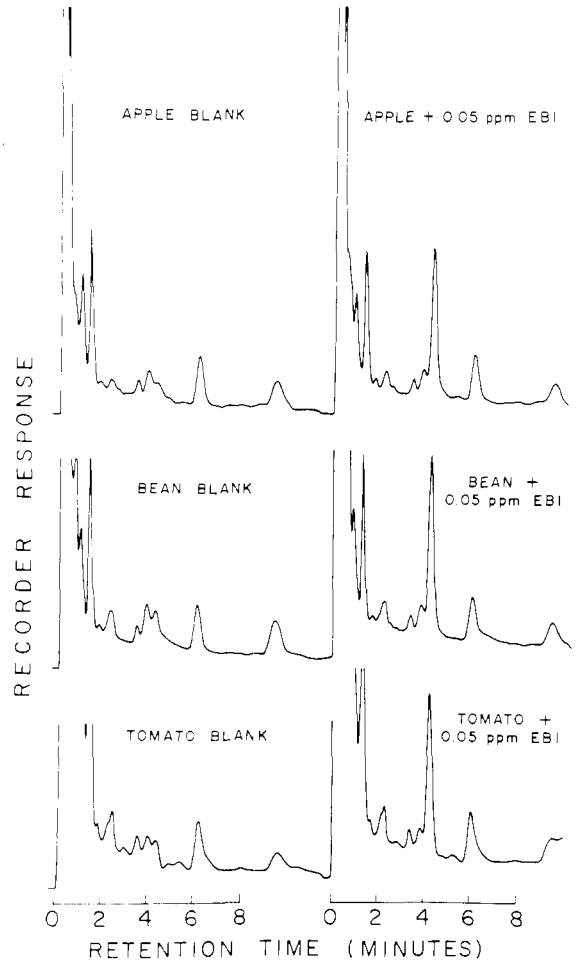


Figure 1. Gas-liquid chromatograms of final extracts of different commodities with and without the addition of 0.05 ppm of EBI. Each injection represents the equivalent of 1 mg of sample.

Table II. Linearity of Recovery of EBI from Beans

EBI added, ppm	EBI found,[a] ppm	Recovery, %
0.050	0.046	92.0
0.100	0.095	95.0
0.500	0.466	93.2
1.00	0.978	97.8
5.00	5.36	107
10.0	10.5	105

[a] Values are the means of duplicate determinations.

Table III. Recovery of EBI from Lettuce in the Presence of Maneb or Zineb

EBI added, ppm	Zineb (5.0 ppm) EBI found, ppm	Zineb (5.0 ppm) Recovery, %	Maneb (5.8 ppm) EBI found, ppm	Maneb (5.8 ppm) Recovery, %
0	0.004		0.008	
0.094	0.088	93.6	0.100	106
0.944	0.808	85.6	0.972	103

gon–methane (95:5) carrier gas. Typical operating parameters were as follows: column oven temperature, 190°C; detector temperature, 300°C; carrier gas flow rate, 30 ml/min. Samples were quantitated by comparison of the peak height to that of the standard.

RESULTS AND DISCUSSION

Typical chromatograms of extracts of various commodities fortified with EBI are shown in Figure 1. The lower limit of detection with a 2:1 signal:background ratio is 0.02 ppm. Since the presence of ethylenethiuram monosulfide in samples would lead to erroneous results due to its decomposition to EBI on GLC (Newsome, 1975), it was necessary to remove it by partitioning with HCl. No interference above normal background was observed when the monosulfide was added to samples at a level of 1 ppm.

The recoveries obtained from various commodities fortified with EBI are shown in Table I. The recovery was found to be linear with the amount of EBI added between 0.05 and 10 ppm (Table II) with an overall yield of 98.3%.

As shown by the data in Table III, the presence of either of the parent compounds, maneb or zineb, does not interfere with the method.

LITERATURE CITED

Engst, R., Schnaak, W., Rattba, H., *Nachrichtenbl. Dtsch. Pflanzenschutzdienstes (Braunschweig)* **22**, 26 (1968).

Ludwig, R. A., Thorn, G. D., Unwin, C. H., *Can. J. Bot.* **33**, 42 (1955).

Newsome, W. H., *J. Agric. Food Chem.* **23**, 348 (1975).

Thorn, G. D., Huston, B., *Can. J. Chem.* **37**, 2099 (1959).

Thorn, G. D., Ludwig, R. A., "The Dithiocarbamates and Related Compounds", Elsevier, Amsterdam, 1962.

