determinations and represent those used in calculating the residues reported herein. The 4-μg spike used calculates as a 0.08-ppm residue which is characteristic of the harvest residues found in the apples and apple products tested. As a further verification of the assay procedure duplicate samples of McIntosh apples from Geneva were analyzed both in the Geneva Pesticide Laboratory and the Celamerck, Ingelheim, West Germany, Pesticide Laboratory. Table II lists the residues found in this fruit at various periods after application as determined in the two laboratories. The agreement between laboratories is excellent indicating a reliable method.

The results of field testing of triforine on apples are summarized in Table III. Applications at the rates of between 8 and 16 oz of active ingredient per acre were applied to three varieties in 1971 at four different locations. Between 1 and 13 applications were applied through the growing season. Periodic samples were taken from last application to harvest and residues determined. In all cases the harvest residue was determined to be between 0.03 and 0.08 ppm. The average rate constant (k) was calculated to be 0.044. Similar experiments run during 1972 at Geneva but with shorter application to harvest intervals resulted in harvest residues from 0.05 to 0.24 ppm depending on application rate. The rate constants were slightly higher than those obtained during 1971, averaging 0.055.

Pilot plant processing of the 1972 fruit and subsequent analysis indicated the vast majority of the residue that was present in the apples at harvest (<0.24 ppm) was recovered in the pomace. Only minor quantities (<0.035 ppm) were recovered in either juice or sauce.

In 1972 and 1973 extensive trials on sour cherries were carried out in East Lansing, Mich., Geneva, Switzerland, and Lockport, N.Y. From one to eight applications at rates of between 6 and 25 fluid oz/100 gal were applied to the foliage. Harvest residues (Table IV) were found to range between 0.1 and 0.3 ppm 1 week after application depending upon application rate. The rate constant was found to average 0.10 or about twice that found in the apple experiments.

The application of a 20% emulsifiable concentrate to peaches at rates of between 8 and 16 fluid oz/100 gal resulted in harvest residues of between 0.7 and 1.1 ppm 11 days after application. Residues in blueberries sprayed at the same rate were determined to be between 0.5 and 0.8 ppm 7 days after the application. Thirty-five days past application, the residue had decreased to 0.1 ppm. Prune triforine residues of between 0.2 and 0.4 ppm were found 9 days after treatment at the above rates. Approximately 0.3 ppm of triforine was recovered from grapes sprayed four times, 15 days after the last application.

The rate constant for prunes, peaches, and grapes ranged between 0.03 and 0.09, averaging 0.06. The rate constant on blueberries was about three times that or 0.17. The specific conditions and residues from the field trials are given in Table V.

ACKNOWLEDGMENT

We wish to thank S. D. Gibbs and R. A. Marafioti for technical assistance.

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Received for review June 1, 1976. Accepted August 24, 1976. Funded in part by Northeast Regional Research Project No. 36. Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 2286, May 5, 1976.

Distribution and Dissipation of Captafol Applied to Apple Trees

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Seasonal changes of captafol residues on semidwarf apple trees were determined following a single application of Difolatan for early season apple scab control. Initial wood deposits of 126–128 $\mu g/cm^2$ declined to 36–2 $\mu g/cm^2$ at harvest at tree heights of 1.5 and 3.0 m, respectively. Deposits on cluster leaves declined from 6.4 $\mu g/cm^2$ (May 1) to 0.98 $\mu g/cm^2$ (June 6). The minimum deposit of captafol necessary for protection of leaves against apple scab was judged to lie between 0.1 and 1.0 $\mu g/cm^2$. During a 4-mm rainfall, rainwater collected under sprayed trees, with a wood deposit of 97 $\mu g/cm^2$ captafol, contained 0.65 $\mu g/ml$ of captafol. At harvest, whole apple residues were 0.0062 $\mu g/g$ with the highest residues associated with the peel. A simple thin-layer chromatographic technique was used to purify apple extracts prior to gas chromatographic analysis.

