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Uptake of Ethoprop (Mocap) by Ten Vegetables Grown in Soil Treated for Control of Nematodes

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An analytical method was developed for the analysis of the nematocide ethoprop (*O*-ethyl *S*,*S*-dipropyl phosphorodithioate) in vegetable crops. The method was rapid and efficient with recoveries nearly 100% for samples fortified at levels as low as 0.01 ppm. Ethoprop was found at harvest at levels above 0.01 ppm in onion (0.12, 0.52, 1.34 ppm), carrot (0.14, 0.34, 0.81 ppm), radish (0.12, 0.33, 0.66 ppm), and eggplant (0.027, 0.044, 0.086 ppm) which were grown in soil treated 1 week before planting with 30, 60, and 120 lb of ethoprop 10% granules/acre (3.4, 6.7, 13.4 kg/ha active ingredient). Ethoprop was not detected (<0.01 ppm) in beet, cabbage, cantaloupe, pea, and tomato. Skin, core, or roots of certain selected vegetables sampled had higher concentrations of ethoprop than had the whole vegetable.

Ethoprop (*O*-ethyl *S*,*S*-dipropyl phosphorodithioate), a nematocide–insecticide, is currently registered for use on sugarcane, soybean, corn, banana, plantain, peanut, sweet and white potatoes, pineapple, snap and lima beans, cabbage, and cucumber with a tolerance level at harvest set at 0.02 ppm. The objective of this study was to develop an efficient and rapid method suitable for analysis of this chemical in various vegetable crops in order to accumulate the chemical data required to support minor use pesticide registration requirements for the establishment of appropriate tolerances for this chemical in vegetables.

RESIDUE ANALYSIS

Preparation of Samples. All samples were analyzed within 2 weeks after freezing. The frozen samples were washed by hand under cold tap water to help remove traces of soil. All samples except tomato and cantaloupe were chopped in a food mill into small pieces. The greens 3 cm above the onion bulbs were discarded and the bulbs chopped. Both pea and pod were chopped. Tomatoes were thawed at 25 °C and slurried in a Vitamix 3600 blender. Cantaloupes were thawed and halved, seeds were discarded, and the pulp was slurried.

Sample Analysis. For sample analysis, 100-g portions of the chopped or slurried vegetable, 10 mL of 10% sulfuric acid, and 250 mL of methylene chloride were blended together for 3 min in a Waring Blendor. The blend was filtered by gravity through filter paper into a flask that contained anhydrous granular sodium sulfate. A 83-mL portion of the filtrate was concentrated to near dryness on a Rinco evaporator at about 20 °C under a water aspirator vacuum. Five milliliters of ethyl acetate was added to the concentrate to dissolve the residue, the ethyl acetate solution was centrifuged to remove any insoluble material, and 5 μL of the supernatant was injected into a gas chromatograph (see Figure 1 for GC conditions). The response was compared with that of ethoprop standards. Standard solutions were prepared from analytical grade ethoprop (Mocap) supplied by Mobil Oil Corp. at 95.8% purity. All ethoprop concentrations are reported with the phosphorus filter positioned in the flame photometric detector.

Extraction Efficiency of Method. For the determination of the efficiency of extraction, 100-g portions of chopped or slurried vegetable grown in untreated plots were fortified at levels between 0.01 and 0.2 ppm by adding 1 to 20 μg of ethoprop standards before blending and analyzed as were the samples.

Confirmation by Mass Spectrometry. A methylene chloride extract of a 200-g portion of chopped onions (replicate 4; 6 pounds/acre treatment level) (0.89 ppm) was concentrated under vacuum, diluted to 10 mL with methylene chloride, and rinsed into a 10 mm i.d. glass column that contained 14 g of 60–200 mesh silica gel 45 cm deep. The column was eluted with methylene chloride, and 25-mL fractions were collected. The fifth through seventh fractions were combined, evaporated to near dryness, taken up in 0.5 mL of ethyl acetate, and 2 μL injected into a Hewlett-Packard Model 5930A GC mass spectrometer with 5932A Data System that contained a 5% OV-17 gas chromatographic column held at a temperature of 220 °C. This represented an injection into the GC–MS estimated at approximately 700 ng of ethoprop.

