Residues of Maneb, Ethylenethiuram Monosulfide, Ethylenethiourea, and Ethylenediamine on Beans and Tomatoes Field Treated with Maneb

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Maneb, ethylenethiourea (ETU), ethylenethiuram monosulfide (ETM), and ethylenediamine (EDA) were measured on crops of beans and tomatoes at 0, 1, 2, 3, 6, 9, and 14 days after treatment with maneb. The levels of all residues declined with time, beans containing more of each compound than tomatoes. After 14 days beans contained the following amounts (parts per million) of compound: maneb, 13; ETU, 0.11; ETM, 0.25; EDA, 0.09. The corresponding values for tomatoes were: maneb, 10; ETU, 0.07; ETM, 0.03; EDA, 0.05.

Ethylenebis(dithiocarbamates) are widely used as agricultural fungicides and have been shown to degrade under laboratory conditions to several compounds including ethylenethiuram monosulfide (ETM), ethylenethiourea (ETU), and ethylenediamine (EDA) (Hylin, 1973; Ludwig et al., 1954). The rate of disappearance of maneb, as measured by a carbon disulfide evolution procedure, has been examined on two crops, lettuce and kale, under field conditions (Yip et al., 1971). From this study it was found that maneb persisted at appreciable levels 14 days after application while ETU declined to undetectable amounts within 7 days.

Residues of ETU and ETM on tomatoes treated in the field with maneb have been measured semiquantitatively and found to reach maximum values 5 days after application, declining to trace amounts within 10 days (Engst et al., 1968). The purpose of the present study was to determine the levels of maneb existing on crops with different surface characteristics, i.e. beans and tomatoes, and monitor its decline in relation to that of three of its decomposition products, ETU, ETM, and EDA.

EXPERIMENTAL SECTION

Field Experiment. The field experiment was conducted during the summer of 1974 at the Ottawa Research Station, Canada Department of Agriculture. The crops employed were string beans (Sanilac variety) and tomatoes (Ottawa 78 variety). The test plot of beans consisted of two 30-ft rows approximately 2 ft apart, while that of tomatoes consisted of 20 plants distributed in two 30-ft rows. Untreated plots of each crop were maintained as controls. An aqueous suspension of an 80% maneb formulation (Dithane M-22, Rohm and Haas Co.) was applied by hand sprayer at a rate of 3 lb/acre per 100 gal. Both beans and tomatoes were sprayed to run-off, 0.5 gal of the suspension being consumed in the treatment of each crop. Beans received seven treatments and tomatoes eight at intervals of 7 days. Total rainfall during the test period was 4.25 in. for beans and 4.61 in. for tomatoes.

Sampling. Sampling was commenced immediately after the final application of maneb. Each crop row was divided into 10-ft sections, providing six sample locations for each crop. The sample size from each location was 75 g of beans and 500 g of tomatoes.

Upon receipt at the laboratory, samples of beans were chopped finely, while those of tomato were blended in a Waring Blendor. Subsamples were taken for immediate ETM analysis and the remainder was frozen at −18° for later analysis of other components.

Soil samples were taken from 15 × 15 cm sections along a row of beans. They were removed from below plant foliage to monitor accumulated runoff. Samples were obtained 15 days after the final application of maneb and were removed from depths of (a) 0.5 in., (b) from 0.5 to 1.5 in. and (c) 1.5–2.5 in.

Analytical Methods. Maneb was analyzed by hydrolysis to ethylenediamine and gas–liquid chromatography of the bis(trifluoroacetate) derivative essentially as described (Newsome, 1974). Because of the large amounts of maneb encountered, the acid hydrolysate was diluted to 50 ml with glass distilled water and a 5.0-ml aliquot was subjected to ion exchange chromatography. After elution of the ethylenediamine with saturated $NaHCO_3$, a 100-μl aliquot was added to 50 μl of concentrated HCl for evaporation to dryness prior to trifluoroacetylation.

Free ethylenediamine was determined by extraction with cold dilute HCl, followed by ion exchange chromatography and trifluoroacetylation as described for maneb (Newsome, 1974).

The analysis of ETM was performed exactly as described (Newsome, 1975). Briefly, the method involved extraction of the sample with toluene followed by partitioning of the ETM into HCl. After basification with Na_2CO_3, the ETM was extracted into toluene for gas–liquid chromatographic analysis.

