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## Worker Environment Research: Residues from Carbaryl, Chlorobenzilate, Dimethoate, and Trichlorfon Applied to Citrus Trees

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Carbaryl, chlorobenzilate, dimethoate, and trichlorfon insecticide formulations were applied at the highest recommended dosages to California lemon and orange trees. Dislodgable foliar residues are herein reported to provide a basis for determining potential exposures of agricultural workers who come into continuous and prolonged contact with the treated foliage. Fruit was sampled about 60 days postapplication, and the edible portions (pulp) of the fruit after rind removal were analyzed for the presence of persisting residues; analytically significant pulp residues were absent.

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Field workers are constantly exposed to minute amounts of insecticide residues in the agricultural environment. Exposure is aggravated when labor involves prolonged and continuous contact with foliar surfaces bearing insecticide residues. The dislodgable foliar residues are transferred to workers' skin and clothing where they can eventually penetrate into the skin or can become airborne and be inspired. This health problem is currently referred to as the "reentry problem" in reference to worker reentry into a field or grove after an insecticide application has been made. Although sulfur, with its capacity to cause eye irritations, may be claimed to have caused the first reentry problem in agriculture, the problem as currently evaluated is limited to the use of cholinesterase-inhibiting compounds with emphasis on the organophosphorus insecticides. This problem is reviewed by Gunther et al. (1977).

However, workers are exposed to residues of insecticides that are potentially oncogenic, mutagenic, or teratogenic. Such exposure will not result in easily demonstrable physiological effects such as blood cholinesterase depression and may lead to adverse long-term health effects. Currently four major insecticide/ acaricides widely used in California citriculture have been placed on the U.S. Environmental Protection Agency's Rebuttable Presumption Against Registration (RPAR) or pre-RPAR

review list. These compounds are carbaryl, chlorobenzilate, dimethoate, and trichlorfon. The issuance of an RPAR does not constitute a ban or necessarily mean that the affected registration will be cancelled or suspended. It does mean that the Agency has taken the initial position that the use of the insecticide may pose an unacceptable risk on the basis of available information.

Dislodgable foliar residue data are reported here for these four compounds after their application to California citrus trees to provide a basis for determining potential exposures of workers during the postapplication period. Persisting residues in the edible portion of the fruit were also sought. Applications were made at the highest dosage recommended by the California Agricultural Experiment Station in relation to method of application and/or tree size.

### EXPERIMENTAL SECTION

**Application.** Treatments were made on mature orange trees located on the Irvine Ranch, Tustin (Orange County), CA, on Aug 11, 1978, and on mature lemon trees located on the Citrus Research Center (Field 5, Block H), Riverside (Riverside County), CA, on Sept 22, 1978, using an oscillating boom spray rig. For carbaryl, chlorobenzilate, dimethoate, and trichlorfon the formulations used were Sevin 80W, Acaraben 4E, Cygon 4E, and Dylox 80W, respectively. Application rates were 11.5 lb of AI (1200 gal)<sup>-1</sup> acre<sup>-1</sup> (13 kg (112 hL)<sup>-1</sup> ha<sup>-1</sup>) carbaryl, 3.0 lb of AI (1200 gal)<sup>-1</sup> acre<sup>-1</sup> (3.4 kg (112 hL)<sup>-1</sup> ha<sup>-1</sup>) chlorobenzilate,

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1.25 lb of AI (500 gal)<sup>-1</sup> acre<sup>-1</sup> (1.4 kg (47 hL)<sup>-1</sup> ha<sup>-1</sup>) dimethoate, and 4.0 lb of AI (500 gal)<sup>-1</sup> acre<sup>-1</sup> (4.5 kg (47 hL)<sup>-1</sup> ha<sup>-1</sup>) trichlorfon.

**Plots.** For each insecticide, the plot consisted of five adjacent rows of either seven orange trees or six lemon trees each. For sample collection, the inner three rows were each considered as three replicate treatment plots. End trees of each row were not sampled. Thus, each sample was taken from five orange or four lemon trees.

**Sampling. Foliage.** Using a leaf punch sampler, 2.54-cm diameter disks were excised from each of 40 mature leaves free of surface moisture and collected directly in an 8-oz (240-mL) jar. The portion of the tree about 1.2–1.8 m above ground was sampled. The procedure used was to punch leaf disks at 45° intervals around each of five orange trees or at 36° intervals around each of four lemon trees. Duplicate samples were collected from each of three replicate "treatment" plots at each sampling interval. Samples in transit to the laboratory were kept in a cold ice chest. Samples were processed within 24 h of collection.

