crop. Application formulation variables appear to have a moderate ability to affect these levels, but the conversion of parathion to paraoxon and the intoxication potential, Ψ (see Spear et al., 1975), are more strongly affected by ambient weather and foliar dust. That parathion is the only pesticide affected by these factors is doubtful. The need to quantitate the sensitivity of parathion and other organothiophosphates to these factors is vital for the verification of safe worker reentry intervals.

Supplementary Material Available: Listing of all available residues and dislodgeable residues for each plot and day post-application (DPA) from which model coefficients were estimated (5 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

- Adams, J. D., Iwata, Y., Gunther, F. A., *Bull. Environ. Contam. Toxicol.* **18**, 000 (1977).
- Atkins, E. L., Blinn, R. C., Fukuto, T. R., Gunther, F. A., *J. Econ. Entomol.* **54**, 455-456 (1961).
- Bobb, M. L., *J. Econ. Entomol.* **47**(1), 190-191 (1954).
- Brunson, M. H., Koblitsky, L., *J. Econ. Entomol.* **45**, 953-957 (1952).
- California, State of, Air Resources Board, "California Air Quality Data", Vol. VI-VII, 1974-1975.
- Carman, G. E., Gunther, F. A., Blinn, R. C., Garmus, R. D., *J. Econ. Entomol.* **45**, 767-777 (1952).
- Fahey, J. E., Hamilton, D. W., Rings, R. W., *J. Econ. Entomol.* **45**(4), 700-703 (1952).
- Gunther, F. A., Ott, D. E., Ittig, M., *Bull. Environ. Contam. Toxicol.* **5**, 87-94 (1970).
- Gunther, F. A., Barkley, J. H., Westlake, W. E., *Bull. Environ. Contam. Toxicol.* **12**, 641-644 (1974).
- Iwata, Y., Westlake, W. E., Gunther, F. A., *Arch. Environ. Contam. Toxicol.* **1**, 84-96 (1973).
- MacLean, H. R., Futagaki, S., Leffingwell, J. T., *Bull. Environ. Contam. Toxicol.* **18**, 247-250 (1977).
- Popendorf, W. J., Spear, R. C., Selvin, S., *Environ. Sci. Technol.* **9**, 538-585 (1975).
- Spear, R. C., Popendorf, W. J., Leffingwell, J. T., Milby, T. H., Davies, J. E., Spencer, W. F., *J. Occup. Med.* **19**, 406-410 (1977a).
- Spear, R. C., Popendorf, W. J., Spencer, W. F., Milby, T. H., *J. Occup. Med.* **19**, 411-414 (1977b).
- Spear, R. C., Popendorf, W. J., Leffingwell, J. T., Jenkins, D., *J. Agric. Food Chem.* **23**, 808-810 (1975).
- Sutherland, G. L., Widmark, G., *J. Assoc. Off. Anal. Chem.* **54**, 1316-1317 (1971).
- U. S. Department of Commerce, National Weather Records Center, "Local Climatological Data-Fresno, California", May, June, July, 1974, 1975.

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