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Environmental Fate of Methyl Eugenol[1,2]

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Methyl eugenol was found to be attractive to males of Dacus dorsalis Hendel (oriental fruit fly) by STEINER (1952) and has been used successfully as a synthetic lure in subsequent fruit fly control programs (STEINER et al. 1965, 1970). However, the proposed use of methyl eugenol in a male annihilation program will involve aerial distribution of cigarette filters saturated with the lure and with malathion over fruit fly infested areas. Therefore, it is important to determine the fate of methyl eugenol in the environment after such application. The present report describes the fate of methyl eugenol in soil and water and in tomatoes, a representative crop that might be affected by its use in a fruit fly control program.

MATERIALS AND METHODS

Chemicals. Samples of nonradioactive eugenol and methyl eugenol were obtained from commercial sources. Also, a supply of ^{14}C-labeled methyl eugenol was prepared by mixing 25 mg of eugenol with 2.15 mg ^{14}C-labeled methyl iodide (11.0 mCi/mmole) in 1 mL acetone and heating the solution in the presence of 100 mg anhydrous potassium carbonate in a sealed tube for 3 h at 100°C. Unreacted eugenol was removed from the reaction mixture by extraction from a diethyl ether solution with 0.05 N NaOH. Radiochemical purity of the ^{14}C-labeled methyl eugenol was > 99% as determined by thin later chromatography (TLC); the specific activity was 9.5 mCi/mmole.

Persistence of Methyl Eugenol in Soil and Water. For tests of the persistence in soil, 100 g of Lufkin fine sandy loam (see BULL et al. 1970 for description)

[1] In cooperation with the Tex. Agric. Exp. Stn., Texas A&M University, College Station, TX.

[2] Mention of a pesticide does not constitute a recommendation for use by the USDA nor does it imply registration under FIFRA as amended. Mention of a proprietary product does not constitute an endorsement by the USDA.

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was mixed with 15 mL H_2O in a beaker; then 2 mL of a hexane solution containing 10 mg of methyl eugenol were distributed uniformly over the soil surface. Samples were held at constant temperatures (22 or 32°C) in an environmental chamber programmed for 14 h light:10 h dark. Three beakers were removed from the chamber at preset posttreatment intervals (0, 24, 48, 72, and 96 h), and the soils were extracted 5 times with ca. 20-mL portions of dichloromethane. The combined extracts were concentrated under vacuum and adjusted to 3.0 mL with hexane. Analyses were performed by gas chromatography (GC) using a 2 m x 2-mm ID glass column packed with 1.5% SP2250 + 1.95% SP2401 on 100/120 Supelcoport at a column temperature of 140°C. Methyl eugenol had a retention time of 3.6 min.

In another experiment, cigarette filters were each treated with 0.5 mL of methyl eugenol and placed in beakers containing Lufkin fine sandy loam, either by embedding the filter in the soil or by placing it on top of the soil. Samples were held at 32°C in an environmental chamber programmed for 14 h light:10 h dark. At 0, 2, 7, and 12 days posttreatment, triplicate samples of this preparation were removed from the chamber, and the filter and soil were analyzed separately. Soil samples were extracted as previously described; filters were shredded and extracted with ca. 95 mL hexane in 15- to 20-mL portions, and the combined extracts were filtered and adjusted to 100 mL for GC analysis. The samples from both tests were concentrated to ca. 1 mL and analyzed with TLC using precoated plates (silica gel 60, F-254, Brinkmann Instruments) and solvent mixtures of either (a) hexane-acetone (85:15 v/v) or (b) hexane-chloroform-methanol (80:10:10 v/v/v). Radioactive materials were located on TLC plates by autoradiography with x-ray film. The plates were also exposed to shortwave UV light to detect nonradioactive compounds.

Residues of unextractable ^{14}C in soil were determined by combusting samples at 1000°C in an oxygen atmosphere as described by BULL et al. (1970).