Captafol, *N*-(1,1,2,2-tetrachloroethylthio)-3a,4,7,7a-tetrahydrophthalimide, is an important fungicide recently introduced for the control of apple scab (*Venturia inaequalis* (Cke.) Wint.). It is applied to trees using the single application technique (SAT), at or just prior to the appearance of leaf tissue in early spring and has given adequate scab control for as long as 53 days (Northover, 1975).

The prolonged fungicidal activity of captafol is due to its persistence (Neely, 1970, 1971) and its redistribution

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(Gilpatrick et al., 1971; Yamada, 1973; Yamada et al., 1969). The fate of captafol on large apple trees was examined by Gilpatrick et al. (1971). Because the trend is toward smaller trees, the present study was undertaken to determine the persistence and redistribution of captafol on semidwarf apple trees.

Several captafol residue studies have been published (Baker and Flaherty, 1972; Dubin and English, 1974; Gilpatrick et al., 1971), but there was little mention of analytical methodology. The efficiency of pesticide recovery by using fortification techniques is not necessarily the same as that from weathered samples (Chiba and Morley, 1968). Therefore, this study determined the relative efficiency of tumbling and sonification extraction methods, benzene vs. benzene–acetone as solvents, and the efficiency of extraction of weathered and fortified captafol deposits. Furthermore, it examined the suitability of the captafol SAT procedure for control of apple scab in semidwarf trees, and determined the harvest residues of apples to aid in the establishment of a tolerance.

EXPERIMENTAL SECTION

Spray Application. Experimental plots consisted of 16 mature semidwarf McIntosh apple trees within a 2-ha orchard. Trees were 3.5 m high and spaced 8.3 × 8.3 m (150 trees/ha). Fungicide-treated plots were randomized in two blocks and separated by one or two rows of unsprayed trees.

Captafol was used at 22 kg/ha as a 39% flowable formulation of Difolatan 4.8F (4.8 lb of captafol/Imperial gal) (Chevron Chemical (Canada) Ltd., Oakville, Ontario). Unsprayed plots were included as controls. The chemical was applied on April 24, 1974, at 1.5 cm green bud stage, with a Swanson airblast orchard sprayer operated at 3.2 km/h. The sprayer delivered 1.1 kl/ha of spray with 60% directed into the top half of the trees. Dodine, 1.1 kg/ha (Cyprex 65W, Cyanamid of Canada Ltd., Rexdale, Ontario), was applied on June 20 and July 9 over all plots to minimize mid- and late-season scab infection.

Sample Collection. One- to three-year old branches 10–60 cm long were collected randomly from heights of 1.5 and 3.0 m on both sprayed and unsprayed trees. A post-spray sample was taken 2 h after the deposits had dried; subsequent samples were collected at weekly or biweekly intervals until July 4, and a final sample was taken at harvest, Sept 16. Early season samples were subdivided into wood and cluster leaves. Samples taken on and after June 6 were subdivided into wood, cluster leaves, and axillary leaves on shoots in the axils of cluster leaves. Duplicate 4.5-kg samples of mature apples were harvested on Sept 16 for the determination of harvest residues. All plant material was weighed and quickly frozen immediately after collection and stored at −12 °C until extraction.

Redistribution Study. To study the redistribution of captafol during a light rain, branches from unsprayed trees were moved to a captafol-treated plot. Branches were held in 1-l. glass jars supported at the 1.4-m level midway between the center and periphery of each of the four central trees of a captafol-treated plot. Also, two glass jars fitted with glass funnels (15 cm diameter) were positioned under each of the same four captafol-treated trees to collect the rainwater passing through the tree canopy. On May 15, 1974, after a 4-mm overnight rainfall, the rainwater was collected and analyzed. Cluster leaves from the excised branches and from branches in the control plot were taken for analysis of residues.

Disease Assessment. On Aug 6, 20 terminal shoots and 400 immature apples were harvested from a height of 3 m in each plot and examined for apple scab lesions. The disease incidence of the leaves which developed before May 23 was recorded separately from that of leaves which unfolded and were susceptible to scab infection after May 24 and before June 20, when the first dodine application was made.

