Supplementary Material Available: Synthesis of radiolabeled oxamyl and the mass spectrum of metabolites A and A' (10 pages). Ordering information is given on any current masthead page.

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Decomposition of Oxamyl in Soil and Water

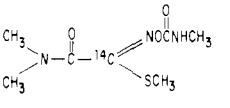
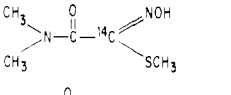
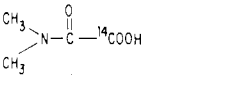
John Harvey, Jr.* and Jerry C-Y. Han

Oxamyl was stable in water at pH 5 or lower, but hydrolyzed rapidly to the oximino compound (I) at pH 9. Ultraviolet light accelerated hydrolysis and caused the formation of the syn–anti isomer of I. In river water exposed to sunlight, oxamyl hydrolyzed immediately to I, which gradually was converted to its isomer and to *N,N*-dimethyloxamic acid (III) and CO_2. In soil [^{14}C]oxamyl degraded rapidly to $^{14}CO_2$. Traces of I and a polar fraction were extractable, and radioactivity became incorporated into normal soil organic matter. Under anaerobic conditions, oxidation to CO_2 and incorporation into organic matter were delayed. These results were confirmed in field studies where the half-life of oxamyl was about 1 week.

We have already described in a previous paper (Harvey et al., 1978) the synthesis of [^{14}C]oxamyl and the metabolic fate of Vydate oxamyl insecticide–nematicide in crop plants. Because the application of oxamyl to crops unavoidably brings the compound into contact with soils and water, its fate in these media is of considerable importance. Bromilow (1973) has reported a half-life of about 2 weeks for oxamyl (Du Pont 1410) in fallow soil in pots kept outdoors in late summer.

This paper describes investigations of the decomposition of oxamyl in water and its decomposition and movement in soils under laboratory and field conditions. The structures and designations of compounds which were encountered in this work but described in our previous paper are shown in Scheme I.

Scheme I

COMPOUND	NAME	STUCTURE
OXAMYL	METHYL N',N'-DIMETHYL-N[(METHYLCARBAMOYL)OXY]-1-THIOOXAMIMIDATE	
(I)	OXIMINO METABOLITE METHYL N-HYDROXY-N',N'-DIMETHYL-1-THIOOXAMIMIDATE	
(III)	N,N-DIMETHYLOXAMIC ACID	

EXPERIMENTAL SECTION

Equipment and Methods. Liquid scintillation counting (LSC), combustion analysis (CA) of solid samples, thin-layer chromatography (TLC) on silica gel developed with ethyl acetate, and high-performance liquid chromatography (HPLC) were all carried out as described in Harvey et al. (1978).

A Bendix Time-of-Flight Model 12-107 mass spectrometer (MS) was used to characterize metabolites after purification.

Effect of pH on Aqueous Solutions of Oxamyl. The stability of [^{14}C]oxamyl was evaluated in 0.01 M solutions of sodium acetate (pH 4.7), sodium chloride (pH 6.9), and sodium bicarbonate (pH 9.1). [^{14}C]oxamyl was introduced at an initial concentration equivalent to 16 oz/100 gal (~1200 ppm). The solutions were kept in stoppered glass flasks at room temperature in the laboratory. Aliquots were withdrawn at appropriate time intervals and analyzed by thin-layer chromatography. The results are shown in Figure 1.

Decomposition in Water Exposed to UV Light. The Brandywine River is a pastoral stream in northern Delaware from which the City of Wilmington draws its water supply. Water drawn from the Brandywine in February, pH 6.5, and distilled water, pH 6.2, was used in these experiments. Th pH of the samples remained unchanged throughout. [^{14}C]Oxamyl solutions were prepared at 1 ppm and 1000 ppm in both distilled and river water. Control samples were transferred into glass bottles and placed in the dark at 24 °C for 10 days. The remaining samples were stirred in beakers exposed to a Blak-Ray XX-15 long wavelength lamp (A. H. Thomas Co.) continuously for 7 days. This lamp emits wavelengths between 300 and 400 nm with an intensity of 1200 μW cm^{-2} when placed 7 in. above the surface of the test solutions. This is equivalent to about half the intensity of summer sun-

