Persistence of Azodrin Residues on and in Valencia Oranges and in Laboratory-Processed Citrus Pulp Cattle Feed

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Residues of the new pesticide phosphoric acid dimethyl ester, ester with *cis*-3-hydroxy-*N*-methyl crotonamide (Azodrin), were determined on and in Valencia oranges and in citrus pulp cattle feed prepared from the treated fruit. The residue half-life for the high- and low-volume treatments was 13 and 16 days, respectively. Washing the fruit 12 days after treatment had little effect on the residue, indicating rapid penetration of the pesticide into the rind. Residues did not survive the processing into the citrus pulp cattle feed. The high-volume treatment resulted in traces of persisting residues in the edible portion of the fruit.

The compound phosphoric acid dimethyl ester, ester with *cis*-3-hydroxy-*N*-methylcrotonamide (Azodrin), is a promising pesticide for the control of mites and thrips on citrus. This paper reports the magnitudes of persisting residues on and in mature Valencia oranges subjected to full- and low-volume spray treatments, and in citrus pulp cattle feed prepared from the treated fruits. The data presented here are to establish the residue behavior of Azodrin for the purpose of assisting in the determination of tolerances required and minimum permissible intervals between application and harvest.

Menzer and Casida (1965) have reported that Azodrin is metabolized to yield trace amounts of the *N*-hydroxy analog and the unsubstituted amide. As the levels of these metabolites have been shown to be too low to be of significance, no attempt was made to detect them in the present study.

PROCEDURE

Mature Valencia orange trees were sprayed on Feb. 16, 1968, with approximately 2000 gal per acre of a full-volume spray mixture containing 0.5 lb of Azodrin in 100 gal, or approximately 10 lb of technical grade Azodrin per acre. A second set of plots was treated with a low-volume spray at the rate of 1.0 lb of technical grade Azodrin per acre in 100 gal of spray. An upwind, untreated plot was maintained as a control. The plot arrangement and size and sampling procedures were as described by Gunther (1969). Samples of 32 full-sized fruits each were collected (Gunther, 1969) before spraying and at 4-, 7-, 12-, 17-, 24-, 38,- 52-, 61-, 66-, 87-, and 108-day intervals after spraying. At the 12-, 24-, and 52-day intervals, both washed and unwashed samples were analyzed to determine the probable effects of commercial washing practices on residues. Pulp (edible portion) samples were analyzed on the 38-, 66-, and 108-day samplings to determine the extent of penetration, if any, into the edible part of the fruit.

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Cattle feed was prepared in the laboratory from about 100 lb of fruit picked at the 38-day interval using the procedure described by Gunther (1969). Analyses were made of the rind before processing, of the ground rind after liming and pressing, and of the finished feed after drying to approximately 10% water content.

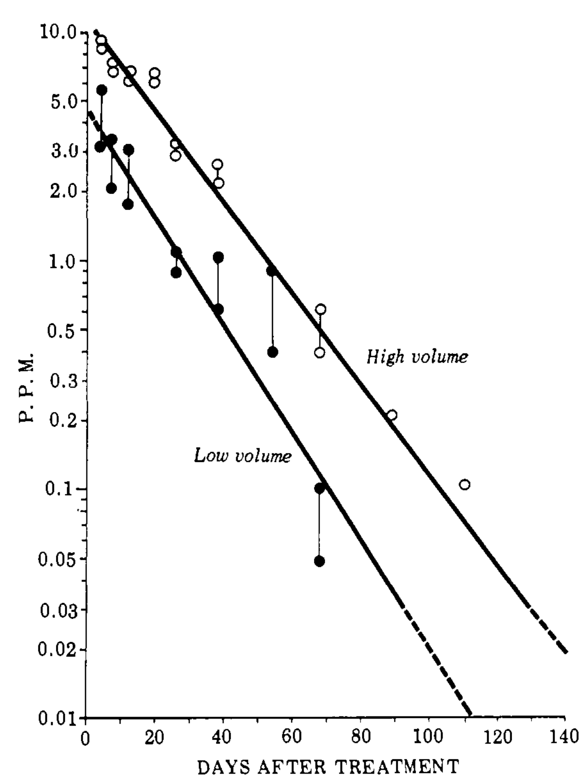

Figure 1. Persistence of Azodrin on and in Valencia orange rind after two different treatments

Low-volume spray with 1.0 lb of technical grade Azodrin per acre in 100 gal of water and full-volume spray with about 2000 gal per acre of spray containing 0.5 lb of technical grade Azodrin per 100 gal