The persistence of methyl eugenol in water was determined by adding 10 mg of the chemical to 100 mL of water contained in a 250-mL beaker. Samples were aged in a constant temperature chamber (22 or 32°C) and triplicate samples were taken at 0, 24, 48, 72, and 96 h posttreatment. The water was extracted 3 times with dichloromethane (50 mL/extraction), and the combined extracts were concentrated and analyzed by GC. The extracted aqueous fraction was analyzed for residual methyl eugenol by high performance liquid chromatography with a 24 cm x 0.5-mm μ-Bondapak/C-18 column and methanol-water (70:30) as solvent.

The dissipation of methyl eugenol from a cigarette filter suspended in air was determined by injecting 0.5 mL into each filter and suspending them ca. 1 m above ground level in an open field near College Station, TX, in June 1979. Three filters were analyzed for methyl eugenol by GC as previously described at each preset interval (0, 1, 2, 4, 7, and 12 days posttreatment).

Soil Leaching Studies. The leaching of methyl eugenol in sand, Houston clay, and Lufkin fine sandy loam was evaluated with the soil-TLC method described by HELLING (1971). Each soil was coated (500 µm) on 20 x 20-cm glass plates, and the plates were air dried. ^{14}C-labeled methyl eugenol was applied to each soil plate along with samples of ^{14}C-labeled diflubenzuron and potassium 3,4-dichloro-5-isothiazolecarboxylate (PDIC), which were included in each analysis as reference materials. Diflubenzuron has limited solubility in water (0.0002 mg/mL); PDIC is very soluble (485 mg/mL). Treated plates were developed in water in an enclosed TLC chamber until the solvent front migrated 10-12 cm. Radioactive material was then located by exposing the plates to x-ray film.

Fate of Methyl Eugenol in Field-Grown Tomatoes. Mature, red cherry-type green tomatoes were each treated topically with 1 mg of ^{14}C-labeled methyl eugenol (0.48 mCi/mmole) dissolved in 20 µL of 60% ethanol. Three tomatoes were harvested immediately after treatment, and additional triplicate samples were harvested at 1, 3, 7, and 14 days posttreatment. Unabsorbed (external) methyl eugenol was recovered by rinsing each tomato with ca. 50 mL dichloromethane, and absorbed (internal) radioactivity was recovered by homogenizing the tomato with dichloromethane and reextracting the residue twice with dichloromethane and twice with methanol. Aliquots from combined solvent extracts were radioassayed by conventional liquid scintillation, and then extracts were concentrated under vacuum to a convenient volume for analysis by GC and TLC. Residues were analyzed for unextractable radiocarbon by the combustion procedure described by BULL & IVIE (1976).

In another test, a cigarette filter containing 0.5 mL ^{14}C-labeled methyl eugenol was placed at the base of a tomato plant, and triplicate samples of mature green tomatoes were harvested at 0, 1, 3, 7, and 14 days. External and internal extracts were prepared and assayed as described.

Since preliminary tests indicated that methyl eugenol rapidly disappeared from the surface of mature green tomatoes, the compound was also applied to frosted glass slides (1 µg/slide) to assess its volatilization from an inert surface. The slides were placed outside, and at 0, 1, 2, 4, 8, and 24 h posttreatment, 3 slides were rinsed with hexane and prepared for quantitation by GLC.

RESULTS AND DISCUSSION

Persistence in Soil and Water. Methyl eugenol dissipated rapidly from both soil and water. At 32°C, 98% of the material was lost within 96 h, and 77 and 81% were lost from water and soil, respectively, after 96 h at 22°C (Fig. 1 and 2). Methyl eugenol had a half-life of ca. 6 h in soil and water at 32°C, and a half-life of 16 h and 34 h in soil and water at 22°C. TLC analyses of soil and water extracts at the various exposure times revealed methyl eugenol as the only radiolabeled compound. It is possible that methyl eugenol could have been demethylated to form eugenol, thus losing the ^{14}C-label; however, no eugenol was detected by either GC or TLC analyses. Persistence of methyl eugenol in water was very similar for treatment rates of 1 mg/100 mL water and 10 mg/100 mL water (Fig. 2).

