priming was necessary to obtain a stable response, and similar responses were obtained with the reference standards prepared in pure ethyl acetate or in cleaned sample extracts.

The extraction efficiency of the described method for weathered field samples was evaluated. Aliquots of corn tissues collected from plots treated with bendiocarb at 2.5 kg of a.i./ha were extracted separately by the following methods: (1) blending with ethyl acetate as described herein, (2) refluxing with hydrochloric acid (Cook et al., 1969; Robinson, 1982), and (3) refluxing with dichloromethane (Whiteoak et al., 1978). Bendiocarb residues detected by methods 2 and 3 were about 60% of those detected by method 1, indicating that the described method is more effective for extracting bendiocarb from weathered field samples than previous proposed methods. Moreover the ethyl acetate extracts contained less coextractives than the acid extracts.

The Abbotsford silt loam was chosen for recovery study because it is similar to the sandy silt loam in the experimental plots at Agassiz. Percentage recoveries for fortified corn tissues and soil are presented in Table I. Each mean percentage with its standard deviation was derived from four replicates. The mean recoveries of bendiocarb ranged from 86.7 to 98.1% for both corn tissues and soil. Since 0.3 ng of bendiocarb gives about 30% full-scale delfection at 10 × 1 attenuation and the cleaned extracts can be concentrated to 0.5 mL for GLC analysis, the limit of detection of the described method may well be below 0.01 ppm for corn tissues and soil.

Residues in Corn Tissues. Bendiocarb residues detected in various corn tissues are given in Table II. Only small amounts of residues (<0.05 ppm) were found; thus, very little bendiocarb was accumulated in corn after soil treatment with this chemical. The residue concentration in leaves plus stems, husks, and cobs correlated with the rate of soil treatment with bendiocarb. After soil application of bendiocarb at the higher rate, i.e., 2.5 kg of a.i./ha, significantly higher concentrations of residue were found in those tissues ($P = 0.05$). However, there was no significant difference in residues accumulated in kernels after soil application of bendiocarb at 1.7 or 2.5 kg of a.i./ha. The addition of Eradicane in the soil treatments appeared to have no significant effect on the accumulation of bendiocarb in various corn tissues ($P = 0.05$). When soil treatments with bendiocarb were at the same rate, there was no difference in residues in various corn tissues whether or not the herbicide, Eradicane, was included in the soil treatments. Taking into consideration all four treatments of soil in this study, there was a significant difference in residue concentrations in various corn tissues ($P = 0.05$). They were in the order of kernels < cobs and husks < leaves plus stems. There was no significant difference between cobs and husks.

Registry No. Bendiocarb, 22781-23-3; Eradicane, 51990-04-6.

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Leaf, Fruit, and Soil Surface Residues of Carbosulfan and Its Metabolites in Florida Citrus Groves

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Carbosulfan was applied to a Florida orange grove in the fall of 1981 and again 3 months later at one-fourth the fall rate. Dissipation was rapid from fruit and leaf surfaces in each experiment but was significantly more rapid during the fall than in winter. Persistence of carbosulfan along the soil dripline exceeded that on fruit or leaf surfaces in each experiment. Very little carbosulfan was detected midway between trees. The major observed metabolite of carbosulfan was carbofuran. In each experiment, carbofuran was more persistent on leaf surfaces than the parent compound. Safe worker reentry intervals, estimated from toxicity studies on rats, were determined to be 3 days for the fall application rate of 4 lb of a.i./acre and 1–2 days for the winter rate of 1 lb of a.i./acre.

Carbosulfan (CS) [2,3-dihydro-2,2-dimethyl-7-benzofuranyl [(di-*n*-butylamino)thio]methylcarbamate] is a derivative of carbofuran (CF) and a candidate broad-spectrum pesticide for Florida citrus. Degradation of CS has been studied in soil (Clay et al., 1980) and plants (Umetsu et al., 1979). Principal metabolites reported were CF, 3-hydroxycarbofuran, and 3-ketocarbofuran. CS has an oral LD_{50} of 209 mg/kg (rat) vs. 11 mg/kg (rat) for CF ("Farm Chemicals Handbook", 1982). The safe reentry of harvesters into pesticide-treated fields requires an understanding of the environmental behavior of toxic compounds and their metabolites. This study was undertaken

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to determine standard-usage levels and disappearance rates of CS and its principal metabolites for worker reentry purposes.

