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Received for review May 19, 1987. Accepted October 26, 1987.

Presented at the Association of Official Analytical Chemists Meeting, Washington, DC, Oct 27-31, 1985. The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Metabolism of Methabenzthiazuron in the Soil of Pea Crops

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The herbicide methabenzthiazuron (MBT) was presowing applied onto the soil of pea fields in four regions with three different soil types. MBT, (2-benzothiazolyl)urea (IV), 2-(methylamino)benzothiazole (V), and 2-aminobenzothiazole (VI) were observed in all soil types. Concentrations of compound IV in soil greatly varied with the soil type. The amines V and VI represented a majority of the soil bound residue. The half-life in soil of MBT was 2 months when concentration of compound IV was low and 1 month when it was high. The half-life of the total of ureas was 2 months in all regions, and that for the total of ureas + identified metabolites was 6 months.

The urea derivative methabenzthiazuron [1,3-dimethyl-3-(2-benzothiazolyl)urea, MBT, I] is a very effective herbicide in grain and certain vegetable crops including peas. However, MBT has a rather long life in soil and may, by its remnant residues, be phytotoxic to some crops grown after the one for which the herbicide was applied (Van Himme et al., 1984). Several studies have been reported on the fate of MBT in soil, under laboratory conditions. After a [^{14}C]MBT-treated soil was aged for 6 months, the amount of ^{14}C activity remaining in the soil was equivalent to 50–60% of the MBT originally applied (Cheng and Führ, 1976). Only 50–70% of the ^{14}C remaining in the soil could be extracted; however, over 90% of the ^{14}C in the extracts was identified as the parent MBT. The main metabolite in the extract (5% of its ^{14}C content) was 1-methyl-1-(2-benzothiazolyl)urea, II (Mittelstaedt et al., 1977). However, low concentrations of 1-methyl-3-(2-benzothiazolyl)urea (III) may also be present in the soil extract, as III was formed during in vitro microbial decomposition of MBT (Wallnöfer et al., 1976; Goettfert et al., 1978).

In the present study, the fate of MBT in the soil of pea crops grown in four different regions of culture is studied. Identification and measurement of extractable and bound residues of MBT for up to 6 months after treatment with herbicide MBT are reported here.

EXPERIMENTAL SECTION

Pea Crops and Treatments. The peas (cv. Minarette, used for canning) were grown in fields located in three regions of culture different as to their soil types (Table I). The soil characteristics were determined in 1986. Each field was subdivided into four plots corresponding to four replications. MBT was applied to soil just before sowing the peas at a rate of 2 kg of MBT/ha by spraying an emulsion of Tribunil (wettable powder obtained from Bayer Belgium, containing 70% w/w MBT) in water (400 L/ha). MBT was applied on top of soil and incorporated into the top 3 in. of soil, and then the seeds were sown. At harvest, samples of about 1 kg of dehulled peas were collected at random from each plot.

Thin-Layer (TLC) and Gas–Liquid (GLC) Chromatographies, Mass (MS) and Infrared (IR) Spectrometries, and Nuclear Magnetic Resonance (NMR). TLC was performed using DC-Plastikfolien Kieselgel 60F254 plates, 20 × 20 cm and 0.2 mm thick, Merck. All the mobile-phase solvents described by Cheng and Führ (1976) were used, some of them successively, to resolve MBT and its metabolites. The R_f with the eluting solvents generally used were as follows. (1) Chloroform: I, 0.25; II, 0.17; III, 0.05; IV, 0.03; V, 0.16; VI, 0.10. (2) Ethyl acetate: I, 0.64; II, 0.63; III, 0.45; IV, 0.45; V, 0.68; VI, 0.64. Acetonitrile: I, 0.87; II, 0.88; III, 0.81; IV, 0.78; V, 0.82; VI, 0.73. Identification was done by single-dimensional TLC development. With the mobile-phase solvents giving low R_f values, after first development the TLC plate was dried and redeveloped as such. This procedure was repeated several times, making it possible to resolve the standards when applied as a mixture onto the TLC plate.

