

cated 1.4% of it to the shoots (Table III). During the same period, radioactivity in the nutrient solutions in which these plants were grown decreased from an average of 86.2% on day 1 to 4.6% on day 7 (Figure 1). Autoradiograms of treated plants showed that most of the radioactivity was concentrated in the roots, lower stem, and leaf sections nearest the stalk, but that some activity was present throughout the plant, including the meristematic tissues.

One-month-old sorghum growing in solutions treated with 5 ppm of the compound (Table IV) absorbed 1.8% of the radioactivity and translocated 0.7% of it to the shoots within 1 hr; after 7 days in these treated solutions, the roots contained 42.9% and 1.4% had been translocated to the shoots. When roots of 7-day-treated plants were placed in untreated nutrient solutions, radioactivity leached from the roots to the cultures, indicating that much of the radiolabeled material was present in a free form (Table IV). Autoradiograms of treated plants showed that radioactivity was present in the stems 1 hr after treatment, but only the 7- and 14-day plants showed ^{14}C in the leaf blades, concentrated along the center veins.

Older Plants. In 2- and 3-month-old corn plants grown 7 days in treated cultures, most of the translocated chemical was in the lower 12 in. of each plant (Table V). There was no evidence of radioactivity in the husks, silk, or ear of a 3-month-old plant, and detectable ^{14}C activity in the vegetative portion was less than in the 2-month-old plants.

In 3-month-old sorghum (Table VI), the pattern of radioactivity in the vegetative portions was similar to that in corn; most was concentrated in the lower sections and only trace amounts appeared in the uppermost internodes. However, unlike the corn ear, both the seeds and the stripped heads (rachis, branches, and racemes) contained detectable radioactivity (Table VI). Radioactivity in the heads varied widely (range <0.01–0.08 ppm) and apparently was related to vigor of growth as evidenced by fresh head weights. Separate analyses of seeds and stripped heads also showed considerable variation; radioactivity in the seeds ranged from 38 to 100% of that in the total head.

Soil Translocation Studies. The effect of soil composition on the availability of 4- ^{14}C aminopyridine for absorption by 1-month-old corn plants is shown in Table

VII. Although composition had an effect on the amount of chemical available for absorption, the total amount actually absorbed by the plants from any of the four soils was very small (maximum, 0.28% of the 10 ppm applied).

CONCLUSIONS

The nutrient culture studies showed that 4- ^{14}C aminopyridine was readily absorbed by roots of corn and sorghum plants but that the quantity of radioactivity translocated into the upper vegetative tissues appeared to be inversely proportional to plant age. Small quantities of radioactivity were also detected in seeds of 3-month-old sorghum grown 7 days in treated cultures. However, shoots of young corn grown in soil treated with 4- ^{14}C aminopyridine contained only small quantities of radioactivity, illustrating the tenacity with which 4-aminopyridine and/or metabolites are adsorbed onto soil colloids. Thus, it is unlikely that detectable quantities of the chemical would be present in plants grown under field conditions because of soil absorption of chemical and the extremely low application rates used.

ACKNOWLEDGMENTS

We thank personnel of the Phillips Petroleum Co. for providing the radiolabeled 4-aminopyridine and Ann H. Jones of the Denver Center for editing this manuscript.

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Received for review October 19, 1973. Accepted December 26, 1973. Reference to company or trade names does not imply endorsement of commercial products by the U. S. Government.

Fate of Benomyl on Field Soil and Turf

Frederic J. Baude,* Harlan L. Pease, and Richard F. Holt

Benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate] degradation to MBC (methyl 2-benzimidazolecarbamate) and AB (2-amino-benzimidazole) and the disappearance of these secondary products were studied in the field on bare soil and turf in four areas of the United States using ^{14}C -labeled and unlabeled parent

compound. The "half-life" of the total benzimidazole-containing residues is about 3–6 months on turf, representing a vegetative situation, and about 6–12 months on bare soil. The major portions of the residues were found in the top 4 in. of soil.