Plot Size, Soil Treatment, Planting, and Sampling Dates. Vegetables were grown in light sandy soil with irrigation as needed in plots located at the University of Maryland Experimental Farm, Salisbury, Md. Each plot measured 30 ft by 33.33 ft. Ethoprop, except in the untreated control plots, was dispersed at the soil surface as a 10% granular formulation and worked into the soil to a depth of 1–2 in. with a spiked tooth harrow; vegetables

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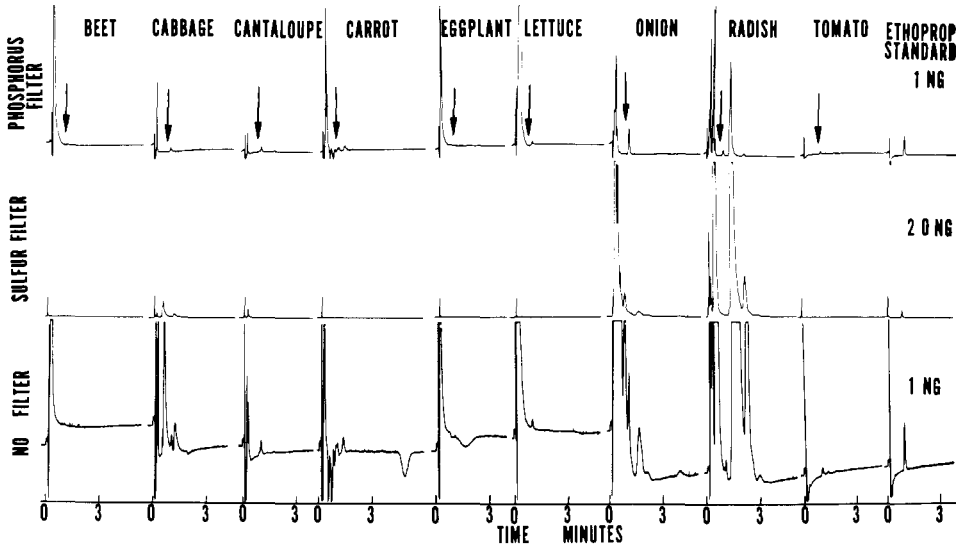

Figure 1. Gas chromatograms for vegetables grown as controls in untreated plots (33.3 mg of plant/5 μL of injected extract). (Tracor Model 550 Gas Chromatograph with a 5 ft × 0.25 in. o.d. 3% OV-1 on 80/100 mesh HP Chromosorb W column at 160 °C; electrometer attenuation: sulfur and phosphorus filters, $10^4 \times 4$; no filter, $10^4 \times 8$). Arrows indicate retention time of ethoprop.

were planted 1 week after soil treatment. Seven vegetables were planted on April 21, 1976, in each of 16 plots (four replicates at 0, 3, 6, 12 lb of ethoprop/acre) and sampled at the following times after planting: onion, radish, 6 weeks; lettuce, cabbage, pea, 8 weeks; carrot, beet, 12 weeks. Three vegetables were planted on May 5, 1976, in each of 16 additional plots and sampled at the following times after planting: eggplant, 11 weeks; tomato, 13 weeks; cantaloupe, 14 weeks. Samples were washed to remove loose soil, frozen within several hours, and stored at −20 °C at Beltsville, Md.