Table I. Azodrin Residues in Rind and Pulp of Field-Treated Valencia Oranges

Days after spraying	Residue (ppm)[a] Treatment I[b] Rind Unwashed	Treatment I Rind Washed	Treatment I Pulp	Treatment II[c] Rind Unwashed	Treatment II Rind Washed	Treatment II Pulp	Treatment III[d] Rind Unwashed	Treatment III Pulp
Pretreatment	ND[e]	...	ND[e]	ND[e]	...	ND[e]	ND[e]	ND[e]
4	9.0 ± 0.3	...	...	4.3 ± 1.2	...	...	...	...
6	...	...	...	...	...	...	3.1 ± 1.0	...
7	7.2 ± 0.4	...	ND[e]	2.7 ± 0.7	...	...	...	...
12	6.5 ± 0.4	6.6 ± 1.5	...	2.4 ± 0.6	2.2 ± 0.1	...	0.7 ± 0.2[f]	...
19	6.4 ± 0.7	...	ND[e]	1.5 ± 0.1	...	ND[e]	0.5 ± 0.1	0.4 ± 0.2
26	3.1 ± 0.3	3.7 ± 0.1	...	1.0 ± 0.2	0.5 ± 0.2	...	...	...
38	2.4 ± 0.2	...	0.17 ± 0.05	0.8 ± 0.2	...	ND[e]	0.2 ± 0.1	...
54	0.9 ± 0.1	0.7 ± 0.2	...	0.06 ± 0.03	0.06 ± 0.03	...	...	...
61	...	...	...	...	...	...	0.04 ± 0.03	ND[e]
68	0.5 ± 0.1	...	0.15 ± 0.03	0.06 ± 0.03	...	0.05 ± 0.03	...	...
89	0.20 ± 0.03	...	...	ND[e]	...	...	...	...
108	0.10 ± 0.03	...	0.09 ± 0.03	ND[e]	...	ND[e]	...	...

[a] Corrected for recovery of 65%. Based on the analyses of 72 fortified control samples, the laboratory recovery was 65 ± 13%. Four replicated samples for each sampling interval, 6 for each control sampling interval. [b] 10 lb of technical grade Azodrin per acre. [c] 1.0 lb of technical grade Azodrin per acre. [d] Retreatment of 1.0 lb plot at the same rate 81 days after first treatment. [e] None detectable. The lower limit of detectability was 0.03 ppm in the presence of rind or pulp extractives. No residue was detected at any time in untreated control samples collected on every sampling date. [f] No reduction after washing (0.7 ± 0.2 ppm).

Table II. Azodrin Residues in Cattle Feed Prepared from the Rind of Field-Treated Valencia Oranges 38 Days after Both Treatments (Full-Volume and Low-Volume)

Dosage (actual) per acre, lb	Azodrin residues (ppm)[a,b] Ground rind	Ground, limed, and pressed
10	2.4 ± 0.2	0.9 ± 0.2
1.0	0.7 ± 0.2	0.3 ± 0.1

[a] Corrected for recovery of 65 ± 10% and for background (ND) from six untreated control samples, each stage; six replicates for each sample stage. [b] There was no detectable residue of Azodrin in the dried finished cattle feed. The lower limit of detectability was 0.03 ppm.

The method of analysis was that of Shell Chemical Co. (1967), with modifications as follows.

The rind samples were chopped in a Hobart food cutter to pieces less than 1/8-in. in diameter and each 500-g subsample was tumbled at 58 rpm end-over-end in a 2-quart jar with 1000 ml of methylene chloride for 1 hr. The extract was recovered by filtration through Sharkskin filter paper. Each pulp sample (500 g) was tumbled with 500 ml of solvent in the same manner, then stored in a cold room at about 4° C for 2 days before filtering (Gunther, 1969). Each sample of dried cattle feed (250 g) was equilibrated with 1000 ml of solvent and processed in the same manner as the rind samples.

An Aerograph 500-D gas chromatograph fitted with a phosphorus detector (cesium bromide pellet) was used for the analytical step. A 3-ft glass column, 2 mm i.d., packed with 2% Reoplex-400 on 80/100 mesh Gas Chrom Q (N_2 carrier gas, H_2 17–30 ml per min, air 200–300 ml per min), operated at 187° C (inlet 210° C), gave excellent resolution of the Azodrin peak and was employed for the routine analyses.

RESULTS AND DISCUSSION

The residues of Azodrin found in the rind and pulp of field-treated Valencia oranges are shown in Table I. Residues found in rind used for making cattle feed, and in the ground, limed, and pressed rind are given in Table II. Figure 1 shows the disappearance rate of Azodrin after application by the two different methods. There is apparent agreement in the rates of disappearance for the two treatments as shown by the slopes of the two lines, although the low-volume treatment did not afford an easily fitted line (the 89- and 110-day samples for the low-volume treatment were obviously borderline for minimum detectability). The residue half-life for the low-volume spray is 13 days, while that for the full-volume spray is 16 days. By extrapolation, the full-volume treatment had an initial deposit of 10 ppm, whereas that for the low-volume spray was about 4 ppm on a rind basis (Valencia oranges have 18.7 ± 6.3% rind). During the preparation of cattle feed, the Azodrin residues were reduced to nondetectable levels, over 50% being lost during the grinding and liming process, and the remainder during drying.

Washing in a manner to simulate commercial washing in packing houses did not remove an appreciable part of the residue, indicating a rapid penetration of this pesticide into the oils and waxes in the rind. There is evidence of slow penetration into the pulp of the fruits from the higher dosage, but the data are not adequate to establish definite levels of longevity of these low residues.

Variation among field replicated analytical samples was much greater for the low-volume treatment than for the high-volume treatment (Figure 1).

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