GLC was performed with a Tracor 550 apparatus, using a flame photometric detection. Injection port and detector temperatures were at 300 and 180 °C, respectively. Glass column (1.80 m × 2 mm (i.d.)) filled with 1% OV17 + 5% OV210 on 80–100-mesh Gas Chrom Q was used. Nitrogen carrier gas was used at a flow rate of 30 mL/min. Retention times for 2-aminobenzothiazole (VI) and for 2-(methylamino)benzothiazole (V) were 2.7 and 3.4 min, respectively. By the GLC, MBT and II were detected as V; III and (2-benzothiazolyl)urea (IV) were detected as VI.

Mass spectra were reached with the Varian MAT 311 (70 eV; m/e, relative abundance, %) apparatus employed in the electron impact (spectra described here) and chem-

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0021-8561/88/1436-0642$01.50/0

Table I. Soil Types of the Pea Fields Used in the Study

location	soil type	pH	% organic matter	% sand	% silt	% clay
Melle	loam	6.1	2.5	38.9	50.3	10.8
Ingooigem	sandy loam	5.9	2.6	60.3	29.6	10.1
Gembloux (School for Horticulture)	silt loam	5.5	2.4	10.2	74.8	15.0
Gembloux (Research Station for Fruits and Vegetables)	silt loam	5.9	2.2	10.7	74.3	15.0

ical ionizaton (isobutane) modes.

The IR spectra (KBr disks; cm^{-1}) were recorded with the Perkin-Elmer 297 apparatus. The ^1H NMR spectra were recorded in DMSO-d_6 with the Jeol PMX60SI 60-MHz apparatus; chemical shifts are reported in parts per million (ppm) from an internal standard of tetramethylsilane.

Standards of MBT and Its Metabolites. *1. Methabenzthiazuron (MBT).* Tribunil (100 g) in ethyl acetate (250 mL) was heated to reflux with stirring for 30 min. The hot mixture was filtered, and the solids were extracted twice as described above. The filtrates were pooled and concentrated to about 100 mL in a vacuum evaporator at 30 °C, and MBT was crystallized: yield 80%; MS, 221 (5, M^+), 164 (55, M – CH_3NCO), 149 (2, M – CH_3NHCON), 136 (43, 164 – CH_2N), 109 (5, 164 – $NCNCH_3$); ^1H NMR 2.83 (d, 3 H, CH_3), 3.40 (s, 1 H, NH), 3.67 (s, 3 H, CH_3), 7.00–7.50 (m, 2 H, aromatic), 7.50–8.00 (m, 2 H, aromatic).

2. Ureas II–IV. Procedure A. Amine (37 mmol) V or VI (obtained from Janssen, Belgium), urea (20 mmol), and acetic acid (3 mL) were mixed, and the resultant mixture was heated in an open flask over a bare flame for 1 min. The crude cold product was recrystallized from aqueous ethanol.

Procedure B. Amine V or VI (50 mmol) was dissolved in acetic acid (24 mL) and water (45 mL) at 35 °C. A solution of potassium cyanate (100 mmol) in water (45 mL) at 35 °C was added dropwise. The suspension was stirred for 15 min at 35 °C and kept overnight at 20 °C. Water (20 mL) was added; the mixture was cooled at 0 °C. The urea was filtered and recrystallized from aqueous ethanol.

Nonoptimized yields of isolated II and IV synthesized by procedure A were, respectively, 35 and 48%; with procedure B, these yields were, respectively, 85% and 0. Urea III was obtained from the Department of Chemistry (Louvain-la-Neuve) and was synthesized by reaction of 2-aminobenzothiazole with methyl isocyanate in benzene heated at reflux.

1-Methyl-1-(2-benzothiazolyl)urea (II): MS, 207 (11, M^+), 164 (100, M – HNCO), 136 (77, 164 – CH_2N), 108 (23, 164 – $NCNHCH_3$); IR, 3420, 3240 (NH_2), 1710 (CO), 1615, 1580, 1460, 1420, 1290, 1260, 1230, 1160, 1130, 1080, 1050, 1020, 930, 880, 750, 720; ^1H NMR 3.03 (s, 2 H, NH_2), 3.33 (s 3 H, CH_3), 6.90–7.90 (m, 4 H, aromatic).