RESULTS AND DISCUSSION

Mobil Oil Corporation provided a method by which ethoprop was extracted with hexane from an acidified sample macerate, that required a sample cleanup and cosweep distillation prior to gas chromatography with detection by flame photometry. We found, however, that ethoprop was separated sufficiently by gas chromatography from ir ɔrferences that occur in crops to allow injection of the sample extract directly into the gas chromatograph, thus eliminating clean-up steps that could be a possible source of loss for the pesticide residue. The chromatograms shown in Figure 1 were obtained after over 200 injections of extracts of samples and illustrate the satisfactory separation of ethoprop from coextractives in vegetables by our direct method. The chromatograms obtained with the phosphorus filter in position in the flame photometric detector correspond very closely to those obtained throughout the duration of the work. We also found a relatively high concentration of sulfur-containing compounds in several vegetables that account for additional chromatographic peaks during operation of the detector in the phosphorus mode. Apparently a small percentage of the light emitted by these sulfur-containing compounds is transmitted through the phosphorus 526-nm interference filter. Nevertheless, interfering peaks at the retention time of ethoprop (indicated by the arrows in Figure 1) were absent. Recoveries of fortified samples by our method were nearly 100% in all cases (Table I).

Because of our concern that coextractives would interfere with confirmation of GC–MS on an onion sample, they were separated from ethoprop by silica gel column chromatography. The mass spectrum of a standard of ethoprop ($M^+ = 242$) closely corresponds to that of ethoprop extracted from onion grown in treated soil (Figure 2). The fragmentation pattern with masses at m/e 200, 167, 158, 139, 125, and 97 may be explained through successive eliminations of C_3H_6, HS, and C_2H_4, as proposed

Table I. Ethoprop Found in Control Samples Fortified with Known Amounts of Ethoprop

Crop	Ppm added	Ppm found
Beet	0.01	0.012
Cabbage	0.01	0.012
Cantaloupe	0.01	0.01
Carrot	0.10	0.108
Eggplant	0.01	0.01
Lettuce	0.01	0.01
Onion	0.20	0.23
Peas (English)	0.01	0.008
Radish	0.20	0.22
Tomato	0.01	0.01

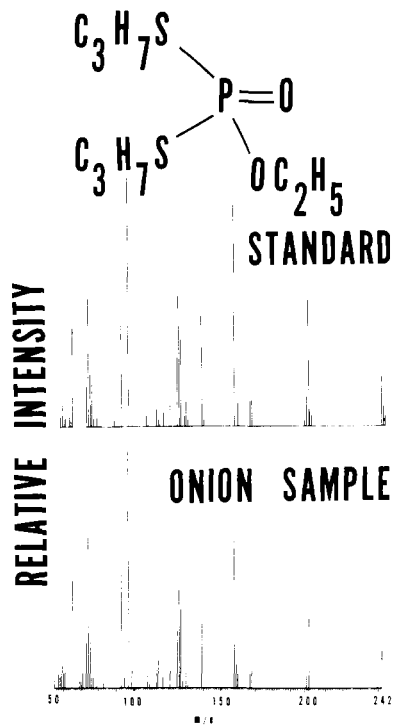

Figure 2. Confirmation by GC–MS of ethoprop in sample of onion grown in treated soil.

Table II. Ethoprop (ppm) in Ten Vegetable Crops Grown in Soil Treated Prior to Planting with 10% Ethoprop Granules

Vegetable crop	Treatment level, lb of ethoprop/acre, four replicates[a]		
	3 lb	6 lb	12 lb
Onion	0.07, 0.10, 0.13, 0.19	0.32, 0.41, 0.47, 0.89	1.09, 1.16, 1.45, 1.64
	0.12 ± 0.026[c]	0.52 ± 0.126	1.34 ± 0.128
Carrot	0.08, 0.09, 0.17, 0.23	0.15, 0.17, 0.31, 0.74	0.28, 0.86, 0.96, 1.14
	0.14 ± 0.035	0.34 ± 0.137	0.81 ± 0.186
Radish	0.08, 0.09, 0.13, 0.18	0.26, 0.30, 0.33, 0.44	0.60, 0.65, 0.67, 0.71
	0.12 ± 0.023	0.33 ± 0.039	0.66 ± 0.023
Eggplant	0.014, 0.029, 0.031, 0.034	0.036, 0.041, 0.05, 0.05	0.061, 0.082, 0.085, 0.116
	0.027 ± 0.004	0.044 ± 0.007	0.086 ± 0.011
Beet, Cabbage, Cantaloupe, Pea, Tomato	<0.01	<0.01	<0.01
Lettuce[b] (salad bowl variety)	<0.01, 0.05, <0.01	0.02, 0.03, 0.03, 0.08	0.03, 0.05, 0.23
		0.04	

[a] All residues <0.01 ppm at a treatment level of 0 lb/acre. [b] Poor sampling contributed to large amount of soil in frozen samples of leaves. [c] Mean ± standard error of mean.