ETU analyses were carried out as described by Pecka et al. (1975), which is a modification of an earlier procedure (Newsome, 1972).

Gas–liquid chromatography was performed on a Hewlett-Packard 5700 A instrument fitted with a ^{63}Ni electron capture detector. All analyses were carried out on a single 6 ft × 4 mm i.d. glass column packed with 5% butanediol succinate on 100–120 mesh Chromosorb W, HP. The column was conditioned at 200° for 48 hr before initial startup. Detector and injection block settings of 300 and 200°, respectively, were used throughout the experiment. The argon–methane (95:5) carrier gas flow rate and oven temperature were varied, depending on the compound analyzed. For ETU and ETM, an oven temperature of 195° was used, while for ethylenediamine trifluoroacetate the temperature was 180°. A carrier flow rate of 80 ml/min was used for the analysis of ETU and ethylenediamine trifluoroacetate, while 35 ml/min was employed for ETM.

Recoveries of maneb, ETM, ETU, and EDA added to both crop materials were greater than 90%. The recovery of ETM and ETU added to soil was quantitative, whereas a 71% yield of EDA was obtained. The method for maneb was not suitable for soil as described, only 10% being recovered from fortified samples.

RESULTS AND DISCUSSION

The level of all residues analyzed was higher on beans than on tomatoes (Figures 1–3, Table I) and may be a reflection of the larger surface area of the former. Beans were found to contain low levels of EDA which declined with time while tomatoes did not contain amounts greater than

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Table I. Ethylenediamine in Beans and Tomatoes after Treatment with Maneb

Elapsed time, days	Ethylenediamine found, ppm ± SE	
	Tomato	Bean
0	0.053 ± 0.008	0.239 ± 0.036
3	0.068 ± 0.006	
9	0.051 ± 0.002	0.187 ± 0.017
14	0.047 ± 0.002	0.094 ± 0.058
Control[a]	0.073 ± 0.037	0.039 ± 0.013

[a] Sampled at 0 days.

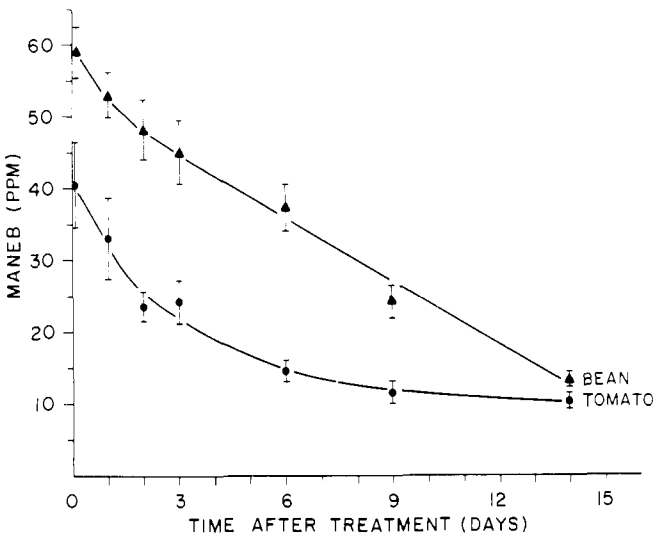

Figure 1. Residues of maneb on beans and tomatoes harvested at various intervals after treatment. Values are the means of single determinations performed on six samples. Vertical bars represent the standard error of the mean.

the control value (Table I). With the exception of EDA, significant amounts of all residues remained after 14 days, although none was found to accumulate. The decline of residues did not appear related to periods of rainfall recorded over the sampling interval and corresponds to observations with other crops (Yip et al., 1971).

The amount of maneb found 14 days after the final application was similar to that found on lettuce and kale by the CS_2 method (Yip et al., 1971), but in the present study a slower initial rate of decline was observed (Figure 1). Samples of control crop analyzed for maneb resulted in values of 0.123 ppm for beans and 0.065 ppm for tomatoes.

Residues of ETU decreased to 0.1 ppm after 6 days on beans and after 2 days on tomatoes (Figure 2). Small amounts persisted 14 days after spraying.