(2-Benzothiazolyl)urea (IV): MS, 193 (15, M^+), 176 (6, M – NH_3), 150 (100, M – HNCO), 123 (23, 150 – HCN); IR, 3400 (NH, NH_2), 1690 (CO), 1650, 1600, 1550, 1450, 1330, 1300, 1280, 1050, 880, 760.

3. 2-(Methylamino)benzothiazole (V). MBT (100 g) was heated with stirring to reflux in 250 mL of 6% g/g Claisen alkali (6 g of KOH was dissolved in 25 mL of water, cooled and diluted, to 100 mL with methanol) for 3 h. The cooled mixture was concentrated to 80 mL in a vacuum rotavapor at 30 °C and V crystallized: yield 85%; MS, 164 (25, M^+), 149 (28, M – CH_3), 136 (27, M – CH_2N); IR, 3250 (NH), 1620, 1580, 1480, 1450, 1410, 1330, 1310, 1280, 1155, 1120, 1080, 1040, 1020, 930, 880, 750, 720; ^1H NMR 2.90 (d, 3 H, CH_3), 3.27 (s, 1 H, NH), 6.77–7.40 (m, 2 H, aromatic), 7.40–8.03 (m, 2 H, aromatic).

Soil and Pea Analyses. Soil (100 g) was heated to reflux with acetone–water (8:2, v/v, 200 mL) with stirring for 15 min. The sample mixture was filtered, and the extraction of the solid was repeated as described above using acetone–water (1:1, v/v, 200 mL). After extraction, the extracts were pooled and concentrated to about 80 mL in a vacuum rotavapor at 30 °C. The aqueous solution was saturated with sodium chloride and extracted with ethyl acetate (2 × 200 mL). The ethyl acetate fraction was dried with anhydrous Na_2SO_4 and concentrated to 40 mL in a vacuum evaporator at 30 °C and then with a stream of nitrogen to 1 mL. The concentrated ethyl acetate extract was applied as a band on a TLC plate, along with the standards. MBT and its metabolites were separated by means of successive TLC, using the mobile-phase solvents described by Cheng and Führ (1976). Bands were separated, extracted with ethyl acetate, and analyzed further by GLC and, for some samples, by MS. At the 0.1 ppm level, recoveries in soil of I–IV were higher than 88%; for V and VI, they were higher than 80%. Separate experiments indicated that, during the extraction procedure, the ureas were not hydrolyzed into the corresponding amines. Recoveries were not better when the fourfold solvent cold extraction procedure as described by Cheng and Führ (1976) was used. The acetone–water extract thus contained compounds I–VI present as such in soil.

The acetone-extracted soil was further extracted with 200 mL of the 6% g/g Claisen's potassium hydroxide (see above) by heating to reflux for 30 min with stirring. After filtration, the extract was neutralized with concentrate HCl and again made basic (pH 11) by addition of a small amount of aqueous KOH (20%, g/g). Water (40 mL) was added; the mixture was concentrated to about 80 mL in a vacuum rotavapor at 30 °C and extracted with ethyl acetate (2 × 150 mL). The ethyl acetate extract was analyzed further as described above as the acetone–water extract. At the 0.1 ppm level, recoveries for compounds V and VI were higher than 80%. During the Claisen's potassium hydroxide extraction procedure, compounds I and II were hydrolyzed into V; III and IV were hydrolyzed into VI. However, compounds V and VI observed in the alkaline extract was present as such in the soil. Indeed, the ureas were completely extracted by the acetone–water extraction, as indicated by the recovery experiments performed 15 days after their incorporation into soil. Dehulled peas were analyzed by the procedures described above for the soil; however, extraction was carried out with use of a Sorvall Omnimixer.

RESULTS AND DISCUSSION

In all four crop locations, no weeds were observed in the test plots. In the harvested dehulled peas, the concentrations MBT and of its metabolites were ≤0.02 ppm relative to the fresh weight, i.e. the limit of sensitivity of the analytical method. In soil, MBT and its metabolites were observed only in the 0–10-cm soil layer; in the 15–30-cm layer, their concentrations were ≤0.02 ppm.