EXPERIMENTAL SECTION

Application and Plots. A mature Valencia orange grove owned by the University of Florida was used for both experiments. Tree spacing was 25 × 25 ft or 70 trees/acre. Trees were approximately 12 ft high. This grove was in excellent horticultural condition and its treatment with pesticides was under the strict control of the authors.

The pesticide applied was FMC 35001 (brand name, Advantage), whose active ingredient is carbosulfan. Treatment began on Aug 20, 1981. Four pounds of CS a.i. per acre was applied as the 2.5 emulsifiable concentrate with an air-blast sprayer to four 0.75-acre random plots. This application was made in order that the entire experiment match the grower practice of three applications annually but was not sampled. Four random control plots were left unsprayed.

On Sept 21, 1981, the same sprayed plots were resprayed with the same machine and rate of CS. One hour prior to this second application (experiment 1) and for 35 days thereafter, samples of fruit, leaves, and soil were taken and analyzed for CS, CF, 3-hydroxycarbofuran, and 3-ketocarbofuran. Experiment 2 was begun on Dec 29, 1981, and also extended over a 35-day period; the same plots were used except that the application rate was reduced to 1 lb of CS a.i./acre. Volume per acre for all applications was 750 gal.

Sampling. Forty circular, 1 in. diameter, random leaf punches were taken from each plot and 10 fruit were clipped into 3.5-gal pickle jars on each sampling day. Soil samples were taken at the dripline and also midway between trees by vacuuming soil from each plot through a 40-mesh screen. Soil samples were not random in that a pattern of sampling was followed that avoided resampling the same area of soil. These sampling methods have been described in detail (Iwata et al., 1977; Spencer et al., 1977). Samples were returned on ice to the laboratory and processed immediately. None of the field samples was stored.

Extraction. *Fruit.* Ten oranges were tumbled in their collection jar for 10 min with 100 mL of Surten–phosphate buffer detergent (0.01 M, pH 8.0). Surten is the ICN (Plainview, NY) name for a 70% solution of sodium dioctyl sulfosuccinate. The Surten solution was 2 mL of a 1:25 dilution of the 70% solution in 1000 mL of sodium phosphate buffer. The Surten solution was decanted to a separatory funnel and the fruit tumbled for an additional 10 min in 100 mL of Surten–buffer solution. The second wash was combined with the first, 60 g of NaCl was added to the separatory funnel, and the combined washes were extracted 3× with 100 mL of methylene chloride. One or two milliliters of 4% w/v sodium lauryl sulfate was added to break emulsions.

Each 100 mL of extract was filtered through a Whatman No. 1 filter containing sodium sulfate. The combined extracts (3 × 100 mL) were taken almost to dryness on a rotary evaporator at 40 °C and brought up in 10 mL of ethyl acetate for GLC analysis.

Leaves. Each leaf disk sample was shaken 2× with 40 mL of Surten–phosphate buffer (0.01 M, pH 8.0) at 200 cpm for 10 min. The Surten washes were combined in a separatory funnel, 30 g of NaCl was added, and the washes were extracted 3× with 50 mL of methylene chloride. One or two milliliters of 4% w/v sodium lauryl sulfate was added to break emulsions. The combined extracts were taken almost to dryness on a rotary evaporator at 40 °C and transferred to 10 mL of ethyl acetate of GLC analysis.

Table I. Recoveries of Carbosulfan (CS) and Metabolites from Fortified Samples

compound	substratum	fortification	% recovery
carbosulfan	leaf and fruit	50 μg (0.125 μg/cm², leaf; 0.025 μg/cm² fruit)	68 ± 5[a]
carbofuran	leaf and fruit	50 μg	61 ± 4
3-OH	leaf and fruit	50 μg	71 ± 5
3-keto	leaf and fruit	50 μg	64 ± 4
carbosulfan	soil	1 ppm	82 ± 4
carbofuran	soil	1 ppm	84 ± 3
3-OH	soil	1 ppm	88 ± 3
3-keto	soil	1 ppm	87 ± 2

[a] Mean of four replications ± standard error of the mean.