Fortification. For recovery tests, samples were fortified with a Difolatan 4.8F water suspension: wood with captafol at 100 and 1000 μg/g, and leaves at 300 μg/g; all samples were dried slowly at 24 °C and extracted by the tumbling method (see Main Extraction Methods) with benzene and Na_2SO_4 (anhydrous, BDH, Analar). Rainwater samples were fortified at the 2 μg/ml level and the procedure described under Main Extraction Methods was followed.

Comparison of Tumbling and Ultrasonic Methods and Solvents for Extraction of Weathered Wood and Leaf Samples. Three 40-g samples of wood, cut into 2.5-cm lengths, and bearing captafol deposits weathered for 29 days, were placed in 450-ml glass jars with 150 ml of benzene and 30 g of Na_2SO_4. The jars were tumbled on a Fisher-Kendall mixer at 60 cycles/min for 30 min. Samples in three similarly prepared jars were treated with an ultrasonic probe (Bronwill Biosonik, Bronwill Scientific) at 50 000 Hz for 5 min. The benzene was decanted and four subsequent extractions from the same samples were made each using 150 ml of fresh benzene. The captafol content of each of the five extracts was determined.

The tumbling method was used with wood (40 g) and leaves (20 g) to test the relative extraction efficiency of three solvent systems. Benzene–acetone (9:1), benzene–acetone (1:1), and pure benzene with Na_2SO_4 were used in three sequential extractions, and each replicated three times.

Main Extraction Methods for Wood, Leaves, and Rainwater. Samples consisted of 40 g of wood, cut into 2.5-cm lengths, or 20 g of leaves. Each was weighed accurately, placed in a 450-ml glass jar, and tumbled for 30 min with 30 g of Na_2SO_4 and 150 ml of benzene. The extraction was repeated once and the jar was then rinsed three times with 30 ml of benzene; the rinses were combined with the extracts and the volume adjusted to 400 ml with benzene. After mixing, 50 ml was retained for analysis.

The rainwater collected in each of the sampling jars during the redistribution study was measured. The jars and corresponding funnels were each rinsed three times with 50 ml of water and twice with 25 ml of acetone. Rinsings and rainwater were combined and the volume adjusted to 700 ml with water. Two successive extractions were made with 50 ml of benzene. The extracts were combined, dried over Na_2SO_4, adjusted to 100 ml, and analyzed.

Extraction and Cleanup of Apple Samples. Apples (1 kg) were randomly taken from the 4.5-kg harvested sample. One-half of each apple was diced into small pieces including peel (whole apple sample). The remaining halves were separated into peel and flesh (excluding core) subsamples. Four-hundred grams of whole apple and flesh was separately macerated in 300 ml of acetonitrile, and 80 g of peel was macerated in 150 ml of acetonitrile with a Polytron Homogenizer (Brinkman Instruments Ltd., Model PT-10-35) with a PT 20 ST sawtooth generator for 2 min. Each homogenate (200 g) was mixed with 10 g of Celite and filtered. The filter cake was rinsed with acetonitrile and the rinse was added to the filtrate. The combined filtrate was mixed with 1.5 l. of water and extracted three times with 150 ml of benzene. The benzene

extracts were combined, washed three times with 100 ml of water, dried over 100 g of Na_2SO_4, concentrated in a vacuum evaporator to 25 ml, and analyzed.

Apple extracts were cleaned up for gas chromatographic analyses (GLC) by the thin-layer chromatographic technique (TLC) of Morley and Chiba (1964) with minor modifications. Each concentrated extract, equivalent to 5 g of fresh sample, was streaked on a 5 × 10 cm precoated TLC sheet (Eastman Chromagram sheet, 13181 silica gel, No. 6060) and developed in a small tank with 2% acetone in hexane. After drying, the sheet was developed in the same direction with 10% acetone in hexane. A narrow strip which included the captafol band (R_f 0.45) was cut from the sheet and extracted with 10 ml of benzene in a 20-ml vial. This extract permitted gas chromatographic analysis without interference. The TLC procedure was completed within 1 h to avoid captafol degradation on the sheet.