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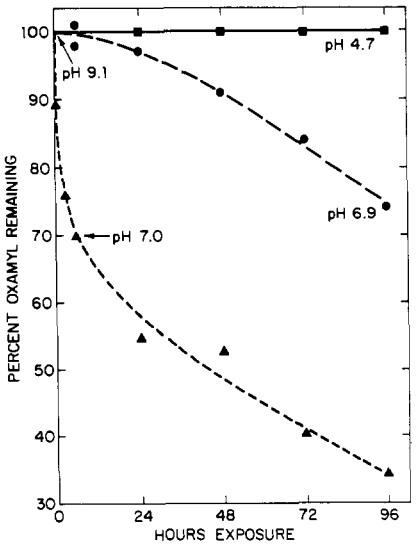

Figure 1. Stability of [^{14}C]oxamyl in aqueous solutions.

Table I. Breakdown of [^{14}C] Oxamyl in Distilled and River Water in the Laboratory under Ultraviolet Light

	Hours Exposure	Percentage composition: Oxamyl	I	I Isomer	Polar fraction
1 ppm oxamyl					
Distilled water	0	100	0	0	0
(UV light)	3	93	7	0	0
	19	93	7	0	0
	48	90	8	0	2
	96	79	9	2	10
	168	61	18	3	18
Dark (control)	240	98	2	0	0
1 ppm oxamyl					
River water	0	100	0	0	0
(UV light)	3	75	24	0	1
	19	15	65	10	10
	48	1	67	12	20
	96	2	51	25	22
	168	2	51	24	23
Dark (control)	240	98	2	0	0
1000 ppm oxamyl					
Distilled water	0	100	0	0	0
(UV light)	3	94	6	0	0
	19	82	16	0	2
	48	67	27	4	2
	96	38	44	15	3
	168	28	43	25	4
Dark (control)	240	96	4	0	0
1000 ppm oxamyl					
River water	0	100	0	0	0
(UV light)	3	89	11	0	0
	19	72	24	3	1
	48	50	34	14	2
	96	37	46	14	3
	168	22	39	36	3
Dark (control)	240	84	16	0	0

shine at noon (Wilmington, Del.). The temperature of the exposed solutions rose to 31 °C after 30 min and remained constant for the duration of the test. At intervals of 0, 3, and 19 h, 2, 4, and 7 days, aliquots of the UV-exposed water samples were removed and analyzed for total radioactivity by LSC and for composition by TLC. Identification of the major components was confirmed by MS analysis of materials isolated from the TLC plates. Loss of total ^{14}C activity during the course of the experiment was less than 2% in all samples. The results of these studies are shown in Table I.

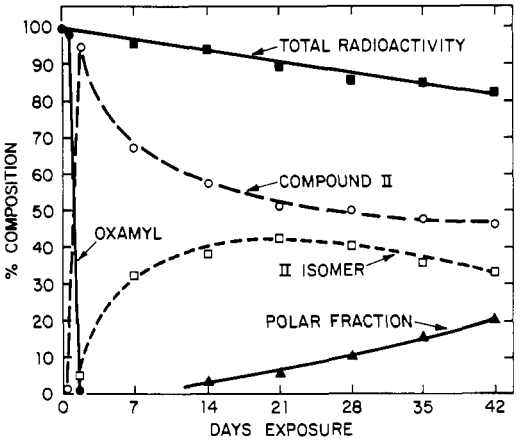

Figure 2. Decomposition of [^{14}C]oxamyl in river water.

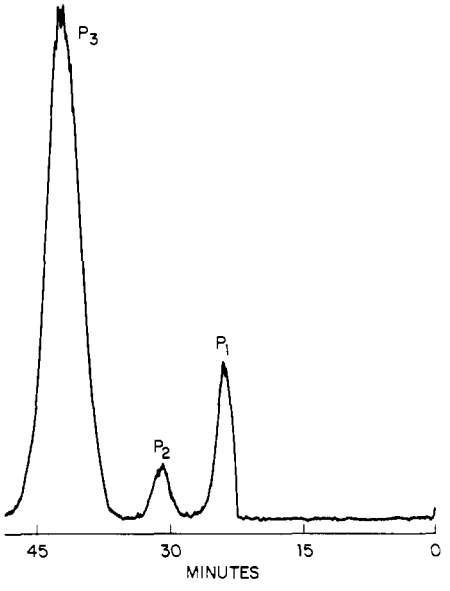

Figure 3. Separation of ^{14}C decomposition products in river water on Sephadex G15/water.