Soil. Ten grams of each soil sample was weighed into a 100-mL beaker immediately upon return to the laboratory. Fifty milliliters of methanol was added and each sample was sonicated at 15 000 kHz for 30 s. Sonicated samples were covered with foil, the sediment was allowed to settle for 20 min, and a 30-mL aliquot was taken. This aliquot was reduced to dryness on an N_2 evaporator at 40 °C in a brown sample bottle, and 10 mL of ethyl acetate was added for GLC analysis.

Processed samples were stored at −20 °C in ethyl acetate.

Gas–Liquid Chromatography. GLC was performed as per Greenhalgh and Belanger (1981) on a Hewlett-Packard 5730A equipped with a nitrogen–phosphorus detector and a 1.8 m × 2 mm silanized glass column packed with 4% SE-30/6% SP 2401 on 100/120 Supelcoport.

Operating conditions were as follows: injection port 200 °C; detector 300 °C; N_2 50 mL/min; H_2 4 mL/min; air 60 mL/min. A temperature program of 190 °C (2-min hold), 4 °C/min, final temperature 210 °C (4-min hold), separated CF and CS. 3-Hydroxy- and 3-ketocarbofuran were not base line separated but separated well enough for quantitative estimation.

The temperature program was varied slightly, depending upon the condition of each column. For instance, a column might initially be programmed for 180 to 210 °C with an 8-min final hold. With use, each column became more sensitive and retention times changed slightly. A change of about 30 s in the retention of CS allowed a reduction in the final hold. Standards were chromatographed after every three samples. Quantification of samples was by comparison with peak heights of standards.

On the basis of GLC detection limits of approximately 50 pg for CS and CF and 250 pg for 3-hydroxy- and 3-ketocarbofuran, limits for quantification were approximately 0.001 μg/cm² for leaves and 0.0003 μg/cm² for fruit (CS and CF), 0.005 μg/cm² for leaves and 0.001 μg/cm² for fruit (3-hydroxy- and 3-ketocarbofuran), 0.01 ppm for soil (CS and CF), and 0.05 ppm for soil (3-hydroxy- and 3-ketocarbofuran).

Recoveries of CS and metabolites from fortified Surten washes and soil are listed in Table I; values reported in the tables that follow have been corrected for recoveries. Because the spray application covered both sides of the leaf and both sides of leaves were extracted, residue values were calculated by using the combined areas of the upper and lower leaf surfaces.

Analytical standards of CS (94.2% pure), CF (99.6%), 3-hydroxycarbofuran (99%), and 3-ketocarbofuran (99%) were provided by Dr. Jack Graham, FMC Corp., Princeton, NJ.

Calculation of Reentry Interval. Reentry intervals for 4 and 1 lb of a.i./acre application rates in experiments

Table II. Surface Concentration of Carbosulfan (CS): Experiment 1

day	fruit, μg/cm²	leaf, μg/cm²	soil dripline, ppm	soil midline, ppm
1	0.759[a] ± 0.306[b]	0.782 ± 0.266	0.81 ± 0.28	0.05 ± 0.01
2	0.387 ± 0.040	0.288 ± 0.037	1.56 ± 0.77	0.03 ± 0.01
3	0.209 ± 0.029	0.194 ± 0.066	0.33 ± 0.19	0.01 ± 0.01
7	0.082 ± 0.007	0.044 ± 0.010	0.49 ± 0.33	ND
14	0.006 ± 0.001	0.004 ± 0.003	0.10 ± 0.10	ND
21	0.001 ± 0.000 (3)	ND[c]	0.11 ± 0.11	0.20 ± 0.12
29	0.001 ± 0.000 (6)	ND	ND	ND
35	0.000 (6) ± 0.000 (4)	0.000 (6) ± 0.000 (6)	ND	ND

First-Order Half-Lives, Dissipation Rate Constants (k), and Correlation Coefficients (R)

	fruit	leaf	soil dripline	soil midline
half-life, day	2.0 ± 0.1[d]	1.8 ± 0.1	4.2 ± 1.4	0.8 ± 0.2
k, day^{-1}	0.35 ± 0.02	0.38 ± 0.03	0.17 ± 0.06	0.86 ± 0.26
R	0.99	0.99	0.86	0.96
n	5[e]	5	5	3

[a] Mean of four replications. [b] Standard error of the mean. [c] ND = not detected. [d] Root mean square error. [e] Number of data points.