Since it has been shown that ethylenebis(dithiocarbamates) added to foods degrade to ETU when cooked (Newsome and Laver, 1973; Watts et al., 1974), it was considered appropriate to ascertain what levels would be generated from maneb on crops subjected to normal weathering processes in the field. Accordingly, beans sampled 9 days after spraying and tomatoes obtained 6 days after spraying were boiled for 15 min in water, cooled, and extracted with ethanol. Analyses for ETU showed a total (cooking water + sample) of 11.14 ± 0.22 ppm in beans and 3.19 ± 0.48 ppm in the case of tomatoes. Thus, it would appear that residues of the parent compound can represent a considerable source of ETU.

ETM was found to decrease rapidly on both crops the first day after treatment and then decline slowly thereafter

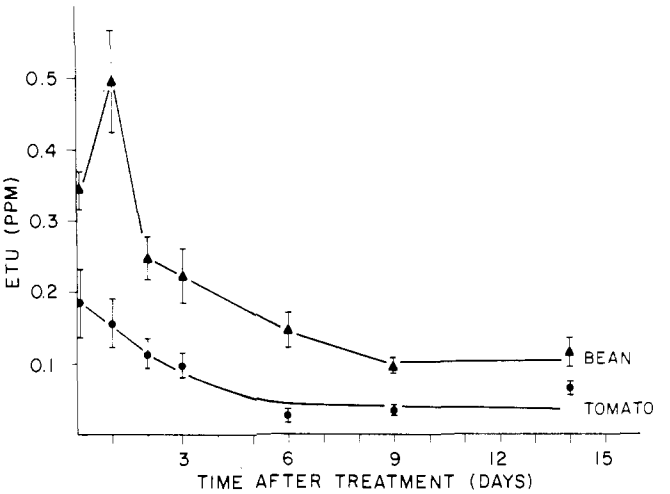

Figure 2. Residues of ETU on beans and tomatoes after treatment with maneb. Symbols as in Figure 1.

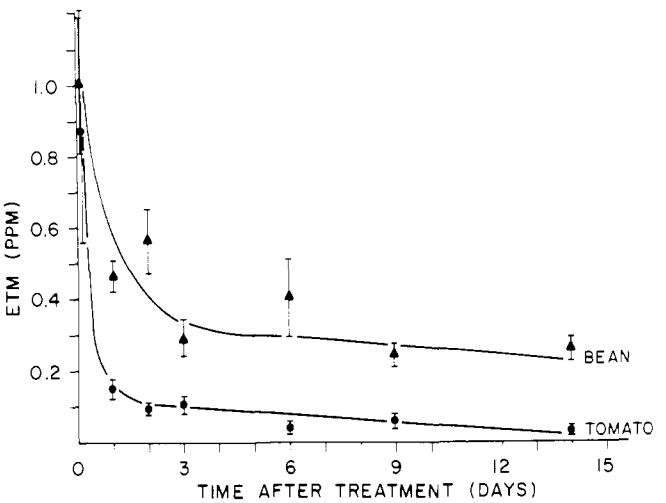

Figure 3. Residues of ETM on beans and tomatoes after treatment with maneb. Symbols as in Figure 1.

Table II. Residues in Soil 15 Days after Treatment with Maneb[a]

Soil depth, in.	ETM, ppm	ETU, ppm	EDA, ppm
0–0.5	0.539 ± 0.056	0.353 ± 0.096	0.119 ± 0.015
0.5–1.5	0.081 ± 0.021	0.046 ± 0.023	0.044 ± 0.009
1.5–2.5	0.044 ± 0.025	0.076 ± 0.060	0.044 ± 0.004

[a] Values are the mean ± standard error of three determinations.

(Figure 3). Considerably more ETM was found on beans compared to tomatoes. No increase or accumulation of ETM was found as has been reported previously (Engst et al., 1968). The metabolism and toxicological significance of ETM remain to be examined.

The residues of ETM, ETU, and EDA found in soil are given in Table II. From the data it is evident that penetration below the first 0.5 in. is slight but that the level of each compound is higher than on the plant. Further studies are required to determine the dynamics of ethylenebis(dithiocarbamate) degradation in soil and the availability of various products to the plant.

