Persistence of the Insecticide/Acaricide Phosalone on and in Oranges and in Laboratory-Processed Citrus Pulp Cattle Feed

William E. Westlake,* Janet R. O'Neal, Francis A. Gunther, and Glenn E. Carman

Residues of phosalone [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl)methyl phosphorodithioate] were determined on and in mature Valencia oranges and in dried citrus pulp cattle feed prepared from the field-treated fruit. The residue half-life was 40–45 days, and about half of the residue remaining 35 days after treatment persisted into the dried cattle feed. Residues in the edible part of the fruit did not exceed 0.03 ppm at any time and were not detectable in samples taken 30 and 79 days after spraying.

Phosalone [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl)methyl phosphorodithioate], Rhodia, Inc., is a promising insecticide and acaricide for use on citrus. This paper reports the magnitudes of the persisting residues on and in mature Valencia oranges sprayed in the field with the compound, and in dried citrus pulp cattle feed prepared in the laboratory from the field-treated fruits. Selected sequential samples were also analyzed for the oxygen analog of phosalone, a possible metabolite.

PROCEDURE

Plots of mature Valencia orange trees were manually sprayed on June 23, 1969, using spray mixtures containing 1.0 or 0.5 pt of a phosalone 3 lb/gal emulsifiable concentrate (6 oz and 3 oz, respectively, of technical phosalone) in 100 gal, at the rate of approximately 25 gal per tree. The amount of material applied represented the maximum and minimum requirements anticipated for the use of phosalone on citrus as a replacement material. The field plot design and sampling procedure and the preparation of the fruits for analysis were as described by Gunther (1969). Samples were collected prior to treatment, and at 3-, 7-, 14-, 21-, 30-, 45-, 79-, and 105-day intervals after spraying. A composite sample was taken from the plots treated with the higher dosage 35 days after spraying for processing into dried citrus pulp cattle feed (Gunther, 1969).

The method of analysis was based upon that of Guardigli *et al.* (1971) with the following modifications. All samples were processed to the point of extraction, then frozen until analyses could be made. Residues were recovered by blending 50 g of sample with 150 ml of acetonitrile for 5 min in a Sorvall Omni-Mixer at a speed setting of 5, except that for the dried cattle feed, 25-g samples were blended with 200 ml of acetonitrile. The mixer container was cooled in an ice bath during the blending process. The macerated samples were filtered through loose glass wool plugs in funnels, into 1000-ml separatory funnels, and the mixer container and residues in the funnels washed with two successive 25-ml portions of acetonitrile, then with two successive 50-ml portions of hexane. The cake in the funnels was pressed to remove additional solvent.

Department of Entomology, University of California, Citrus Research Center and Agricultural Experiment Station, Riverside, California 92502.

To each solution in the separatory funnels was added 500 ml of 2% sodium chloride solution and the contents were shaken thoroughly. The aqueous phase was then drained into a second separatory funnel and the hexane phase drained through anhydrous sodium sulfate, prewet with hexane, into a 500-ml round-bottomed flask. The aqueous phase in the second separatory funnel was washed with two successive 50-ml portions of hexane that were drained through the sodium sulfate into the same round-bottomed flask, and the sodium sulfate was washed with an additional 50 ml of hexane. The combined filtrates were evaporated to an oily residue on a rotary vacuum evaporator at a water bath temperature of 50–60° C.

A chromatographic column (Shell-type, 25 mm o.d.) was packed with a plug of glass wool, 12 cm of Florisil, and 1 cm of anhydrous sodium sulfate, in that order, and prewet with benzene. The residue in the evaporating flask was dissolved in 10 ml of benzene and introduced on to the column, after which the flask was rinsed with two successive 5-ml portions of benzene that were, in turn, poured on to the column. Benzene (40 ml) was then added to the column, followed by 200 ml of 5% ethyl acetate in benzene. All eluates were collected in the same 500-ml round-bottomed flask and the solvents completely removed with a rotary vacuum evaporator at a water bath temperature of 50–60° C. The residue was transferred to a graduated centrifuge tube with acetone and brought to the proper volume for injecting in the gas chromatograph.

An Aerograph Model 1520B gas chromatograph fitted with a phosphorus-sensitive detector (cesium bromide flame tip)

Table I. Recovery of Phosalone from Orange Rind, Pulp, and Cattle Feed

	Recovery, %		
ppm added	Rind	Pulp	Cattle feed
0.1		88, 107, 113	
0.2	96	88	
0.25	77, 115		
0.5	91, 107	94, 98, 100, 109, 90	
1.0	90, 90, 100, 96, 83		107
2.0	112, 102		96