Table III. Ethoprop Found in Select Parts of Several Vegetables (Soil Treatment Level 12 lb/acre)

Beets	Skin	0.02 ppm
Cabbage	Core	0.098 ppm
Carrots	Vascular tissue	0.095 ppm
	Outer core (cortex)	0.22 ppm
	Skin (peel)	2.1 ppm
	Side root hairs	20 ppm
Lettuce	Roots	0.14 ppm
Onions	Roots and bottom 0.125 in. of bulb	2.2 ppm

by Jorg et al. (1966) for the dimethoxyphosphorodithioates.

The method reported here for the analysis of ethoprop was not designed to measure the residues of the metabolites of ethoprop. Menzer et al. (1971) showed that ethoprop is metabolized in bean and corn plants to metabolites that are not likely to be considered toxic in any way. In nearly all cases, these metabolites were at concentrations below those found for ethoprop. Furthermore, when fed to rats, ethoprop was changed rapidly to metabolites that would not be expected to present a toxic hazard to man (Iqbal and Menzer, 1972).

Residues of ethoprop are given in Table II for ten vegetables. The amount of residues found in onion, carrot, radish, and eggplant is directly proportional to the amount of the nematocide applied to the soil. That residues in beet were undetected (<0.01 ppm) while residues in other root crops such as onion, carrot, and radish were significantly higher could not be correlated with the relative pH, water content, relative concentration of sulfur-containing compounds, or surface area at the soil/vegetable interface of the vegetables. The close agreement among the replicates in the amount of ethoprop taken into four of the vegetables indicates that the ethoprop granules were applied fairly uniformly by the spiked tooth harrow and that irrigation and rain distributed the ethoprop equally into the soil in all four replicates.

The question of whether the small residue found in several of the root crops resulted solely from the failure to remove adhering soil particles sufficiently or from entrapment of soil particles during the growth of the crop was considered. We therefore determined the amount of ethoprop in specific parts of several vegetables (Table III) as follows: Beet skin, cabbage core, lettuce and onion roots were separated from the whole vegetable. Carrots were selected at random from three replicates (12 lb/acre treatment level). Root hairs (5 g) were obtained from 30 carrots. The skin of the carrots was removed with a potato peeler. Peeled carrots were quartered lengthwise, and the cortex was separated from the vascular tissue with a knife. The amount of ethoprop was determined after extraction with an appropriate amount of methylene chloride.

Ethoprop was detected in the cabbage core (0.098 ppm) whereas none was found in the whole vegetable (<0.01 ppm). The amount of residue found in the peel of the carrot did not, on a weight basis, account for the total amount of residue found in the whole vegetable since the peel represents a very small percentage of the carrot. In fact, ethoprop was found in the cortex and vascular tissue of the carrot. A higher amount of ethoprop was found in the roots of lettuce and onions than in the leaves and bulb.

The mechanism that would account for the concentrations of ethoprop found in these vegetables undoubtedly is highly complex. It is certainly a function of the concentration of ethoprop available in the soil during the growth of the vegetable and the rates of uptake and metabolism that may be unique for each of these vegetables.

The rate of loss of ethoprop from soil has been described by others. The half-life of ethoprop has been reported to be between 3 and 12 days in the field and 30 days in steam-sterilized soil when beans were grown in that soil in plant growth chambers (Menzer et al. 1971). Biological activity against certain insects disappeared after 8 weeks when ethoprop was incorporated into sandy loam (Harris and Hitchon, 1970).