Benlate benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate] fungicide is at the present time being used primarily by agriculture in the United States as a

plant foliar crop protectant. A certain amount of the total material from these uses will be found on the surface of the soil, due to overspray and weathering, and in the soil, due to cultivation. Therefore, studies to determine the fate and behavior of benomyl in soil in the field were undertaken. This information has been developed using [2- ^{14}C]benomyl, formulated as Benlate, 50% WP, on small

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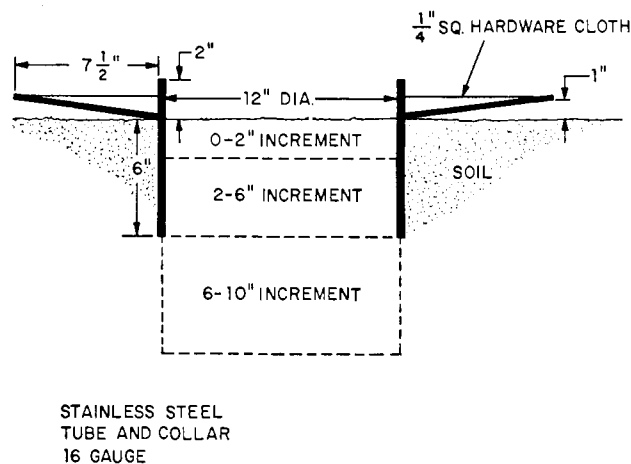


Figure 1. Section view of soil tube test plot and collar in Delaware and North Carolina.

confined outdoor bare soil plots and by using commercial Benlate on larger unconfined outdoor bare soil and turf plots in four different agricultural areas of the United States.

Previously, the persistence of soil-incorporated benomyl in field plots of irrigated cotton has been estimated by bioassay techniques with *Phymatotrichum omnivorum* (Hine *et al.*, 1969). These data indicate an approximate "half-life" of about 3 months. Separate studies have demonstrated the immobility of benomyl and its degradation products in soil under rigorous greenhouse conditions (Rhodes and Long, 1974).

EXPERIMENTAL SECTION

Chemicals. Analytical standards of benomyl, methyl 2-benzimidazolecarbamate (MBC), and commercial Benlate (52% benomyl, 48% inert ingredients) were provided by E. I. du Pont de Nemours & Co., Inc., Biochemicals Dept., Wilmington, Del. 2-(3-Butylureido)benzimidazole (BUB) was prepared as has been described (Baude *et al.*, 1973). All radiolabeled materials were synthesized in our laboratories (Gardiner *et al.*, 1974).

AB was used directly as obtained commercially (Eastman Kodak 4037).

Equipment. Samples were counted for ^{14}C using a Nuclear-Chicago liquid scintillation system Model 6801. A Varian-Aerograph/Berthold Model 6000-2 automatic/integrating tlc radioscanner was used to detect and measure ^{14}C on tlc plates (silica gel, Merck, F-254, 0.25 mm). Samples were combusted for total ^{14}C in a Packard Tri-Carb Model 305 sample oxidizer or by wet combustion (Smith *et al.*, 1964).

Test Plot Methods with ^{14}C Benlate. In early June at a test farm near Newark, Del., an unshaded plot of previously tilled soil (Keyport silt loam) covered with weedy grasses was rototilled to a depth of about 1 ft. Stainless steel tubes with a collar (Figure 1) were pushed into the prepared soil. Two weeks later the surface soil in each tube was treated with $[2-^{14}\text{C}]$ benomyl, formulated as Benlate, 50% WP, by pipetting as evenly as possible a suspension in water (15 ml). Treatment rates were equivalent to 2 and 5 lb of active ingredient (ai)/acre. Additional water (15 ml) was used to wash the vial the fungicide was weighed in, the holding vial for the suspension, and the disposable pipet. Later in the laboratory, the glassware was extracted with methanol. Correction (usually 1% or less) was made for the $[2-^{14}\text{C}]$ benomyl remaining on the glass as determined by liquid scintillation counting techniques. Any weed seedlings growing on the surface of the soil were removed prior to treatment; however, any seedlings which appeared subsequent to the treatment were

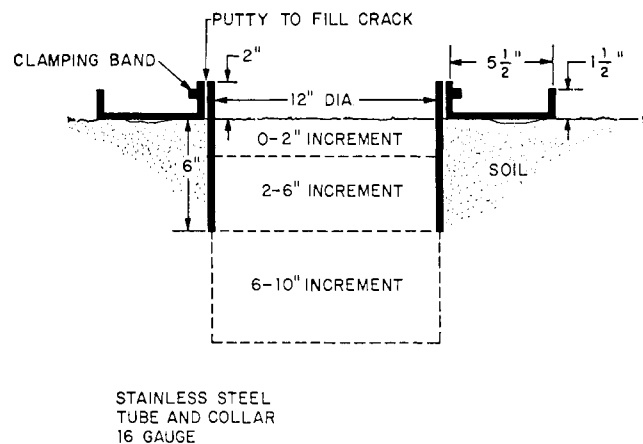


Figure 2. Section view of soil tube test plot and collar in Florida.

