Persistence of *O,O*-Diethyl *S*-(2-Chloro-1-phthalimidoethyl)-phosphorodithioate (Torak) on and in Lemons, Oranges, and Dried Citrus Pulp Cattle Feed, and Toxicity of the Residues to Mites

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Residues of Torak [*O,O*-diethyl *S*-(2-chloro-1-phthalimidoethyl)phosphorodithioate] were determined on and in Valencia oranges, Eureka lemons, and citrus pulp cattle feed prepared from treated oranges. The residue half-lives were 40–60 days on oranges and 60–80 days for lemons. Concentrate spray applications gave higher initial deposits and somewhat longer residue half-lives than did full volume sprays. The difference in deposits may be due in part, at least, to the sampling technique used. There was a rapid penetration of the pesticide into the rind but none into the peeled fruit. Washing was ineffective in removing Torak residues. There was no evidence of the presence of the oxygen analog, a potential metabolite. Bioassay evaluations were made at each sampling interval to establish the effect of type of application and kind of fruit on toxicity to mites. Low volume applications were effective longer than the dilute applications, and residues were effective for a longer period on oranges than on lemons.

Torak [*O,O*-diethyl *S*-(2-chloro-1-phthalimidoethyl)-phosphorodithioate], a product of Hercules, Inc., is a promising insecticide and acaricide for controlling thrips and mites on citrus. The initial deposits and the rates of dissipation required to establish tolerances and make recommendations for the use of this pesticide were determined for oranges and lemons. The rind and the peeled fruits (pulp) were analyzed separately to determine the extent of penetration, if any, and dried citrus pulp cattle feed was prepared from the rind of treated oranges and analyzed. This paper reports the data resulting from the study.

PROCEDURE

Plots of Eureka lemons and mature Valencia oranges were sprayed with an emulsive concentrate formulation of Torak containing 4 lb of technical ingredient per gallon. The oranges were sprayed on June 23, 1969, and the lemons on September 16, 1969, with dosages, expressed as actual ingredient, as follows.

ORANGES: Plot 1. Concentrate spray, 5 lb/A, in 50 gal. Plot 1R. As plot 1 but resprayed August 8. Plot 2. Concentrate spray, 10 lb/A, in 50 gal. Plot 3. 800 gal/A, 5 oz/100 gal of spray. Plot 3R. As plot 3 but resprayed August 8. Plot 4. 800 gal/A, 10 oz/100 gal of spray. Plot 7. Untreated control.

LEMONS: Plots 1 and 2. As for oranges, Plot 3. 400 gal/A, 10 oz/100 gal of spray. Plot 4. As plot 3 but 5 oz/100 gal. Plot 5. As plot 1, but resprayed October 16. Plot 6. As plot 4, but resprayed October 16. Plot 10. Untreated control.

The trees used in this study were parts of a young grove of oranges and lemons and were approximately one-half the size of fully grown ones. As the dilute spray applications were directed manually, the volume of spray applied was, accordingly, about one-half the amount normally used in a mature grove. The air-blast sprayer used for the concentrate

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sprays ran continually, and the amount applied per acre by this method was almost the same as would have been used for a fully grown grove. The amount of the toxicant applied to a tree by each method was considered to be approximately equal.

The field plot design and sampling procedure, and the preparation of the fruits (*e.g.*, washing and peeling) were as described by Gunther (1969). The sampling intervals are given in the Tables below. At every other sampling date double samples were collected and one-half of each was washed before processing to determine the probable effect of commercial washing practice in the packinghouse. After peeling, the samples were processed and analyzed by the gas chromatographic method of Hercules Inc. (Ford, 1968) with the exception of minor differences in equipment and operating conditions as follows.

A Varian Aerograph 1520B gas chromatograph was used, fitted with a phosphorus detector (cesium bromide pellet) and a 5 ft × $^1/_8$ in. stainless steel column packed with 3% SE-30 on Gas Chrom Q, 80/100 mesh, or Varaport 30, 100/120 mesh. The temperatures were: column, 225–235° C; injector, 250° C; and detector, 250° C. The nitrogen carrier gas flow rate was 30 ml/min and air and hydrogen flow rates as required for proper performance.