Decomposition in River Water Exposed To Sunlight. Twenty liters of water, drawn from the Bradywine, were placed in a 6-gal battery jar. The surface of the water in the jar was exposed outdoors directly to sunlight, and the water was maintained in a constant state of moderate agitation with a Little Giant (Cole-Parmer Instrument Co.) submersible pump. [^{14}C]Oxamyl (20.1 mg; 81.0 μCi) ~1 ppm was dissolved in the water. Water lost by evaporation was replaced at frequent intervals with distilled water. At intervals throughout the course of the experiment, small aliquots were removed and analyzed for total radioactivity by LSC and for composition by TLC. The results of these analyses are shown in Figure 2. At the end of 6 weeks, the experiment was discontinued, and the metabolites present was used for identification studies.

The water was removed from the jar, and all interior surfaces exposed to the water were rinsed with fresh water. As much as possible of the biological residue (algae, bacteria, etc.) was scraped off these surfaces and analyzed for carbon-14. A 12-L portion of the clear water was concentrated under reduced pressure in a rotary evaporator to 500 mL without loss of radioactivity or change in composition. A portion of this concentrate was resolved into three fractions by HPLC of 1.0-mL aliquots on a 6 mm × 1000 mm column of Sephadex G15 (Pharmacia Fine Chemicals, Inc.) equilibrated with water at 0.66 mL min^{-1} (Figure 3). The fraction collected 22.5–26 min (P_1) and

Table II. Composition of a Solution of [^{14}C]Oxamyl in River Water after 6 Weeks Exposure to Sunlight

Compound	Percentage
Oxamyl	0
I } (P_3)	46
I isomer } (P_3)	34
Polar compounds	
N,N-Dimethyloxamic acid, III (P_1)	14
Polar compound a } (P_2)	3
Polar compound b } (P_2)	3
	100

the fraction collected 30–34 min (P_2) were shown to contain only polar ^{14}C material, i.e., radioactivity that remained at the origin of a TLC plate. A third fraction (P_3), collected in the interval 38–47 min, contained two nonpolar ^{14}C compounds which were subsequently separated and purified by TLC and identified by MS.

Fractions P_1 and P_2 were individually purified by evaporation of the aqueous solutions, transfer of the ^{14}C residues to methanol, and passage through a 6 mm × 1000 mm column of Sephadex LH20 (Pharmacia Fine Chemicals, Inc.) equilibrated with methanol at 0.66 mL min^{-1}. After concentration of the single ^{14}C fraction from each injection, the compounds were further purified by passage through a 6 mm × 1000 mm column of Porasil A (Waters Associates) equilibrated with methanol at 0.66 mL min^{-1}.

Fraction P_1 was finally purified and identified by HPLC on a 2.8 mm × 1000 mm column packed with XE255 strong anion-exchange resin on <37 μm glass beads (Kirkland, 1970) equilibrated with 0.004 M phosphate buffer, pH 5.3, at 0.50 mL min^{-1}. An authentic sample of III had a retention time of 17–21 min under these conditions and cochromatographed with P_1. The identification of P_1 as *N,N*-dimethyloxamic acid was confirmed by mass spectrum analysis.

An aliquot of P_2 was not retained on the anion-exchange column. The remainder of the methanolic solution was evaporated to dryness, and the radioactivity taken up in tetrahydrofuran (THF). Adsorption chromatography of the THF solution on a 2.8 mm × 1000 mm column of Porasil A equilibrated with THF (0.5% H_2O) at 0.5 mL min^{-1}) resolved the fraction into two radioactive peaks. Purification was incomplete, however, and MS analysis was unable to provide a structure for either before the supply of compound was exhausted. These results are summarized in Table II.