MBT did not hinder pea growth at all and did not reduce the weight yield of pea at harvest, when the comparison was made at Melle with herbicide-untreated plots made clean by hand. The same was observed with other crops that are nonsensitive to MBT, the opposite of the ones sensitive to it for which the use of MBT is not recommended. These observations suggest that MBT has no influence on soil fertility and probably also on soil microbial activity.

Table II. Concentration of Methabenzthiazuron and Its Metabolites in the 0–10-cm Soil Surface Layer of Pea Crops[a]

sampling date[b]	post-treatment, days	cum rainfall, mm	concn of compd as equiv of methabenzthiazuron,[c] mg/kg dry soil: acetone–water extract[d] $ArNCH_3CONHCH_3$,[e] I	acetone–water extract[d] $ArNHCONH_2$, IV	acetone–water extract[d] $ArNHCH_3$, V	acetone–water extract[d] $ArNH_2$, VI	methanol–water–KOH extract[d] $ArNHCH_3$, V	methanol–water–KOH extract[d] $ArNH_2$, VI	total
1. Crop at Melle									
27–3	6	0	1.32 ± 0.07	nd	nd	nd	nd	nd	1.32
12–5	52	76	0.75 ± 0.04	nd	0.15 ± 0.02	nd	0.21 ± 0.02	nd	1.11
8–7[f]	109	236	0.50 ± 0.03	nd	0.20 ± 0.02	nd	0.22 ± 0.01	nd	0.92
6–9	169	399	0.35 ± 0.02	0.02 ± 0.01	0.18 ± 0.02	nd	0.12 ± 0.02	nd	0.67
19–11	243	572	0.22 ± 0.01	0.02 ± 0.01	0.11 ± 0.02	nd	0.13 ± 0.01	0.01 ± 0.01	0.49
2. Crop at Ingooigem									
16–5[g]	0	0	1.36 ± 0.07	nd	nd	nd	nd	nd	1.36
27–6	42	64	0.70 ± 0.04	nd	0.14 ± 0.01	nd	0.22 ± 0.02	nd	1.06
18–7	63	92	0.63 ± 0.03	0.01 ± 0.01	0.18 ± 0.02	nd	0.18 ± 0.01	0.01 ± 0.01	1.01
30–7[f]	75	105	0.55 ± 0.03	0.02 ± 0.02	0.13 ± 0.01	nd	0.18 ± 0.01	0.01 ± 0.01	0.89
3. Crop at Gembloux (School for Horticulture)									
5–5[g]	0	0	1.29 ± 0.06	nd	nd	nd	nd	nd	1.29
3–6	29	81	0.73 ± 0.04	0.10 ± 0.01	0.17 ± 0.02	nd	0.19 ± 0.01	nd	1.19
16–6	42	166	0.39 ± 0.02	0.37 ± 0.03	0.15 ± 0.01	0.01 ± 0.01	0.18 ± 0.02	0.01 ± 0.01	1.11
4–7[f]	60	177	0.24 ± 0.01	0.44 ± 0.02	0.19 ± 0.01	0.03 ± 0.02	0.21 ± 0.01	0.02 ● 0.02	1.13
4. Crop at Gembloux (Research Station for Vegetables and Fruits)									
20–5[g]	4	0	1.36 ± 0.02	nd	nd	nd	nd	nd	1.36
25–6	40	99	0.65 ± 0.03	0.10 ± 0.01	0.13 ± 0.01	0.01 ± 0.01	0.24 ± 0.01	0.01 ± 0.01	1.14
1–8[f]	77	133	0.41 ± 0.02	0.23 ± 0.02	0.19 ± 0.02	0.02 ± 0.01	0.23 ± 0.02	0.03 ± 0.02	1.11

[a] In the 10–30-cm soil layer and in the pea self harvested for canning, concentrations of MBT and of its metabolites were lower than 0.02 mg/kg of dry soil or fresh pea or were not detected. [b] Day–month, year 1986. [c] Means of four repetitions ± SD; nd = not detected. [d] Ar = benzothiazolyl-2-. [e] Methabenzthiazuron. [f] Pea harvest. [g] Pea sowing; at Melle, 2–5.