The retention time of Torak, under the conditions cited, was *ca.* 4.2 min, while that of the oxygen analog, a potential metabolite, was *ca.* 3.8 min. The oxygen analog would have been detected, if present, at levels of 0.1 ppm or higher although quantitation below 0.5 ppm would be uncertain; there was no indication of the presence of this analog in any of the samples. Figure 7 shows a chromatogram of a control sample of orange rind and one of orange rind to which has been added 1 ppm of Torak and 0.5 ppm of the oxygen analog.

Quantitation was by peak height with injection of a standard following each sample injection. The detector response was linear over a range greater than that required for this study but variations in response during the day precluded the use of a standard curve. The injection of a standard in an amount approximating the Torak content of the sample injected permitted accurate measurement of the unknowns.

The recoveries of Torak added to orange rind, pulp, and dried citrus pulp cattle feed extracts and lemon rind and pulp

Table I.   Percent Recoveries of Torak Added to Extracts from Control Samples

Sample	0.1	0.2	0.3	0.5	1	2	3	4	5
Orange rind					98 ± 8	100 ± 8	105 ± 3	88[a]	100 ± 5
Orange pulp	95 ± 9	93 ± 11	110[a]	91 ± 9					
Lemon rind					93[a]	106 ± 6	110 ± 9		101 ± 9
Lemon pulp	100 ± 12	106[a]	92[a]	99 ± 19					
Cattle feed									
Ground rind					102[a]		110[a]		97[a]
Limed and pressed rind					95[a]		95[a]		93[a]
Dried feed						91[a]			95[a]

(Column heading: Level of fortification (ppm))

[a] Duplicate samples only.

Table II.   Residues (ppm) of Torak on and in Valencia Orange Ring (Average of Triplicate Field Samples)[a]

Interval after spraying (days)	1	2	3	4	1R	3R	Untreated control
3	9.1	18.5	4.9	6.7			<0.1
7	8.4	17.2	3.2	5.5			<0.1
7W[b]	9.2	15.5	7.9	8.0			0.3
10					14.8	7.4	<0.1
10W[b]					12.3	6.5	<0.1
14	7.8	17.4	4.0	6.5			<0.1
25					6.5	4.3	<0.1
28	9.1	14.9	2.8	5.6			0.3
28W[b]	8.0	13.2	2.6	4.3			0.1
38					5.4	3.3	<0.1
38W[b]					6.3	2.4	<0.1
42	5.2	9.1	2.2	4.5			<0.1
56	4.9	10.5	2.1	5.0			0.1
56W[b]	5.4	6.9	1.7	3.6			0.1
59					6.1	3.3	<0.1
70	5.1	9.8	1.5	1.4			<0.1
79					3.7	2.5	<0.1
79W[b]					3.6	2.4	<0.1
84	2.4	5.1	1.0	2.8			<0.1
84W[b]	3.9	5.1	1.0	2.1			<0.1
104	3.6	7.0	1.0	1.8			<0.1
125	2.1	4.3	0.7	1.9			<0.1
125W[b]	2.5	4.3	0.7	1.4			<0.1

(Column heading: Plot no.)

[a] Corrected for appropriate recovery.   [b] Samples washed before processing.

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extractives are shown in Table I.   Untreated control samples and fortified controls were analyzed at each sampling interval as a continuing check on the procedure.

