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A Seasonal Comparison of Parathion Degradation on Oranges in Arizona

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Increasing concern with the health hazards presented by residues of pesticides on crop foliage has been motivated by the change in use patterns within the United States from organochlorine insecticides to the more dangerous organophosphorus (OP) materials (FEDERAL WORKING GROUP ON PEST MANAGEMENT 1975). The exact nature of exposure to pesticide residues and the various contributing factors involved in an exposure-response relationship in poisoning cases are not completely understood. It is clear, however, that the contributing factors are multiple in nature with many interactions. For instance, recent work by BAILEY (1974), reviewing early data on farmworker pesticide poisoning episodes in California, indicated that geographical location is a significant factor in the incidence of worker poisoning. The geographical pattern of poisoning episodes provides some evidence that rainfall, among other climatological factors, is an important parameter in residue persistence. The importance of geographical location in relation to pesticide exposure problems of agricultural workers has also been emphasized by DAVIES (1973) in his review of the much broader problem of pesticides in the environment.

Another consideration of climatological significance is seasonal variation. It is obvious that seasonal variation greatly influences weather variables such as temperature, humidity, total sunlight, and dew point. GUNTHER (1977) compared parathion residues on oranges in California using seven monthly applications and noted that parathion dissipated more rapidly during warmer climatic conditions and immediately following rainfall. The following study was undertaken to compare the degradation of parathion applied to orange trees in the fall and winter seasons in Arizona.

MATERIALS and METHODS

Experimental Design

An experimental field at the University of Arizona Experiment Station, Yuma, Arizona, was the site selected. Two neighboring plots of twelve trees each were utilized, one plot at each season. At each sampling period, four quadrants per tree were sampled giving a composite sample of 48 leaf punches. A second replicate of 48 punches was then taken from the same locations on the twelve trees, in order to evaluate sampling variability.

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Samples were taken immediately following application and on days 1, 3, 5, 7, 14, 21, 28, and 42 following application, beginning in both October, 1975, and February, 1976.

Insecticide Application

Wettable powder formulation of parathion was applied to the orange trees at a rate of 8 lbs of active ingredient per acre by an air blower (speed) orchard sprayer.

Sample Collection

Leaf disc samples were collected through the use of a leaf punch similar to that described by GUNTHER et al (1973, 1974). Leaf discs were collected by punching one leaf disc from each of 4 sides of every sample tree. Care was taken not to shake the limb nor disturb the leaves on the trees while punching a leaf. Each leaf disc was automatically deposited in the collection bottle as it was punched from the leaf. When the desired number of discs was collected, the bottle was immediately placed in a dry ice container and held there until transfer to the analytical laboratory.

Materials

All solvents used throughout the study were nanograde (Mallinckrodt) and all water used for punch extraction was distilled in glass. Silane-treated glass wool (Applied Science Labs) and Sur-Ten® surfactant, di-n-octyl-sulfosuccinate (Aldrich Chemical) were also used.

Extraction Procedure for Leaf Punches and Filters

The leaf punch extraction procedure used is a modification of the methods of GUNTHER (1974) for analysis of dislodgeable pesticide residues. The major modification in the Gunther procedure was the replacement of benzene with chloroform to extraction of the aqueous phase.

Gas Chromatographic Analysis and Data Reduction

Gas chromatographic analysis was carried out on a Tracor MT 220 gas chromatograph equipped with a flame photometric detector. This system was connected via Perkin-Elmer Model GC-1 interfaces to a Perkin-Elmer PEP-1 GC Data System. A 76 cm x 4 mm ID column of 5% OV-101 on Chromasorb-G was used for analysis of parathion and paraoxon. Column conditions were as follows: Temperature 185°C, nitrogen flow 90 ml/min. Inlet and detector temperatures were 225 and 235°C, respectively, for all analyses.

Areas for peaks of both standards and samples obtained from the GC trace were computed. From the curve of peak area versus ng, calculations of ng/µl for each injection of each unknown were made.

Methods of Data Analysis

Leaf punch data were transformed before analysis by a logarithmic transformation in order to make the variability homogeneous at each time point. Such a transformation also linearized the decay curves of parathion so that the half-life of parathion on leaf surfaces could be estimated from the slope of the regression line. Data were analyzed using a two-way analysis of variance with replications. This model tests for differences in mean levels between plots (seasons), mean levels among days of sampling, and the plot-by-day interaction. This interaction tells whether the differences between plots are consistent over time and can be interpreted as telling whether curve shapes are the same.