**Fruit.** After 52- and 59-days postapplication, orange and lemon fruit, respectively, were sampled. Three replicate field samples were collected for each citrus variety and each sample of 32 fruit consisted of two fruit picked from each quadrant of each of four trees.

**Processing. Dislodgable Foliar Residues.** For carbaryl and chlorobenzilate, the procedure of Iwata et al. (1977) was used. Briefly, the leaf disk sample was shaken three times with 100 mL of water containing a wetting agent to remove surface residues. Then, the combined aqueous wash was extracted two times with 50 mL of an organic solvent. The solvents were CHCl<sub>3</sub> for carbaryl and hexane for chlorobenzilate.

For dimethoate and trichlorfon, the procedure of Iwata et al. (1977) was modified to accommodate the relatively high water solubility of these compounds—2–2.5% for dimethoate and 12–15% for trichlorfon (Gunther et al., 1968). Only a single 100-mL aqueous wash was used so as to limit the amount of water. The aqueous wash was then nearly saturated with 25 g of NaCl and extracted three times with CHCl<sub>3</sub>.

**Fruit.** Fruits were washed and dried to remove surface residues and thus avoid contamination of the pulp (edible portion). The rind was removed and a core sample was removed from each fruit. From the composite core sample taken from a 32-fruit sample, duplicate 100-g subsamples were frozen until processed further.

**Analysis. Foliage. Carbaryl.** Extracts were analyzed using a slight modification of the cleanup and subsequent colorimetric procedure described in "A Method for the Determination of Residues of Carbaryl on Plant Foliage" (1974) available from Union Carbide Corporation. Briefly, the sample in 50 mL of CHCl<sub>3</sub> was added to a 5-cm Florisil column (22 mm i.d.) and the column eluted with 100 mL of CHCl<sub>3</sub>. The solvent was removed from an appropriate aliquot of the concentrated column eluate. The carbaryl was hydrolyzed with methanolic KOH and the resulting 1-naphthol was reacted with 4-nitrobenzenediazonium fluoroborate for colorimetric analysis. Analyses were conducted within 48 h of sample collection.

**Chlorobenzilate.** Pretreatment sample extracts contained a large interfering background peak when analyzed by gas chromatography for chlorobenzilate. Therefore, the procedure of Blinn et al. (1954) was used with modification. Chlorobenzilate was hydrolyzed to 4,4'-dichlorobenzilate by adding 5 mL of 10% methanolic KOH to the hexane extract and removing the hexane using a rotary evaporator

and a 50 °C water bath; the residue was heated an additional 5 min after solvent removal. Nonpolar materials, including 4,4'-dichlorobenzophenone if present, were removed by adding, swirling, and decanting two successive 25-mL portions of hexane. After evaporating off residual hexane, 25 mL of glacial acetic acid and 1.0 g of CrO<sub>3</sub> were added. After 30 min the mixture was transferred to a separatory funnel with 100 mL of water. The 4,4'-dichlorobenzophenone formed was extracted with two 50-mL portions of hexane. Extracts were analyzed by gas chromatography using a <sup>63</sup>Ni electron-capture detector. A 75 cm × 4 mm i.d. glass column packed with 10% DC-200 on 60/80 mesh Gas-Chrom Q was used. Inlet, column, and detector temperatures were 233, 220, and 293 °C, respectively, and nitrogen carrier gas flow was 80 mL/min. A standard curve was used for quantitation by peak height measurements. Final calculations took into account that 1.0 μg of chlorobenzilate was converted to 0.77 μg of dichlorobenzophenone.

**Dimethoate and Trichlorfon.** Extracts were analyzed by gas chromatography using a flame photometric detector. For analysis of dimethoate and dimethoxon, a 120 cm × 4 mm i.d. glass column packed with 10% DC-200 on 60/80 mesh Chromosorb 750 was used. Inlet, column, and detector temperatures were 230, 210 and 220 °C, respectively. For trichlorfon analysis, a 150 cm × 4 mm i.d. glass column packed with 25% Carbowax 20 M on 60/80 mesh Gas-Chrom Q was used. Inlet, column, and detector temperatures were 230, 175 and 230 °C, respectively. For both columns, nitrogen carrier gas flow was 80 mL/min.