Table III. Surface Concentration of Carbofuran (CF): Experiment 1

day	fruit, μg/cm²	leaf, μg/cm²	soil dripline, ppm	soil midline, ppm
1	0.096[a] ± 0.019[b]	0.042 ± 0.015	0.19 ± 0.05	0.10 ± 0.01
2	0.100 ± 0.020	0.041 ± 0.006	0.86 ± 0.11	0.29 ± 0.08
3	0.064 ± 0.010	0.029 ± 0.008	0.47 ± 0.15	0.24 ± 0.06
7	0.075 ± 0.002	0.014 ± 0.002	1.32 ± 0.96	0.32 ± 0.11
14	0.043 ± 0.009	0.004 ± 0.001	0.65 ± 0.27	0.06 ± 0.06
21	0.013 ± 0.002	0.001 ± 0.000 (7)	0.80 ± 0.32	0.24 ± 0.05
29	0.041 ± 0.017	0.001 ± 0.000 (8)	1.42 ± 0.28	0.12 ± 0.06
35	0.041 ± 0.017	0.002 ± 0.000 (5)	trace	ND[c]

[a] Mean of four replications. [b] Standard error of the mean. [c] ND = not detected.

1 and 2 were calculated according to each of two procedures used by Iwata et al. (1983). They derive from recognizing that the total toxic dose received from a mixture of toxic compounds depends on the proportion and toxicity of each individual compound in the mixture. In the first procedure, the safe levels developed by Iwata et al. (1983) for CS and CF were used in conjunction with dislodgeable residue data from experiments 1 and 2 to determine a safe reentry period for total carbamate residues. In the second procedure a modification of the method proposed by the U.S. Environmental Protection Agency (1981), using ED_{10} values for CS and CF from dermal dose–ChE response studies on rats, was used to calculate an allowable exposure level (AEL) in μg kg^{-1} day^{-1} for rats, followed by a total allowable dermal dose in μg/h for humans. From the total allowable dose, a reentry level was obtained from a graph of dose (μg/h) vs. dislodgeable foliar residues (μg/cm²) from data of Popendorf and Leffingwell (1982).

RESULTS AND DISCUSSION

Experiment 1. The unsprayed control plots were uniformly negative for CS and its metabolites as were samples obtained from experimental plots just prior to the spray application.

Table II presents experiment 1 data for CS. The fruit and leaf data were essentially the same for levels and rate of disappearance. First-order half-lives through day 14 were 2.0 days (fruit), 1.8 days (leaves), 4.2 days (soil dripline), and 0.8 days (soil midline). Clay et al., (1980) reported a half-life of about 3 days for CS in Cosad sandy loam. For all practical purposes CS had disappeared between days 7 and 14.

Table III presents the CF data for experiment 1. CF reached about 2.5× the level on fruit as on leaves and disappeared less rapidly. The fruit data were irregular and the individual means contained rather large standard errors. If a first-order analysis is performed on the CF leaf data during days 2–14 (when decay occurs), the results are R = 0.99, k = 0.19 ± 0.01 day^{-1}, and half-life = 3.7 ± 0.2 day. CF was more persistent than CS on leaves, as is normally the case for metabolite vs. parent. Soil data for CF show slower dissipation compared to that of leaves and fruit. Since CS was applied to leaves, fruit, and soil, transfer of CS and CF to soil would be expected. Any such transfer would increase the apparent CF level and decrease the disappearance rate. Dripline data for soil CF indicates the most persistence; the greatest potential for transfer to soil and leaves would occur at the dripline. The structure of the soil midline and soil dripline data for CF is similar

Table IV. Surface Concentration of 3-Hydroxy- and 3-Ketocarbofuran: Experiment 1

day	fruit, μg/cm²	leaf, μg/cm²	soil dripline, ppm	soil midline, ppm
	3-Hydroxycarbofuran			
1	trace	ND[c]	ND	ND
2	trace	ND	ND	ND
3	ND	ND	ND	ND
7	ND	trace	ND	ND
14	0.004[a] ± 0.002[b]	ND	ND	ND
21	0.000 (7) ± 0.000 (4)	ND	ND	ND
29	trace	trace	ND	ND
35	ND	ND	ND	ND
	3-Ketocarbofuran			
1	trace	ND	ND	0.14 ± 0.13
2	0.000 (5) ± 0.000 (5)	ND	ND	ND
3	0.000 (6) ± 0.000 (6)	ND	ND	ND
7	trace	trace	ND	ND
14	trace	ND	ND	ND
21	0.000 (8) ± 0.000 (5)	ND	ND	ND
29	trace	ND	ND	ND
35	0.000 (2) ± 0.000 (2)	ND	ND	ND

[a] Mean of four replications. [b] Standard error of the mean. [c] ND = not detected.