Gas Chromatography. A Varian Model 600 D, equipped with a tritium electron capture detector, was operated as follows: temperature—column 205 °C, detector 215 °C, injector 220 °C; flow rate, 31 ml/min of high purity nitrogen. Two glass columns (90 × 0.32 cm) were used. One, packed with 5% QF-1 on 60/80 mesh Gas-Chrom Q, had a retention time of 2.5 min for recrystallized captafol (Chevron Chemical Co.) and a relative retention to aldrin of 7.6 under the above conditions. The corresponding figures for the other column, packed with 3% OV-3 on 80/100 mesh Gas-Chrom Q, were 3.4 min and 3.7, respectively. All solvents were of high purity and glass-distilled.

RESULTS AND DISCUSSION

GLC and TLC Techniques. Both QF-1 and OV-3 worked well as the stationary phase for gas chromatographic analysis. The QF-1 column was slightly less sensitive, but more stable than the OV-3 column. In the past, XE-60, a much more polar stationary phase (Baker and Flaherty, 1972), and Dow-11, a nonpolar phase (Kilgore and White, 1967), were both satisfactory for captafol analyses.

The cleanup of fruit extracts was essential because the coextractives masked captafol residues below 0.03 μg/g. Kilgore and White (1967) recommended a modified charcoal–Attaclay procedure for cleanup, because ordinary column cleanup techniques using charcoal, Florisil, silicic acid, and alumina gave low recoveries. The TLC cleanup method used here, however, is rapid, simple, inexpensive, and effective. The strongest interfering coextractive with a retention time very close to captafol on both the QF-1 and OV-3 columns had an R_f of 0.85 on the TLC sheet. As the R_f value for captafol was 0.45, the separation was excellent. Indeed this procedure may prove very useful for analyses of captafol residues on different crops. However, the whole cleanup procedure should be completed within 1 h, as captafol decomposes appreciably if kept on the sheet for more than 2 h. The recoveries of captafol from fortified apples at 0.03 μg/g ranged from 87 to 97%.

Recovery Tests with Fortified Samples. Recoveries of captafol from fortified wood, leaf, and water samples were more than 98% in all cases after two successive extractions with benzene. Several workers have used benzene for captafol extraction by swirling (Pereira et al., 1974) or by shaking (Dubin and English, 1974), but no recovery data are given. Kilgore and White (1967) also used benzene, but with a rolling technique and reported an average recovery of 93% from fortified fruit samples. Baker and Flaherty (1972) used acetonitrile and a mechanical blending technique with recoveries ranging from 87 to 93%. Chiba and Morley (1968) reported that although recoveries of fortified dieldrin from soil samples ranged from 91 to 97% with five solvent systems, recoveries from weathered samples were much lower, and ranged from 36 to 67%. Therefore, the extraction efficiencies of naturally weathered samples were examined.

Table I. Percent Recoveries of Weathered Captafol Deposits from Wood and Leaf Samples by Ultrasonic and Tumbling Methods Using the Successive Extraction Technique

Success. extractn	Wood		Leaves/ tumbling
	Ultrasonic	Tumbling	
1	99.43 ± 0.26[a]	98.96 ± 0.36[a]	90.99 ± 5.07[a]
2	0.40 ± 0.11	0.77 ± 0.26	6.08 ± 3.81
3	0.09 ± 0.09	0.19 ± 0.05	2.93 ± 2.15
4	0.08 ± 0.07	0.09 ± 0.03	
5	0.01 ± 0	0.01 ± 0	
Total	100.01	100.02	100.00

[a] Mean recovery of three replicates and standard deviation, respectively.

Successive Extractions with Weathered Samples. Table I shows that both ultrasonic and tumbling procedures with benzene extracted practically all the residues from weathered wood in the first extraction and that there was little difference between the two methods. Although the tumbling procedure was the slower, it was chosen as the standard method for the full experiment because of its relative quietness.

Three sequential extractions of captafol from weathered wood in benzene with Na_2SO_4, acetone–benzene (1:9), and acetone–benzene (1:1) by the tumbling method gave better than 98% recovery with the first extraction and complete recovery with the second extraction. Since the three solvent systems were equally effective, benzene–Na_2SO_4 was chosen for the full experiment because it gave the least interference in gas chromatographic analyses.