Decomposition in Soils Metabolite Study. A glass soil-metabolism apparatus was set up as described by Harvey and Pease (1973). Moist Keyport silt loam, pH 4.7 (Delaware), was placed in the chamber and treated with [^{14}C]oxamyl (0.98 μCi) at a rate equivalent to 4 lb/acre. Air was drawn slowly through the chamber and the connected trapping system for 42 days. Total radioactivity in the gas traps was determined by LSC at 21 and 42 days and $^{14}CO_2$ content by precipitation with barium chloride solution. At the end of the experiment, the soil was removed from the apparatus and ball-milled with water. After centrifuging, the supernatant liquid was decanted through glass wool and the extraction repeated. The extracted soil was air-dried at room temperature. Radioactivity in the extracts was determined by LSC; in the dry extracted soil by wet combustion. The composition of the soil extract was determined by TLC. The organic matter in a 50-g sample of the air-dried soil after extraction was fractionated according to the precedure described by Ivarson and Stevenson (1964).

The experiment was repeated under anaerobic conditions. [^{14}C]Oxamyl (7.12 μCi) at 6 ppm was mixed thoroughly in a ballmill with air-dry Keyport silt loam, after which the moisture content was adjusted to 87% field capacity. The soil was placed in the metabolism chamber, and a stream of nitrogen was forced very slowly through the chamber above the soil and then through the trapping system for 42 days. Fractions were analyzed as described above. The results of these studies are shown in Table III.

Table III. Decomposition of [^{14}C]Oxamyl in Soil in a Metabolism Chamber (42-Day Exposures)

Distribution of radioactivity	% of original treatment	
	Aerobic	Anaerobic
Carbon dioxide	51	3
Soil extract		
Oxamyl	4	8
Compound I	<1	41
Polar fraction[a]	11	42
Unextracted residue	26	6
Total recovery	93	100

[a] Polar fraction = that material which remains at origin of silica gel TLC plate developed in ethyl acetate.

Table IV. Decomposition of [^{14}C]Oxamyl in Soil under Aerobic Laboratory Conditions[a]

Time of exposure, days	Oxamyl in soil extract % O.T.[b]	Unextracted residue[c] (% O.T.)	Total (% O.T.)
North Carolina soil			
0	99	0	99
2	87	2	89
7	58	10	68
14	42	14	56
28	28	13	41
Florida Soil			
0	100	1	101
2	92	4	96
7	68	13	81
14	53	17	70
28	28	19	47

[a] Distribution of radioactivity (applied 2.28 μCi = 0.615 mg). [b] O.T. = original ^{14}C treatment. [c] Determined by combustion analyses after extraction with methanol.

Decomposition in Soil, Laboratory Rate Study. Additional aerobic laboratory studies were conducted with [^{14}C]Oxamyl incorporated at 6 ppm into Cecil loamy sand, pH 6.8 (North Carolina) and Leon Immokalee fine sand, pH 6.4 (Florida). The treated samples were maintained in partially covered beakers in the laboratory at 25 °C and 30% field moisture capacity. After 0, 2, 7, 14, and 28 days, samples were taken and analyzed as previously described. No attempt was made to trap $^{14}CO_2$. The results of the aerobic rate study are shown in Table IV.

An anaerobic rate study was carried out with [^{14}C]oxamyl incorporated at 6 ppm into Keyport silt loam, pH 4.9 (Delaware). The treated samples with moisture content adjusted to 87% field capacity were placed in glass centrifuge bottles with polyethylene-lined screw caps. Each container was evacuated five times and refilled each time with nitrogen, after which the caps were tightened and the bottles stored in the dark at room temperature. One bottle was opened and analyzed within several hours (0 day); the others 7, 14, and 28 days after treatment. The results of these studies are shown in Table V.

Mobility in Soil, Laboratory Conditions. Soil TLC values were determined on a number of soils as described by Rhodes et al. (1970). The results are shown in Table VI.