Table V. Surface Concentration of Carbosulfan (CS): Experiment 2

day	fruit, μg/cm²	leaf, μg/cm²	soil dripline, ppm	soil midline, ppm
1	0.243[a] ± 0.056[b]	0.243 ± 0.021	0.65 ± 0.24	ND
2	0.193 ± 0.026	0.165 ± 0.029	1.29 ± 0.68	ND
3	0.199 ± 0.041	0.157 ± 0.009	0.41 ± 0.13	0.06 ± 0.06
8	0.103 ± 0.024	0.022 ± 0.004	0.33 ± 0.11	ND
14	0.026 ± 0.009	0.006 ± 0.004	0.18 ± 0.04	ND
21	0.013 ± 0.004	0.001 ± 0.001	ND	ND
28	0.001 ± 0.000 (9)	ND[c]	ND	ND
35	trace	ND	ND	ND

First-Order Half-Lives, Dissipation Rate Constants (k), and Correlation Coefficients (R)

	fruit	leaf	soil dripline	soil midline
half-life, day	4.2 ± 0.4[d]	2.4 ± 0.2	5.9 ± 2.0	
k, day^{-1}	0.17 ± 0.02	0.29 ± 0.02	0.12 ± 0.04	
R	0.98	0.99	0.86	
n	5[e]	5	5	

[a] Mean of four replications. [b] Standard error of the mean. [c] ND = not detected. [d] Root mean square error. [e] Number of data points.

Table VI. Surface Concentration of Carbofuran (CF): Experiment 2

day	fruit, μg/cm²	leaf, μg/cm²	soil dripline, ppm	soil midline, ppm
1	0.041[a] ± 0.007[b]	0.013 ± 0.002	1.38 ± 0.13	0.49 ± 0.17
2	0.044 ± 0.003	0.025 ± 0.002	1.03 ± 0.25	0.63 ± 0.10
3	0.069 ± 0.010	0.034 ± 0.003	0.32 ± 0.04	0.23 ± 0.02
8	0.036 ± 0.005	0.007 ± 0.000 (8)	0.46 ± 0.28	0.12 ± 0.09
14	0.090 ± 0.028	0.003 ± 0.002	0.56 ± 0.10	0.16 ± 0.03
21	0.039 ± 0.010	0.002 ± 0.000 (2)	ND[c]	ND
28	0.005 ± 0.003	ND	trace	ND
35	0.005 ± 0.002	ND	trace	ND

[a] Mean of four replications. [b] Standard error of the mean. [c] ND = not detected.

in that a local maximum is reached on day 7. With the soil dripline data, however, this local maximum is exceeded on day 29. This irregularity in the CF soil dripline data may be due to variation in runoff and transfer at the dripline. After 35 days CF was barely detectable on the soil surface.

Table IV presents the 3-hydroxycarbofuran and 3-ketocarbofuran data for Experiment 1. These two metabolites were generally below detection limits on leaves and soil. Fruit had low and uncertain levels of each metabolite.

Experiment 2. Control plots were uniformly negative for CS and its metabolites as well as for samples obtained from the experimental plots just prior to this experiment.

Table V presents experiment 2 data for CS. As with experiment 1, fruit and leaf residue levels were essentially the same, with the dissipation rate somewhat larger for leaves. The first-order half-lives through day 14 were 4.2 days (fruit), 2.4 days (leaves), and 5.9 days (soil dripline). Soil midline levels were essentially zero. CS had virtually disappeared between day 14 and day 28 postapplication.