RESULTS and DISCUSSION

An analysis was conducted to assess the decay pattern of parathion applied to orange trees in Arizona at two different times: October, 1975, and February, 1976. The statistical analyses are summarized in Tables 1 to 3 and the graphs of residue levels over time are shown in Figures 1 and 2. No statistically significant differences were observed between October and February in the rate of decay of parathion on or from leaf surfaces but the average amount of parathion residue was greater in February. Further, no differences were seen in the average amount of paraoxon found in October or February.

For parathion and paraoxon residues, a significant difference was found in curve shapes, however. This could be explained in part by daily weather variations since additional studies carried out by this laboratory indicate no difference in curve shape for studies of parathion evaluated on neighboring plots at the same time (GEHRICH et al. 1976). The comparison of slopes measures differences in decay processes over the entire course of the particular study of concern. This process would not be affected by daily fluctuations caused by outside influences unless they were consistent. Two study plots can have the same slopes but differences in curve shapes because comparable fluctuations due to outside influences occurred on different days. It is very possible, then, that for studies conducted at different times, comparisons which reveal differences in curve shape but no differences in slope may be reflecting day-to-day variations of outside influences. Therefore, significant day-by-plot variation in residue levels could be attributable to short-term climatological effects.

Figure 3 shows the difference between the two study periods with regard to several climatological variables collected by the National Weather Service. Winter temperatures were roughly ten degrees below the fall temperatures during the first two weeks of the studies and ten degrees above the fall temperatures during the last two weeks of the studies. Minutes of sunshine were equivalent between the studies at the start of the sampling

TABLE 1

Analysis of Variance of Parathion Residues (Transformed Data)

S.V.	d.f.	S.S.	M.S.	F	p
Months (Oct vs. Feb)	1	0.4976	0.4976	173.38	p<.001
Days	8	19.5025	2.4378	849.41	p<.001
Days x Months	8	0.2059	0.0257	8.97	p<.001
Replicates	18	0.0516	0.0029		
TOTAL	35	20.2576			

TABLE 2

Statistical Comparison of Slopes of Decay Curves of Parathion on Leaf Surfaces (Transformed Data)

Month	Intercept	Slope	$S^2_{y.x}$	R^2	Half-Life (Days)	95% C.I.
October	3.467	-0.056	0.028	0.958	5.4	(3.6-7.1)
February	3.648	-0.052	0.014	0.975	5.8	(4.4-7.1)

Comparison	Significance
October vs. February	Not statistically significant, $\alpha=.05$

TABLE 3

Analysis of Variance of Paraoxon Residues (Transformed Data)

S.V.	d.f.	S.S.	M.S.	F	p
Months (Oct vs. Feb)	1	0.0037	0.0037	2.80	N.S.
Days	8	2.0364	0.2545	192.84	p<.001
Days x Months	8	0.4973	0.0622	47.10	p<.001
Replicates	18	0.0238	0.0013		
TOTAL	35	2.5612			