**Fruit.** A 100-g sample of pulp was macerated with 300 mL of acetone for 5 min in a Waring Blendor jar. The extract was vacuum filtered through a Büchner funnel. The volume collected was measured; a theoretically recoverable value of 400 mL was used for final calculations.

**Carbaryl.** The acetone was removed from the extract on a rotary evaporator until about 130 mL of liquid remained. Then, 150 mL of coagulation solution (1.0 g of NH<sub>4</sub>Cl, 2 mL of 85% H<sub>3</sub>PO<sub>4</sub>, and 4 mL of concentrated HCl in 400 mL of H<sub>2</sub>O) was added and the mixture vacuum filtered through a Büchner funnel containing about 2 cm of Celite 545. After adding 10 mL of saturated NaCl solution, the mixture was extracted twice with 50-mL portions of CHCl<sub>3</sub>. The extract was concentrated to 50 mL, and subsequent steps were identical with those for dislodgable residues except that the entire sample was used for the colorimetric determination of residues in pulp.

**Chlorobenzilate.** The acetone extract was partitioned with 100 mL of benzene and the organic phase passed through a funnel containing Na<sub>2</sub>SO<sub>4</sub>. The benzene extract was concentrated using a rotary evaporator to remove as much of the solvent as possible. Then, 100 mL of 10% methanolic KOH was added and the mixture refluxed for 2 h. The methanol was removed using a rotary evaporator. The residue was twice washed by adding, swirling, and decanting 50-mL portions of benzene. After removing traces of benzene using a rotary evaporator, 50 mL of saturated NaCl solution was added. With the flask chilled in an ice-water bath, 12 mL of concentrated HCl was added. The mixture was extracted three times with 50-mL portions of diethyl ether. After removing all traces of ether, 25 mL of glacial acetic acid and 3 g of CrO<sub>3</sub> were added, and the mixture was refluxed for 10 min. After adding 100 mL of water to the cooled mixture, it was twice extracted with 50-mL portions of hexane. The concentrated hexane extract was then analyzed for 4,4'-dichlorobenzophenone.

Table I. Recovery of Compounds from Fortified Aqueous Leaf Washes

compound	fortification <sup>a</sup>		recovery, % <sup>b</sup>
	μg	μg/cm <sup>2</sup>	mean ± SD
carbaryl	4000	10	90 ± 3
	400	1.0	95 ± 3
	40	0.10	90 ± 6
	10	0.025	80 ± 0
	4	0.010	74 ± 1
chlorobenzilate <sup>c</sup>	400	1.0	88 ± 3
	40	0.10	93 ± 1
	4	0.010	95 ± 8
dimethoate <sup>d</sup>	400	1.0	93 ± 5
	40	0.10	101 ± 5
	4	0.010	95 ± 8
dimethoxon	400	1.0	90 ± 3
	40	0.10	105 ± 6
	4	0.010	75 ± 7
trichlorfon <sup>d</sup>	400	1.0	96 ± 5
	40	0.10	91 ± 4
	4	0.010	89 ± 4

<sup>a</sup> Forty leaf disks (2.54-cm diameter) have a total surface area of 405 cm<sup>2</sup>. <sup>b</sup> Three replicate samples were used. <sup>c</sup> Analyzed directly as chlorobenzilate. <sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub> was used rather than CHCl<sub>3</sub> for these tests.

**Dimethoate and Trichlorfon.** A 50- (or 100) mL aliquot of the acetone extract was shaken gently for 30 s with 50 (or 100) mL of CHCl<sub>3</sub>. The lower organic layer was passed through a funnel containing Na<sub>2</sub>SO<sub>4</sub> and the solvent then was removed. The residue was dissolved in acetone for analysis.

**Procedural Recovery Studies. Dislodgable Foliar Residues.** Three replicate aqueous leaf washes were fortified separately with compounds of interest to determine recoveries. Results are given in Table I; all recoveries were ≥74%. In addition, the chlorobenzilate procedure was tested to determine recoveries when analyzed as dichlorobenzophenone; three replicate hexane extracts of leaf washes were fortified with chlorobenzilate. Recoveries for samples fortified with 400, 40, and 4.0 μg were 108 ± 4, 112 ± 7, and 102 ± 13%, respectively. No correction factors have been applied to the residue data presented herein for the field samples.