ANALYTICAL RESULTS

Oranges. Table II summarizes the data for the Valencia orange plots and Table III summarizes the residues found in the citrus pulp cattle feed before and after drying.   The data for the plots receiving only one treatment are shown graphically in Figures 1 and 2 for the concentrate and full volume sprays, respectively.   The individual values for the three field replicates have been plotted for each sampling interval,

Table III.   Torak Residue in Citrus Pulp Cattle Feed[a]

Sample	A	B	C	Control
Chopped rind (washed)	4.1	4.8	4.4	<0.1
Chopped, limed, and pressed rind	5.9	6.1	3.3	<0.1
Finished product (dried to ca. 10% water content)	9.1	8.7	9.7	<0.1

(Column heading: Residue, ppm[b])

[a] Taken 28 days after spraying from plot 4.   [b] All values corrected for recovery.
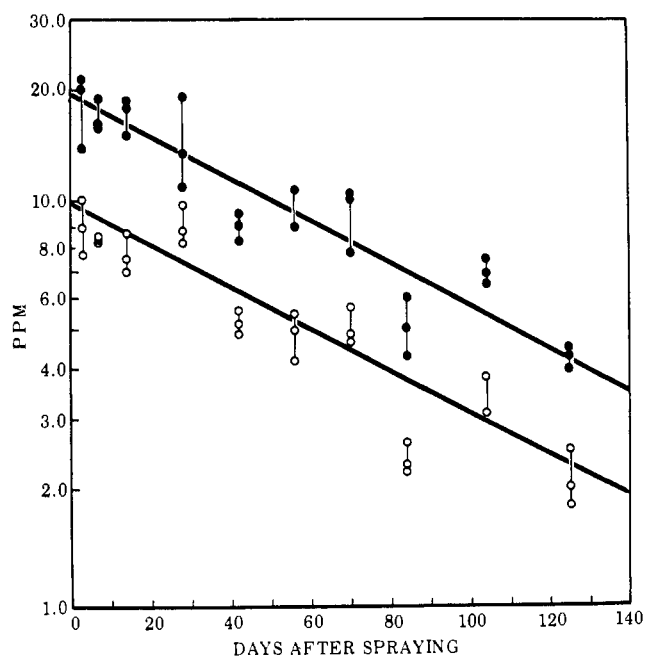
Figure 1.   Persistence curves for Torak in and on Valencia oranges following treatment with concentrate sprays.   O—O = 5 lb per acre; ●—● = 10 lb per acre
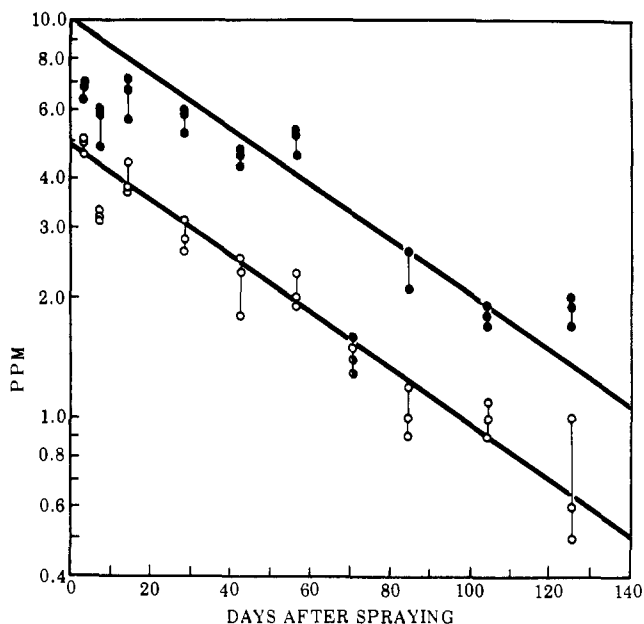
Figure 2. Persistence curves for Torak in and on Valencia oranges following treatment with full-coverage sprays. O—O = 5 oz per 100 gal of spray; ●—● = 10 oz per 100 gal of spray
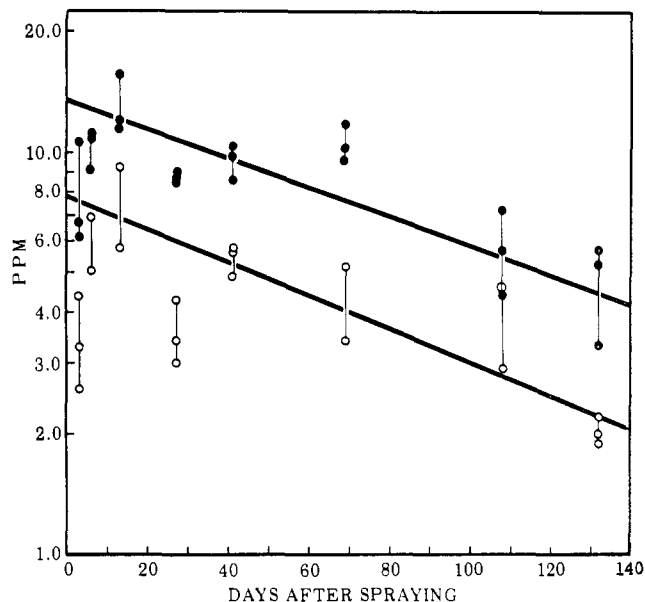

