

## Decomposition of Methomyl in Soil

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Laboratory studies of soils treated with [ $^{14}\text{C}$ ]methomyl show that methomyl degrades rapidly to [ $^{14}\text{C}$ ]carbon dioxide as the end product. Under field conditions in Delaware, only 1.8% of the applied [ $^{14}\text{C}$ ]methomyl remained intact in the soil after 1 month exposure, while 70.7% of the applied radioactivity had been lost from the soil by volatilization, presumably as [ $^{14}\text{C}$ ]carbon dioxide based on the laboratory studies. The small amounts of residual radioactive compounds which could be extracted from this soil consisted of methomyl, *S*-methyl *N*-hydroxythioacetimidate, and traces of a mixture of very

polar compounds. Methomyl and its hydrolysis product had completely disappeared from treated soil after 1 year. Similar results were obtained in Florida and North Carolina. To account for the small, unextractable balance of  $^{14}\text{C}$  activity, evidence is presented for reincorporation of  $^{14}\text{C}$  into normal components of the soil organic matter following breakdown of [ $^{14}\text{C}$ ]methomyl into  $^{14}\text{CO}_2$  or other small fragments. A runoff study with nonradiolabeled methomyl under farm use conditions shows that methomyl does not move laterally into untreated areas with runoff water.

This paper is the third in a series of three. The first two papers describe the synthesis of radiolabeled methomyl and its fate in rats (Harvey *et al.*, 1973) and the metabolic fate of methomyl in tobacco, corn, and cabbage (Harvey and Reiser, 1973). A review of pertinent literature is given in the first paper. Since the application of methomyl to crops brings the compound into contact with soil, its fate in this medium is of importance. This paper describes investigations of the metabolism of methomyl in soils under laboratory and field exposure conditions.

### EQUIPMENT AND METHODS

The preparations of *S*-methyl[1- $^{14}\text{C}$ ]N-[(methylcarbamoyl)oxy]thioacetimidate (radiolabeled methomyl) and of the *S*-oxide and the *S,S*-dioxide of methomyl were described earlier by Harvey *et al.* (1973). Procedures for countercurrent fractionation, determination of radioactivity, and the preparation of thin-layer chromatographic plates were also described in the same paper.

### DECOMPOSITION IN SOIL, LABORATORY STUDY

Three soils were used in the following experiment. The first was a Keyport silt loam with pH 4.7. The second soil was the same Keyport silt loam with the pH adjusted to 7.9 by liming. The third was a soil collected from the San Joaquin Valley of California of pH 7.9.

An apparatus was set up in the laboratory, as shown in Figure 1. The chamber in which the soil was placed consisted of two glass parts joined together with an O-ring seal and a pressure clamp. The bottom section was 3 in. in diameter and 4.5 in. deep. In it was placed 400 g of moist soil, firmed as for planting. Onto the surface of the soil was pipetted as evenly as possible an aqueous solution of [ $^{14}\text{C}$ ]methomyl. The top of the vessel was sealed in place and connected to the series of traps with Tygon tubing. Each trap was fritted, and contained 28 ml of 1 *N* sodium hydroxide solution. The oxidizing furnace between trap no. 2 and trap no. 3 maintained at dull red heat a 6-in. section of 1-in. diameter quartz tubing filled with cupric oxide. A gentle stream of air was drawn through the apparatus continuously for a period of 42 days, after which the apparatus was disassembled and the fractions were analyzed.

Radioactivity in the traps was determined by liquid scintillation counting. In each experiment all the volatile radioactivity was found in the first sodium hydroxide

trap. Quantitative precipitation of the radioactivity in each of the radioactive sodium hydroxide solutions with barium chloride indicated that the only significant source of radioactivity in the trap was carbon dioxide.

At the end of the experiment the soil was removed from the apparatus and transferred to four 250-ml screw-cap centrifuge bottles. The bottles were filled with methanol, capped, and shaken continuously for 20 min. The slurry was centrifuged and the supernatant liquid was decanted. The soil was extracted twice with methanol and four times with water in this manner. The extracts were cloudy suspensions which were clarified by filtration through a bed of Celite Filter Aid on a sintered glass funnel. The radioactivity in the extracts was determined by liquid scintillation counting.