Table I. Percentage of Residue Remaining in Soil as Intact $[2-^{14}\text{C}]$ Benomyl

Time interval	Rate, lb of ai/acre	Fla.	N. C.	Del.
4 weeks	2	0	27	0
	5	0	7	0
12 weeks	5		0	
	2		0	
6 months	2		0	
	5		0	

pulled periodically and allowed to decompose on the treated surface.

In late May at a test farm near Clayton, N. C., stainless steel tubes with a collar (Figure 1) were pushed into unshaded unprepared barren ground (Cecil loamy sand). The surface soil in the tubes was then treated and weeded as previously described. In addition, fertilizer (10-10-10, 500 lb/acre) was periodically handspread on the treated areas.

In March at a test farm near Bradenton, Fla., an unshaded plot of previously tilled soil (Leon Immokalee fine sand) was rototilled to a depth of about 1 ft. Stainless steel tubes with a collar (Figure 2) were pushed into the prepared soil. The soil in each tube was removed to a depth of 6 in. and screened through 0.5-in. hardware cloth. This soil was replaced in the tubes with tamping. The surface soil in the tubes was then treated, weeded, and fertilized (10-10-10, 420 lb/acre) as previously described.

At exposure times of 0 days, 1 month, 3 months, 6 months, 1 year, and 2 years, the soil in selected tubes at the three locations was sampled *in toto* for analysis. Increments were taken from the surface to 2 in. below the surface (*ca.* 2.5 kg in. $^{-1}$ increment), 2-6 in. below the surface, and 4 in. directly below the tube. Any soil in the collar was collected and the collar washed with acetone. The acetone washes were added to the collar soil and the acetone allowed to evaporate. In Florida, a band of soil 1 in. deep and 1.5 in. on either side of the outer lip of the collar was collected and checked for any ^{14}C -labeled materials which might have escaped the collar due to the mechanical action of the wind and rainfall. Soil samples were shipped to Wilmington and kept frozen until analysis.

Test Plot Methods with Commercial Benlate Benomyl Fungicide. Soil and lawn turf plots were selected at the three test sites previously mentioned and at a fourth site near Rochelle, Ill. (Flanagan silt loam). Duplicate test plots were 12-15 ft by 20-25 ft with buffer zones to prevent cross contamination. Cultivation of the bare soil plots was accomplished with a subsurface blade or wheel hoe. The turf areas were mowed and the clippings allowed to decompose on the surface.

Table II. [2-¹⁴C]Benomyl Soil Disappearance Test in Delaware

	0 day, 2 lb of ai/a, μCi	4 weeks		12 weeks, 5 lb of ai/a, μCi	6 months		12 months, 5 lb of ai/a, μCi	24 months, 5 lb of ai/a, μCi
		2 lb of ai/a, μCi	5 lb of ai/a, μCi		2 lb of ai/a, μCi	5 lb of ai/a, μCi		
Total [2- ¹⁴ C]benomyl applied to each tube	24.04 ^a	22.40 ^a	31.19 ^b	58.37 ^a	23.58 ^a	33.49 ^b	31.55 ^b	32.44 ^b
Rainfall total, in.			3.0	11.7		20.5	41.6	91.4
Total ¹⁴ C activity remaining in								
Collar		0.53 (2%) ^c	0.96 (4%)	1.56 (3%)	0.42 (2%)	0.88 (4%)	0.51 (3%)	0.34 (2%)
0-2 in.	21.92	19.21 (90%)	22.29 (85%)	42.82 (86%)	15.62 (85%)	16.30 (75%)	15.56 (86%)	12.83 (77%)
2-6 in.		1.39 (7%)	2.81 (11%)	5.00 (10%)	2.14 (12%)	3.96 (18%)	1.69 (9%)	3.05 (18%)
6-10 in.		0.16 (1%)	0.13 (<1%)	0.19 (<1%)	0.27 (1%)	0.55 (3%)	0.30 (2%)	0.48 (3%)
Total ¹⁴ C activity remaining	21.92	21.29	26.19	49.57	18.45	21.69	18.06	16.70
% remaining of total applied to each tube	91	95	84	85	78	65	57	51

^a Specific activity of 0.715 μCi mg⁻¹. ^b Specific activity of 0.396 μCi mg⁻¹. ^c Numbers in parentheses indicate the per cent of the total recovered ¹⁴C activity in the particular fraction for each separate test.