Pretreatment samples indicated dislodgable residue levels of <0.03 μg/cm<sup>2</sup> of carbaryl, <0.003 μg/cm<sup>2</sup> of chlorobenzilate, and <0.001 μg/cm<sup>2</sup> of dimethoate, dimethoxon, and trichlorfon. Extracts of samples collected from untreated control plots contained no background interferences or determinable residues when diluted or concentrated to the same volume as used for analysis of treated sample extracts.

**Citrus Pulp.** No attempt was made to determine the efficiency of the extraction procedures used. They are assumed to be adequate based on the solvent properties of acetone, the 5-min blending time used, and the fact that citrus pulp consists of very little solid matter to be extracted. Procedural recoveries of insecticides added to the pulp prior to acetone blending are given in Table II. No correction factors have been applied to the residue data presented herein for the field samples.

Extracts of samples collected from untreated control plots contained no determinable residues when diluted or concentrated to the same volume as used for the analysis of treated samples.

## RESULTS AND DISCUSSION

**Dislodgable Foliar Residues.** Residue data are shown in Figures 1 and 2. The 0-day postapplication residue data for Figure 2 obtained for samples collected after the sprayed trees had dried were 4.6 ± 0.3, 1.4 ± 0.1, 2.7 ± 0.3, and 0.84 ± 0.08 μg/cm<sup>2</sup> for carbaryl, chlorobenzilate,

Table II. Recovery of Insecticides Added to Orange Pulp

insecticide	fortification, ppm	recovery, % <sup>a</sup>
		mean ± SD
carbaryl <sup>b</sup>	1.0 <sup>c</sup>	85 ± 5
	1.0 <sup>d</sup>	81 ± 2
	0.10 <sup>e</sup>	73 ± 9
	0.050 <sup>f</sup>	64 ± 10
	0.050 <sup>f</sup>	72 ± 2
chlorobenzilate	0.010 <sup>f</sup>	79 ± 6
	0.050 <sup>c</sup>	107 ± 5
dimethoate	0.010 <sup>c</sup>	110 ± 6
	0.10 <sup>c</sup>	103 ± 5
trichlorfon	0.10 <sup>c</sup>	103 ± 5
	0.010 <sup>d</sup>	109 ± 3

<sup>a</sup> Three replicate samples used. <sup>b</sup> Samples corrected for background as determined from unfortified samples. <sup>c</sup> Fifty-milliliter aliquot of acetone extract used. <sup>d</sup> One-hundred-milliliter aliquot of acetone extract used. <sup>e</sup> Two-hundred-milliliter aliquot of acetone extract used. <sup>f</sup> Entire acetone extract used.

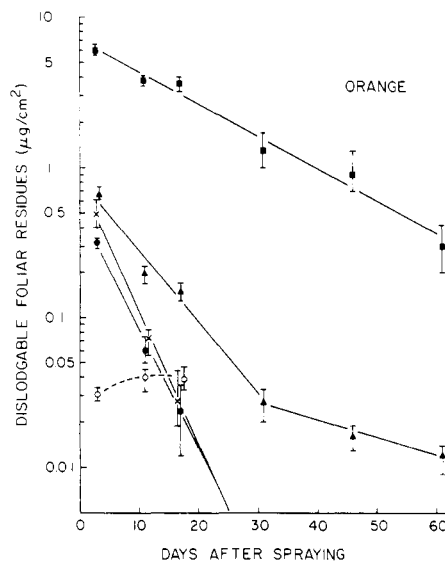


Figure 1. Dislodgable foliar residues of carbaryl (■), chlorobenzilate (▲), dimethoate (●), dimethoxon (○), and trichlorfon (x). Each point is the mean of six field samples; the range of values is given by the vertical lines.