Table V. Decomposition of [^{14}C]Oxamyl in Soil, Anaerobic Conditions

Fractions	Distribution of radioactivity, % of original treatment after: 0 days	7 days	14 days	28 days
Soil extract				
Oxamyl	95	38	40	2
Compound I	5	55	40	61
Polar fraction[a]		9	15	33
Unextracted residue	7	7	6	5
Total recov.	107	109	101	101

[a] Polar fraction = that material which remains at origin of a silica gel TLC plate developed in ethyl acetate.

Table VI. Soil TLC R_f Values for Oxamyl

Soil	pH	Soil organic matter, %	R_f value
Muck (Fla.)	6.7	83.5	0.53
Muscatine brown silt loam (Ill.)	6.4	6.0	0.69
Keyport silt loam (Del.)	5.4	2.1	0.79
Cecil loamy sand (N. C.)	5.8	0.7	1.00

Table VII. Decomposition of [^{14}C]Oxamyl in Three Soils under Field Conditions

Distribution of radioactivity	Time of exposure: 1 week	1 month	3 months
A. Delaware (Keyport silt loam)			
Rainfall (in inches)	0.4	3.4	12.1
Volatility losses (% O.T.[a])	5.4	73.0%	93.3
Soil extract (% O.T.[a])			
Oxamyl	0.3	<0.05	<0.005
Compound I	0.3	<0.05	<0.005
Polar fraction	67.0	8.0	0.3
Unextracted residue (% O.T.[a])	27.0	18.9	6.4
	1 week	1 month	5 months
B. North Carolina (Cecil loamy sand)			
Rainfall (in inches)	0.4	1.3	17.3
Volatility losses (% O.T.[a])	14.2	66.8	87.7
Soil extract (% O.T.[a])			
Oxamyl	55.4	1.4	<0.05
Compound I	13.3	3.3	<0.05
Polar fraction	10.3	7.6	0.08
Leachate (% O.T.[a])	0.0	0.0	
Oxamyl			0.1
Compound I			0.2
Polar fraction			0.1
Unextracted residue (% O.T.[a])	6.8	20.9	11.7
	1 week	1 month	3 months
C. Florida (Leon immokalee fine sand)			
Rainfall (in inches)	0.0	6.5	23.6
Volatility losses (% O.T.[a])	33.0	65.5	79.1
Soil extract (% O.T.[a])			
Oxamyl	28.8	5.0	
Compound I	5.8	2.0	
Polar fraction	26.1	17.3	
Leachate (% O.T.[a])	0.0	0.0	
Oxamyl			0.07
Compound I			5.98
Polar fraction			.75
Unextracted residue (% O.T.[a])	6.3	10.2	14.1

[a] O.T. = original treatment.

The K value (Freundlich adsorption constant) was determined in three soils: Cecil loamy sand, Keyport silt loam, and Butlertown silt loam. In each case the value was <0.1, indicating that oxamyl has no adsorption onto soil when shaken for 72 h in a system containing 25 g of soil and 30 g of water.

Table VIII. Distribution of ^{14}C (μCi) in Soil Profile

1 week		1 month		3 months
Delaware (Keyport silt loam)				
13.3		1.0		0.1
[5.3][a]	3 in.	[3.0][a]	3 in.	[1.1][a]
0.4		0.2		0.0
[0.1][a]	7 in.	[0.5][a]	7 in.	[0.2][a]
0.2		0.2		0.0
[0.0][a]	11 in.	[0.4][a]	11 in.	[0.1][a]
0.0		0.4		0.0
[0.0][a]	15 in	[0.1][a]	15 in	[0.0][a]
1 week		1 month		5 months
North Carolina (Cecil loamy sand)				
10.5		2.0		0.0
[0.8][a]	3 in.	[3.3][a]	3 in	[1.8][a]
5.1		0.5		0.0
[0.6][a]	7 in.	[1.0][a]	7 in	[0.5][a]
0.0		0.0		0.0
[0.0][a]	11 in.	[0.0][a]	11 in.	[0.0][a]
0.0		0.0		0.0
[0.0][a]	15 in.	[0.0][a]	15 in.	[0.0][a]
1 week		1 month		3 months
Florida (Leon immokalee fine sand)				
10.3		0.2		0.0
[1.1][a]	3 in.	[1.3][a]	3 in.	[1.4][a]
0.2		0.3		0.0
[0.2][a]	7 in.	[0.4][a]	7 in.	[0.5][a]
0.0		2.2		0.0
[0.0][a]	11 in.	[0.3][a]	11 in.	[0.2][a]
0.0		2.3		0.0
[0.0][a]	15 in.	[<.1][a]	15 in.	[0.1][a]

[a] Residue not extractable with water.