Figure 3. Persistence curves for Torak in and on Eureka lemons following treatment with concentrate sprays. O—O = 5 lb per acre; ●—● = 10 lb per acre

rather than the average values in the tables, to show the variation. The deposits were proportional to the amounts applied for both types of spray, and the concentrate sprays deposited twice as much as the full volume treatments. The higher deposits for the concentrate sprays may be due, in part at least, to the method used in sampling. Fruits were collected at about shoulder height, the area where the output of the air-blast sprayer used for the concentrate sprays is centered and where the maximum deposit would be encountered. The dilute sprays being manually controlled, on the other hand, were more uniformly distributed over the trees. Although deposits in the area sampled were less than those on the concentrate-sprayed trees, the average for all of the trees may have been approximately equal. The residue half-life for the con-

centrate spray was about 60 days and that for the full volume spray was about 40 days, showing a substantial difference for the two types of application. A rapid penetration of the pesticide into the rind is indicated by the slow but uniform rate of decline throughout the entire period. Washing the fruit in a manner to simulate commercial packinghouse procedure had no effect at any time, offering further evidence of rapid penetration.

Table IV. Residues (ppm) of Torak on and in Lemon Rind (Average of Three Replicates)[a]

Interval after spraying (days)	Plot no.					
	1	**2**	**3**	**4**	**5**	**6**
3	3.4	7.9	2.8	3.0		
6	6.3	10.6	5.1	4.8		
6W[b]	6.5	10.0	5.1	3.4		
11					9.6	6.6
13	8.1	13.1	5.0	5.3		
27	3.6	8.6	4.3	3.7		
27W[b]	3.5	11.3	4.7	3.6		
28					6.1	5.4
39					10.2	6.3
39W[b]					9.6	6.1
41	5.4	9.6	4.4	3.1		
69	4.5	10.5	3.5	3.1		
69W[b]	4.6	9.5	3.7	2.8		
78					7.9	4.5
108	4.0	5.8	1.6	1.8		
132	2.0	4.7	1.2	1.5		
132W[b]	2.1	6.3	1.3	1.5		

[a] Corrected for recovery. [b] Samples washed before processing. All untreated control samples contained no detectable residue (<0.05 ppm).
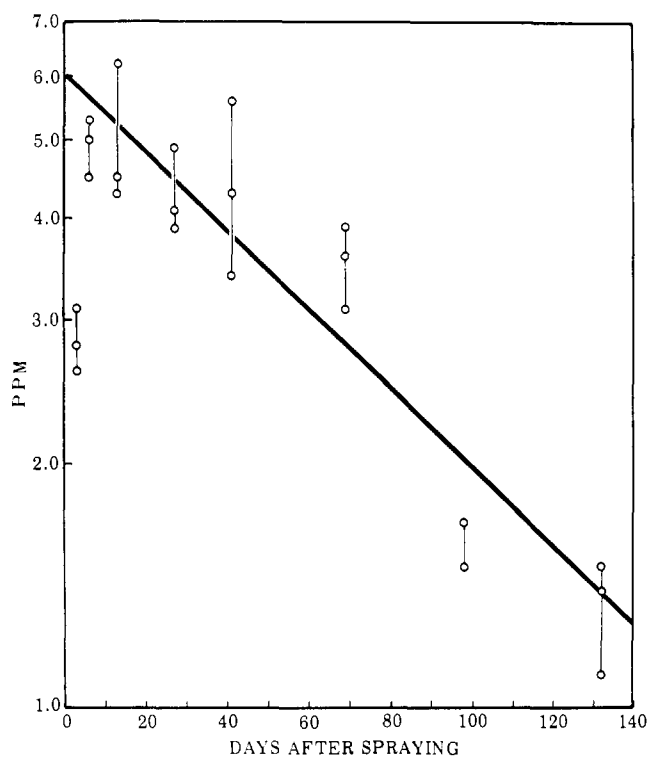

