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WORKER REENTRY AND RESIDUES OF ETHION, PARATHION, AND CARBOPHENOTHION (TRITHION) ON FLORIDA CITRUS[1,2]

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Abstract. **The degradation rate and oxon metabolite levels of ethion, parathion, and carbophenothion (trithion) were compared under different environmental conditions. The oxon metabolite levels observed were low and never exceeded the residue level of the parent compound. Residue data was related to temperature, rainfall, free water on leaves, and time. These parameters accounted for 90 to 98% of the residue disappearance. These results indicate that under present weather conditions in Florida, the potential for a worker reentry illness is low.**

On May 10, 1974, the Environmental Protection Agency published reentry standards of 24 to 48 hr for 12 organophosphate insecticides designed for the protection of field workers (1). These regulations were instituted as a deterent to recurring harvester illnesses in perennial crops in the Western United States (4). The cause of picker organophosphate intoxications has been linked to several factors including: (1) production of a highly toxic oxon metabolite in the environment, (2) stabilization of the parent compound and its oxon metabolite through attachment to dust and dry weather conditions, and (3) transfer of residues attached to dust from foliage and the soil surface to field workers (4).

The present study was conducted to determine the effect of weather conditions on the residues of ethion, parathion, and carbophenothion, and their oxon metabolites on 'Valencia' leaves in Florida citrus groves.

Materials and Methods

A mature bearing 'Valencia' orange grove in good condition located in Polk county was selected for this study. Treatments replicated 4 times in a randomized block design were applied to plots of 4 trees each. Four unsprayed plots were included as controls. Experiment 1 was conducted from May 29 through June 15, 1975 during hot, wet weather and experiment 2 from November 10 through December 15, 1975 during a cool, dry period.

Identical treatments for both experiments were applied with a handgun at 600 psi in a diluent volume of 1200 gal/acre. Treatments included: (1) ethion 4E (0,0,0',0'-tetraethyl-S,S'-methylene bisphosphorodithioate) at 0.5 pt/100 gal, 0.75 pt/100 gal, 0.75 pt/100 gal plus 0.5% 435 spray oil, 0.75 pt/100 gal plus 0.7% 435 spray oil, and 1.5 pt/100 gal, (2) parathion (0,0-diethyl 0-p-nitrophenyl phosphorothionate) at 8 oz 4E/100 gal and 6.3 lb. 15 WP/100 gal and (3) carbophenothion (S-((p-chlorophenylthio)methyl) 0,0-diethylphosphorothiolothionate) at 3/8 pt 8E/100 gal and 3/4 pt 8E/100 gal.

Forty leaf discs taken at random in each plot represented a sample. Samples were processed and extracted according to Gunther et al. (3). Other analytical details, weather monitoring, and statistical methods have been previously described (6, 7, 8).

Results and Discussion

The oxons of ethion, carbophenothion, and parathion were identified by thin-layer chromatography, gas-liquid chromatography, high-pressure liquid chromatography, and GC-mass spectral analyses. The absolute chemical identification of these products from 3 different organophosphates confirms that these compounds are produced in Florida. However, the oxon of carbophenothion was detected only on the day of application and consequently only the parent compound data are reported here (Fig. 1). For ethion, 2 oxon products are possible. Only the monoxon of ethion was detected in these experiments and remained at very low levels below the residue level of the parent compound (Fig. 1). Only data resulting from the 1.5 pt/100 gal ethion rate is illustrated in Fig. 1. The other ethion rates produced lower residues of both parent compound and the monoxon metabolite. Paraoxon also remained at levels lower than the parathion residue in both experiments. In experiment 1, parathion reached such a low level in so short a time that only the results of experiment 2 are presented (Fig. 1).

The multiple correlations of pesticide residue data with weather data shown in Table 1 indicate that all of the residues disappear more quickly with increased temperature and moisture. Correlations of the residue data with temperature (heating degree days), rainfall, and leaf wetness were significant at the 5% level or better. In these experiments, residue decay which occurred in 14 days under hot, wet weather took 35 days under dry, cool conditions (Fig. 1). The organophosphate insecticides hydrolyze rapidly into non-toxic products under Florida weather conditions and, consequently, the potential for a worker reentry illness is much lower in Florida citrus groves as compared to those in California.

Previous Florida residue data agree well with the data presented here (10, 11). On the other hand, California studies (Fig. 2) show levels of oxon metabolites higher than the parent compound and relative to Florida compounds are long-lived. The possibility exists that rates of application in the two regions might account for these differences. The California recommendation for red scale calls for 6.3 lb. AI/acre of the wettable powder applied in 1,000 gal diluent (12). Florida recommends 1.25 lb. AI/acre applied as an emulsifiable concentrate in 1,000 to 1,500 gal diluent (2). The weakness with this supposition is that insecticides generally follow a first-order decay pattern, i.e., the more compound present the more rapid its disappearance. A comparison of the data in Fig. 1 and 2 shows that the opposite can happen. California parathion residues disappear more slowly than Florida parathion residues, though in a first order fashion. As shown by the Florida data, these differences are probably related to regional weather conditions.