Table III. Half-Life (Days) of Methabenzthiazuron, Total Ureas, and Total Ureas + Identified Metabolites in the Soil of Pea Crops.

crop location	MBT	total ureas	total ureas + metabolites
Melle	75	75	170
Ingooigem	55	55	125
Gembloux (School for Horticulture)	30	55	170
Gembloux (Research Station for Vegetables)	40	55	170

The rigorous soil extraction procedure in this study resulted in higher concentrations of metabolites, which, in previous studies, were not observed at all or were observed in very low concentrations (Table II). In the present work, concentrations in soil of the ureas II and III were always low, ≤0.02 ppm. Both compounds correspond to the monodemethylation of MBT. In previous studies conducted in laboratory conditions, MBT was found as the primary extractable residue from soil, and the monodemethylated ureas corresponded to ≤5% of the extractable residue (Mittelstaedt et al., 1977). In the present work however, significant concentrations of the didemethylated urea IV, not observed in previous studies, were detected. Moreover, at both locations at Gembloux, unlike at Melle and Ingooigem, concentrations in soil of compound IV may be as high as those of MBT. The rate of the reductive demethylation pathway thus varied from one region of culture to the other. The rate of reductive demethylation is surprising, since this metabolic reaction is not usually important in the superficial soil layer.

The amino compound V (generated by hydrolysis of the ureas I and II) and the amino compound VI (from hydrolysis of III and IV) were observed in significant concentrations in soil, unlike the results of the previous studies. The alkaline extraction of soil, applied after the hot acetone–water one, released additional amount of compounds V and VI. These probably corresponded for a large part to the unidentified soil-bound residues reported in previous studies that used [^{14}C]MBT (Cheng and Führ, 1976).

Reductive demethylation and hydrolysis are thus the main metabolic reactions. These reactions operate competitively and also consecutively. Moreover, other metabolic reactions are responsible for the degradation of MBT and its identified metabolite residues in the soil. The half-life ($t_{1/2}$) values for MBT, total ureas, or MBT + identified metabolites in soil are presented (Table III). In both locations, Gembloux and Ingooigem, the fate of MBT in soil was observed during 2–2.5 months (the time for the pea crop). At Melle, soil sampling and residue analysis were performed before and after the pea crop, i.e. over a period of about 6 months. Comparison of the half-lives for compounds in the four crop locations has been made. For MBT, the half-life values were shorter at Ingooigem (55 days) than at Melle (75 days) and still shorter (about 35 days) at both locations in Gembloux on account of MBT didemethylation. For the total of the ureas, the half-life values were similar (55 days) at Ingooigem and at both locations at Gembloux but shorter than at Melle (75 days). The half-lives for the total ureas + identified metabolites were similar at each location (170 days), except at Ingooigem (125 days) where it was shorter. These differences in the half-life values could result from various factors, such as soil texture, pH, and microbial activity, the presence or absence of pea crop (Melle), rainfall, and temperature (season).

In conclusion, the half-life value for MBT ranged from 30 to 75 days; for the total of urea compounds, it was about 2 months, and it was about 6 months for the total of MBT and its metabolites in soil.

Registry No. I, 18691-97-9; II, 53065-94-4; IV, 32568-55-1; V, 16954-69-1; VI, 136-95-8; tribunil, 18691-97-9.

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Received for review May 2, 1987. Accepted October 26, 1987. This work was supported by the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture, IRSIA, Belgium (Grant No. 4868A).