Figure 4. Persistence curve for Torak in and on Eureka lemons following treatment with a full coverage spray containing 5 oz per 100 gal
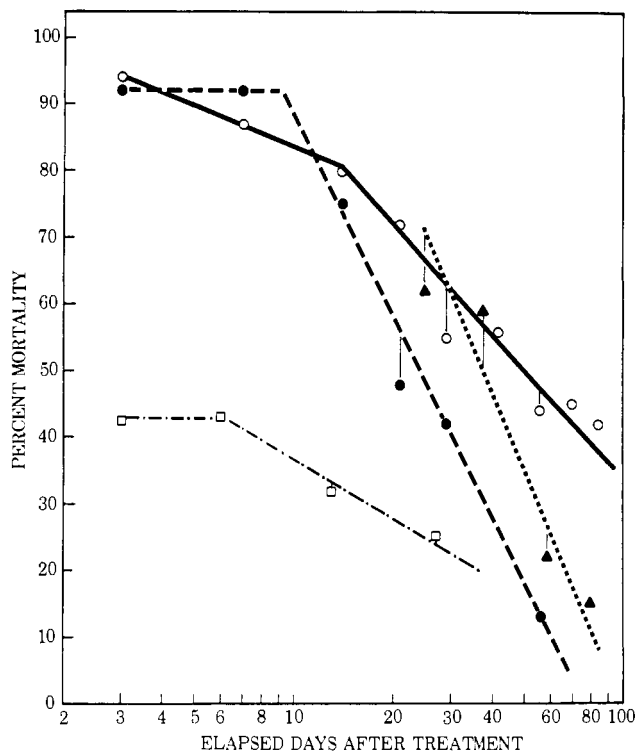
Figure 5. Toxicity of Torak residues on oranges and lemons to mites at various intervals after application. O—O = oranges, low volume spray; ●- - -● = oranges, dilute spray; ■- - -■ = lemons all treatments; ▲····▲ = oranges, overtreatment

Analyses of the pulp (edible portion) of the samples collected at the 7-, 21-, 42, 75-, and 125-day intervals showed no detectable Torak (<0.05 ppm), proving that the pesticide penetrated only into the rind.

The data for the citrus pulp cattle feed prepared from oranges picked 28 days after spraying show a loss of about 50% of the Torak during the processing. The theoretical
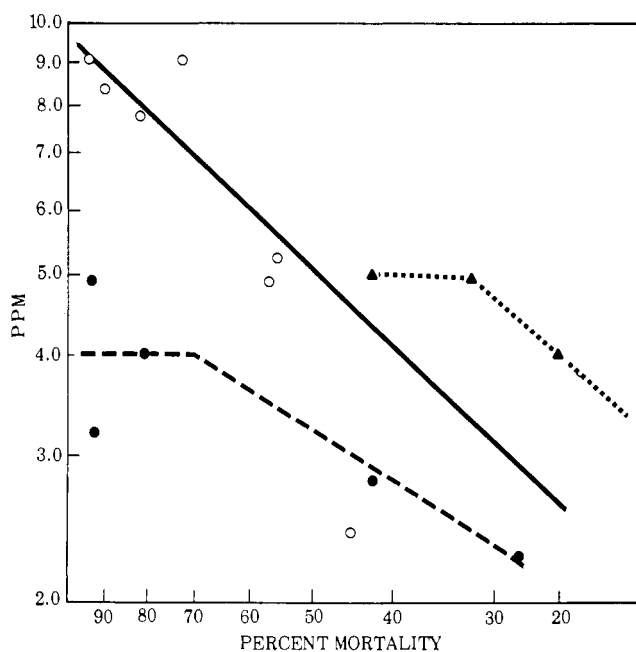

