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Dislodgeable Residues of Carbophenothion in Florida Citrus: Implications for Safe Worker Reentry

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Carbophenothion (S-((p-chlorophenylthio)methyl) 0,0-diethylphosphorothiolothionate) is an organophosphate insecticide used on both Florida and Brazilian citrus. An estimated 23,000 acres of Florida citrus (Griffiths et al. 1983) and 73,000 acres of Brazilian citrus (Campos et al. 1983) were sprayed with carbophenothion in 1982.

A previous study concentrated on dislodgeable residues of carbophenothion on leaves and fruit in Florida (Thompson and Brooks 1976). Nigg et al. (1978) reported dislodgeable residues of carbophenothion oxon as well as carbophenothion on orange leaves. The purpose of this study was to investigate the dislodgeable residues of carbophenothion and its oxon on both leaves and soil in the same experiment and to determime whether citrus harvesters were at apparent risk. The presence of the sulfoxide and sulfone of carbophenothion was not assessed.

MATERIALS AND METHODS

The experimental field was a mature Valencia orange grove. This grove and grove practices have been previously described (Nigg et al. 1978). Carbophenothion was applied to four random 48-tree plots at rates of 5 and 10 lb ai/acre (1X and 2X rates). The 32 inside trees received full coverage, whereas the outer 16 trees received partial coverage. Leaves and surrounding soil from only the 32 inside trees were subsequently sampled. Approximately 210 gal of spray mixture per plot or 4.4 gal per tree was applied at 200 psi with airblast equipment. Two random unsprayed plots were used as controls. All plots were buffered with two rows of trees. The first application was made on January 19, 1983. All treatments received one inch of rainfall immediately following application and an additional 0.22 inches a short time later. Carbophenothion was consequently reapplied as described above on January 24, 1983.

Leaf and soil samples were taken prior to the first application, prior to the second application (leaf only), and on days 1, 3, 5, 7, 15, 22 and 28 postapplication. In addition, a sample of the Trithion 8E (8 lb/gal carbophenothion) was taken and analyzed for carbophenothion and carbophenothion oxon.

Forty circular, 2.54 cm diameter, random leaf discs from each of the four treatment plots (replications) were excised directly into a jar. 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 which avoided resampling the same area of soil. These methods have been previously described (Nigg et al. 1984).

Leaf samples were extracted using the standard dislodgeable method (Iwata et al. 1977). Carbophenothion and its oxon were recovered from the dislodgeable washes with two 40 ml CH_2Cl_2 extractions. Twenty ml of saturated NaCl solution was added to the first extraction and liberal amounts of NaCl to the second to increase recoveries and break emulsions. The CH_2Cl_2 was filtered through 20 g of Na_2SO_4 and the Na_2SO_4 rinsed with an additional 20 ml of CH_2Cl_2. The CH_2Cl_2 was rotary evaporated to dryness at 40°C in a 250 ml boiling flask containing 4 drops of paraffin oil. Sample extracts were transfered to 10 ml volumetric flasks with three rinses of 2,2,4-trimethylpentane, made to volume, transfered to 2 oz brown bottles over about 1 g of dry Na_2SO_4, and stored at -20°C.

Soil samples were processed for gas chromatography by manually shaking the sample, weighing 10 g of soil into a 100 ml beaker, adding 2 ml of deionized water, covering with aluminum foil, and placing the sample at 4°C overnight (16-18 hr). The sample was removed from the refrigerator, 40 ml of acetone was added, and the sample was sonicated at 15 kHz for one minute. The beaker was re-covered with aluminum foil, the sediment allowed to settle for 5 min, and a 20 ml aliquot taken. This aliquot was added to a 50 ml volumetric flask containing three drops of paraffin oil and evaporated at 50°C in a N_2 evaporator. Following a 5 min cooling period, 5 ml of toluene and 40 ml of 2% Na_2SO_4 were added, and the flask capped and shaken vigorously. The layers were allowed to separate and the toluene layer was brought into the neck of the flask by the addition of deionized water. This layer was removed with a disposable pipet to a brown-glass sample bottle containing about 1 g of dry Na_2SO_4 and stored at -20°C prior to GLC analysis.

Recoveries from fortified substrates were as follows. Leaves fortified with 1 $\mu g/cm^2$ carbophenothion and carbophenothion oxon: 95 ± 1% and 91 ± 4%, respectively; with 10 $\mu g/cm^2$: 96 ± 1% and 93 ± 2%, respectively; soil fortified with 1 ppm: 87 ± 2% and 91 ± 3%, respectively; with 10 ppm: 87 ± 3% and 92 ± 5%, respectively. Data were not corrected for recoveries. The minimum detectable level of both compounds was 1 ng/injection; all injections were 5 μl. The detection limits were: 0.005 $\mu g/cm^2$ (leaf) and 0.2 ppm (soil).

Table 1. Carbophenothion dislodgeable residues on leaf, soil-middle, and soil-dripline surfaces (mean of four replications ± std. dev.).