W. H. Newsome

Food Research Division
Bureau of Chemical Safety
Health Protection Branch
Health and Welfare Canada
Tunney's Pasture, Ottawa K1A 0L2, Ontario, Canada

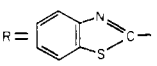
Received for review June 30, 1975. Accepted September 19, 1975.

Extraction of Methabenzthiazuron from the Soil

A fourfold solvent extraction procedure involving the use of acetone–ethyl acetate and acetone–chloroform combinations was developed for quantitative extraction of the herbicide methabenzthiazuron (MBT) from the soil. The recovery of MBT from soils spiked with [^{14}C]MBT 1 day before extraction was consistently over 95%, with each of the first three extractions removing over 60% of the MBT present or remaining in the soil. After a MBT-treated soil was aged for 6 months, 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, and the pattern of MBT removal from the aged samples was similar to that from spiked samples. It appears that the unextracted ^{14}C is either tightly bound by soil components or partially metabolized and could no longer be extracted by this procedure.

The herbicide methabenzthiazuron [*N*-(2-benzothiazolyl)-*N*,*N*'-dimethylurea or MBT] is used both in the fall and in the spring for weed control in cereal crops. It is degraded in the soil only at moderate rates (Cheng et

Table I. Thin-Layer Chromatographic R_f (× 100) Values of MBT and Related Test Chemicals in Different Solvents

Test chemical R= 	Solvent						
	Benzene	Carbon tetrachloride–acetonitrile (100:3)	Chloroform	Ethyl acetate	Acetonitrile	Methanol	Acetone
1. R-N(CH_3)CONHCH_3 (MBT)	3	13	27	64	87	80	91
2. R-N(CH_3)CONHCH_2OH	1	1	9	42	79	81	89
3. R-N(CH_3)CONH_2	1	4	16	61	86	81	91
4. R-NH_2CONHCH_3	0	1	5	47	81	81	90
5. R-NH_2CONHCH_2OH	0	0	1	44	64	81	90
6. R-NH_2CONH_2	0	0	2	45	77	80	90
7. R-NHCH_3	2	6	16	68	83	82	90
8. R-NH_2	3	4	10	64	77	75	87
9. R-OH	3	7	18	86	91	85	93

al., 1974). Thus, at the end of a growing season, significant amounts of MBT could still remain in the soil. Jarczyk (1969, 1972) has proposed a method for extracting MBT from the soil for either colorimetric or gas chromatographic analysis. The procedure involves mixing MBT-containing soil with an acetone–chloroform (1:1) mixed solvent at a 1:2 soil:solvent ratio in a blender, filtering the mixture to separate the extract from soil residue, and repeatedly washing the residue with additional aliquots of solvent. Recovery of MBT from spiked soil samples was found to range between 80 and 100%. However, the effect of aging on the extractability of MBT from soil was not evaluated. The objectives of this study were to compare the efficiency of solvents for extraction of MBT from spiked and aged soil samples, to evaluate by exhaustive extraction the step-by-step extractability of MBT in the soil, and to suggest alternatives which could improve the procedure for extraction of MBT from soils.

EXPERIMENTAL SECTION

Materials and Methods. All analytical grade experimental chemicals and [benzothiazolyl-2-^{14}C]MBT were supplied by courtesy of Farbenfabriken Bayer AG. For determination of total ^{14}C in the soil, a sample was combusted in a high-temperature induction furnace to convert soil C to CO_2, which was trapped in a NaOH solution and measured for its ^{14}C activity by the liquid scintillation technique using PCS solubilizer (Amersham/Searle Corporation) as fluor (Cheng and Farrow, 1976). After the soil sample was extracted by appropriate solvent, the ^{14}C activity of soil extract was measured by the liquid scintillation technique using toluene containing 2,5-diphenyloxazole and 1,4-bis[2-(5-phenyloxazolyl)]-benzene as fluor. Thin-layer chromatograms of experimental compounds were obtained by developing single 20 × 20 cm precoated silica gel F-254 glass plates in a Desaga tank under normal saturation of solvent, and detection and quantitation of compounds were made either visually under ultraviolet radiation or by autoradiography. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5751G instrument using a Model 15161A nitrogen detector (Jarczyk, 1972).