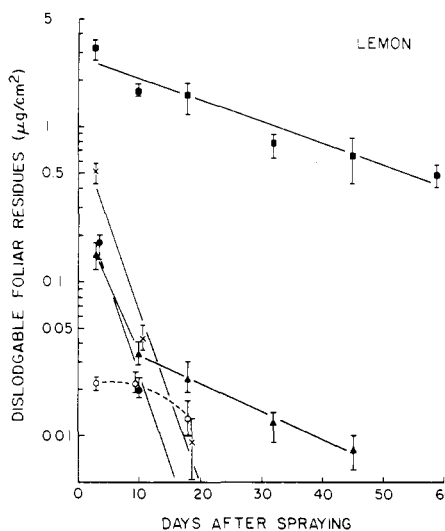
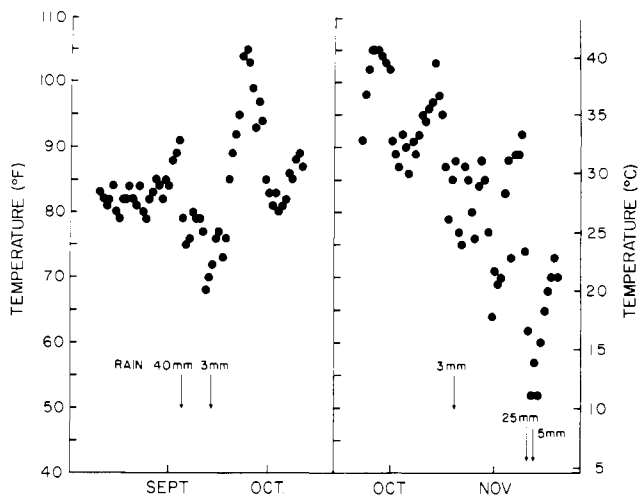


Figure 2. Dislodgable foliar residues of carbaryl (■), chlorobenzilate (▲), dimethoate (●), dimethoxon (○), and trichlorfon (x). Each point is the mean of six field samples; the range of values is given by the vertical lines.

trichlorfon, and dimethoate, respectively. These residue data were not used for the calculations presented below and serve only to confirm that no gross errors in appli-



**Figure 3.** Maximum daily air temperature and rainfall data for the experimental study period on orange (left) and lemon (right) trees.

cation rates were made. Since both climatic and geographic factors for the orange and lemon tree applications differed, it should not be inferred that the residue data differences are a result of citrus variety. A plot of the daily maximum air temperature is shown in Figure 3 for the two experimental periods. For orange trees, the immediate 3-week postapplication period had maximum air temperatures between 79 and 85 °F while for lemon trees it was between 86 and 105 °F.

The dislodgable residue data presented here are only indicative of what levels workers might encounter after an insecticide application because of the numerous variables that are operative under normal agricultural practices. No attempt is made to unravel the complex relationship between available foliar residue levels and their ultimate biological effect on workers who come into contact with them. The work reported herein is the first step toward evaluating potential worker exposure hazard.

**Carbaryl.** This insecticide was the most persistent of the four compounds studied. Since 1-naphthol could be carried through the dislodgable residue procedure and quantitated as carbaryl, two replicate samples from each sampling of both orange and lemon foliage were analyzed by omitting the methanolic KOH addition step in the analytical procedure. Residue levels for 1-naphthol were less than 0.02  $\mu\text{g}/\text{cm}^2$  for all samples analyzed.

Dissipation of carbaryl over the 61-day period examined was first order. The dissipation curves were described by  $\ln y = -0.050x + \ln(7.2)$  with a correlation coefficient ( $r$ ) of 0.99 for residues on orange foliage and  $\ln y = -0.032x + \ln(2.8)$  with  $r = 0.97$  for residues on lemon foliage. Persistence half-lives were 14 and 22 days, respectively. Foliar residues after 5 days, the recommended waiting interval for fruit harvest, were 5.6 and 2.4  $\mu\text{g}/\text{cm}^2$  on orange and lemon, respectively. The 60-day residue values were 0.36 and 0.41  $\mu\text{g}/\text{cm}^2$  for orange and lemon, respectively. A 40-mm (1.6-in.) rainfall on day-25 postapplication on orange trees and a 25-mm (1.0-in.) rainfall on day-50 postapplication on lemon trees did not appear to remove any significant amount of carbaryl residues from the foliage at the shoulder-height level of the tree from where samples were collected.

For comparison purposes, half-life values were calculated for the dissipation of dislodgable residues of carbaryl on cotton. The data of Ware et al. (1975, 1978) were used with the assumption of a first-order dissipation over the 96-h period studied. Using the data of Ware et al. (1975), the

half-life was 13 days ( $r = 0.29$ ) after application of Sevin 80WP and 3 days ( $r = 0.87$ ) after application of Sevimol 4EC. Using the data of Ware et al. (1978), the half-life was 1.3 days ( $r = 0.96$ ) after application of Sevin 80WP and 1.2 days ( $r = 0.96$ ) after application of Sevimol 4EC. The half-life of residues on cotton appear to be best represented by 1–3 days, if the 13-day half-life is disregarded due to the poor correlation coefficient (0.29) obtained for the linear regression analysis of the data.