Field Decomposition and Leaching Studies. Early in June, stainless steel cylinders (4 in. diameter × 15 in. long) were driven into undisturbed soil near Newark, Del. (Keyport silt loam); Clayton, N.C. (Cecil loamy sand); and Bradenton, Fla. (Leon Immokalee fine sand), and treated with [^{14}C]oxamyl at 6 lb/acre as described by Harvey and Pease (1973). Because of the low adsorptive capacity of the North Carolina and Florida soils, cylinders in these locations were equipped as Harvey and Pease have described to collect water passing through the soil columns. All cylinders were fully exposed to normal weather conditions throughout the exposure periods. At selected intervals, cylinders were removed from the ground and the soil column sectioned in increments for analysis. The results of these studies are shown in Tables VII and VIII. The organic matter in two 50-g samples of air-dried soil from the 0–3 in. depth of 5 months exposure in North Carolina was fractionated as described by Ivarson and Stevenson (1964).

Leaching–Disappearance Study in Field Soil. To evaluate the practical significance of possible downward movement of oxamyl residues in soils, a 1200 ft^2 area of prepared soil bed was surface treated with Vydate Oxamyl Insecticide/Nematicide at 5.65 lb of active ingredient/acre. The soil was a Matapeake silt loam (1.5% organic matter, pH 6.0) located on a farm in northern Delaware. Twenty-four hours after treatment, 1.0 in. of artificial rainfall was applied to the plot. A second inch was applied on the seventh day. By 30 days after treatment, there was a total of 8.5 in. of artificial plus natural rainfall.

Just prior to treatment, three 4 in. diameter by 5 in. long steel collection tubes were pushed nearly flush into the ground at random locations near the center of the test plot. Within 1 h after treatment, the soil inside the three special

Table IX. Residue Data (Treatment Date: June 6, 1973)

Days after treatment	Depth, in.	Total rainfall, in.	Residue, ppm, calcd as oxamyl
[a]	0-4		<0.04
	4-8		<0.04
	8-12		<0.04
	12-18		<0.04
	18-24		<0.04
	24-30		<0.04
0[b]	0-4		3.2[b]
	0-4		3.6
	0-4		3.0
2	0-4	1.0[c]	2.5
	4-8		0.06
	8-12		0.04
	12-18		0.04
	18-24		<0.04
	24-30		<0.04
5	0-4	1.0	1.3
	4-8		0.14
	8-12		0.07
	12-18		0.04
	18-24		0.04
	24-30		0.04
9	0-4	2.0[c]	1.5
	4-8		0.15
	8-12		0.15
	12-18		0.11
	18-24		0.05
	24-30		0.04
15	0-4	3.1	0.73
	4-8		0.09
	8-12		0.07
	12-18		0.05
	18-24		0.05
	24-30		0.04
23	0-4	6.2	0.23
	4-8		0.04
	8-12		0.06
	12-18		0.09
	18-24		0.06
	24-30		0.04
30	0-4	8.5	0.13
	4-8		<0.04
	8-12		<0.04
	12-18		<0.04
	18-24		0.04
	24-30		<0.04
60	0-4	14.1	<0.04
	4-8		<0.04
	8-12		<0.04
	12-18		<0.04
	18-24		<0.04
	24-30		<0.04

[a] Two weeks prior to treatment; control samples taken from test area. [b] Special zero-day samples (see text) to establish initial residue level in 0-4 in. soil increment. [c] First rainfall was by irrigation 24 h after treatment (1.0 in.). Second rainfall was by irrigation on the seventh day after treatment (1.0 in.).

collection tubes was very carefully removed with a spoon (0–4 in. depth). The samples were packaged separately from frozen immediately. These special samples were used to establish the 0-day residue level on the basis of a 0–4 in. depth.