Evaluation of Solvents. The solvent extraction method is based on the quantitative partitioning of the pesticide chemical from the soil–water system to an immiscible organic solvent system. In selecting a suitable organic solvent system for extraction of MBT from the soil, considerations were given to the affinity of MBT for the solvent, miscibility of the solvent with water, and ease of handling of the solvent in the extraction process. The R_f values of a number of test chemicals on thin-layer chromatographic plates developed in various solvents were used as a means of indicating the affinity of the chemicals to the solvents. As shown in Table I, all test chemicals have greater affinity for the more polar solvents (acetone and methanol) than for the nonplar solvents (benzene and carbon tetrachloride). Affinity decreases with decreasing polarity (e.g., acetonitrile > ethyl acetate > chloroform). Whereas acetone is miscible with water, ethyl acetate and chloroform are not. In a three-component system of water–acetone–ethyl acetate or chloroform, most of the acetone and a negligible amount of water could be partitioned into ethyl acetate or chloroform to form a two-phase system, depending on the ratios of the three components. Ethyl acetate, being lighter than water, forms an organic phase over the water phase, and chloroform, being denser than water, forms an organic phase under the water phase. Preliminary tests have shown that for a 1:1:2 water–acetone–ethyl acetate or chloroform system, over 99% of the MBT added to the water phase could be partitioned to the organic solvent phase in two extractions. In the initial extraction of soil, the acetone–ethyl acetate combination yielded a clearer extract than the acetone–chloroform combination, but repeated extractions of the sample yielded extracts equally clear from both solvent combinations. Advantages of using chloroform compared with using ethyl acetate are that chloroform is more effective in eliminating water from the organic phase and that the denser organic phase formed can be handled more readily in the separation process. The proposed method for extraction of MBT from the soil incorporates these considerations in the procedure.

Proposed Extraction Method. A fourfold solvent extraction procedure was developed and involves the following steps. (1) Weigh 10 g of soil into a 300-ml Erlenmeyer extraction flask and soak the soil with 5 ml of water for 15 min. (2) Add 15 ml of acetone to the wet soil, cover the flask, and mix the contents of the flask on a shaker for 20 min. (3) After shaking, add 20 ml of ethyl acetate to the flask, mix the contents thoroughly by hand, and allow the soil to settle. (4) Decant carefully as much as possible the clear supernatant liquid extract into a 250-ml separatory funnel. (5) For a second extraction, repeat steps 2, 3, and 4. Then, combine the extracts in the same separatory funnel. (6) For the third and fourth extractions, each time repeat step 2. After shaking, add 20 ml of chloroform to the flask, mix the contents thoroughly, and allow the soil to settle before decanting the clear supernatant liquid extract into the same separatory funnel. (7) Wash the soil residue in the extraction flask twice, each with 10 ml of chloroform, and decant the chloroform extract into the same separatory funnel after each washing. (8) Add 20 ml of water and 20 ml of chloroform to the separatory funnel, mix the contents thoroughly, and allow the liquids to separate into two phases. (9) Drain the organic solvent (lower) phase from

Table II. Characteristics of the Soils Used in the Extraction Studies

Soil type	Location	pH	% carbon	% sand	% silt	% clay
Cisne silt loam	Illinois	5.0	0.9	25	58	17
Flanagan silt loam	Illinois	5.5	2.3	13	60	27
Palouse silt loam	Washington	5.9	1.5	12	61	27
Walbeck humic sand	Germany	6.2	3.2	80	10	10
Walla Walla silt loam	Washington	6.1	0.9	23	62	15

the separatory funnel into a 400-ml round-bottomed flash-evaporating flask. (10) Extract the water (upper) phase remaining in the separatory funnel twice with 20 ml of chloroform, each time draining the chloroform (lower) phase into the same flash-evaporating flask. (11) After flash-evaporating the solvents, collect the contents of the flask for analytical determination.

Extraction from Spiked Samples. Five soils of different properties and origins (Table II) were spiked in duplicate with [benzothiazolyl-2-^{14}C]MBT 1 day before extraction. To each 10-g air-dried soil sample was added 1 ml of [^{14}C]MBT solution containing 16200 dpm of ^{14}C and 50 or 500 μg of MBT in acetone (equivalent to 5 or 50 ppm of MBT in soil). After the solvent had evaporated, the soil was thoroughly mixed and then extracted according to the proposed method. Recovery of added MBT from the soil ranged from 95 to 99% regardless of soil properties or MBT concentration (Table III). It was also found (data not shown) that the particle size of spiked soil samples (4 and 100 mesh) had no effect on MBT recovery.

By determining the ^{14}C in each extract separately, each of the first three extractions was found to remove over 60% of the MBT present or remaining in the soil. Only the fourth extraction removed a smaller proportion of the remaining MBT.