**Chlorobenzilate.** Dissipation of chlorobenzilate over the 61-day period studied could be conveniently described by an initial first-order "degradation" curve, followed by a first-order "persistence" curve (Gunther and Blinn, 1955). For oranges, the dissipation curves were described by  $\ln y = -0.11x + \ln(0.85)$  with  $r = 0.99$  and  $\ln y = -0.027x + \ln(0.060)$  with  $r = 0.99$ , respectively, with half-lives of 6.3 and 26 days, respectively. For lemons, the dissipation curves were described by  $\ln y = -0.21x + \ln(0.28)$  with  $r = 1.00$  and  $\ln y = -0.042x + \ln(0.049)$  with  $r = 0.99$ , respectively, with half-lives of 3.3 and 17 days, respectively. Chlorobenzilate has no indicated waiting interval for harvest. After 60-days postapplication, residue levels were 0.01  $\mu\text{g}/\text{cm}^2$  on orange foliage and less than 0.01  $\mu\text{g}/\text{cm}^2$  on lemon foliage.

**Dimethoate.** Dissipation of dimethoate over the 31-day period studied appeared to be first order; however, there were only three sampling dates before residue levels dropped below 0.003  $\mu\text{g}/\text{cm}^2$  and sample collections were discontinued. Dissipation curves were described by  $\ln y = -0.19x + \ln(0.53)$  with  $r = 0.99$  for residues on orange foliage and  $\ln y = -0.27x + \ln(0.37)$  with  $r = 0.99$  for residues on lemon foliage. Persistence half-lives were 3.6 and 2.6 days, respectively. Dimethoate oxon was present but no sample contained more than 0.05  $\mu\text{g}/\text{cm}^2$ . At 4-days postapplication, the current reentry waiting interval, residues on orange foliage were 2.5  $\mu\text{g}/\text{cm}^2$  dimethoate and 0.03  $\mu\text{g}/\text{cm}^2$  oxon and on lemon foliage were 0.13  $\mu\text{g}/\text{cm}^2$  dimethoate and 0.02  $\mu\text{g}/\text{cm}^2$  oxon. At 15-days postapplication, the recommended waiting interval for harvest, residues on orange foliage were 0.03  $\mu\text{g}/\text{cm}^2$  dimethoate and 0.04  $\mu\text{g}/\text{cm}^2$  oxon and on lemon foliage were <0.01  $\mu\text{g}/\text{cm}^2$  dimethoate and 0.02  $\mu\text{g}/\text{cm}^2$  oxon.

Woodham et al. (1974) have reported on the combined surface residues of dimethoate and its oxon after application of dimethoate to grapefruit trees. Unfortunately, due to differing methods of data presentation no direct comparisons can be made.

**Trichlorfon.** Dissipation over the 31-day period studied appeared to be first order; however, there were only three sampling dates before residue levels dropped below 0.005  $\mu\text{g}/\text{cm}^2$  and sample collections were discontinued. Dissipation curves were described by  $\ln y = -0.21x + \ln(0.84)$  with  $r = 0.99$  for residues on orange foliage and  $\ln y = -0.27x + \ln(0.92)$  with  $r = 0.99$  for residues on lemon foliage. Persistence half-lives were 3.3 and 2.6 days, respectively. Trichlorfon is an organophosphorus insecticide but has no assigned reentry waiting interval; the acute dermal  $\text{LD}_{50}$  for rats is more than 2000 mg/kg (Pesticide Index, 1976). Foliar residues at 21 days, the recommended waiting interval for harvest, were 0.01  $\mu\text{g}/\text{cm}^2$  for orange trees and less than 0.005  $\mu\text{g}/\text{cm}^2$  for lemon trees.

**Citrus Pulp Residues.** Orange and lemon fruit were sampled 52- and 59-days postapplication, respectively. After washing the fruit to prevent internal contamination, samples of the edible portion of the fruit after rind removal were analyzed for residues.