Other soil samples were taken at time intervals indicated in Table IX. All these other samples were obtained by use of a 36-in. long × 0.75 in. diameter steel soil sampling tube which was pushed into the ground only once for each core (down to a depth of either 12 or 30 in.). A typical sample consisted of the composite of 12 cores taken from random locations inside the test plot for the 0–4, 4–8, and 8–12 in. increments. Eight cores were composited for the 12–18, 18–24, and 24–30 in increments. All samples were frozen pending analysis. All core holes in the ground were filled with sand to minimize atypical soil conditions in subsequent time periods.

Prior to analysis, each composite increment was thawed, air-dried, and dry ballmilled for 4 h to insure homogeneity. The final samples were then subdivided to secure representative 25-g aliquots and analyzed by the method of Holt and Pease (1976). The entire method was checked from freezer storage to air-drying to dry ballmilling to analysis. Average recovery of oxamyl was 94%. Average recovery of the corresponding oximino compound was somewhat lower (72%), but this compound is not a major residue in soil. The results of this leaching–disappearance study are shown in Table IX.

RESULTS AND DISCUSSION

Water. The stability of oxamyl in aqueous solutions is markedly influenced by pH (Figure 1). At an initial concentration equivalent to 16 oz/100 gal, oxamyl was entirely stable at pH 4.7 for at least 11 days. It hydrolyzed slowly to the corresponding oximino compound (I) in neutral solution (pH 6.9) with 3% hydrolysis occurring after 24 h and 9% after 48 h. Hydrolysis was quite rapid at pH 9.1 with 30% conversion in the first 6 h. However, the hydrolysis reaction neutralized the buffer during this period, and the subsequent rate of conversion was equivalent to the rate in neutral solution. In these studies, the portion of oxamyl that disappeared was converted quantitatively to the oximino compound, and no loss of ^{14}C activity was observed.

The decomposition of oxamyl when exposed to ultraviolet light was investigated in both distilled water and river water (Table I). In both types of water, oxamyl was not only converted to the corresponding oximino compound (I) at an accelerated rate, but decomposition was more extensive. The initial hydrolysis product (I) was converted gradually to a material which was slightly less polar than I, i.e., it advanced further on TLC plates than the oximino compound itself. The mass spectrum of this material showed the same mass peaks as that of I, but the ratios between peak heights varied. Accordingly, this compound was assigned the structure of the geometrical isomer of I. In addition, small amounts of very polar materials began to appear in quantities insufficient for structure identification. In the dark, hydrolysis to I was much less even after 10 days, and no further degradation products were formed. At both levels of compound, decomposition was more rapid in river water than in distilled water. These results suggest that natural salts and microorganisms may play a role in the breakdown reactions.

The decomposition of oxamyl in river water exposed to sunlight outdoors for 6 weeks was even more extensive (Figure 2). Total radioactivity in solution declined during the course of the experiment by 17%. This loss was due to volatilization, presumably as carbon dioxide. Only 0.5% of the original radioactivity was recovered in the biological residue (algal and bacterial growth). Although only 3% of the oxamyl hydrolyzed to the corresponding oximino compound, I, during the initial 16-h period (overnight), complete hydrolysis occurred during exposure to sunlight the next day. Compound I was converted gradually into its geometrical type isomer, and both of these, after attaining an apparent equilibrium state degraded further into a mixture of polar compounds that remained at the origin of the TLC plates.

At the conclusion of the exposure period, the water was harvested and the radioactive compounds fractionated by gel filtration chromatography. The major component P_3 (80%) was resolved into two compounds in roughly equal

amounts, which were positively identified as I and the geometrical isomer of I by MS analysis.

Two minor components were present to the extent of 14 and 6%, respectively. The larger, P_1, was isolated as a pure compound and identified on the basis of mass spectrum and anion-exchange chromatography as III. The smaller component, P_2, which was not anionic, was separated further into two equal fractions by adsorption chromatography, neither of which have been further characterized. These results are summarized in Table II. No metabolites were observed which corresponded to the S-oxidation products of oxamyl or the oximino compound.