N.S. - Not statistically significant, $\alpha=.05$

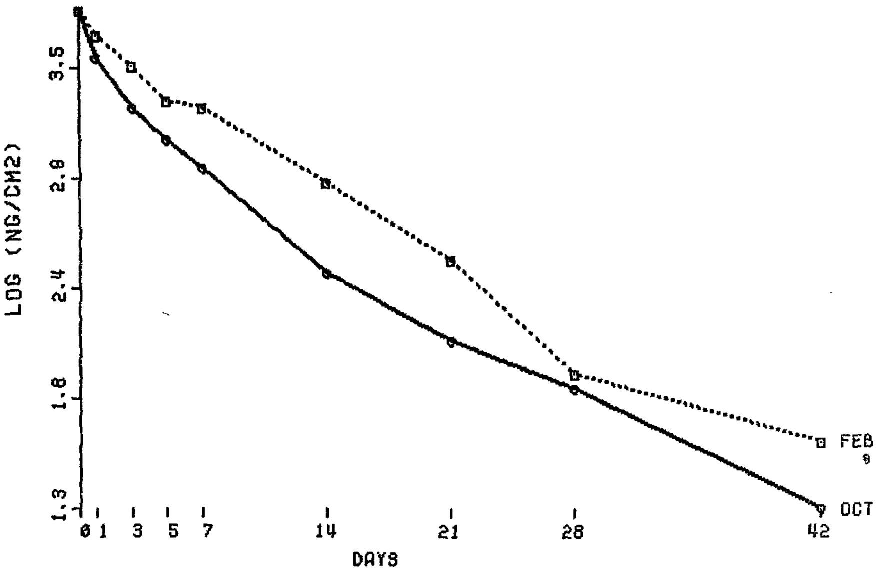

FIGURE 1

The Decay of Parathion W.P. on Leaf Surfaces
During October and February

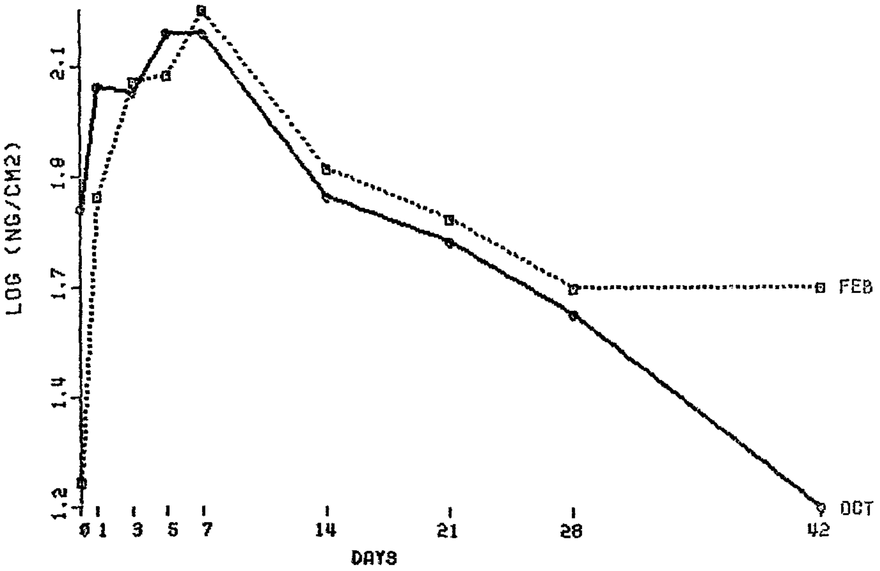

FIGURE 2

The Formation of Paraoxon on Leaf Surfaces
During October and February

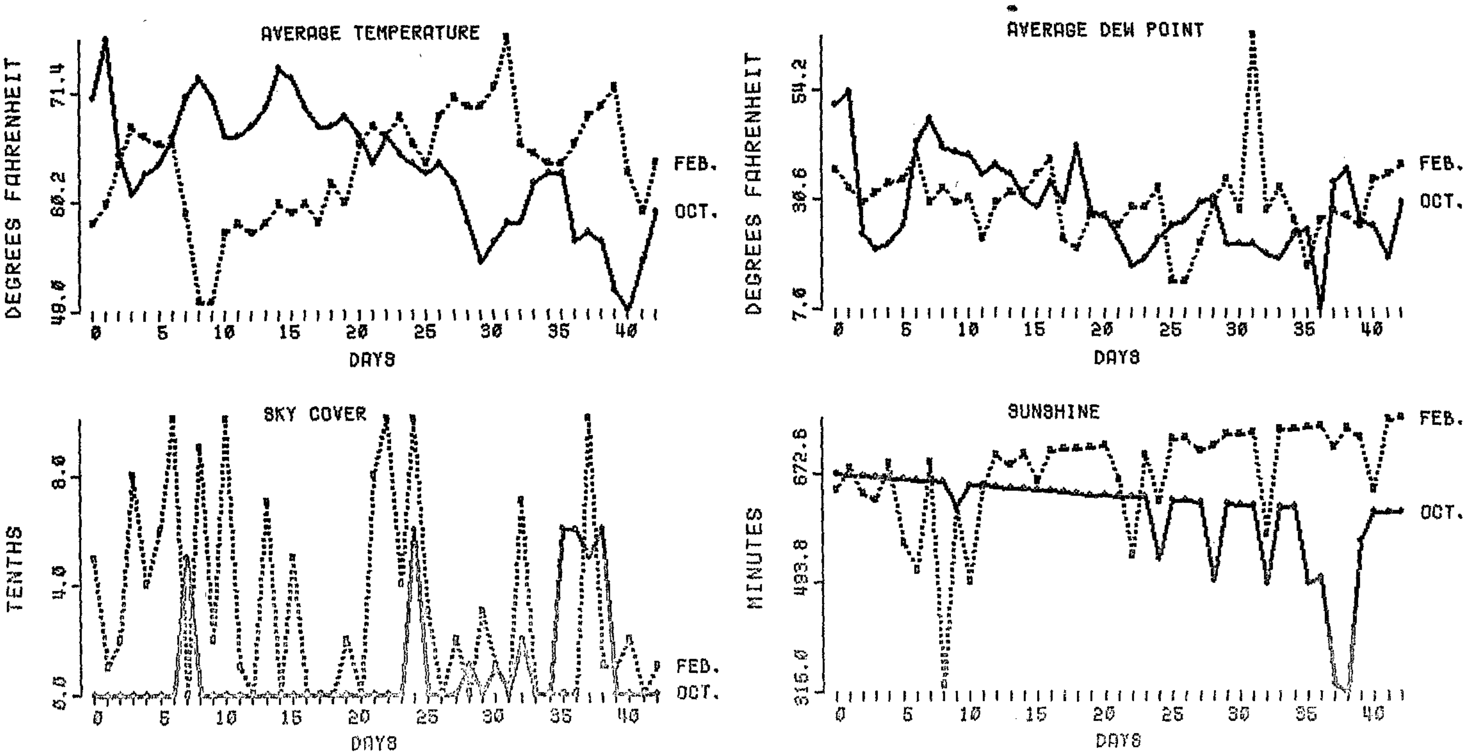

FIGURE 3

Comparison of Weather Variables Over Two Seasonal Studies of Parathion Degradation period but increased over the course of the winter study, while decreasing over the course of the fall study. Sky cover was generally greater during the winter study. No large differences in dew-point could be seen between the two seasons. Rainfall was not a significant factor with .02 inches on Day 8 of the winter study and .03 inches on Day 38 of the fall study. Although these differences are easy to describe, additional work is needed to identify the relevant functions of the climatological variables and to determine how these variables effect residue decay.

The studies presented in this report involving the comparisons of parathion for differing seasons is influenced by a number of variables. In dealing with these variables and their effects on pesticide decay, environmental forces, especially light and air composition, which affect chemical transformation, must be taken into consideration. For example, light intensity is strongly affected by season and climate (CROSBY 1969). It has been shown that sunlight alone can induce changes in chemicals, and evidence suggests that the ultra-violet (UV) wave lengths are most responsible. The chlorinated compound dieldrin applied to glass plates undergoes photoalteration to photodieldrin, a compound of increased toxicity. Parathion exposed to UV light isomerizes to the S-ethyl isomer and probably paraoxon (CROSBY 1969). The overall photochemical transformations of organophosphorus compounds are most probably an interaction of light and air to give oxidative products such as oxons.

Other factors may also greatly affect the environmental decay of pesticides. TAKADE et al. (1976), in a study of the environmental fate of the organophosphorus insecticide phenthoate, found that the decay rate of radioactive phenthoate was virtually the same during March as it was in August-September. However, they found that much more phenthoate oxon was found in the late summer months as compared to the late winter. The study was conducted in Riverside, California, and the late summer months in that area are periods of high temperature and air pollution. Therefore, the possibility exists that oxidants found in air pollution, acting in concert with high temperature, were responsible for the formation of penthoate oxon.

SUMMARY

A study comparing the leaf residue decay of parathion wettable powder (8 lbs per acre) on oranges was carried out on neighboring plots in Arizona beginning in October, 1975, and February, 1976. While identical amounts of parathion were present immediately after spraying and the half-life of parathion was the same in both months, there was, on the average, more parathion residue during February. Graphs of parathion and paraoxon levels over time differed between months (in excess of sampling variability). This most likely was due to the daily influences of climatological variables which were obviously different in October and February.

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