**Carbaryl.** Five of six samples of orange pulp did not contain determinable amounts of carbaryl (0.01 ppm); one

sample contained 0.02 ppm. The six lemon pulp samples contained 0.01, 0.01, 0.03, 0.06, 0.07, and 0.09 ppm carbaryl with a mean  $\pm$  SD value of  $0.05 \pm 0.03$  ppm. Three lemon pulp samples analyzed with the omission of the alkaline hydrolysis step showed that the apparent carbaryl residues were not due to determinable amounts of 1-naphthol (0.01 ppm) in the final extract. No further efforts were made to confirm the identity of apparent carbaryl residues present due to the trace levels found and therefore the difficulty involved. Gunther et al. (1962) treated lemon trees at 7.5 and 15 lb of AI (1500 gal)<sup>-1</sup> acre<sup>-1</sup> and orange trees at 12.5 and 25 lb of AI (2500 gal)<sup>-1</sup> acre<sup>-1</sup> and reported no determinable amounts of carbaryl (0.2 ppm) or 1-naphthol (0.1 ppm) in the pulp of the fruit samples collected. Lower levels of detection were achieved here by use of additional sample cleanup.

**Chlorobenzilate.** Neither orange nor lemon pulp contained determinable amounts of chlorobenzilate (0.01 ppm). Gunther et al. (1955) treated lemon trees at 2.5 and 7.5 lb of AI (1000 gal)<sup>-1</sup> acre<sup>-1</sup> and reported that 14- and 28-day samples analyzed colorimetrically contained trace amounts (<0.2 ppm) of chlorobenzilate. Subsequent samples of pulp were reported to be indistinguishable from control samples. Lower levels of detection were achieved here by use of additional sample cleanup and use of gas chromatography with electron-capture detection.

**Dimethoate and Trichlorfon.** None of the samples contained determinable amounts of dimethoate or trichlorfon (0.01 ppm). Gunther et al. (1965) treated orange trees with dimethoate at 11 and 22 lb of AI (2250 gal)<sup>-1</sup> acre<sup>-1</sup> and analyzed pulp samples colorimetrically with a lower limit of detection of 0.08 ppm. Pulp residues for fruit sampled between 3- and 59-days postapplication were all no higher than levels reported for control samples (0.1–0.2 ppm). Woodham et al. (1974a) treated grapefruit trees with dimethoate at 2.5 lb/acre. The range of residue values reported was 0.01–0.19 ppm for pulp samples obtained 7- and 14-days postapplication; no determinable amount of dimethoxon was reported (0.05 ppm) in grapefruit pulp.

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**Supplementary Material Available:** Data used to plot Figures 1 and 2 and standard deviations for mean residue values (2 pages). Ordering information is given on any current masthead page.

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## Transformation of [<sup>14</sup>C]Diclofop-methyl in Small Field Plots

Allan E. Smith

The degradation of the herbicidal ester [<sup>14</sup>C]diclofop-methyl, in soil, applied at a rate of 1.25 kg/ha, was studied under field conditions in small sandy loam plots. The plots, following treatment in May of 1978, were extracted at regular intervals using aqueous acidic acetonitrile and the extracts analyzed using radiochemical and gas chromatographic techniques to monitor the herbicide breakdown. In addition, the polar solvent extracted soils were oxidatively combusted to determine bound residue formation. During the growing season there was a loss of extractable, and an increase in nonextractable, radioactivity so that by October only 15% of the applied <sup>14</sup>C was solvent recoverable, while 37% was associated with the soil in a bound form. At all sampling dates the major soil transformation product was diclofop-acid, with 4-(2,4-dichlorophenoxy)phenol as a minor metabolite. Minute traces of 4-(2,4-dichlorophenoxy)phenetole and four other degradation products were also detected.

Diclofop-methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate] is applied as a postemergence treatment for the control of wild oats and other annual grasses in a variety of crops.

Laboratory studies with the <sup>14</sup>C-ring-labeled herbicide have shown (Smith, 1977; Martens, 1978) that in moist soil the ester underwent a rapid hydrolysis to diclofop, the corresponding propionic acid. Small amounts of 4-(2,4-dichlorophenoxy)phenol were also isolated from the treated soils (Smith, 1977; Martens, 1978) together with 4-(2,4-dichlorophenoxy)phenetole (Smith, 1977) and traces of other degradation products including [<sup>14</sup>C]carbon di-

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