The average recovery of captafol from weathered leaf deposits with the first two extractions was 97.1% (Table I), which showed that captafol deposits weathered for 29 days were readily recovered from wood and leaves. This contrasts sharply with the poor recovery of weathered pesticides from soil (Chiba and Morley, 1968).

Dissipation of Captafol Residues on Wood and Leaves. To facilitate a comparison of captafol residues with their biological activities, the residues were first calculated as usual on a weight/weight basis (μg/g), and then converted to surface deposits (μg/cm^2) from a knowledge of the weight–surface relationship for wood and leaves. The surface area of a 400-g wood sample was determined by carefully peeling the bark and measuring its width and length. The surface area/weight relationship of leaves was determined by weighing 100 leaf disks each with a combined upper and lower surface area of 10 cm^2. The conversion rates for wood and leaves were 5.4 and 100 cm^2/g, respectively.

The initial captafol deposits on wood were 126 and 128 μg/cm^2 at heights of 1.5 and 3.0 m in the tree canopy (Figure 1). During the ensuing 29 days there was 93 mm of rain and the residues declined to 76 and 83 μg/cm^2 at the two levels, respectively. Thereafter, captafol dissipation was appreciably slower at 1.5 m than at 3.0 m resulting in harvest residues of 35.9 and 2.1 μg/cm^2, respectively, but showed no direct relationship to the amount of rainfall. The slower net dissipation of captafol at 1.5 m than at 3.0 m was probably due to redistribution of

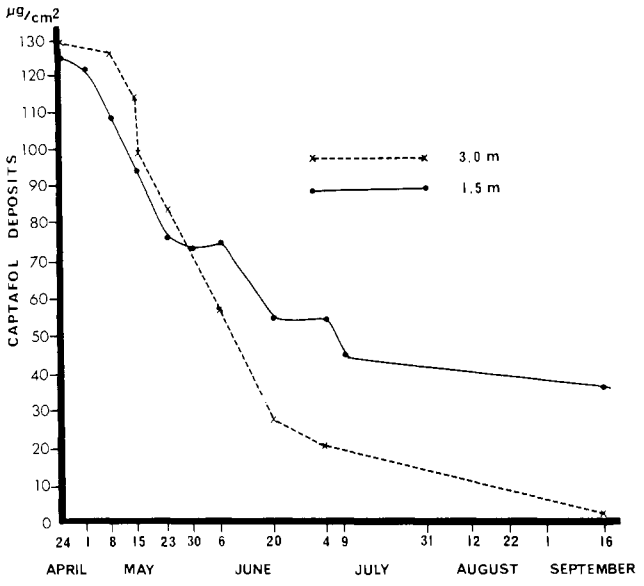

Figure 1. Seasonal dissipation of captafol residues on wood at 1.5 and 3.0 m.

Table II. Dissipation of Captafol Deposits on Leaves ($\mu g/cm^2$) at 1.5 and 3.0 m

Date	1.5 m	3.0 m	Types of leaves
May 1	6.40		Cluster leaves
May 8	3.20	4.97	Cluster leaves
May 15	1.06	1.15	Mixture of cluster and axillary leaves
May 23	0.56	0.64	Mixture of cluster and axillary leaves
May 30	0.22		Mixture of cluster and axillary leaves
June 6	0.98	0.47	Cluster leaves
	0.15	0.091	Axillary leaves
July 4	0.79	0.39	Cluster leaves
	0.068	0.048	Axillary leaves
Sept 16	0.18	ND[a]	Cluster leaves
	ND	ND	Terminal leaves

[a] Not detectable at 0.005-ppm level.

captafol from higher parts of the canopy. These values tended to be higher than those observed on large trees (Gilpatrick et al., 1971).

On May 1, 7 days after the trees were sprayed, the captafol residue on cluster leaves at 1.5 m was 6.4 $\mu g/cm^2$. It declined to 0.98 $\mu g/cm^2$ after 43 days (June 6) and to 0.18 $\mu g/cm^2$ after 145 days (Sept 16) (Table II). At 3.0 m, the early season residues on cluster leaves were similar to those at 1.5 m, but during June and July they declined more rapidly and were not detectable at harvest.