After the extractions were complete, the soil was air dried at room temperature in a large stainless steel tray. The dry residue was broken up and passed through a no. 20 sieve. Representative samples were analyzed by wet combustion. The material balance of recovered radioactivity is shown in Table I.

**Fractionation of Soil Extracts.** The combined soil extracts were concentrated to a convenient volume (10–25 ml) under reduced pressure in a rotary evaporator on a water bath. Recovery of radioactivity in the concentrate averaged 85%. An aliquot of the aqueous concentrate was used as the first lower phase in a 100 transfer countercurrent distribution using the benzene–water system. The distribution of radioactivity obtained for the extract of Keyport silt loam soil, pH 4.7, is shown in Figure 2. The extracts of the other soils gave similar results. The compositions of the soil extracts are summarized in Table I. No radioactivity was found in tubes no. 60–100 for any extract.

In each case, the material in tubes no. 30–55 cochromatographed with methomyl on silica gel tlc plates developed with ethyl acetate. Similarly, the material recovered from tubes no. 10–25 cochromatographed with *S*-methyl *N*-hydroxythioacetimidate.

The quantity of the extremely polar material in tubes no. 0–5 was too small to permit purification and identification.

### FIELD DECOMPOSITION STUDIES

Late in June, three 4-in. diameter  $\times$  15-in. long stainless steel cylinders were driven into an undisturbed Keyport silt loam soil near Newark, Del., allowing  $\frac{1}{2}$  in. of each cylinder to protrude above the soil surface. The top  $1\frac{1}{2}$  in. of soil was removed from each enclosed column of soil. Onto the exposed surface was pipetted 5.0 ml of an

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**Table I. Decomposition of [<sup>14</sup>C]Methomyl in Three Soils under Laboratory Conditions (42-Day Exposures)**

Soil	Keyport silt loam	Keyport silt loam	Soil from California
pH	4.7	7.9	7.9
Treatment	10.6 $\mu$ Ci 4.0 lb/acre	11.5 $\mu$ Ci 4.3 lb/acre	14.6 $\mu$ Ci 5.5 lb/acre
Distribution of radioactivity	% OT <sup>a</sup>	% OT <sup>a</sup>	% OT <sup>a</sup>
Carbon dioxide	39	31	45
Soil extract			
Methomyl	48	44	31
s-Methyl N-hydroxy-thioacetimidate	1	2	1
Polar fraction	1	1	1
Unextracted residue	14	18	12
Total recovery	103%	96%	90%

<sup>a</sup> OT = original treatment.

aqueous solution of 4.15 mg (8.90  $\mu$ Ci) of [<sup>14</sup>C]methomyl. This was equivalent to 4.5 lb/acre of the subject compound. The soil which had been removed was replaced. Each column was irrigated with 60 ml of water. Weed seedlings as they appeared were severed at the surface and the severed top was allowed to decompose on the surface of the soil.

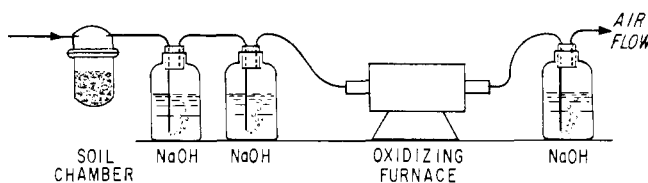
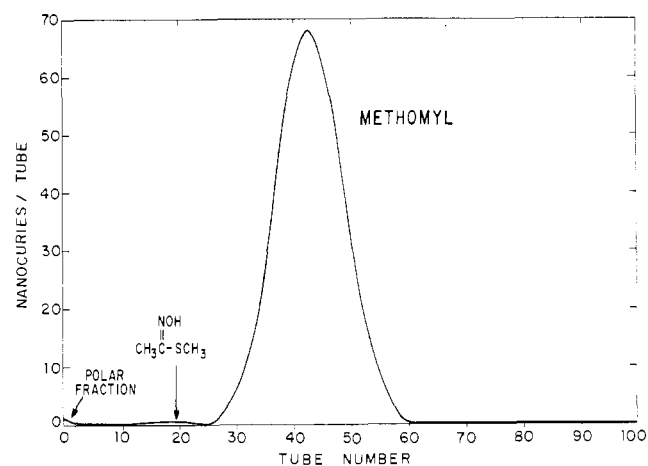
Single cylinders were dug up after 1, 3, and 12 months. The soil was extruded from the cylinder, sectioned as shown in Table II, and analyzed for total radioactivity by wet combustion. The top layer from each cylinder was then analyzed as described for the laboratory study. The results are included in Table III.