Table II. Phosalone Residues in Valenica Oranges, ppm

Interval after spraying,[b] days	Residues, ppm[a]							
	Plot 1				Plot 2			
	A	B	C	avg	A	B	C	avg
				Rind				
3	3.8	3.6	3.7	3.7	3.6	2.7	2.5	2.9
7	5.1	4.2	5.4	4.9	3.9	3.4	3.2	3.5
14	5.0	5.0	5.5	5.1	3.4	3.1	3.3	3.3
21	5.1	5.3		5.2		3.8	3.0	3.4
30	3.4	3.2	4.4	3.7	2.4	2.5	2.2	2.4
45	3.5	2.6	3.4	3.2	2.0	2.0	1.8	1.9
79	1.7	1.5	1.9	1.7	1.1	0.9	0.7	0.9
105	1.5	1.2	1.6	1.4	0.9	0.7	0.6	0.7
				Pulp				
3	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02
7	0.03	0.03	0.03	0.03	0.01	0.01	0.02	0.01
14	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01
30	ND	ND	ND	ND	ND	ND	ND	ND
79	ND	ND	ND	ND	ND	ND	ND	ND

[a] ND—none detectable, less than 0.01 ppm. [b] Plot 1 sprayed with 1 pt of Zolone 187 (3 lb/gal EC formulation) in 100 gal of spray; plot 2 sprayed with 0.5 pt of above formulation in 100 gal of spray; about 25 gal applied per tree on June 23, 1969.

Table III. Residues in Orange Rind and Citrus Pulp Cattle Feed Produced from It (35-Day Sample)

Plot	Replicate	Residues, ppm		
		Rind I[a]	Rind II[b]	Cattle feed[c]
1	A	3.1	1.6	1.6
	B	2.5	1.8	2.3
	C	2.8	1.5	2.4
2	A	2.2	1.3	3.8
	B	1.9	1.3	3.2
	C	3.2	1.7	3.5

[a] Fruit peeled as for residue samples. [b] Fruit washed, cut in half, and juiced, rind and adhering rag analyzed. [c] Processed dry cattle feed.

was used for quantitation as this type of detector is more specific and much less affected by plant extractives than the electron capture detector. A stainless steel column, 4 ft × 1/8 in. o.d. packed with 10% SE-30 on 60/80 mesh Gas Chrom Q and operated at 237° C, was used. The injection port and detector oven temperatures were 287 and 243° C, respectively.

Phosalone oxygen analog was determined in the unwashed rind and in the pulp of samples collected at the 7-, 21-, and 45-day intervals from the plot receiving the higher treatment, using the method of Guardigli *et al.* (1971).

RESULTS AND DISCUSSION

Table I gives the recoveries of known amounts of phosalone added to the various substrates, and Table II shows the residues found in the unwashed citrus rind and pulp samples at the various sampling dates. Values for each individual replicate are given, as well as the average for each plot.

Table III shows the residues found in the dried citrus pulp cattle feed, in the unwashed rind, and in the rind from oranges that were washed and then juiced. The rind from the juiced fruit contains a small amount of "rag" that is not included with the rind of peeled fruit. About half the rind residue was removed by washing, indicating slow penetration of phosalone into the rind, even after 35 days.

The residue half-life of phosalone is 40–45 days, as determined by plotting the data in Table II. The values for both plots through the 21-day samples also indicate unusually slow penetration of this insecticide/acaricide into rind tissues; low values for the first few days after treatment are typical, as it has been found that reliable samples are difficult, if not impossible, to obtain during the first few days after spraying (Gunther, 1969) from the unavoidable handling involved, with consequent dislodgment of surface deposits. These data show that, under Southern California conditions, the initial deposit at the higher dosage is approximately 5 ppm in the orange rind or 1 ppm in the whole fruit.

The data in Table III, for the dried cattle feed and the rind before processing, show a twofold concentration due to the loss of water. As the theoretical concentration in drying from 80 to 10% water content is 4.5:1, approximately 50% of the insecticide was lost in processing.

The minimum detectable amount of phosalone oxygen analog was 0.1 ppm. Of the three replicates analyzed at each of the three sampling intervals, only one, at the 45-day interval, appeared to contain a detectable amount; this was attributed to contamination in the laboratory.

The residue half-life of 40–45 days is similar to that found by Guardigli *et al.* (1971) in citrus grown in Florida despite the climatic differences (*e.g.*, high temperature and no precipitation in Southern California *vs.* somewhat lower temperature and substantial precipitation in Florida).

ACKNOWLEDGMENT

The assistance of James H. Barkley and Dorothy L. White for processing and analysis, and Joseph L. Pappas, Gene F. Wood, and Ordell L. Wolfe for field work is gratefully acknowledged.

LITERATURE CITED

Guardigli, A., Chow, W., Martwinski, P. M., Lefar, M. S., J. AGR. FOOD CHEM. **19,** 742 (1971).
Gunther, F. A., *Residue Rev.* **28,** 1 (1969).

Received for review June 17, 1971. Accepted August 16, 1971. Research supported in part by a grant-in-aid from Rhodia, Inc.