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Herbicide and Insecticide Residues in Tailwater Pits: Water and Pit Bottom Soil from Irrigated Corn and Sorghum Fields

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Water and soil sediment samples from tailwater pits used to collect irrigation runoff were analyzed for herbicide and insecticide residue. Herbicide residues were more frequently found and generally more persistent than were insecticide residues. Atrazine residue occurred more frequently than other pesticides in both pit bottom soil and water samples. Propazine and fonofos residues were also common. The maximum amount of atrazine detected was 1068.3 ppb in bottom soil and 1074.1 ppb in water. Propazine also was detected at a high level, 429.0 ppb in bottom soil and 153 ppb in water. Insecticides such as fonofos were found at 771.2 ppb in bottom soil and 5.9 ppb in water. Analyses detected residues of 11 additional pesticides: alachlor, carbofuran, cyanazine, dimethoate, disulfoton, EPN, EPTC, parathion, phorate, R25788, and terbutryn. In general, pesticide residues were small enough that water from irrigation tailwater pits could be reused to irrigate crops in the same or other fields. In a few cases, however, herbicide residues were concentrated sufficiently that particularly sensitive crops might be damaged if irrigated with water from the pits. Insecticide residues were usually not detected at the end of the growing season. Residues of fonofos were sufficient in five pits (1974) to kill fish if the pit bottom soil had been roiled and to be a potential hazard to birds and mammals.

In the development of irrigation systems for farm land, collecting basins are excavated to impound runoff from fields during irrigation (Hay and Pope, 1977). They also may collect water during and after heavy rainfall. These basins, called tailwater pits, collect water which may be pumped back to the high end of the field, or onto another field, and reused for irrigation (Figure 1). Tailwater pits provide drinking water for pheasants, doves, rabbits, coyotes, and occasional deer and are resting sites for waterfowl. (Vegetation is discouraged from growing in the water or on the shore of well-managed pits. Thus, they are relatively unimportant as feeding and nesting sites). Consideration has also been given to the use of tailwater pits for fish rearing, livestock drinking water, and for swimming.

Pesticides are utilized extensively in the production of corn and grain sorghum, and other crops, on irrigated land in southwest Kansas. One would expect irrigation water and silt to carry measurable pesticide residues into the tailwater pits. Farmers have asked if herbicide residues may accumulate and cause crop damage when tailwater is reused for irrigation. Those contemplating other uses for the water are also concerned.

In 1973 and 1974 we conducted the study reported herein to help answer such questions. Extraction–cleanup methods and gas chromatographic procedures were adapted for analyses of water and soil for pesticide residues.

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MATERIALS AND METHODS

Thirty-six tailwater pits in Haskell County, Kansas, each receiving water from one or more fields of corn or grain sorghum, were sampled. Most fields were 160 acres (65 ha) in size. The surface soils of all the fields were Richfield, Ulysses, or Richfield–Ulysses silt loam, and all fields had from 0 to 3% slope (Hamilton et al., 1968).

The fields and pits were managed by 28 different farmers. Our purpose was to determine the occurrence of pesticide residues under actual agricultural conditions. Therefore, the investigators did not try to influence tillage and irrigation practices nor to coordinate pesticide use. Information about pesticide use in fields draining into the tailwater pits was obtained in June or July of each year by questionnaires and interviews. Additional information was added to each record after pesticide applications were made.

For 1973, our plan included sampling each pit before the first runoff of the growing season, immediately after the first runoff, at midseason, in late summer, and during autumn. However, we could not visit all pits daily and irregular patterns of rainfall and irrigation upset the timing of our first two samplings. In 1974 we sampled each pit in May, June, July, August, and November without regard to dates of runoff into specific pits.

Although the closest field associated with each pit was recorded as either corn or sorghum, in 1973 it was not known what crops were grown in nonadjacent fields which drained into some of the pits. In 1974 we attempted to identify all of the fields which drained into each pit and to record the crops grown in them. Thus, some pits were known to have received runoff from both corn and sorghum.

Water samples (3.8 L) were collected into clean glass jugs from the edges of pits near their inlets. At each sampling we took 1 gal (3.8 L) of tailwater and 1 qt (0.95 L) of

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