An additional cylinder was driven into a Leon Immokalee fine sand soil on a test farm near Bradenton, Fla., and another into a Cecil loamy sand soil on a test farm near Clayton, N. C., in May. Because of the sandy nature of these soils and lower absorptive capacity, an additional step was added to the procedure. Each cylinder was immediately dug up and a filter trap was attached to the bottom of the cylinder, which allowed water to elute freely from the bottom of the soil cylinder. Water passing through the soil columns during the test period was then collected in a 2-l. capacity glass vessel at the bottom of each cylinder. Each assembled device was then reburied in the soil to its original depth. Each cylinder was treated with [<sup>14</sup>C]methomyl as previously described. After heavy rains, water was withdrawn from the vessel under each cylinder without disturbing the soil and analyzed for radioactivity. No radioactivity was ever found in the eluate. The cylinder from Florida was harvested after 3 months, and that from North Carolina after 5 months. Each was sectioned as follows: 0-3 in. depth; 3-7 in. depth; 7-11 in. depth; and 11-15 in. depth. Each fraction was analyzed as previously described. The results are shown in Tables II and III.

Two 50-g samples of the soil organic matter remaining in the top layer of North Carolina soil after exhaustive extraction with water were fractionated according to the procedure described by Iverson and Stevenson (1964). Hot 0.1 N sodium hydroxide extracted 62% of the residual radioactivity, which was subsequently found to be divided between the soil fractions as follows: humatmelanic acid, 2%; fulvic acid, 16%;  $\alpha$ -humus, 22%;  $\beta$ -humus, 5%; and a volatile component lost during concentration, 17%. The soluble humin fraction (6 N HCl) contained 12% of the original soil residual radioactivity, while 26% was not extracted by either alkali or acid (insoluble humin).

#### RUNOFF STUDIES

A hillside farm site in Maryland was selected with a Tinton loamy sand and a 10% slope. The site was cleared


**Figure 1.** Laboratory apparatus for soil metabolism study.

**Figure 2.** Countercurrent fractionation of soil extract (laboratory study, Keyport silt loam, pH 4.7).

**Table II. Residual Radioactivity in Soil Treated with [<sup>14</sup>C]Methomyl under Field Conditions**

Depth, in.	Radioactivity remaining after				
	Delaware			Florida, months, % OT <sup>a</sup>	North Carolina, 5 months, % OT <sup>a</sup>
	1 month, % OT <sup>a</sup>	3 months, % OT <sup>a</sup>	12 months, % OT <sup>a</sup>		
0-3	28.1%	18.9%	14.4%	8.9%	11.1%
3-4.5	0.9	0.3	0.4		
3-7				0.7	3.8
4.5-6	0.2	0.1	0.1		
6-8	0.1	0.0	0.1		
7-11				0.1	0.1
8-10	0.0	0.0	0.0		
10-12.5	0.0	0.0	0.0		
11-15				0.0	0.2
12.5-15	0.0	0.0	0.0		
Total	29.3%	19.3%	15.0%	9.7%	15.2%

<sup>a</sup> OT = original treatment = 8.9  $\mu$ Ci.

of vegetation by rototilling prior to treatment. A 5 ft  $\times$  5 ft area was treated with methomyl at 2 lb/acre. On the uphill side, a ditch was dug to prevent gross amounts of water from washing out the test site. On the downhill side, an adjacent 5 ft  $\times$  5 ft area was left untreated. At the base of the untreated area, a gutter was installed to collect runoff water. This gutter was covered to prevent direct collection of rain water.