Day	Leaf 1X ($\mu g/cm^2$)	Leaf 2X ($\mu g/cm^2$)	Soil-mid. 1X (ppm)	Soil-mid. 2X (ppm)	Soil-drip 1X (ppm)	Soil-drip 2X (ppm)
-5[a]	ND[c]	ND[c]	ND[d]	ND[d]	ND[d]	ND[d]
0[b]	.20 ± .08	.57 ± .11	--	--	--	--
1	1.03 ± .13	1.98 ± .35	8.9 ± 4.9	14.5 ± 6.0	8.2 ± 1.9	14.5 ± 4.9
3	.55 ± .12	1.15 ± .18	16.1 ± 3.3	17.2 ± 3.3	12.3 ± 2.0	26.6 ± 5.8
5	.35 ± .06	.76 ± .19	6.5 ± 2.0	11.1 ± 2.6	6.4 ± 1.2	11.7 ± 2.9
7	.20 ± .04	.47 ± .08	6.0 ± 1.6	10.9 ± 5.1	6.4 ± 1.9	10.1 ± 2.8
15	.05 ± .02	.14 ± .05	2.2 ± 1.2	3.6 ± 1.0[e]	1.1 ± 0.7	4.6 ± 2.4
22	.03 ± .01	.10 ± .01	1.0 ± 0.7	1.8 ± 0.6	0.6 ± 0.2	2.6 ± 0.9
28	.02 ± .01	.05 ± .01	0.8 ± 0.1	1.8 ± 1.1	0.6 ± 0.3	1.8 ± 1.2

[a] Sampled before first application; [b] Sampled before second application; [c] Detection limit = 0.005 $\mu g/cm^2$; [d] Detection limit = 0.2 ppm; [5] Mean of three replications

Table 2. Carbophenothion oxon dislodgeable residues on leaf, soil-middle, and soil-dripline surfaces (mean of four replications ± std. dev.).

Day	Leaf 1X ($\mu g/cm^2$)	Leaf 2X ($\mu g/cm^2$)	Soil-mid. 1X (ppm)	Soil-mid. 2X (ppm)	Soil-drip 1X (ppm)	Soil-drip 2X (ppm)
-5^{a}	ND^{c}	ND^{c}	ND^{d}	ND^{d}	ND^{d}	ND^{d}
0^{b}	.005 ± .001	.011 ± .002	--	--	--	--
1	.021 ± .002	.035 ± .004	.23 ± .06	.34 ± .13	.37 ± .22	.54 ± .15
3	.018 ± .004	.029 ± .004	.99 ± .16	.84 ± .39	.95 ± .29	1.14 ± .09
5	.010 ± .002	.019 ± .004	ND^{d}	.38 ± .11	ND^{d}	.51 ± .10
7	.009 ± .002	.018 ± .001	.25 ± .08	.51 ± .20	.39 ± .17	.78 ± .31
15	ND^{c}	ND^{c}	ND^{d}	ND^{e}	ND^{d}	ND^{d}
22	ND^{c}	ND^{c}	ND^{d}	ND^{d}	ND^{d}	ND^{d}
28	ND^{c}	ND^{c}	ND^{d}	ND^{d}	ND^{d}	ND^{d}

[a] Sampled before first application; [b] Sampled before second application; [c] Detection limit = 0.005 $\mu g/cm^2$; [d] Detection limit = 0.2 ppm; [e] Mean of three replications

Table 3. Carbophenothion and carbophenothion oxon on leaf, soil-middle (SM), and soil-dripline (SD) surfaces, from unsprayed control plots.

	Day 1						Day 3					
	Leaf ($\mu g/cm^2$)		Soil (ppm)				Leaf ($\mu g/cm^2$)		Soil (ppm)			
Plot	1	2	1		2		1	2	1		2	
			SM	SD	SM	SD			SM	SD	SM	SD
Carbo	.018	.021	1.9	.8	ND[b]	ND[b]	.013	.007	ND[b]	ND[b]	ND[b]	ND[b]
Carbo-oxon	ND[a]	ND[a]	ND[b]	ND[b]	ND[b]	ND[b]	ND[a]	ND[a]	ND[b]	ND[b]	ND[b]	ND[b]

[a] Detection limit = 0.005 $\mu g/cm^2$; [b] Detection limit = 0.2 ppm

Table 4. Half-lives for carbophenothion dissipation from leaves and soil.

		Half-life (days)	R[a]	N[b]	Weather cond.	Combined data (2X 1X)	Combined data Half-life (days)
Leaf	1X	4.5 ± 0.4[c]	.98	7	cool-dry	2.6 ± 0.7[d]	
	2X	5.2 ± 0.5	.98	7	cool-dry		
							4.9 ± 0.3[c] (leaf)
Soil-mid.	1X	6.4 ± 0.7	.97	7	cool-dry	1.7 ± 0.4	
	2X	7.5 ± 0.8	.97	7	cool-dry		
							6.8 ± 0.4 (soil)
Soil-drip.	1X	5.7 ± 0.7	.96	7	cool-dry	2.7 ± 1.1	
	2X	7.7 ± 0.9	.97	7	cool-dry		

[a] Correlation coefficient between ln (concentration) and days post-application; [b] Number of data pairs; [c] Standard error; [d] Mean (2x residue ÷ 1x residue) ± std. dev.

