Post-Application Slough-Off of Pesticide Deposits on Orange Trees

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Toxicant loss from fruit and leaf surfaces after a pesticide application was considered by GUNTHER and BLINN (1955) to be composed of 3 separate steps. The first step, occurring immediately after the pesticide spray had dried, was postulated to be a rapid loss within a few hours to a few days of the loosely adhering deposits consisting of pesticide sorbed to formulation carrier and to natural dust on the plant. The following step was a dissipation of toxicant from the more tenaciously adhering deposits through volatilization and decomposition of the compound by the action of sunlight and moisture. The duration of this step could be several days to several weeks. The final step was dissipation of the residues at a greatly reduced rate through a combined action of dislodgment, volatilization, chemical degradation, and penetration into subsurface tissues.

The occurrence of the second and final steps, designated on semi-logarithmic plots of pesticide dissipation as the degradation and persistence curves, respectively, was reviewed by GUNTHER (1969) for about 40 insecticides and acaricides on citrus fruit. WESTLAKE et al. (1973) demonstrated this phenomenon on both citrus fruit and foliage for the newer insecticide dioxathion. Much interest has been currently generated with respect to foliar residues because of the current belated emphasis on worker safety in pesticide-treated groves. The visible accumulation of dust on foliage has been recorded by many workers (CARMAN et al. 1952) and quantitatively demonstrated by WESTLAKE et al. (1973) and POPENDORF et al. (1975) on California citrus trees. The occurrence of high foliar residues may be augmented by the trend toward use of low-volume spray applications (CARMAN et al. 1972). Not only does this type of application deposit greater quantities of pesticide, but the use of only about 100 gal of spray/A eliminates the cleansing effect of removing foliar dust achieved by dilute spray applications. In addition to foliar dust, dust on the orchard floor has also been suggested as a source of toxicants to field workers (GUNTHER et al. 1975, SPENCER et al. 1975). This dust presumably can be transferred to foliage and workers through worker or mechanical activity and wind action.

As little work has been directed towards evaluating the initial step of toxicant loss (sloughed residues) from foliage and its role as a potential problem for worker safety, the

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present project was undertaken to study the significance of this initial loss and its contribution to orchard soil dust residues. Thus, an experiment was conducted to estimate the amount of sloughed residues over a 5-day period for 3 parathion formulations, and to determine the magnitude and distribution of sloughed residues over the orchard floor. Concurrently, dislodgable foliar parathion and paraoxon levels were determined after the applications with wettable powder (WP) and emulsifiable concentrate (EC) formulations.

MATERIALS AND METHODS

Treatment. Parathion was applied to Valencia orange tree plots located at the Citrus Research Center, Riverside, CA. For the study involving the comparison of sloughed residues from trees after dilute and low-volume applications, plots were sprayed with a 25WP parathion formulation on September 26, 1975 at a rate of 12.5 lb a.i./2,000 gal/A with an oscillating boom and the low-volume spray was applied at 100 gal/A with a Kinkelder® sprayer. For the study involving the comparison of sloughed residues from trees after dilute application of 3 different formulations, plots were sprayed with a 25WP, 4EC or 2 lb/gal Penncap® E (encapsulated) formulation. Applications were made using an oscillating boom on November 14, 1975 at a rate of 12.5 lb a.i./2,000 gal/A. In all experiments, sprays were applied to plots of trees so as to duplicate the normal spraying conditions employed in a commercial citrus grove. The formulation study was repeated on May 20, 1976, with the 25WP and 4EC formulations; application was by manually spraying the trees to give especially thorough coverage. The concentration of a spray mixture was 0.63 lb a.i./100 gal. Each tree selected for the sloughed residue study was located near the center of the treated plot. For the September application, the tree selected for the dilute application sampling was 15.7 ft in height and had an in-row width of 16.5 ft and an across-row width of 15.0 ft. The tree selected after a low-volume application was 15.3 ft in height and had an in-row width of 15.8 ft and an across-row width of 16.3 ft. Trees used for the formulation studies were located in the same field and had similar dimensions.

Collection of Sloughed Residues. The sloughed residues were collected by placing 6 sets of racks, each designed to hold 10 or 13 wide-mouth 1-pt Mason jars at 1-ft intervals, beneath a tree as described by CARMAN et al. (1977). The trees chosen were, as nearly as possible, symmetrical. After parathion application, the trees were allowed to dry for approximately 2 hr and the Mason jars were placed in the racks under a selected tree for a 5-day period. The jars were then capped and stored at 4°C. Prior to analysis, each jar interior was thoroughly rinsed (extracted) with 10 ml of acetone and the parathion present was quantitated by gas chromatography (GC).