Table III. [2-¹⁴C]Benomyl Soil Disappearance Test in North Carolina

	0 day, 2 lb of ai/a, μCi	4 weeks		12 weeks, 5 lb of ai/a, μCi	6 months		12 months, 5 lb of ai/a, μCi	24 months, 5 lb of ai/a, μCi
		2 lb of ai/a, μCi	5 lb of ai/a, μCi		2 lb of ai/a, μCi	5 lb of ai/a, μCi		
Total [2- ¹⁴ C]benomyl applied to each tube ^a	10.00	12.69	32.11	31.53	12.69	29.38	32.54	31.04
Rainfall total, in.			1.3	12.6		19.0	42.7	85.7
Total ¹⁴ C activity remaining in								
Collar		0.09 (<1%) ^b	0.13 (<1%)	0.40 (2%)	0.08 (1%)	0.29 (2%)	0.26 (2%)	0.34 (3%)
0-2 in.	9.94	11.42 (99%)	26.42 (99%)	15.04 (78%)	6.58 (85%)	13.82 (73%)	8.47 (53%)	6.13 (62%)
2-6 in.		0.04 (<1%)	0.09 (<1%)	3.78 (20%)	1.10 (14%)	4.57 (24%)	7.09 (45%)	3.01 (31%)
6-10 in.		0.00	0.06 (<1%)	0.05 (<1%)	0.00 (0%)	0.06 (<1%)	0.06 (1%)	0.35 (4%)
Total ¹⁴ C activity remaining	9.94	11.55	26.70	19.27	7.76	18.74	15.88	9.83
% remaining of total applied to each tube	99	91	83	61	61	64	49	32

^a Specific activity 0.396 μCi mg⁻¹. ^b Numbers in parentheses indicate the per cent of the total recovered ¹⁴C activity in the particular fraction.

During May and June, single treatments of Benlate benomyl fungicide, 50% WP, at 2, 10, and 20 lb of ai/acre were applied. Additional plots of soil and turf received five treatments of 2 lb of ai/acre about 10 days apart for a total of 10 lb of ai/acre. All of the above involved use of the commercial material in water suspension as a surface treatment (no incorporation).

At selected sampling dates, 12 soil cores (0.75 in. diameter) were randomly collected from each plot and divided into increments of 0-4, 4-8, and 8-12 in. These samples were composited, shipped, and kept frozen until analysis.

Analysis of ¹⁴C-Labeled Samples. The analysis of the soil from the [¹⁴C]Benlate treatments is divided into three sections: (1) determination of the [2-¹⁴C]benomyl, the parent compound at both application rates in the 0-2-in. increment; (2) determination of the disappearance rate ("half-life") of the parent compound together with all degradation products containing ¹⁴C in the soil at all treatment rates, sampling intervals, and increments; (3) determination of [2-¹⁴C]MBC and [2-¹⁴C]AB, the degra-

dation products of the parent compound, in the 0-2-in. increment at the highest application rate at selected time intervals.

The determination of the intact parent compound in the soil proceeded according to a method already described and developed for plants (Baude *et al.*, 1973). This method involves the conversion of benomyl to a stable derivative BUB, 3-butylureidobenzimidazole; MBC in the same procedure hydrolyzes to AB. An aliquot (100 g of the 2 lb/acre treatments and 70 g of the 5 lb/acre treatments) of each of the 0-2-in. frozen soil increments was refluxed in 1 N aqueous sodium hydroxide (100 cm³) for 1 hr. After cooling, the mixture was centrifuged and the liquid decanted from the solids. The decanted liquid was extracted with ethyl acetate (3 × 150 ml). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and stripped on a rotating evaporator *in vacuo*. The residue was taken up in methanol (2 ml) and an aliquot streaked on a tlc plate containing fluorescent indicator. The plates were developed for 15 cm with an ethyl ace-