The residues on axillary leaves in June were appreciably lower than those on cluster leaves (Table II). This difference was because the axillary leaves developed after spray application and acquired captafol only by redistribution. In contrast, the tips of several cluster leaves in each floral bud were partially exposed when captafol was applied resulting in residues higher than those acquired through redistribution.

Redistribution of Captafol. The rainwater, collected under the canopies of captafol-sprayed trees during a 4-mm rainfall, May 14–15, contained captafol at a mean concentration of 0.65 $\mu g/ml$. Leaves from check trees supported within the lower canopy of captafol-treated trees acquired 0.058 $\mu g/cm^2$ of redistributed captafol. Captafol residues on wood at this time were 97 $\mu g/cm^2$ (Figure 1).

Terminal Captafol Residues Associated with Apple Fruits. Mature apples contained very low captafol residues. The concentrations of captafol in peel, whole apples, and flesh were, respectively, 0.015, 0.0062, and 0.0032 $\mu g/g$. The very low flesh residue was consistent with the activity of captafol as a nonsystemic fungicide. These residues are well below the current Canadian tolerance levels established for other edible fruits: 5 $\mu g/g$ for sweet cherries, 15 $\mu g/g$ for tomatoes, and 30 $\mu g/g$ for peaches. There is no established tolerance for captafol residues of apple fruit in Canada, but 0.25 $\mu g/g$ is established in the United States (Szkolnik, 1975).

Apple Scab Control in Relation to Captafol Deposits. In the captafol-treated plots, 5% of the terminal leaves became infected from four Mills' scab infection periods (Mills and LaPlante, 1954) during the 29-day interval (April 24–May 23) prior to petal fall. During the succeeding 28-day post-petal fall interval (May 24–June 20) there were a further four Mills' periods which caused moderate infection of 20% of terminal leaves and 6% of fruits. Scab infection in the unsprayed plots was severe with 30% terminal leaf infection before petal fall, and 65% terminal leaf and 63% fruit infection after petal fall. The protection provided by captafol was adequate in the initial 29-day interval but became inadequate by commercial standards between 29 and 57 days after captafol application.

Apple scab protection of semidwarf trees was therefore somewhat inferior to that of standard McIntosh trees (Northover, 1975) in which only 6% of foliage and 3% of fruit infection occurred during a 53-day interval. Unavoidable differences between rainfall, inoculum levels, and the number, severity, and timing of Mills' periods may also have contributed to the above difference between the two studies.

The captafol deposits on terminal leaves at 3.0 m during the post-petal fall interval were considered to have resembled those on axillary leaves at 3.0 m because of their similarity of leaf texture and tree location. Deposits of less than 0.1 $\mu g/cm^2$ were associated with inadequate scab control during the post-petal fall interval (Table II). This contrasted with deposits of 0.64–1.15 $\mu g/cm^2$ on bulked axillary and cluster leaves prior to petal fall (May 23), when scab control was adequate. The minimum deposit of captafol, redistributed under field conditions, necessary for protection against apple scab therefore appears to lie between 0.1 and 1.0 $\mu g/cm^2$ (Table II). Loss of adequate protection was associated with wood residues of less than 80 $\mu g/cm^2$ (May 23), equivalent to less than 62% of the initial surface deposit.

The faster dissipation of captafol residues on wood at 3.0 m than at 1.5 m after petal fall (May 23) (Figure 1) was associated with lower leaf residues at the higher level. This explains why apple scab developed first in the upper canopy of standard trees (Northover, 1975).

Since captafol is registered and recommended commercially on standard apple trees for protection against scab until petal fall, the present results suggest that this recommendation may also be applicable to semidwarf apple trees.

ACKNOWLEDGMENT

The authors acknowledge with appreciation the skillful technical assistance of M. G. Howard, mainly for field work, R. G. Richards for laboratory work, and C. T. Lund for data processing.

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Received for review June 1, 1976. Accepted October 4, 1976.