In spite of these differences, the Environmental Protection Agency in partnership with the Agrichemical Industry has used California data to set regulations for Florida citrus.

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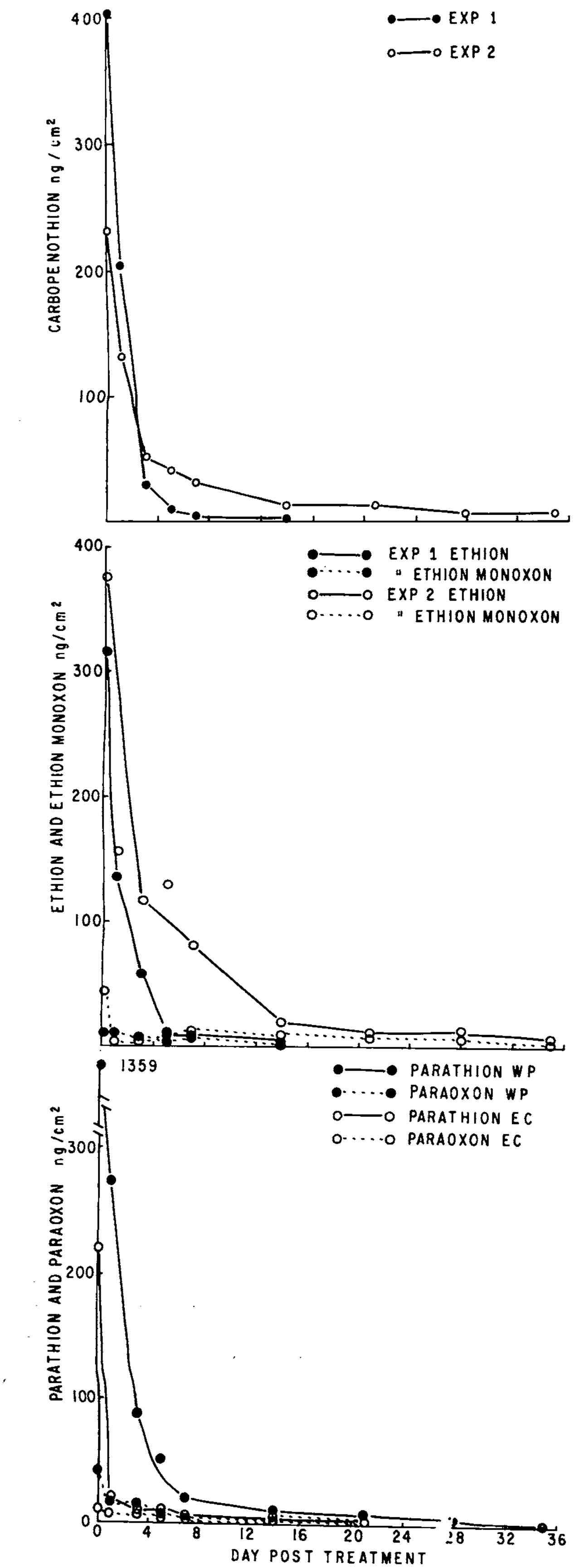

Fig. 1. Disappearance of dislodgeable residues of carbophenothion (top), ethion, ethion monoxon (middle), parathion and paraoxon (bottom) on 'Valencia' orange leaves.

This practice probably results in over-regulation of the Florida citrus industry and is unjustified based on all available information.

A more equitable and accurate approach to worker reentry and general pesticide regulations is to combine the suggestions of Serat (9) and Nigg et al. (6, 7, 8). The basis of these suggestions is the known toxicology and weather-related decay behavior of a compound. Suitable regulations would then be based on residue decay differences between climatic regions, differing toxicities of pesticides, and would more suitably apply to the region concerned.

