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Residues of Ethoprop in Eight Vegetables*†

T. W. Hunt, R. B. Leidy, T. J. Sheets, and H. E. Duncan

Pesticide Residue Research Lab and Department of Plant Pathology, North Carolina State University, Raleigh, NC 27607

Ethoprop (O-ethyl S,S-dipropyl phosphorodithioate) is a nonsystemic nonfumigant nematicide and soil insecticide. It was introduced by Mobil Chemical Company in 1967 under the trade name Mocap and is now marketed as Mocap 10-G (10% granular) and Mocap 6 E.C. (0.72 kg/L emulsifiable concentrate). Ethoprop is applied at rates of 1.7 to 6.7 kg/ha as a preplant incorporated treatment.

Ethoprop is presently registered for use on banana, lima bean, snap bean, cabbage, corn, cucumber, peanut, pineapple, soybean, and sweet and white potatoes. A tolerance of 0.02 ppm has been established for all of these crops (GOVERNMENT PRINTING OFFICE 1979).

The objectives of this research were to develop an efficient method of analysis and to determine the residues of ethoprop in selected vegetables.

MATERIALS AND METHODS

A field test with ethoprop was conducted at the Central Crops Research Station near Clayton, NC in 1976. The experimental design was a randomized split plot with four replications. Each subplot was 3.8 m long and 11 m wide with 1.5 m borders between the main plots. Ethoprop (Mocap 10-G) was applied at rates of 0, 3.4, 6.7, and 13.4 kg/ha to a Dothan loamy sand (Plinthic paleudult; fine loamy, siliceous, thermic) with a pH of 5.7 and 0.5% organic matter. The nematicide was spread uniformly by hand over the soil and incorporated with a powered garden tiller. Incorporation was accomplished by tilling the soil twice in one direction and once in the direction perpendicular to the first to a depth of 13 to 15 cm. Half of each plot was treated on July 9. On July 13, one row each of snap bean (Phaseolus vulgaris L. cv. Poinsett) were planted and one row of tomato (Lycospersicon esculentum Mill. cv. Manapal)

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† Use of product names does not imply endorsement of the products named nor criticism of similar ones not mentioned.

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transplanted in these halves of the plots. The remaining half of each plot was treated on August 20. One row each of turnip (Brassica rapa L. cv. Purple Top, White Globe), radish (Raphanus sativus L. cv Cherry Belle), lettuce (Lactuca sativa L. cv. Butter Crunch), and onion (Allium cepa L. cv. Yellow Globe Danver) were planted into these halves of the plots on the same day.

Two foliar applications of carbaryl and one foliar application of methomyl were made during the growing season to control insects. Rows were shortened to 6.4 m by removal of excess plants. The edible portions of all plants of marketable size and quality were harvested from each plot and transported to the laboratory. Table 1 shows the number of days between planting and harvest.

Table 1. Number of days between planting and harvesting of vegetables

	Harvest			
Vegetable	First (days)	Second (days)	Third (days)	Fourth (days)
Cucumber	58	62	66	73
Tomato	80	86	94	104
Turnip root	87	97	108	
Turnip leaf	70	79		
Radish	59	66		
Snap bean	66	77		
Lettuce	87			
Onion	108			

All samples were washed with tap water before processing to remove any treated soil. A Hobart Food Cutter was used to chop all samples except tomato, which was processed with a Waring blender (1-L capacity). Representative samples were stored at -10 C in sealed glass jars.

Several methods of analysis were attempted (MOBIL CHEMICAL COMPANY 1976, SAGREDOS & ECKERT 1976, U.S. DEPT. HEW, FDA 1973). None of these methods gave adequate results. A chromatographic cleanup procedure was developed to eliminate the interfering coextractives.

Samples (50 g) were blended in 200 mL of n-hexane with 50 g of granular anhydrous sodium sulfate for 8 min (U.S. DEPT. HEW, FDA 1973). After settling, a 100-mL portion was added to a 7 by 2.5-cm column of silicic acid topped with 2 cm of anhydrous sodium sulfate. The column was connected to a vacuum manifold system to maintain solvent flow. Rinses of 25 mL of n-hexane and 150 mL of 15%

diethyl ether in petroleum ether were allowed to pass through the column. Two hundred mL of 10% acetone in n-hexane were added to the column, allowed to pass through, collected, and concentrated to 10 mL on a water bath using a modified Kuderna-Danish distillation apparatus.

Gas chromatographic analysis was done with a flame photometric detector. The column was glass (182 cm x 0.4 cm ID) packed with 15% Carbowax 20M on 60-80 mesh Gas Chrom P. Other operational parameters were: N_2 carrier gas, 100 mL/min; column oven, 190 C; detector, 190 C; injection port, 205 C.

RESULTS AND DISCUSSION

Procedural recoveries from eight vegetables fortified with 0.01 and 0.10 ppm of ethoprop before analysis are given in Table 2. At least one recovery was analyzed with each batch of samples using the same vegetable. The average recovery was 95% for 29 fortified samples and ranged from 71 to 112%.