CF (Table VI) fruit data were again too irregular to analyze for growth or dissipation rates. Fruit surface levels of CF were again higher and persisted longer than leaf surface levels. If a first-order analysis is performed on the leaf data during days 3–14, the results are $R = 0.97$, $k = 0.22 \pm 0.05$ day^{-1}, and half-life = 3.2 ± 0.7 day. This decay is significantly slower than CS on leaves, as was the case in experiment 1.

Only unquantificable trace amounts of 3-hydroxycarbofuran and 3-ketocarbofuran were found on fruit during experiment 2 and none at all on leaves or soil.

Experiment 1 vs. Experiment 2. Table VII presents a comparison between experiment 1 and 2 dissipation rates of CS on fruit, leaves, and the soil dripline. Dissipation of CS was significantly more rapid in experiment 1 on leaves and fruit and marginally so along the dripline.

Table VII. Comparison between Experiment 1 and Experiment 2 of Carbosulfan Dissipation Rate Constants (Day^{-1}) through Day 14

surface	k_1 (expt 1)	k_2 (expt 2)	k_1/k_2	conf level that $k_1 > k_2$, %
fruit	0.35 ± 0.02	0.17 ± 0.02	2.11 ± 0.26	99.9
leaves	0.38 ± 0.03	0.29 ± 0.02	1.30 ± 0.14	98.4
soil dripline	0.17 ± 0.06	0.12 ± 0.04	1.40 ± 0.68	72.2

CF dissipation on leaves, however, was essentially the same in the two experiments. The level of CF on leaves and fruit peaked faster in experiment 1 (ca. day 1.5) than in experiment 2 (day 3), but the maximum levels reached were about the same. CF persisted longer along the soil dripline in experiment 1.

Any explanation of observed differnces between experiments 1 and 2 by using the weather data in Tables VIII and IX is questionable on the basis of only two experiments. However, CS disappearance may be enhanced by the hotter and wetter weather conditions prevailing during experiment 1.

Reentry Intervals. Iwata et al. (1983) determined a safe dislodgeable foliar level for CS and CF from dermal dose–ChE response studies conducted on rats. The level for each carbamate was 0.3 μg/cm² of leaf surface. Because CS was as toxic as CF, the safe level for the combined residue was 0.3 μg/cm². Table X indicates that total carbamate residues for experiment 1 are at a safe reentry level 3 days after application of CS at 4 lb of a.i./acre, while the residues in experiment 2 are at a safe reentry level 1 day after the application of 1 lb of a.i./acre.

Table XI indicates that safe reentry levels are reached in these experiments on days 3 and 2, respectively. The

Table VIII. Temperature (°F)

date	max	min	date	max	min
		Experiment 1			
9-21-81	92	72	10-9-81	99	69
9-22-81	90	71	10-10-81	98	69
9-23-81	96	67	10-11-81	97	71
9-24-81	96	65	10-12-81	91	68
9-25-81	97	69	10-13-81	89	64
9-26-81	93	69	10-14-81	86	66
9-27-81	94	65	10-15-81	85	64
9-28-81	90	66	10-16-81	89	51
9-29-81	95	68	10-17-81	90	51
9-30-81	95	66	10-18-81	91	57
10-1-81	98	69	10-19-81	86	59
10-2-81	98	62	10-20-81	88	49
10-3-81	98	65	10-21-81	87	56
10-4-81	97	68	10-22-81	90	65
10-5-81	95	64	10-23-81	97	62
10-6-81	99	58	10-24-81	91	64
10-7-81	98	64	10-25-81	82	67
10-8-81	98	63	10-26-81	93	65
		Experiment 2			
12-29-81	87	60	1-16-82	70	26
12-30-81	78	60	1-17-82	75	44
12-31-81	85	65	1-18-82	81	39
1-1-82	80	62	1-19-82	80	42
1-2-82	83	62	1-20-82	80	45
1-3-82	81	65	1-21-82	82	48
1-4-82	81	61	1-22-82	81	50
1-5-82	69	39	1-23-82	82	50
1-6-82	83	46	1-24-82	84	62
1-7-82	86	53	1-25-82	68	40
1-8-82	77	53	1-26-82	75	41
1-9-82	70	40	1-27-82	65	36
1-10-82	63	34	1-28-82	66	38
1-11-82	50	33	1-29-82	73	43
1-12-82	63	17	1-30-82	76	47
1-13-82	62	41	1-31-82	79	48
1-14-82	70	36	2-1-82	86	61
1-15-82	59	25			