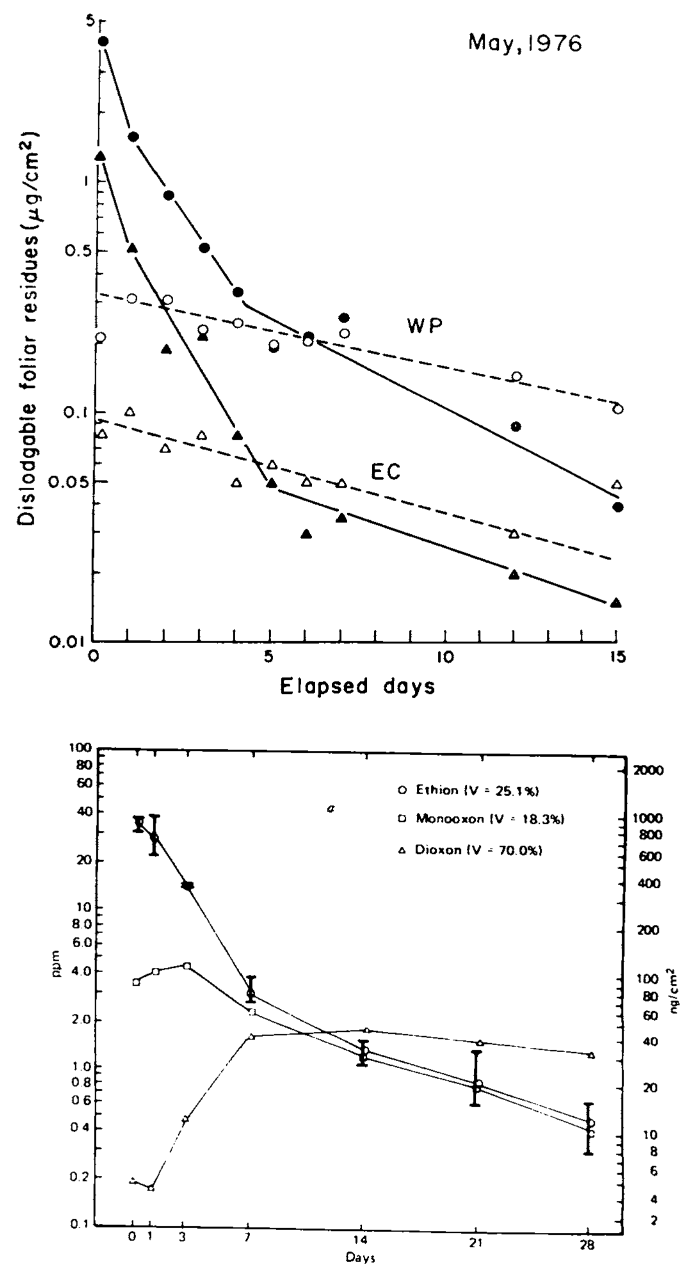

Fig. 2. Dislodgeable residues of WP parathion and paraoxon on California citrus (top, Gunther et al. (4)), dislodgeable residues of EC ethion, ethion monoxon and ethion dioxon on California grape foliage (bottom, Leffingwell et al. (5)).

Table 1. Variable coefficients for parathion, paraoxon, carbophenothion, and ethion decay on 'Valencia' orange leaves.

Compound	Ln initial concn	HDD	CR	CLW	T	Time	% variation explained: Weather + time
Parathion	3.4511	0.0069	−1.2311	−0.0916	−0.0159	35	90**
Paraoxon	3.2822	0.0825	−1.0610	−0.0424	−0.2975	79*	98**
Carbophenothion	4.2014	0.0201	−0.9280	−0.0205	−0.1336	47	93***
Ethion	5.3302	0.0110	−0.8153	−0.0021	−0.1201	57	94***

$\frac{dy}{dt} = (a_0 + a_1x_1 + a_2x_z + ... + a_nx_n)y$) y = pesticide residue, $x_1,..x_n$ = environmental variables.

HDD = Cumulative heating degree days; CR = Cumulative rainfall (inches); CLW = Cumulative leaf wetness (hr); T = time (days).
*Significant at 5% level.
**Significant at 1% level.
***Significant at <1% level.

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WORKER REENTRY IN FLORIDA CITRUS: COMPARISON OF TWO PESTICIDE RESIDUE TECHNIQUES FOR CITRUS FOLIAGE[1,2]

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Abstract. **The official dislodgeable pesticide residue technique was compared with a vacuum method in Florida citrus. Trends in the data for both techniques correlated above 0.9 in 2 expts. The dislodgeable technique recovers 11 times or more pesticide residue compared to the vacuum method and consistently and conveniently provides a better assessment of pesticide residues on the surface of citrus foliage as related to field worker safety.**

Worker reentry acute intoxications in the western United States have been linked to relatively long-lived residues of organophosphate insecticides on foliage and soil surface as well as toxic metabolites produced in the environment (3). Carman et al. (1) first noted pesticide contaminated particulate matter could represent a hazard to agricultural field workers exposed during tillage, picking, pruning, and similar operations. This was supported by subsequent California studies which showed dust and debris was the actual vehicle for pesticide transfer to agricultural field workers (6, 9).

Because exposure of agricultural field workers to pesticides is primarily dermal, the U. S. Environmental Protection Agency recommends a dislodgeable surface particulate technique for reentry pesticide residue data in order to register pesticides. However, in a California study foliage particulate matter collected by vacuuming correlated better with dislodged airborne particulate matter (r = .985) than the recommended EPA technique (r = .687) (7).

The purpose of the study presented here was to assess the vacuuming method in a pesticide residue experiment and determine if vacuuming provides a better measure of foliage surface pesticide residues than the dislodgeable particulate residue technique under Florida conditions.

Materials and Methods

Application methodology was *previously described* (5).

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