Methyl eugenol was lost rapidly from treated cigarette filters that were placed on top of soil or

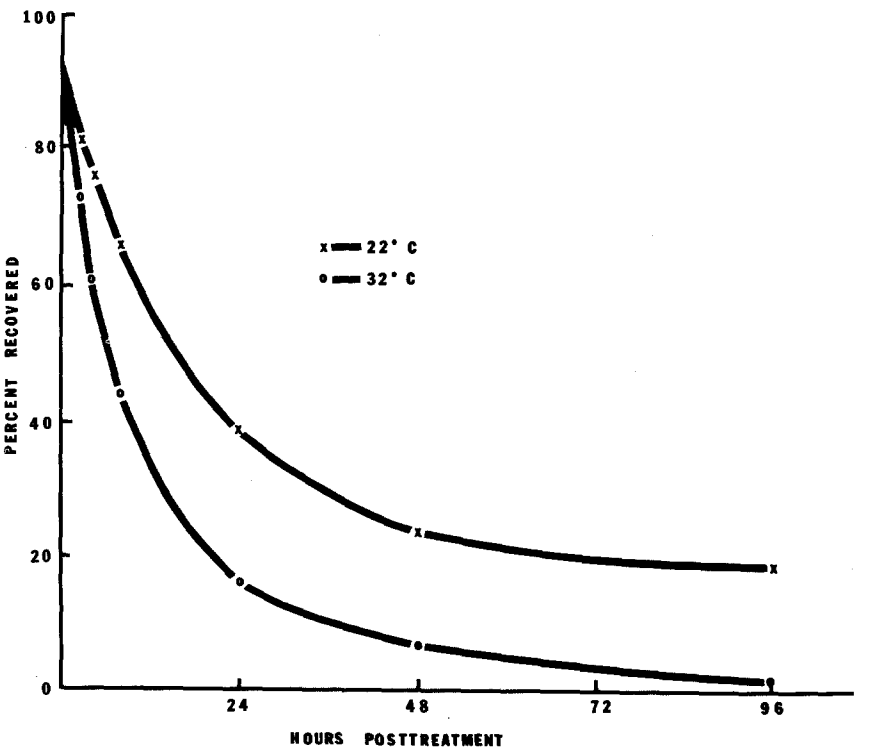

Figure 1. Dissipation curves of methyl eugenol in soil at constant temperatures of 22 and 32°C.