Table IX. Rainfall, Humidity, and Solar Radiation

day	cumulative rainfall, in.	cumulative h at 90%+ rel humidity	cumulative solar radiation, cal/cm²
		Experiment 1	
0	0	7.0	359.1
1	0.58	21.0	793.8
2	0.58	34.0	1152.9
3	0.58	46.0	1682.1
7	0.58	105.0	3515.4
14	0.58	175.0	6066.9
21	0.64	259.5	8883.0
29	0.64	341.5	11718.0
35	4.39	437.0	14042.7
		Experiment 2	
0	0	13.0	359.1
1	0	20.0	680.4
2	0	20.5	945.0
3	0	26.5	1209.6
8	0.35	74.0	2570.4
14	0.35	125.5	4347.0
21	1.70	225.0	6123.6
28	2.00	320.0	8089.2
35	2.08	395.0	9941.4

Table X. Reentry Levels and Intervals for Total Carbamate Residues on Leaves

days after spraying	dislodgeable foliar residues, μg/cm² [a] carbosulfan (CS)	carbofuran (CF)	total carbamates (CS + CF)	reentry level, μg/cm², [b] total carbamates
		Experiment 1		
1	0.782	0.042	0.824	0.3
2	0.288	0.041	0.329	0.3
3	0.194	0.029	0.223	0.3[c]
		Experiment 2		
1	0.243	0.013	0.256	0.3[c]
2	0.165	0.025	0.190	0.3
3	0.157	0.034	0.191	0.3

[a] Values from Tables II, III, V, and VI. [b] Safe reentry level is 0.3 μg/cm² for CS, CF, and total carbamates (CS + CF) according to Iwata et al. (1983). [c] Reentry interval is 3 days for experiment 1 and 1 day for experiment 2.

Table XI. Calculation of Reentry Intervals according to U.S. Environmental Protection Agency (1981) Guidlines[a]

days after spraying	compound ratio,[b] CS:CF	NOEL,[c] μg kg⁻¹ day⁻¹	AEL,[d] μg kg⁻¹ day⁻¹	total allowable CS + CF dose,[e] μg/h	CS + CF reentry level,[f] μg/cm²
		Experiment 1			
1	18.6:1	1198	120	1050	0.21
2	7.0:1	1131	113	989	0.19
3[g]	6.7:1	1127	113	989	0.19
		Experiment 2			
1	18.7:1	1199	120	1050	0.21
2[g]	6.6:1	1125	113	989	0.19
3	4.6:1	1087	109	954	0.19

[a] A slight modification of these guidelines is introduced here that takes into account all toxic residues present on the foliage. [b] Ratios calculated from values in Tables II, III, V, and VI. [c] No effect level (NOEL) calculated from data from dermal dose-ChE response curve (Iwata et al., 1983). NOEL = ED_{10}(25 cm²)/(0.23 kg). Effective ED_{10} for mixture from $1/ED_{10} = P_1/ED_{10,2} + \cdots + P_N/ED_{10,N}$, where P_i = proportion of component i in the mixture (Finney, 1972). $ED_{10,i}$ values were extrapolated from Figure 6, Iwata et al. (1983), and found to be 11.5 and 6.24 μg cm⁻² day⁻¹ for CS and CF, respectively. [d] Allowable exposure level (AEL) = NOEL/SF. Safety factor (SF) = 10. [e] Total allowable dose = (AEL)(body weight, 70 kg)/(duration, 8 h/day). [f] From total dose the reentry level is determined from a graph of whole-body dermal dose (μg/h) vs. dislodgeable foliar residues (μg/cm²) from the data of Popendorf and Leffingwell (1982). Total dose divided by 5100 cm²/h is K_d for citrus for a one-sided dislodgeable residue. [g] Reentry interval (total carbamates from Table X) is about 3 days for experiment 1 and 2 days for experiment 2.