Figure 6. Relationship of toxicity of Torak residues for mites to residues on fruits. O—O = oranges, low volume spray; ●- - - -● = oranges, dilute spray; ▲—▲ = lemons, all treatments
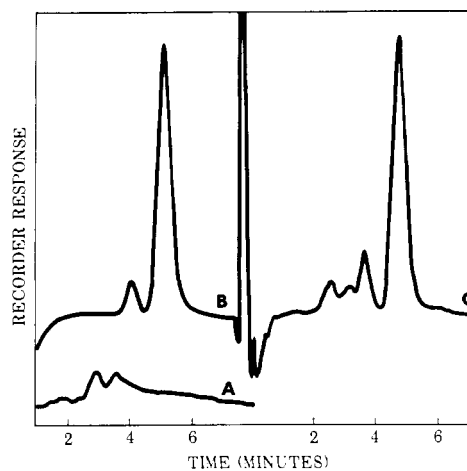
Figure 7. Gas chromatographic responses for: A, untreated control; B, 20 μg of Torak and 10 μg of Torak oxygen analog; C, untreated control fortified with 1.0 ppm of Torak and 0.5 ppm of the oxygen analog. Extract injected equivalent to 20 mg of orange rind

concentration through drying from 80% to 10% water content is 4.5:1; the actual concentration was about 2:1.

Lemons. Table IV includes the residues found in lemon rind following the various treatments. The data for Plots 1 and 2 are shown graphically in Figure 3 and those for Plot 3 are shown in Figure 4. The data for Plot 4 are practically identical to those for Plot 3 and were not included in the Figure. The individual values for the three field replicates are plotted at each sampling interval to show the variation. The deposits for the concentrate sprays are approximately proportional to the amount applied but those for the full volume sprays show no significant difference at the two concentrations used. The difference in deposits for concentrate and dilute sprays was similar to that found for oranges, for the same probable reason. The persistence curves show a residue half-life of 70–80 days for the concentrate sprays and 60–70 days for the full volume treatments. There was, as noted for the oranges, no reduction of residues by washing the fruits before analysis, indicating rapid penetration into the rind.

Analyses were made of the pulp of the fruits at intervals of 6, 27, 69, and 132 days after spraying and no Torak was detected at any time (<0.05 ppm).

BIOASSAY

Each time sample fruits were taken for residue determination, one additional fruit from each of eight trees was used for bioassay evaluations, thus providing eight fruits per sample. In the laboratory 25 citrus red mites were placed on each fruit and, after 48 hr, dead and live mites were counted and reported as percent mortality, as described by Jeppson and Gunther (1970).

Percent mortalities found at each sample interval are represented on semi-log scale in Figure 5. These mortalities plotted in relation to the amount of residue found by chemical analysis are indicated in Figure 6. As there was no difference in mite mortalities from the residues at the two dosages applied to oranges, the average mortality for both was used to obtain the residue values. As the toxicity of the residues to mites on lemons was similar for the two dosages and both methods, the averages of all four treatments were used for values plotted in Figures 5 and 6.

According to these results the residues on oranges were effective longer when applied by low volume methods than by dilute applications and residues from the overtreatment were effective a little longer than the initial application, although time of year could account for this magnitude of difference.

Residues were effective for a much shorter period on lemons than on oranges, regardless of the dosage or method used. Reasons for this difference are not readily apparent. Lemons have more oil sacs per surface area than oranges, which could provide more rapid uptake of the residues into rind oil, in which case the acaricide is not available to the mites either by contact or feeding. Other factors, however, may be involved.

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