Table IV. [2-¹⁴C]Benomyl Soil Disappearance Test in Florida

	0 day, 5 lb of ai/a, μCi	4 weeks		12 weeks, 5 lb of ai/a, μCi	6 months		12 months, 5 lb of ai/a, μCi	24 months, 2 lb of ai/a, μCi
		2 lb of ai/a, μCi	5 lb of ai/a, μCi		2 lb of ai/a, μCi	5 lb of ai/a, μCi		
Total [2- ¹⁴ C]benomyl applied to each tube ^a	28.76	12.77	31.03	30.61	12.04	30.67	32.19	13.13
Rainfall total, in.			6.9	14.3		30.7	51.4	103.7
Total ¹⁴ C activity remaining in								
Collar		0.45 (5%) ^b	0.94 (4%)	0.88 (4%)	0.28 (4%)	0.94 (5%)	0.54 (3%)	0.22 (6%)
Around collar		0.05 (<1%)	0.07 (<1%)	0.19 (1%)	0.05 (1%)	0.12 (1%)	0.19 (1%)	0.07 (2%)
0-2 in.	25.10	8.06 (93%)	21.15 (94%)	20.27 (93%)	6.85 (91%)	16.72 (90%)	15.90 (86%)	3.13 (88%)
2-6 in.		0.09 (1%)	0.30 (1%)	0.32 (1%)	0.30 (4%)	0.82 (4%)	1.76 (10%)	0.15 (4%)
6-10 in.		0.06 (1%)	0.03 (<1%)	0.124 (1%)	0.03 (<1%)	0.06 (<1%)	0.02 (<1%)	0.00 (0%)
Total ¹⁴ C activity remaining	25.10	8.71	22.49	21.78	7.51	18.66	18.41	3.57
% remaining of total applied to each tube	87	68	72	71	62	61	57	27

^a Specific activity of 0.396 μCi mg⁻¹. ^b Numbers in parentheses indicate the per cent of the total recovered ¹⁴C activity in the particular fraction.

tate-methanol-ammonium hydroxide solution (100:25:1, v/v/v). Quantitation proceeded by radioscanning. [2-¹⁴C]Benomyl added to soil at the 2-ppm level and analyzed immediately by this procedure was recovered (87%) as BUB. Results are reported in Table I.

The determination of residual [2-¹⁴C]benomyl together with any ¹⁴C-labeled degradation products in the soil in the various sampling increments was done by combustion techniques. Each soil increment (less the amount taken for the preceding analyses) was thawed, air dried, and ballmilled. Aliquots were then combusted to determine the total ¹⁴C-labeled residue. Results are reported in Tables II-IV.

The determination of [2-¹⁴C]MBC and [2-¹⁴C]AB was made starting with a reported soil extraction method (Kirkland *et al.*, 1973) for MBC and AB. A soil aliquot (usually 50 g but in some cases 25 g) from the 6- and 12-months exposure intervals and 5 lb/acre treatment rates was refluxed for 24 hr with magnetic bar stirring in a solution of 1 N hydrochloric acid (50 ml) and methanol (150 ml). The cooled mixture was centrifuged and the supernatant decanted. The solid residue was washed once with 20% aqueous methanol (150 ml) and again the mixture centrifuged and the supernatant decanted.

The combined supernatants from the 6-month exposure samples were counted for ¹⁴C content and were then

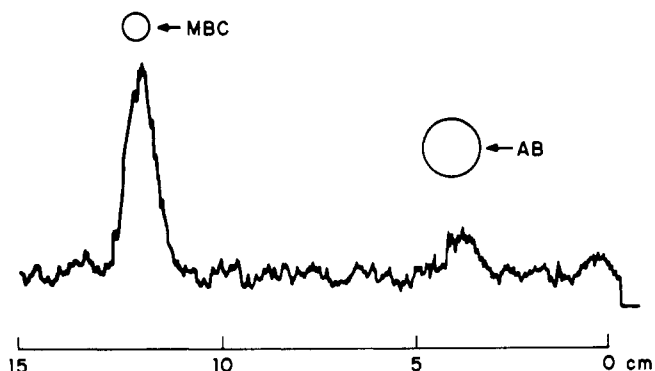


Figure 3. Tlc radioscanner of soil extract (Florida, 0-2-in. increment, 6-months exposure, 5 lb of ai/acre treatment).