Dislodgable Foliar Residues. Duplicate leaf disc samples were collected and each stripped of surface dislodgable parathion and paraoxon residues by 4 successive aqueous strippings followed by 4 successive partitionings into hexane using the procedure of GUNTHER et al. (1974). Hexane extracts were stored at 4°C over Na_2SO_4 prior to GC analysis without cleanup.

Penetrated Residues. A sample of 40 leaf discs was extracted by macerating in a semi-micro Waring blender for 2 min at high speed with about 15 g of Na_2SO_4 and 100 ml of acetone. The mixture was filtered through a coarse sintered glass funnel at reduced pressure. The solid residue was reextracted with 100 ml of acetone. The filtrates were combined, the volume was recorded, and the extract was stored over Na_2SO_4 at 4°C prior to GC analysis without cleanup.

RESULTS AND DISCUSSION

Collection jars were placed under an orange tree to determine the quantity and distribution profile of the post-treatment slough-off of pesticide deposits and residues. Placement was made about 2 hr post-application after the spray had dried. Jars were then left for 5 days under the tree before being collected and analyzed for pesticide content. All treatments were made at a rate of 12.5 lb a.i./A or 62 g of parathion/tree. The trees were approximately 8.5 ft in radius. The mean parathion content in the jars located at one ft intervals from the trunk for 3 experiments is shown in Figure 1. As the data obtained for the individual racks were essentially identical, only the composite picture is presented. Paraoxon was not detected (<0.1 µg) in the jars.

Figure 1 shows the parathion profile resulting from low-volume (100 gal/A) and dilute (2,000 gal/A) applications of a 25WP formulation. As the low-volume application would leave more residues on the tree (CARMAN et al. 1972) the slough-off from this application was somewhat greater than that from a corresponding dilute application. The parathion profiles resulting from a dilute application (12.5 lb a.i./2,000 gal/A) using encapsulated, WP, and EC formulations show, as expected, that the most slough-off was obtained with the encapsulated formulation due to the dislodgment of capsules containing high levels of parathion. The WP formulation gave more sloughed residues than the EC due to dislodgment of parathion-containing solids from the formulation. All slough-off profiles show that the naturally dislodged material is predominantly deposited on the soil and detritus within the tree canopy. Relatively little is deposited on the soil surface between the trees. WINTERLIN et al. (1975) treated peach trees with WP, EC, and encapsulated parathion. Of total parathion foliar residues, dislodgable residues constituted 25% for EC, 47% for WP, and 67% for encapsulated parathion treatments. WOLFE et al. (1975) reported that in studies of a volunteer hand-thinning apples at various intervals after parathion application, both dermal and respiratory exposure were greater when a WP formula-