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Persistence of Dimethoate and Dimethoxon on Cherries

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Two sprays of dimethoate, 10 fluid oz per 100 gal, applied 28 and 14 days prior to harvest on sweet and sour cherry trees, resulted in residues of less than 2.0 ppm of combined dimethoate and dimethoxon at harvest. The recommended use pattern of dimethoate for control of black and western cherry fruit flies in British Columbia should not result in residues at harvest exceeding tolerance levels.

Dimethoate, *O,O*-dimethyl *S*-(*N*-methylcarbamoyl)-methyl phosphorodithioate, is a broad spectrum contact and systemic insecticide that is registered in Canada for control of a wide variety of insect pests. Recently, the use pattern for this material was extended to include control of black cherry fruit fly and western cherry fruit fly. A preharvest interval of 15 days for the last spray application has been set and a residue tolerance of 2 ppm of dimethoate has been established.

Residue studies with dimethoate applied to cherries have previously been conducted in Europe. Beitz et al. (1969) in Germany reported that a 7-day interval to harvest following aerial application of the insecticide should be sufficient, but a further study (Beitz, 1973) indicated that ground spraying led to more persistent residues. Mitic-Muzina et al. (1971) reported that dimethoate degraded more slowly than diazinon and carbaryl on cherries. Residues of dimethoate have also been studied on other tree-fruit crops, including peaches (Mestres and Barrois, 1964) and citrus crops (Woodham et al., 1974a,b).

Experiments were carried out during 1973 to determine the degradation rate of dimethoate and the persistence of its oxygen analog, dimethoxon, on cherries in the Okanagan Valley of British Columbia.

EXPERIMENTAL SECTION

Plots of sweet cherries (Lamberts) and sour cherries (Meteor, Northstar, and English Morello) were treated with dimethoate (Rogor 40% EC) at the recommended rate of 10 fluid oz per 100 Imperial gal. Trees were sprayed to the point of run-off using a portable plot sprayer operated at 300 psi. The first cover spray was applied 6 days after the first cherry fruit fly was trapped and a second cover spray was applied 14 days later. Samples of fruit were taken 14 days after the application of the first cover spray (prior to application of the second cover spray), and then at intervals of 1, 2, 4, 7, and 14 days after the second spray was applied. Sample fruit was frozen and held for later analysis. The sweet cherry test plot consisted of six trees while the sour cherry plot consisted of five trees. Fruit used as controls was picked from trees separated from treated plots by an unsprayed buffer row. The plot pattern (six sweets, five sours) was duplicated for the controls.

Composite samples of sweet cherries and sour cherries were prepared by pooling fruit collected from each plot for each sampling date. The extraction procedure was adapted from that reviewed by Zweig and Sherma (1972). A 1-kg sample of the composite was chopped in a kitchen meat grinder and two 100-g sub-samples were then taken. Each was macerated in an explosion-proof Waring Blendor (Waring Products, Inc.) with 150 ml of residue quality dichloromethane (Caledon Laboratories, Inc., Georgetown, Ontario, Canada) for 5 min. Fifty grams of anhydrous sodium sulfate was then added to the macerate and the mixture was left to stand for 30 min with periodic swirling. Six grams of activated charcoal was added and mixed, and the mixture left to stand for another 2 min. The macerate was filtered through a Millipore glass pad under suction and washed with two 50-ml volumes of dichloromethane. The filtered solution was evaporated to dryness using a rotary evaporator (Buchi Rotavapor-R) and the residue taken up in 1 ml of residue quality acetone (Caledon Laboratories, Inc.).

Chromatographic analyses were carried out on a HP 5715A gas chromatograph (Hewlett-Packard) equipped with a flame photometric detector (Tracor, Inc.) operated in the phosphorus mode (526 nm) and with the following set conditions: oven temperature, 190°; detector temperature, 200°; nitrogen flow rate, 30 ml/min; hydrogen, oxygen, and air flow rates, 125, 25, and 45 ml/min, respectively; attenuation, 1000 × 32. The detector was modified as suggested by Burgett and Green (1974) to prevent solvent flame-out and provide an improved signal-to-noise ratio. On column injection was used.

Chromatography was carried out on a glass column, 6 ft × ⅛ in., packed with 3% OV-17 on Chromosorb W-HP, 80–100 mesh (Chemical Research Services, Inc.). The column was conditioned overnight at 250°, following which re-

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