Table 2. Recoveries of ethoprop from eight vegetables

Vegetable	Fortification (µg/g)	No. of samples	Range (%)	Average (%)
Snap bean	0.01	2	96-108	102
	0.10	2	92-112	102
Tomato	0.01	2	88-90	89
	0.10	1	82	82
Cucumber	0.01	2	78-100	89
	0.10	1	100	100
Lettuce	0.01	3	92-112	101
Onion	0.10	2	94-100	97
Turnip root	0.01	2	82-82	82
	0.10	3	86-105	96
Turnip leaf	0.01	3	100-104	101
	0.10	4	71-104	85
Radish	0.01	1	108	108
	0.10	1	105	105
	All levels	29	71-112	95

The residues found in the eight vegetables grown in soil treated with various rates of ethoprop are presented in Table 3. Residues in all tomato, cucumber, and lettuce samples were below the low detectable limit of 0.005 ppm.

Table 3. Residues (ppm)[a/] of ethoprop in edible portions from eight vegetable crops grown in soil treated with 0, 3.4, 6.7, and 13.4 kg/ha before planting in 1976.

Treatment (kg/ha)	Harvest	Snap bean	Tomato	Cucumber	Lettuce	Onion	Turnip root	Turnip leaf	Radish
0	First	<0.005	<0.005	<0.005	<0.005	<0.005	0.012	<0.005	0.010
	Second	<0.005	<0.005	<0.005			<0.010	<0.005	<0.005
3.4	First	<0.005	<0.005	<0.005	<0.005	0.009	0.017	0.018	0.038
	Second	<0.005	<0.005	<0.005			0.010	<0.005	0.018
6.7	First	0.008	<0.005	<0.005	<0.005	0.035	0.019	0.041	0.079
	Second	<0.005	<0.005	<0.005			0.012	<0.005	0.031
13.4	First	0.018	<0.005	<0.005	<0.005	0.068	0.035	0.281	0.345
	Second	0.005	<0.005	<0.005			0.013	0.036	0.163

[a/] Each value represents an average of four replications.

The highest residues were found in the radish. Residues for both harvests increased with increasing application rates. The residue levels of each treatment of the second harvest were less than half those of corresponding treatments of the first harvest. The decrease was due mainly to two factors, time and radish size. The second harvest was made one week after the first, thus allowing for the loss of some of the ethoprop from the soil by volatization, degradation, and leaching. Nearly 2.3 cm of rainfall occurred between harvests. The average radish weight increased from 9 g to 13 g during this time. This increase in radish size and weight had considerable effect on the reduction of the ethoprop residues. Statistical analysis of the calculated µg per radish values resulted in significant differences between treatments and not between harvests.

Turnip leaves (first harvest) contained the second highest ethoprop residues of all the vegetables. By the second harvest 9 days later, the residues were significantly lower. Ethoprop levels above the low detectable limit were found in two samples from the 6.7 kg/ha treated plots and all samples from the 13.4 kg/ha treated plots. Increased application rates of ethoprop correlated positively with the higher residues.

Ethoprop applied at rates of 6.7 and 13.4 kg/ha caused a reduction in the number of harvestable onion bulbs. The average weight per bulb was not reduced. Ethoprop residues in onions increased directly proportional to the amount applied.

Higher rates of ethoprop did not reduce the number of harvestable turnips or the average weight per turnip. Turnip roots from the first and second harvests contained residues which were not significantly different.

Ethoprop levels in snap beans decreased significantly from the first to the second harvest. A direct relationship was observed between ethoprop levels in snap beans and the rate of ethoprop applied to the soil.

ARGAUER & FELDMESSER (1978) conducted similar experiments to determine the residues of ethoprop in several vegetables. They analyzed onion, carrot, radish, eggplant, beet, cabbage, cantaloupe, pea, and tomato. No residues above their low detectable limit of 0.01 ppm were found in beet, cabbage, cantaloupe, pea, or tomato. Application rates were the same as those in this study. Residues found were 0.12, 0.52, and 1.3 ppm in onion and 0.12, 0.33, and 0.66 ppm in radish for 3.4, 6.7, and 13.4 kg/ha rates of ethoprop, respectively. The residue levels are sixteen times and three times larger than those in this study for onion and radish, respectively. The differences are possible due to the time interval between treatment and harvest.

Onion and radish were harvested 6 weeks after planting, or 7 weeks after treatment by Argauer and Feldmesser, whereas the onions were harvested 15 weeks after treatment and the radishes 8 and 9

weeks after treatment in this study. Both radish and onion were planted the same day the ethoprop was applied in this study. If the amounts of ethoprop found on a crop were directly proportional to the level in the soil, then the differences in the residue levels observed between the two tests were most likely due to the length of time between treatment and harvest. The half life of ethoprop in a sandy loam soil, which was used in both tests, is about 14 days (SMELT 1977). The time interval ratio for radish was 6:9 weeks; thus the residues in radish found by Argauer and Feldmesser would be expected to be more than twice those in this study. The same relationship holds for onion. The time interval ratio here was 6:15, a difference of 9 weeks. With a half life of 2 weeks, the level of ethoprop in the soil at 6 weeks would be greater than 16 times the level at 15 weeks. The ratio of residues on onion from the two experiments was also about 16.

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