One day after treatment, 0.2 in. of natural rain fell and this was supplemented with 1.4 in. of artificial rain before sampling. On the seventh day after treatment, 1.0 in. of artificial rain was applied before sampling. On the fifteenth day, 0.7 in. of natural rain fell, supplemented by 0.8 in. of artificial rain before sampling.

Runoff water, collected in the gutter below the treated and originally untreated areas, was removed and analyzed on the first, seventh, and fifteenth days after treatment. Soil samples were taken 15 days after treatment. One set of samples was taken within the treated area with cores

Table III. Decomposition of [<sup>14</sup>C]Methomyl in Three Soils under Field Conditions

	Location and original treatment				
	Delaware, 4.5 lb/acre			Florida, 4.5 lb/acre, time of exposure, 3 months	North Carolina, 4.5 lb/acre time of exposure, 5 months
	Time of exposure, months				
	1	3	12		
Distribution of radioactivity					
Rainfall during exposure	1.1 in.	11.2 in.	40.5 in.	23.6 in.	17.3 in.
Volatility losses (% OT <sup>a</sup> )	70.7%	80.7%	85.0%	90.3%	84.8%
Soil extract <sup>b</sup> (% OT <sup>a</sup> )					
Methomyl	1.8%	0.3%	0.0%	<0.005%	<0.005%
S-Methyl N-hydroxythioacetimidate	0.2%	0.1%	0.0%	<0.005%	<0.005%
Polar fraction	0.9%	0.7%	0.3%	0.2%	0.04%
Unextracted residue (% OT <sup>a</sup> )	26.4%	18.2%	14.7%	9.5%	15.2%

<sup>a</sup> OT = original treatment. <sup>b</sup> Based on composition of extract of top layer of soil.

taken over the entire plot starting 1 ft within the boundary lines. These samples consisted of 0-4, 4-8, and 8-12 in. depth increments to give additional information on leaching tendencies. Soil samples were taken similarly in the 1-2 ft segment and in the 3-4 ft segment downhill from the treated area. These samples were to provide information on possible residue buildup in untreated soil areas downhill from a treated area. Samples of water and soil were frozen immediately after collection until analyzed. Analyses were conducted according to the method of Pease and Kirkland (1968). No methomyl was detected in any samples of runoff water (<0.01 ppm) or soil (<0.04 ppm), indicating that very little if any surface runoff or leaching of methomyl can be expected following normal use. As indicated in the field studies with [<sup>14</sup>C]methomyl, rapid decomposition leads to very low absolute levels of methomyl in the soil after 15 days.

#### RESULTS AND DISCUSSION

Laboratory studies indicate that methomyl degrades rapidly by microbial action in soil with [<sup>14</sup>C]carbon dioxide as the principal end product. As would be expected, some of this [<sup>14</sup>C]carbon dioxide is reincorporated into normal soil organic matter. Methomyl itself and trace amounts of its hydrolysis product, S-methyl N-hydroxythioacetimidate, appear to be the only residues in which a semblance of the original structure is retained.

Under field conditions loss of methomyl is even more rapid. In Delaware, 71% of the applied radioactivity was lost within 1 month. Only traces of intact methomyl were detected in the soil 1 month after treatment at a rate of 4.5 lb/acre, and none was detected after 1 year. The hydrolysis product, which appeared in trace amounts after 1 and 3 months exposure, was not detected at 1 year. De-

spite the water solubility of methomyl, leaching was slight. No radioactivity was detected below the 8-in. depth of a silt loam soil, and none eluted from the bottoms of 15-in. long cylinders of sandy soil. Decomposition of methomyl was more rapid in North Carolina, and especially rapid in Florida. Fractionation of the unextractable radioactivity remaining in a North Carolina soil 5 months after treatment with [<sup>14</sup>C]methomyl showed that the non-water-soluble residual radioactivity was rather evenly distributed among the normal soil organic fractions, as would be expected from reincorporation of the <sup>14</sup>CO<sub>2</sub> or other small fragments formed from complete breakdown of [<sup>14</sup>C]methomyl.

The runoff study using nonlabeled methomyl applied to the surface of a sandy loam soil followed by the equivalent of fairly heavy rainfall indicated that methomyl is not carried to untreated areas in runoff water and confirmed the other field experiments that show a rapid disappearance of methomyl from treated soils.

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