Photoinduced Additions of Pesticides to Biomolecules. 2. Model Reactions of DDT and Methoxychlor with Methyl Oleate[1]

Wolfgang Schwack[2]

Upon sunlight irradiation, photoinduced additions of pesticides to biomolecules of plant cuticles have been presumed. In order to check this hypothesis, model UV irradiations of DDT (2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane) and methoxychlor (2,2-bis(4-methoxyphenyl)-1,1,1-trichloroethane) in the presence of methyl oleate, as an example of octadecenoic acids often occurring in plant cuticles, were performed. DDT and methoxychlor were extensively added to the C–C double bond of methyl oleate via radical mechanisms. Besides chlorinated stearic acids, several addition products were formed, offering new possibilities to produce "bound residues" in plants.

After spraying, pesticides first contact plant cuticle by absorption with subsequent distribution therein (especially lipophilic compounds) and can be directly affected by sunlight. Components of plant cuticles include alkanes, alkanols, fatty acids, triterpenes, and sterols (epicuticular wax) and a biopolymer of hydroxy fatty acids (cutin).

In my research, photoinduced reactions of pesticides in the presence of biomolecules of plant cuticles are of main interest with special attention to photoaddition reactions producing "bound residues" (Schwack, 1986, 1987). In order to establish the photochemical reactivities of DDT (2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane) and methoxychlor (2,2-bis(4-methoxyphenyl)-1,1,1-trichloroethane) in the presence of plant cuticle constituents, model photoreactions with cyclohexene have been undertaken, which afford addition products in high yields (Schwack, 1984). This paper presents the results of photoinduced addition of DDT and methoxychlor to methyl oleate as an example of octadecenoic acids often occurring in plant cuticles.

EXPERIMENTAL SECTION

Gas Chromatography. A Hewlett-Packard GC 5830A gas chromatograph with FID equipped with a fused silica SE 54 capillary column (25 m × 0.3 mm (i.d.), carrier gas nitrogen) in combination with a 188500A terminal was used. The temperature program was 100 °C, 1 min isothermal, and then 100–300 °C at 5 °C/min.

Mass Spectrometry. Electron impact mass spectra (MS) were recorded on a LKB 2091 mass spectrometer at 15 eV to avoid strong fragmentations. Spectra are reported as mass (^{35}Cl), chlorine isotopes pattern (Cl_n), and relative intensity (percent).

^{1}H NMR Spectroscopy. A Bruker WM 400 spectrometer was used. Signals are reported (δ) downfield from tetramethylsilane as internal standard (δ 0.00).

IR Spectroscopy. IR spectroscopy was carried out with a Beckman IR 4240 spectrometer using capillary films on NaCl plates.

DDT (Zeidler, 1874) and methoxychlor (Zepp et al., 1976) were synthesized following the literature cited and recrystallized four times from *n*-hexane.

Degradation rate analyses were carried out by HPLC as previously described (Schwack, 1984).

Photolyses. DDT (250 mg, 0.71 mmol) and methoxychlor (250 mg, 0.72 mmol) were dissolved in 5 g of methyl oleate (99%, Sigma Chemical Co.), and the resultant mixture was irradiated in a quartz tube for 5 h using a 150-W high-pressure mercury lamp (TQ 150, Hanau Quarzlampen GmbH) equipped with a quartz glass water-cooling jacket. The UV light was filtered by a glass filter WG 295 ($\lambda > 280$ nm, Schott) before reaching the samples. Under these conditions 18% photodegradation of DDT and 24% photodegradation of methoxychlor occurred.

Product Isolation. The reaction mixtures (in 0.5-g aliquots were chromatographed on Bio Beads S-X8 (Bio Rad Lab) with methylene chloride as eluant (glass column, 2 cm (i.d.) × 85 cm, flow rate 1.5 mL/min) to separate the higher molecular weight addition products (first eluted) from the starting materials, using an UV (254-nm) detector (gel permeation chromatography). The combined addition products were separated by preparative TLC (silica gel 60 F_{254}, Merck) with the solvent systems 95:5 *n*-hexane–diisopropyl ether for the DDT products and 96:4 *n*-hexane–ethanol for the methoxychlor products. After rechromatography under the same conditions the addition products were all obtained as colorless oils. Purity control analyses were performed by HPLC using a 5-μm SiO_2 (LiChrosorb (Merck) column (4.6 mm (i.d.) × 25 cm)

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0021-8561/88/1436-0645$01.50/0