Table V. Characterization of ¹⁴C-Labeled Residues in 6-Month 5 lb of Active Ingredient/Acre Benomyl-Treated Soils (0-2-in. Increments)

Location	HCl-MeOH extract, μCi	Final extract prior to tlc, μCi	% [2- ¹⁴ C]-MBC	% [2- ¹⁴ C]-AB
Delaware 0.112 ^a	0.080	0.057	85	15
North Carolina 0.133 ^b	0.110	0.081	69	31
Florida 0.092 ^a 0.184 ^b	0.083 0.140	0.054 0.099	79 73	21 27

^a Total μCi in 25-g samples based on direct combustion analyses. ^b Total μCi in 50-g samples based on direct combustion analyses.

Table VI. Characterization of ¹⁴C-Labeled Residues in 12-Month 5 lb of Active Ingredient/Acre Benomyl-Treated Soils (0-2-in. Increments)

Location and μCi ^a	HCl-MeOH extract, μCi	Unextracted ¹⁴ C, μCi	Final extract prior to tlc, μCi	% [2- ¹⁴ C]-MBC	% [2- ¹⁴ C]-AB
Delaware 0.151 0.151	0.093 0.089	0.051 0.054	0.091 0.091	95 91	5 9
North Carolina 0.078 0.078	0.069 0.069	0.011 0.013	0.074 0.071	65 65	35 35
Florida 0.176 0.176 0.176	0.13 0.13 0.13	0.038 0.030 0.032		100 92 90	0 8 10

^a Total μCi in 50-g samples based on direct combustion analyses.

Table VII. Unlabeled Benomyl Soil Residue, 2, 3, and 10 lb of Active Ingredient/Acre

Location	lb of ai/acre applied	Calcd ppm applied 0-4 in.	Residue found, ppm ^a							
			After 1 year				After 2 years			
			0-4 in.		4-8 in.		0-4 in.		4-8 in.	
			Bare soil	Turf	Bare soil	Turf	Bare soil	Turf	Bare soil	Turf
Delaware	2	1.5	0.63	0.05	0.05	<0.05	0.32	0.09	<0.05	<0.05
	10	7.5	2.8	1.1	0.07	<0.05	1.6	0.56	0.05	0.05
	10 ^b	7.5	3.2	0.60	0.06	0.05	1.3	0.21	<0.05	<0.05
North Carolina	2	1.5	0.47	0.30	0.19	0.09	0.46	0.13	<0.05	<0.05
	10	7.5	2.6	0.71	0.33	0.25	1.4	0.35	0.46	0.17
	10 ^b	7.5		0.82		0.09	2.7	0.37	0.41	0.17
Florida	2	1.5	<0.05	0.05			<0.05	<0.05	<0.05	<0.05
	10	7.5	0.28	0.05	0.08	0.06	0.10	<0.05	<0.05	<0.05
	10 ^b	7.5	0.12		0.06		<0.05	<0.05	<0.05	<0.05
Illinois	3	2.3	0.84		0.13					
	10	7.5	1.5		0.10					

^a Total residues of benomyl and its metabolites containing the benzimidazole moiety (calculated as benomyl). ^b 10 lb of ai/acre total; applied in five sprays about 10 days apart at 2 lb of ai/acre each time.

Table VIII. Unlabeled Benomyl Soil Residue, 20 lb of Active Ingredient/Acre

Location	Calcd ppm applied 0-4 in.	Residue found, ppm ^a											
		After 1 year						After 2 years					
		0-4 in.		4-8 in.		8-12 in.		0-4 in.		4-8 in.		8-12 in.	
		Bare soil	Turf	Bare soil	Turf	Bare soil	Turf	Bare soil	Turf	Bare soil	Turf	Bare soil	Turf
Delaware	15	7.1	1.5	0.13	0.07	0.30	<0.05	1.4	0.44	0.08	<0.05	<0.05	<0.05
North Carolina	15	4.5	2.0	1.7	0.91	0.23	0.15	3.4	0.79	0.50	0.44	0.14	0.17
Florida	15	0.58	0.36	0.06	0.06	0.06		0.68	0.16	<0.05	<0.05	<0.05	<0.05