EPA procedure in Table XI used a safety factor of 10 and the graph of Popendorf and Leffingwell (1982) relating total allowable dose in μg/h to dislodgeable residues in μg/cm² for one-sided residues. Popendorf and Leffingwell suggest that had the residues been divided by two to become two-sided residues, unnecessarily long reentry intervals would be required by the calculated safe reentry levels. Furthermore, the safety factor of 10 employed in the calculation more than compensates. A computation of the safe reentry level is made in Table VIII for each of the first few days of both experiments for a reason. A treated field might be safely reentered very soon after spraying, when a highly toxic metabolite is at low levels and a less toxic parent is at a higher level, but cannot be safely reentered when the metabolite level has increased. That a more toxic metabolite can lead to fieldworker illnesses even with delayed reentry has been documented with the organophosphorus pesticides [for reviews, see Gunther et al. (1977) and Nigg and Stamper (1982)]. In

the case at hand, however, the proportions of parent to metabolite and their individual toxicities are such that the overall mixture presents less hazard to the worker with time, as is evidenced by the decreasing numbers for each experiment in the last column of Table XI. Finally, it might be argued that the conversion factor, K_d, used here to relate total allowable dose (μg/h) to reentry level (μg/cm2) should reflect Florida data rather than the California data of Popendorf and Leffingwell (1982). However, a repeat of the California study, conducted in Florida by two of us (Nigg et al., 1984) yielded K_d = 5300 cm^2/h, in close agreement with the California K_d of 5100 cm^2/h.

CONCLUSIONS

Application of 4 lb or 1 lb of a.i./acre CS resulted in low surface residues on citrus leaf, fruit, and soil surfaces. The 4-lb application resulted on day 1 of experiment 1 in 0.771 $\mu g/cm^2$ on leaves and fruit, while 1 lb resulted on day 1 of experiment 2 in 0.243 $\mu g/cm^2$ on leaves and fruit (see Tables II and III) or a ratio of 3.2 to 1. CS dissipated rapidly under both hot–wet (experiment 1) and cool–dry (experiment 2) condtiions but more rapidly from fruit, leaf, and soil dripline surfaces in experiment 1 than in experiment 2 (see Table VII). Persistence of CS along the soil dripline exceeded that on fruit or leaves during each experiment. The major observed metabolite of CS was CF. (Only very small levels of 3-hydroxy- and 3-ketocarbofuran were observed in both experiments.) CF dissipated less rapidly from leaves than the parent compound during each experiment.

On the basis of the data presented here, the estimated safe worker reentry interval following CS application was 3 days for experiment 1 and 1–2 days for experiment 2.

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Registry No. CS, 55285-14-8; CF, 1563-66-2; 3-hydroxycarbofuran, 16655-82-6; 3-ketocarbofuran, 16709-30-1.

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Synthesis and Biological Activity of Pyrethroids Derived from Halo-4-alkenoic Acids

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Sixty-two examples of pyrethroids derived from halo-4-alkenoic acids have been synthesized. The halo-4-alkenoic acids were prepared by a modified malonic ester synthesis or by allylation of O-silylated ketene acetals. The pyrethroids derived from halo-4-alkenoic acids bearing an alkyl group at C_3 are novel, and the crucial effect of the nature and number of alkyl substituents at C_3 on insecticidal activity of the 5,5-dihalo-4-alkenoic esters has not been reported previously. The observed enhancement of insecticidal activity upon substitution of a single methyl group at C_3 would not have been predicted from known structure/activity trends. Several of the novel esters exhibit good broad-spectrum insecticidal and some miticidal activity, but the most active of the halo-4-alkenoic esters is considerably less active, particularly on lepidopterous larvae, than commercial pyrethroids. Experiments with potential synergists failed to demonstrate that susceptibility to degradative enzymes is a probable reason for the reduced activity of the halo-4-alkenoic esters.

An important component of natural pyrethrins is chrysanthemic acid, which contains a *trans*-isobutenyl moiety at C_3 on the cyclopropane ring. This moiety is essential for high pesticidal activity, but it also limits the metabolic and photochemical stability of the pyrethrins. Insects rapidly oxidize the *trans*-methyl group of the isobutenyl moiety to the corresponding alcohols, aldehydes, and carboxylic acids with loss of insecticidal activity (Yamamoto and Casida, 1966; Yamamoto et al., 1969). The isobutenyl group also undergoes rapid photooxidation to epoxides and various hydroxy, keto, and carboxylic acid derivatives (Ueda et al., 1974; Elliott, 1977). These in-

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