Extraction from Aged Samples. Duplicate soil samples from an experiment studying the effect of decomposing plant roots on MBT degradation in the soil (Cheng et al., 1974) were used to examine the effect of aging on the extractability of MBT from soil. The Walbeck Humic Sand soil had been treated with 5 or 10 ppm of [^{14}C]MBT and incubated in the presence or absence of decomposing plant roots for 6 months under greenhouse conditions. The amount of ^{14}C radioactivity remaining in the soil sample after the aging period ranged from 60000 to 136000 dpm per 10 g of soil, which was equivalent to 50 to 60% of the MBT originally applied (Table IV). The total amount of ^{14}C extracted by the proposed method accounted for approximately 51% of the total ^{14}C in soil samples treated with decomposing roots (samples 1 and 3) and 70% of the total ^{14}C in soil samples absent of decomposing roots (samples 2 and 4). Further examination of the ^{14}C extracted indicated that the pattern of removal of MBT from the aged soil samples was similar to that from MBT-spiked soil samples.

Identification and quantitation of the components of the organic solvent extracts of the aged soil samples after separation by thin-layer chromatography in benzene–methanol (9:1) solvent showed that more than 90% of the ^{14}C in the extract was found to be the parent MBT. Furthermore, the parent MBT could be separated from its metabolites in the soil extracts by a procedure developed by Jarczyk (see Pont et al., 1974) using carbon tetrachloride–acetonitrile (100:3) to elute MBT from a

Table III. Recovery of [^{14}C]MBT from Spiked Soil Samples

Soil	ppm of [^{14}C]MBT in soil	% total ^{14}C recovered	% of total ^{14}C in: 1st extract	2nd extract	3rd extract	4th extract + chloroform wash	Water wash
Cisne	5	97.6	67.9	19.9	7.4	2.3	0.1
	50	98.7	69.7	19.6	7.4	1.8	0.2
Flanagan	5	96.6	63.9	21.2	8.5	2.8	0.2
	50	95.7	60.9	22.7	8.5	3.4	0.2
Palouse	5	97.5	65.4	22.2	7.5	2.2	0.2
	50	96.7	63.6	21.9	7.9	2.8	0.5
Walbeck	5	98.4	70.1	18.6	7.0	2.0	0.7
	50	99.0	66.8	22.0	7.5	2.5	0.2
Walla Walla	5	97.4	67.0	20.1	8.3	1.9	0.1
	50	96.8	66.8	19.8	8.3	1.4	0.5
	Average:	97.4	66.2	20.8 (61.5)[a]	7.8 (60.0)	2.3 (44.2)	0.3

[a] Values in parentheses refer to the ^{14}C extracted as a percentage of the total ^{14}C remaining in the soil after the previous extraction.

Table IV. Recovery of ^{14}C from the Walbeck Humic Sand Soil, after Incubation of the Soil for 6 Months with [^{14}C]MBT in the Presence or Absence of Decomposing Plant Roots

Soil no.[a]	Total ^{14}C in soil, dpm/10 g	^{14}C in total soil extracts, dpm/10 g of soil	% ^{14}C extracted	% of total extractable ^{14}C in: 1st extract	2nd extract	3rd extract	4th extract	Chloroform wash	Water wash
1	60519	31389	51.9	62.6	22.7	9.0	2.0	0.6	3.1
2	71645	46664	65.1	67.0	20.4	8.1	1.7	0.4	2.4
3	117266	59372	50.6	63.8	20.6	9.5	2.2	0.6	3.3
4	139040	100398	73.8	68.2	20.1	7.7	1.5	0.4	2.1
			Average:	65.4	21.0 (60.7)[b]	8.6 (63.2)	1.8 (36.0)	0.5 (15.6)	2.7

[a] Samples 1 and 3 had been incubated in the presence of decomposing plant roots, and samples 2 and 4 incubated without roots. [b] Values in parentheses refer to the ^{14}C extracted as a percentage of the extractable ^{14}C remaining in the soil after the previous extraction.

Table V. Estimation by Gas-Liquid Chromatography (GLC) and ^{14}C Assay of the Percentage of MBT and Degradation Products in Extract Fractions of Two Walbeck Soil Samples Which Had Been Incubated with [^{14}C]MBT for 6 Months

	MBT fraction		Degradation products fraction	
Soil no.	GLC	^{14}C	GLC	^{14}C
1	91.0	91.9	9.0	8.1
2	95.2	94.6	4.8	5.4

silica gel column followed by acetonitrile to elute the metabolites. The proportion of MBT in the soil extracts, as determined by gas chromatography and by ^{14}C assay, was also found to be over 90% (Table V).