Extracts were analyzed on a 1.8 m x 2 mm ID silanized glass column packed with 10% DC 200 on 80-100 mesh Chromosorb WHP (Supelco, Inc., Bellefonte, PA). The Tracor 550 gas chromatograph was equipped with a flame photometric detector in the phosphorus mode. Operating conditions were: column 210°C, detector 190°C, injection 210°C, N_2 40 ml/min, air 100 ml/min, and H_2 60 ml/min. Carbophenothion oxon had a retention time of 3 min 55 sec and carbophenothion 5 min 5 sec, under these conditions.

RESULTS AND DISCUSSION

The formulation showed no detectable carbophenothion oxon.

The residues recovered from leaves and soil are presented in Tables 1-3.

The day 1 carbophenothion level appearing in Table 1 is higher than those found in two previous Florida studies (Nigg et al. 1978; Thompson and Brooks 1976), the former study having been conducted in November-December and the latter in April. Mean

Table 5. Weather data.[a]

Date	Rain-fall (in.)	Air (max/min°F)	Soil 4" max/min°F	Leaf wetness	Evaporation (in./day) (hr)
1983					
Jan 24	0	64/40	67/55	11	8
Jan 25	0	63/41	66/53	18	5
Jan 26	0	66/37	66/53	13	8
Jan 27	0	70/42	68/51	10	8
Jan 28	0.15	80/45	68/56	14	12
Jan 29	0	63/37	66/53	13	7
Jan 30	0	71/37	66/52	11	10
Jan 31	0	82/53	72/56	13	8
Feb 1	0	77/59	74/53	9	11
Feb 2	1.17	83/61	76/63	9	11
Feb 3	1.61	82/55	70/62	16	29
Feb 4	0	68/40	70/56	8	88
Feb 5	0	62/41	66/54	6	25
Feb 6	0	72/43	50/53	2	12
Feb 7	1.00	66/57	65/61	20	16
Feb 8	0	64/37	68/53	4	88
Feb 9	0	62/34	64/49	10	19
Feb 10	.54	69/51	64/55	16	12
Feb 12	2.65	73/52	70/58	2	0
Feb 13	.23	60/52	60/59	23	19
Feb 14	0	66/52	65/57	9	88
Feb 15	0	62/42	62/53	12	88
Feb 16	0	71/45	69/51	9	18
Feb 17	1.07	63/55	62/57	15	14
Feb 18	0	76/49	73/59	11	3
Feb 19	0	74/46	73/57	10	16
Feb 20	0	74/46	70/58	8	17

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[a] Weather data were obtained from the Lake Alfred Citrus Experiment Station, an official U.S. weather reporting station. Methods for these data are in U.S. Dept. of Commerce (1970) reference.

prevailing air temperatures were about the same during these two studies and the present one. The rate of application for both of these previous studies was 12 oz of Trithion 8E/100 gal (2X). The present study used 20 oz of Trithion 8E/100 gal (2X). The first day post application residues were 0.36 $\mu g/cm^2$ (Thompson and Brooks), 0.11 $\mu g/cm^2$ (Nigg et al.) and 1.98 $\mu g/cm^2$ (present study Table 1). The 1.98 $\mu g/cm^2$ level of Table 1 resulted from a double application. The value 0.57 $\mu g/cm^2$, reduced to its probable day 1 value of 0.50 $\mu g/cm^2$, must be subtracted from this, yielding a residue of 1.48 $\mu g/cm^2$ from the second application only. Further reduction by a factor of 12/20 to compensate for the different application rates yields 0.89 $\mu g/cm^2$ (present study) as compared with 0.36 $\mu g/cm^2$ (Thompson and Brooks) and 0.11 $\mu g/cm^2$ (Nigg et al.). Since less water per tree at the same rate per acre tends to produce higher surface residues, this may explain the observed differences (Carman et al. 1977).

The initial residues in Table 1 are in a ratio of approximately 1:2 for the 1X and 2X rates, a ratio which also holds for the oxon data in Table 2. The precise overall mean ratios were 1:2.3 for carbophenothion and 1:1.8 for the oxon. The ratio of oxon to parent is lower in this study compared to Nigg et al. (1978); 0.02 vs. 0.04. The level of oxon in all three studies was low and its disappearance uniform (Table 2). Samples taken from control plots were negative or had low levels of the parent compound (Table 3).

The first order half-life for carbophenothion dissipation from leaves (Table 4) was 4.9 ± 0.3 days. The Nigg et al. (1978) half-life was 7.0 ± 0.7 days and the Thompson and Brooks (1976) half-life was 3.1 ± 0.4 days. Dissipation from soil was with half-life 6.8 ± 0.4 days, only marginally longer than was found for leaves.

From these data, it would appear that carbophenothion would pose little worker reentry hazard under Florida conditions, even at exaggerated rates of application. However, should toxicological data indicate otherwise, the data here can be used to protect fruitpickers from potential health effects of carbophenothion.

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