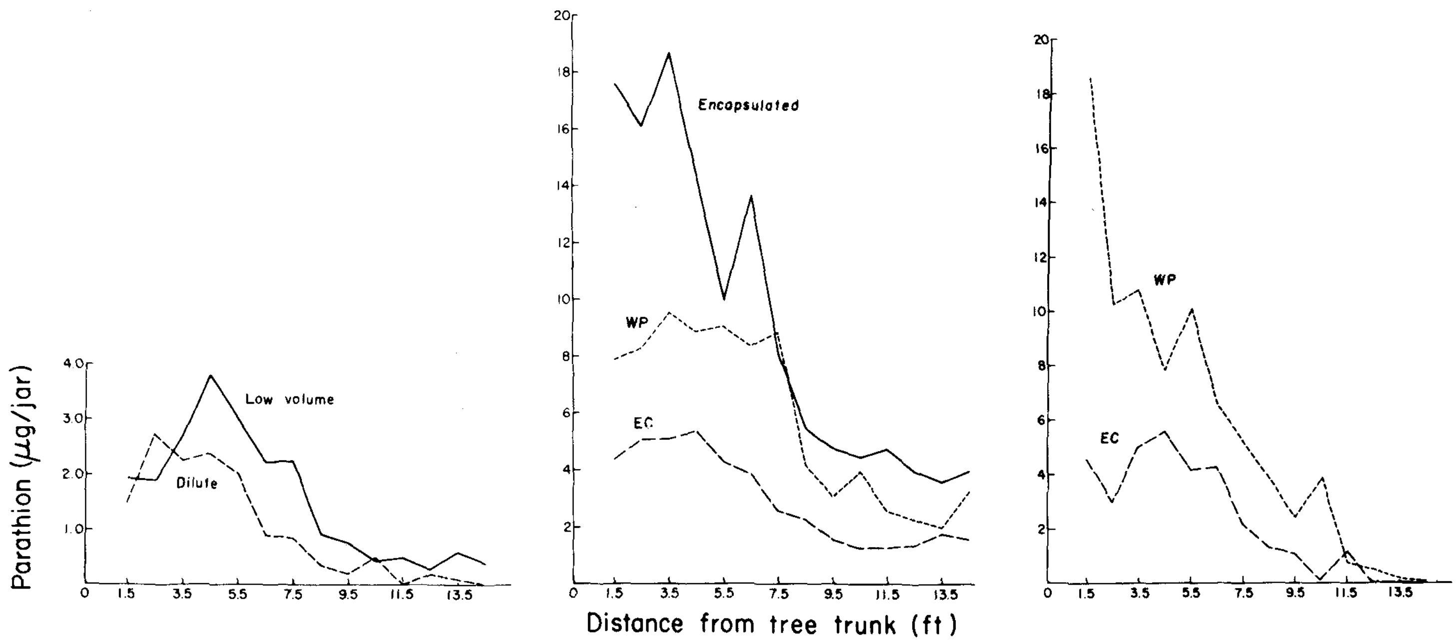

Fig. 1. Mean parathion contents of jars placed under an orange tree at various distances from the trunk; canopy radius was about 8.5 ft. Jars were placed in position about 2 hr post-application and left for 5 days. Left: 12.5 lb a.i. of 25 WP/A using 100 or 2,000 gal of spray (Nov. 1975). Center: 12.5 lb a.i./2,000 gal of spray/A using 25WP, 4EC, and Penncap E (encapsulated) formulations (Nov. 1975). Right: 12.5 lb a.i./2,000 gal of spray/A using 25WP and 4EC formulations (May 1976).

tion was used than an EC. The difference was attributed to the ease with which the dried residue from a WP application dislodged from the foliage during contact or agitation by the worker. Urinary p-nitrophenol excretion by the volunteer indicated slightly more absorption following exposure in WP experimental plots than EC plots.

The second characteristic feature of the profiles is the very low quantities of parathion collected. They do not approach normal soil residue levels such as reported by SPENCER et al. (1975) and show that soil residues principally result from spray drift and runoff during pesticide application. Table I gives the amount of sloughed residue estimated to have fallen onto the orchard floor within a 15-ft radius of the tree trunk. For the November 1975 application, parathion and paraoxon dislodgable residues were determined. Data are plotted in Figure 2. If the initial parathion loss is extrapolated back to 2.5 hr for the EC formulation, parathion loss was 2.1 $\mu g/cm^2$ of leaf area from 2.5 hr after application to the break in the curve at 32.5 hr ([3.0-0.9]$\mu g/cm^2$ of leaf area). Combining this value with the estimated total surface area of a 20-year-old orange tree of 5 x 10^6 cm^2 (GUNTHER et al. 1973), a total loss of 10.5 g of parathion in the 30-hr time period is obtained. A similar treatment for the WP application data gives 7.5 g of parathion lost in a 66-hr time period. This compares with a parathion loss over 5 days of 0.033 and 0.066 g/tree (Table I) for the EC and WP sloughed residues, respectively. As only about 1% of the material was collected as sloughed parathion residues, the results indicate that the major initial loss of parathion is due to a process other than sloughing of foliar dislodgable residues.

The dislodgable foliar parathion and paraoxon levels after a WP and EC application in May 1976 are plotted in Figure 3. Penetrated and total parathion residue data are shown in Figure 4. The total residue curve was obtained by extracting unwashed leaf discs whereas the penetrated residue curve was obtained by extracting leaf discs after having removed the dislodgable residues for separate quantitation. Although absent in Figure 2, Figure 3 shows the 3-step dissipation curve predicted by GUNTHER and BLINN (1955). In Figure 2 dislodgable paraoxon levels increased over a 2- to 3-day period and then remained constant over the experimental period. The increase in the paraoxon level for both formulations ceased when the persistence curve changed to the degradation curve. In Figure 3 paraoxon formation was complete within 1 day and then residues declined very slowly with a half-life of from about 7 to about 10 days. These results from field experiments are in agreement with the greenhouse experiments of ADAMS et al. (1976).

Figure 2 shows that under identical conditions, dislodgable parathion residues dissipate faster after application with an EC than a WP formulation. The results shown in Figure 3, although less definitive, also indicate a somewhat faster dissipation from an EC application.

Table I

Estimation of sloughed parathion residues per tree over a 5-day period for an orange tree treated with 12.5 lb a.i. of parathion/A

Application date	Application: Formulation	Application: gal/A	Parathion (mg)[a/]
Sep. 26, 1975	WP	100	16
	WP	2,000	8.4
Nov. 14, 1975	WP	2,000	66
	EC	2,000	33
	encap.	2,000	96
May 20, 1976	WP	full coverage	45
	EC	full coverage	21

[a/] Tree located in center of plot 15-ft radius.

$$\text{Total mg} = \sum_{n=2}^{14} C_n \, \Pi[n^2-(n-1)^2]$$

where C_n is the soil surface residue in mg/ft^2 for the area between (n-1) and n ft from the trunk; C_n is estimated from the average residue in the jars located (n-½) ft from the trunk.