Binding of "Persistent" and "Nonpersistent" ^{14}C-Labeled Insecticides in an Agricultural Soil

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The extractability and formation of bound ^{14}C-labeled residues in an agricultural loam soil were investigated with the "nonpersistent" insecticides [^{14}C]methylparathion and [^{14}C]fonofos (Dyfonate) and with the "persistent" insecticides [^{14}C]dieldrin and *p,p'*-[^{14}C]DDT. With [^{14}C]methylparathion only 7% of the applied radiocarbon was extractable 28 days after soil treatment, while ^{14}C-bound residues amounted to 43% of the applied dose. With [^{14}C]fonofos, however, still 47% of the applied dose was extractable and 35% of the applied radiocarbon was bound. Only a fraction of the radiocarbon extracted from [^{14}C]methylparathion treated soil was associated with the parent compound, while extractable ^{14}C-labeled residues from the other insecticide-treated soils were primarily due to the presence of the parent compounds. Smaller amounts of soil-bound residues had been formed with the "persistent" insecticides, amounting after 28 days to only 6.5% of the applied [^{14}C]dieldrin and to 25% of the applied *p,p'*-[^{14}C]DDT, while 95 and 72%, respectively, were still recovered by organic solvent extraction. They differed from the organophosphorus compounds in their relatively low binding properties and their high extractability from soils. Contrary to results with [^{14}C]parathion, the mechanism of binding of [^{14}C]fonofos was not dependent on the presence of soil microorganisms. At higher application rates of the insecticides, relatively less radiocarbon was bound, possibly due to saturation of binding sites. Bound residues were found to be either nontoxic to fruit flies or of drastically reduced insecticidal activity. The significance of the formation of insecticide bound residues in soils in reassessing persistence of pesticides is discussed.

During the last three decades of extensive use, insecticides were referred to as either "persistent" or "nonpersistent". In most cases, those insecticide residues which could be extracted from soils or plant material by conventional methods long after they had been applied were the "visible" ones and therefore considered to be "persistent" insecticides. The use of ^{14}C-labeled insecticides, however, has made it possible to detect unextractable ^{14}C-labeled residues by combusting the insecticide contaminated material, after exhaustive extraction, to $^{14}CO_2$. The presence of these bound ^{14}C-labeled residues changed our thinking about "persistent" or "nonpersistent" insecticides, as indicated in a recent publication from our laboratory by Katan et al. (1976). They found that the total radiocarbon (extractable and bound) recovered 28 days after treatment of an agricultural loam soil with [^{14}C]parathion still amounted to 80% of the applied dose. Of this, 35% was extractable and associated with parathion and 45% was bound. It was also found that these bound residues were a product of soil microorganism activity and were primarily amino derivatives of parathion. The production of bound residues in soil was also shown with propanil (Bartha, 1971), fonofos (Flashinski and Lichtenstein, 1974b), and others.

In view of these findings, further studies were conducted in our laboratory with silt loam soil which has been used for both field and laboratory studies with a variety of insecticides during the last 18 years. To obtain additional insight into the phenomenon of extractable and bound residues, investigations were conducted with the "nonpersistent" organophosphorus insecticides, [^{14}C]-methylparathion, [^{14}C]parathion, and [^{14}C]fonofos, and the "persistent" chlorinated hydrocarbon compounds, [^{14}C]-dieldrin and *p,p'*-[^{14}C]DDT.

EXPERIMENTAL SECTION

Materials. [*ring*-^{14}C]Methylparathion (sp act. 2.83 μCi/mg), [*ring*-^{14}C]parathion (sp act. 2 μCi/mg), and *p,p'*-[*ring*-^{14}C]DDT (sp act. 2.09 μCi/mg) were purchased from Amersham-Searle, [*ring*-^{14}C]fonofos (Dyfonate) (sp act. 1.78 μCi/mg) and [*ethoxy*-^{14}C]fonofos (sp act. 1.74 μCi/mg) were obtained from the Stauffer Chemical Company, and [^{14}C]dieldrin (labeled in all positions adjacent to chlorines) (sp act. 2.95 μCi/mg) was obtained from the Shell Development Company. The radiopurity of these insecticides was at least 99% after purification by thin-layer chromatography. A small amount of [^{14}C]DDE was isolated from the originally supplied

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