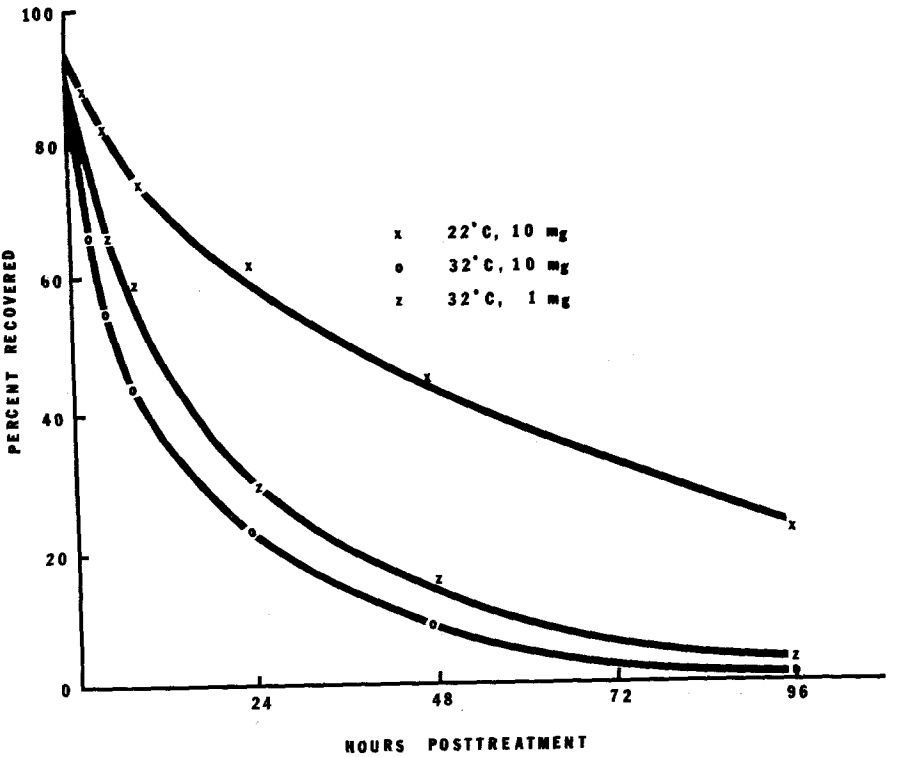

Figure 2. Dissipation curves of methyl eugenol in water at constant temperatures of 22 and 32°C.

embedded ca. 2 cm under the soil surface. With these 2 methods of treatment, 14 and 22% of the treatment dose remained in the filters after 12 days (Fig. 3); and the half-life of methyl eugenol in cigarette filters was ca. 4-4.5 days. No buildup of methyl eugenol was noted in the soil when filters were placed on top of the soil but there was an increase in methyl eugenol in the soil when filters were embedded, probably because there was less direct exposure to the atmosphere. Methyl eugenol was the only radiolabeled compound detected by TLC of the filter extracts. Filters suspended in air lost methyl eugenol at about the same rate as filters on and in the soil; the half-life in suspended filters was ca. 3.5 days, and only 14.5% remained after 14 days exposure (Fig. 4).

Soil Leaching Studies. Leaching studies with the soil TLC technique indicated that methyl eugenol was immobile in the 3 soils tested, although some streaking occurred with sand. The water soluble PDIC migrated with the solvent in sand and loam, and ca. 80% of the

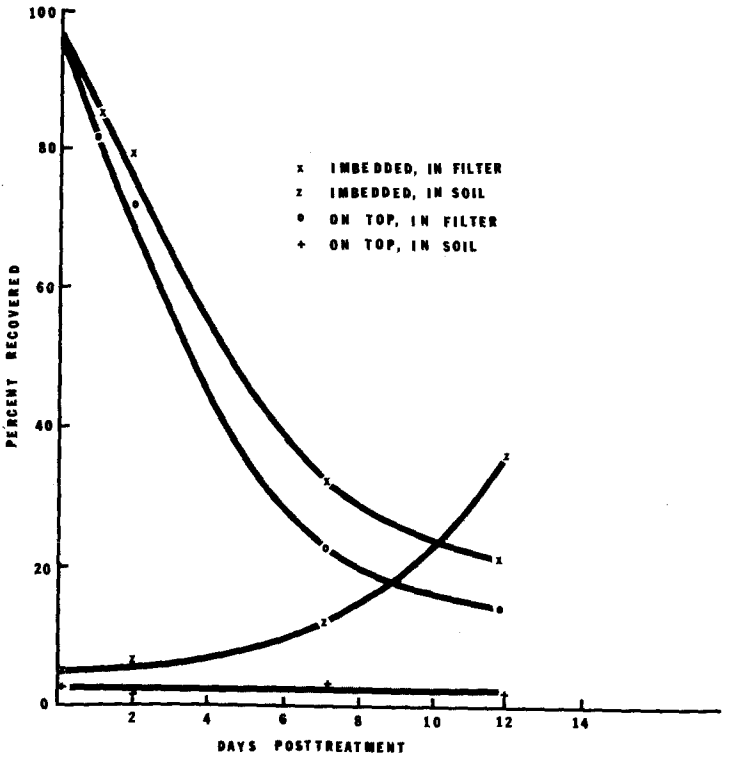

Figure 3. Dissipation curves of methyl eugenol from cigarette filters either embedded in soil or placed on top of soil at a constant temperature of 32°C.

distance traveled by the solvent in clay. Diflubenzuron (only slightly water soluble) was immobile in all of the systems.