^a Total residues of benomyl and its metabolites containing the benzimidazole moiety (calculated as benomyl).

taken to dryness; the residue was taken up in water (100 ml). The solutions were extracted with ethyl acetate (4 × 100 ml) and the combined organic extracts dried over anhydrous sodium sulfate. The residues were taken up in methanol (2 ml). Aliquots were counted for ¹⁴C content and streaked on tlc plates along with the reference compounds AB and MBC dissolved in methanol. Plates were developed in a solution of ethyl acetate, methanol, and ammonium hydroxide (100:25:1, v/v/v). Radioactivity on the developed plates was detected by the tlc radioscanner. A typical scan is shown in Figure 3. Only [2-¹⁴C]MBC and [2-¹⁴C]AB were detected in the extracts. The full results appear in Table V.

The combined supernatants from the 12-month samples were counted for ¹⁴C and taken to dryness; residues were taken up directly in methanol (25 ml). The extracted soils were reanalyzed for ¹⁴C residues to cross-check the values for total ¹⁴C by direct combustion. Aliquots of the solutions were processed as described for the 6-month samples with the following modification. The areas of ¹⁴C activity on the tlc plates of samples from North Carolina and Delaware were ascertained by autoradiography on Kodak No-Screen X-ray film instead of by the radioscanner. Quantitation proceeded by scraping the areas of ¹⁴C activity corresponding to the same R_f values as the reference compounds AB and MBC with subsequent scintillation counting. The results appear in Table VI.

Analysis of Unlabeled Samples. The various soil increments from the different locations were analyzed for MBC (together with benomyl) and AB according to a published method (Kirkland *et al.*, 1973), which utilizes high speed liquid chromatography for residue determination. Representative samples were prepared by ballmilling each entire air-dried soil increment (about 500 g) in 10%

aqueous methanol (300 ml) for 16 hr. The homogeneous slurries were air-dried in shallow stainless trays and then grated and sub-sampled to secure the final material for analysis (50 g). Pieces of turf and weeds were not removed.

Results are reported in Tables VII and VIII as total residues of benomyl and its metabolites containing the benzimidazole moiety (benomyl + MBC + AB), calculated as parts per million of benomyl. AB was detected in many samples from all locations, ranging in amounts up to 25% of the total residue, in general agreement with the results from ¹⁴C studies. All positive values in Tables VII and VIII have been corrected for 86% benomyl-MBC and 58% AB recovery.

RESULTS AND DISCUSSION

We have examined the behavior of Benlate benomyl fungicide on soil and turf in terms of the disappearance of the parent compound, the formation of two degradation products, MBC and AB, and the disappearance of these secondary products. Our approach utilized two experimentally different methods. The first approach utilized [2-¹⁴C]benomyl (the parent compound), formulated as Benlate, 50% WP, and applied in restrictive soil tubes. This type of experiment offered the advantages of quantitation in a total sense insofar as the entire treated soil could be analyzed. Any degradation product containing ¹⁴C could be detected and identified. The disadvantages of this approach are that the free lateral movement of air and water is perturbed and the necessary quantitation dictated the use of pipets (instead of spraying) in applying the fungicide which tended to create uneven distribution. In addition, channeling, along the walls of the steel tubes, although apparently not observed, could have occurred.

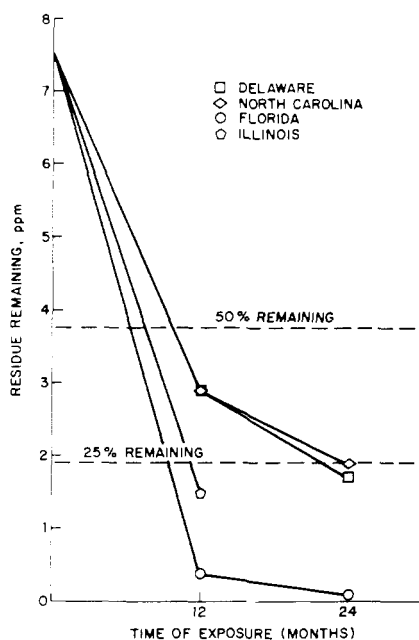


Figure 4. Typical plot of residues remaining in 0-8-in. soil increments (all treatments at 10 lb of benomyl/acre).