Soil. Under aerobic conditions, [^{14}C]oxamyl degraded rapidly in soil to liberate large amounts of $^{14}CO_2$ (51% in 42 days) (Table III). Oxamyl (4%), a trace of the compound I, and a polar fraction (11%) were the only extractable materials. A water-insoluble residue on the soil accounted for the remainder of the radioactivity. Hot 0.1 N sodium hydroxide extracted 63% of the residual radioactivity, which was found to be divided between these soil fractions as follows: hymatomelanic acid, 6%; fulvic acid, 62%; α-humus, 25%; and β-humus, 6%.

Under anaerobic conditions in soil, [^{14}C]oxamyl degraded almost as rapidly as under aerobic conditions (Table III) with only 8% remaining after 42 days. Only 3% of the radioactivity was recovered as $^{14}CO_2$, however, and most of the radioactivity was water soluble, 41% as the hydrolysis product (I) and 42% as a polar fraction. It appears that anaerobic conditions do not interfere with hydrolysis, but do slow total decomposition to carbon dioxide. Only 6% remained unextractable and was not investigated further.

A rate study on a sandy soil from Florida and a loamy sand from North Carolina under aerobic conditions indicated a half-life for oxamyl of 15 and 11 days, respectively (Table IV). Under anaerobic conditions in a Keyport silt loam, the half-life of oxamyl was approximately 6 days (Table V).

Under laboratory conditions, oxamyl appeared to be a rather mobile compound in soil. The soil TLC R_f values reported in Table VI may be compared with a classification method for agrichemicals proposed by Helling and Turner. According to these workers, compounds with R_f 0.00–0.09 are classified as immobile, 0.35–0.64 as moderately mobile, and 0.90–1.00 as highly mobile on a soil similar to Keyport silt loam.

The results of the biodegradation studies under field conditions are shown in Table VII. At all three locations radioactivity was lost rapidly from the soil by volatilization, presumably as carbon dioxide based on the laboratory study. Oxamyl rapidly decomposed in the soil with less than 5% parent compound remaining 1 month after treatment. The corresponding oximino compound (I) was detected in the soils in the early stages, but this also decomposed rapidly. A polar fraction appeared, consisting of radioactivity that remained at the origin of silica gel TLC plates after development with ethyl acetate. The amount of this material decreased rapidly with time after its first appearance. The identity of this transient polar material has not been established.

No water leached through the soil columns in North Carolina or Florida after 1 week because of insufficient rainfall. No radioactivity was detected in the leachate after 1 month at either location. Some radioactivity was detected after 3 months (Florida) and 5 months (North Carolina) but only inconsequential amounts of oxamyl were found as shown in Table VII.

The distribution of radioactivity vertically in the soil profile is shown in Table VIII. The figures in brackets indicate the amount of radioactivity incorporated into the soil in such a manner as to make it unextractable with water. Analysis of this soil organic matter from the 5-month North Carolina soil indicated that the carbon-14 had been incorporated into normal soil organic fractions: sodium hydroxide extracted 76% of the radioactivity not extracted with water. This ^{14}C material was divided between the soil fractions approximately as follows: hymatomelanic acid, 47%; fulvic acid, 13%; α-humus, 32%; and β-humus, 6%; and a volatile component lost during concentration (21%). Soluble humin accounted for 18% of the radioactivity with 6% remaining in the insoluble humin.

These field disappearance and leaching studies confirmed the earlier laboratory data on rate of degradation of oxamyl in soil. The half-life of oxamyl at all three locations was about 1 week or less. However, in regard to leaching, laboratory data indicated high mobility in soil, whereas under normal field conditions very little ^{14}C material got below 15 in. depth in the tests described. Only in Florida on a sandy soil after 3 months and 23 in. of rain did more than 1% of the total ^{14}C reach this depth. It amounted to about 7% of the original ^{14}C, almost all in the form of the oximino compound.

The results of the leaching–disappearance study (Table IX) confirm the results of the field biodegradation study with [^{14}C]oxamyl. Although oxamyl is mobile in soil, based on laboratory evaluations, it appears under practical conditions that degradation of oxamyl takes place so rapidly that no major residues move deep into the soil even under the high rainfall conditions of this test. The half-life of oxamyl in this test was 8 days.

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