Fate of Field-Grown Tomatoes. Methyl eugenol disappeared rapidly from the surface of field-grown tomatoes treated topically with 1 mg of the material. Only 3.8% of the dose was recovered in the external wash after 24 h (Table 1), and none was detected on 3, 7, and 14 days posttreatment. No differences were noted in extractable internal methyl eugenol throughout the test period (including 0-h samples). There was a small increase in unextractable radiocarbon in tomato pulp through 3 days, after which the quantity remained constant. Total internal accumulation of radiocarbon was 4 ppm (based on wet weight) after 14 days. No methyl eugenol was detected in tomatoes from plants that had been exposed to a cigarette filter containing 0.5 mL of methyl eugenol placed at the base of the plant.

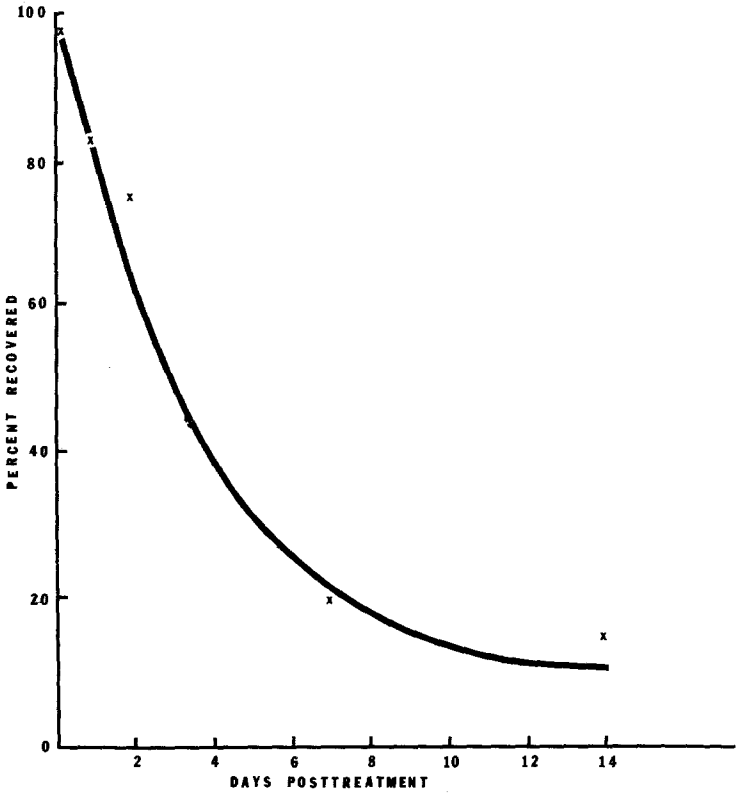

Figure 4. Dissipation curve of methyl eugenol from cigarette filters suspended in air under atmospheric conditions

TABLE 1

Recovery of methyl eugenol from tomatoes treated with 1 mg each

Time post-treatment, days	Quantity of methyl eugenol (µg) recovered in External (wash)	Internal (extract)	Internal (Unextractable)	Total internal accumulations ppm
0	995	23	2	--
1	38	14	15	2.6
3	0	27	35	4.2
7	0	19	41	4.6
14	0	18	40	4.0

The loss of the methyl eugenol was probably the result of evaporation since tests of the volatility of methyl eugenol from a glass surface indicated there was extremely rapid rate of loss with only 17% of the treatment dose (1 mg) remaining after 1 h and 0.4% of the treatment dose was detected after 24 h.

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