The second approach utilized unlabeled benomyl (from commercial Benlate benomyl fungicide) and offered the advantage of spray application over a much larger area. The plots offered no physical restrictions to lateral movement of air and water. This technique suffered the disadvantages, however, of sampling errors due to initial spray nonuniformity and possible erosion during the test period. Also, the subsequent analysis of the soil was subject to the inherently greater variability of residue methods in general in comparison with the accuracy of the ^{14}C techniques.

All the data from both types of tests were collected under conditions in the open field, subject to such variants as rain, wind, soil type, and seasonal temperatures. Although laboratory soil disappearance studies might lead to data which are more internally consistent, we feel our approaches gave results which must be closer to reality.

Intact $[2-^{14}\text{C}]$ benomyl, applied as a solid in aqueous suspension, decomposes rapidly in soil (Table I). Only in North Carolina soil was a detectable residue of intact benomyl observed after 4 weeks; none was found after 12 weeks of exposure. The soil residues consist of $[2-^{14}\text{C}]$ MBC (major) and $[2-^{14}\text{C}]$ AB (minor); see Tables V and VI. The "half-life" of total ^{14}C -labeled residues was about 1 year in the test system employed (Tables II-IV). The only figure not consistent with this evaluation was the 51% total ^{14}C remaining in Delaware soil after 24 months (Table II). Corresponding figures for 24 months in North Carolina and Florida are in agreement, however, and indicate continued, steady degradation of the total ^{14}C -labeled residues.

In the conventional (nonradiolabeled) tests with Benlate benomyl fungicide (Tables VII and VIII), all data on bare soil indicate a "half-life" of total benzimidazole-containing residues of about 6-12 months or less. On turf, the "half-life" is less than 6 months. Figure 4 shows a typical plot used to analyze the data. In this figure, all values are from single 10 lb of ai/acre treatments to bare soil; residues in the 0-4- and 4-8-in. soil increments have been added together for comparisons. The initial parts per mil-

lion value was obtained by calculation from the area of soil sampled (core areas $\times 12$) vs. the average weight of soil in the 0-4-in. increments. Figure 4 shows that the soil residues after 1 year in Delaware and North Carolina were between 25 and 50% remaining, corresponding to a "half-life" of between 6 and 12 months. In Illinois and Florida, the remaining residue (and "half-life") was less. After 2-years exposure in Delaware and North Carolina, the soil residues decreased further to about 25% remaining, corresponding to about a 1-year "half-life."

Other tests have been conducted to evaluate the possible significance of the benomyl soil residues. Separate run-off and leaching studies in the greenhouse have already been referred to (Rhodes and Long, 1974). These tests showed that benomyl and its soil degradation products are highly immobile in soil, a conclusion which is confirmed by the data reported herein. The major portions of soil residues were always found in the uppermost soil increment. Studies on possible effects of benomyl residues on soil microorganisms are also reported separately (Peeples, 1974). These data indicate that long-term microbial populations and respiration rates are not altered by treatment with benomyl at rates up to 80 lb of ai/acre. Only short-term effects, particularly on fungi, are to be expected. Other tests, some of which are based on ^{14}C -labeled materials, have shown that follow-up crops in subsequent growing seasons do not take up remaining benomyl soil residues (Lowen, 1973). Presumably this is the result of tight adsorption of these residues to soil. Chemically, very rigorous extraction methods (boiling MeOH-HCl) must be employed to remove aged residues from soil as shown in Tables V and VI.

CONCLUSIONS

The results of these extensive studies to determine the fate and behavior of benomyl in soil under field conditions show that: (1) MBC is the major and AB the minor degradation product of benomyl in soil and turf; (2) the "half-life" of total benzimidazole-containing residues, as determined after 1 and 2 years of outdoor exposure, is about 3-6 months on turf, representing a vegetative situation, and about 6-12 months on bare soil in different agricultural areas of the United States; (3) the parent compound and its degradation products show little or no downward movement through the soil.

ACKNOWLEDGMENT

The authors are indebted to H. T. Cox, S. J. Denis, F. J. Otto, R. Sutton, and A. W. Welch for contributions to this work.

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Received for review November 20, 1973. Accepted January 24, 1974.