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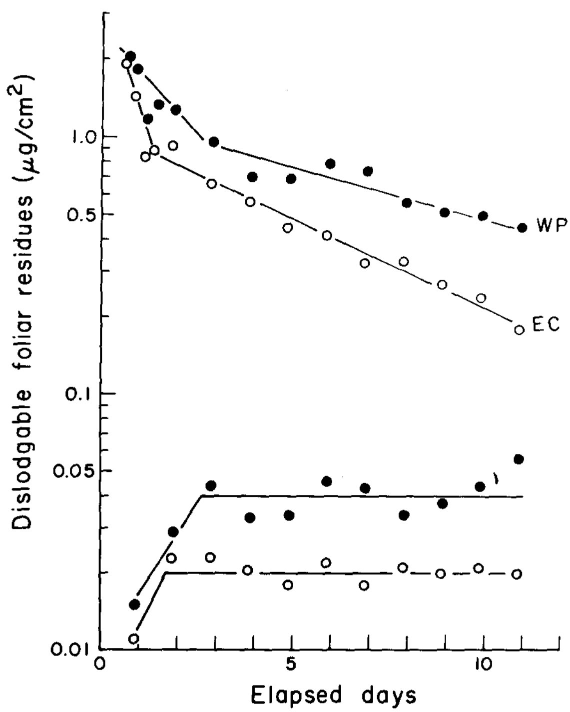

Fig. 2. Dislodgable residues of parathion (top) and paraoxon (bottom) on orange leaves after an application of 12.5 lb a.i./2,000 gal/A using a 25WP (●) or 4EC (O) formulation. Values are a mean of duplicate samples. (Nov. 1975).

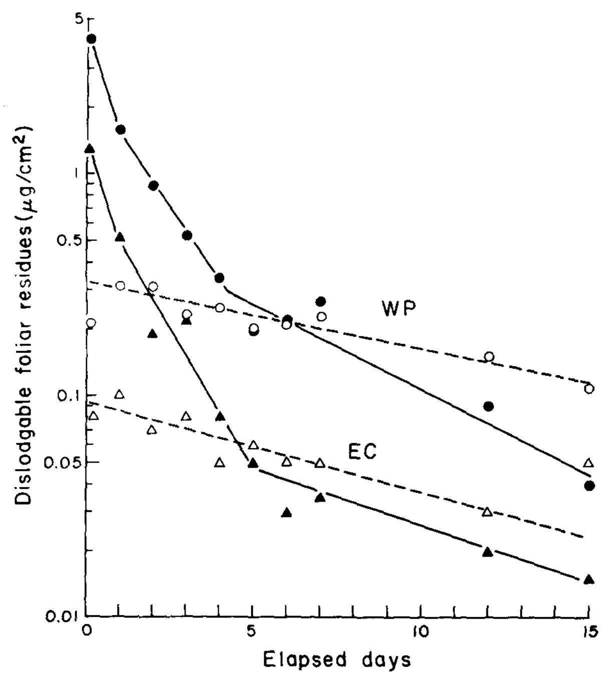

Fig. 3. Parathion (closed symbols) and paraoxon (open symbols) dislodgable foliar residues on orange trees resulting from application of WP (●) and EC (▲) formulations. Values are a mean of duplicate samples. (May 1976).

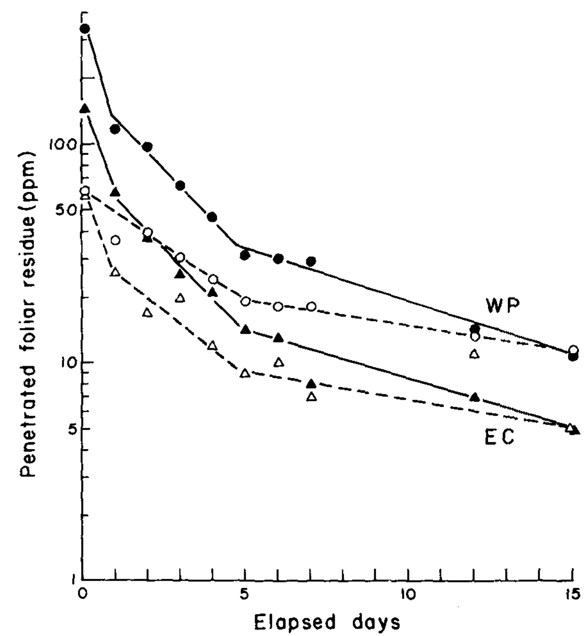

Fig. 4. Total (closed symbols) and penetrated (open symbols) parathion foliar residues recovered from orange trees sprayed with WP (0) and EC (Δ) formulations. Values are a mean of duplicate samples. (May 1976).