Since most of the ^{14}C in the soil extracts was identified as MBT and the proportion of MBT extracted from the soil whether from an aged sample or a spiked sample was similar, it is unlikely that the 30 to 50% of the ^{14}C not extracted by the proposed method would be in a form or state similar to that of the extractable MBT. Recent studies on the fate of substituted phenylureas and acylanilides have shown that many of these compounds and their degradation products could be tightly bound by soil components and become difficult to be extracted from the soil by the solvent extraction approach (e.g., Hsu and Bartha, 1973). MBT is a substituted urea compound with a benzothiazolyl moiety rather than a phenyl moiety; nevertheless, its behavior and degradation could be analogous to that of phenylureas. Thus, some of the ^{14}C in the aged soil samples could be MBT bound tightly by soil components. Moreover, Cheng et al. (1974) have observed that MBT was partially degraded in these aged soil samples and that considerably more MBT was degraded in soil containing decomposing roots than soil without roots. Therefore, one might expect some portion of the pesticide remaining in the soil to be partially metabolized to product(s) which still retain ^{14}C in the benzothiazolyl moiety of the MBT molecule but in a form that is no longer extractable by the proposed method. More drastic treatments of the soil would be required to remove the remaining ^{14}C from the soil.

ACKNOWLEDGMENT

The authors are grateful to Farbenfabriken Bayer AG for the experimental chemicals, to H. J. Jarczyk for performing the gas chromatographic analyses, and to W. Mittelstaedt of Jülich Nuclear Research Center and W. H. Piispanen of Washington State University for assistance in the experimental work.

LITERATURE CITED

Cheng, H. H., Farrow, F. O., *Soil Sci. Soc. Am. Proc.* **40**, in press (1976).
Cheng, H. H., Führ, F., Mittelstaedt, W., *Pestic. Chem., Proc. Int. IUPAC Congr. Pestic. Chem., 3rd*, Paper No. 122 (1974).
Hsu, T. S., Bartha, R., *Soil Sci.* **116**, 444 (1973).
Jarczyk, H. J., *Pflanzenschutz-Nachr. (Am. Ed.)* **22**, 295 (1969).
Jarczyk, H. J., *Pflanzenschutz-Nachr. (Am. Ed.)* **25**, 21 (1972).
Pont, V., Jarczyk, H. J., Collet, G. F., Thomas, R., *Phytochemistry* **13**, 785 (1974).

H. H. Cheng*
Fritz Führ[1]

Department of Agronomy and Soils
Washington State University
Pullman, Washington 99163
[1]Arbeitsgruppe Radioagronomie
Kernforschungsanlage Jülich GmbH
D-517 Jülich, Federal Republic of Germany

Received for review July 17, 1975. Accepted October 6, 1975. Joint contribution from Washington State University and Jülich Nuclear Research Center. Scientific Paper No. 4419, College of Agriculture Research Center, Washington State University, Project 1858. The authors thank Farbenfabriken Bayer AG for financial assistance.

A Simple System to Simultaneously Measure Volatilization and Metabolism of Pesticides from Soils

A new system is described which permits simultaneous measurement of pesticide loss by volatilization and metabolic CO_2 evolution from soils. A polyurethane foam plug effectively trapped volatile dinitroaniline herbicides arising from soil surfaces, while allowing $^{14}CO_2$ to pass through the plugs and subsequently become trapped in alkali solution. Trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) was more volatile than butralin [4-(1,1-dimethylethyl)-*N*-(1-methylpropyl)-2,6-dinitrobenzenamine] when applied to soil surfaces. Volatilization was the major loss mechanism for trifluralin during the first 3 weeks after application. The distribution of volatile products from trifluralin was drastically altered when exposed to an ultraviolet (uv) lamp.

One mechanism by which pesticides disappear from soil surfaces is volatilization. Due to the volatile nature of most dinitroaniline herbicides, they are incorporated directly into the soil to reduce volatilization and photodecomposition losses. Incorporated dinitroanilines are then dissipated mainly by metabolism and, to a lesser extent, by volatilization.

A number of volatility studies (Bardsley et al., 1968; Ketchersid et al., 1969; Parochetti and Hein, 1973; Spencer and Cliath, 1974) have shown that the greatest loss of trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) occurs from warm, moist soils. These same conditions are conducive for rapid microbial metabolism, and studies with soils (Probst et al., 1967; Otto, 1974) and isolated soil microorganisms (Laanio et al., 1973; Kearney et al., 1974) indicated that under certain situations metabolism might be an important loss mechanism. Under flooded conditions volatility was insignificant and metabolism appears to be rapid (Parr and Smith, 1973). Spencer et al. (1973) have prepared an extensive review of the measurement and soil factors affecting pesticide volatilization. One method employed to measure vapors