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Task 1R: Review of THIODICARB

Contract No. 68-01-5830

Final Report

November 5, 1980

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

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THIODICARB

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Hydrolysis of UC 51762 in aqueous buffer solutions, Andrawes, J.R., and P.R. College, Union Carbide Corporation, June 24, 1977, File No. 23794, Acc. No. 099602, Tab 1.

Procedure

[Acetaldehyde-1-^{14}C]thiodicarb (UC 51762; purity 98%) dissolved in 70% ethanol was added to sterilized aqueous buffer solution, which was adjusted to pH 3, 6, or 9, to yield a final concentration of 10 ppm. The buffered solutions were incubated at 25 C in the dark. After thorough mixing, aliquots were removed at zero time and specific intervals for qualitative and quantitative analysis of the degradation products.

Methodology

Organo-soluble hydrolysis products were extracted from the incubated solutions by partitioning the aqueous phase five times with a mixture of chloroform:acetonitrile (1:1). The organic fractions were combined, dried with sodium sulfate, and then concentrated. Aliquots taken from the concentrated extracts were chromatographed on TLC plates. The plates were developed two-dimensionally with two different solvents. Radioactive metabolites were located on plates by radioautography and the standards by short-wave ultraviolet light. Radioactivity in incubated solutions, organic extracts, aqueous phases, and spots on TLC plates was determined by liquid scintillation counting.

Results

The recovered radioactivity of thiodicarb and its metabolites at various sampling times is summarized in Table 1. Linear relationships were obtained from acidic and alkaline conditions by plotting the log of recovered radioactivity against time. Rate constants of 8.04×10^{-2}/day for pH 3 and 7.76/day for pH 9 were estimated by using the first-order rate equation. Only 3% degradation occurred at pH 6 during the 9-day test period (Table 1). Half-life values of 8.6 and 0.9 days were obtained for pH 3 and 9, respectively.

The data indicated that small amounts (2% or less) of water-soluble metabolites were formed at the pH levels tested. Methomyl was the major hydrolysis product. It remained stable after its formation at pH 3 and 6 until the end of the test period. In contrast, methomyl further hydrolyzed at pH 9, forming methomyl oxime.

Table 1. Hydrolysis of radiolabeled thiodicarb in aqueous buffered solutions at 25 C.

pH	Sampling time (days)	Recovered radioactivity[a] (%)		
		Thiodicarb	Methomyl	Methomyl oxime
3	0	98.2	1.8	ND[b]
	0.17	97.1	2.8	ND
	1	92.7	7.3	ND
	4	77	22.4	0.5
	7	59.4	39.6	0.7
	9	47.6	50.9	0.6
6	0	99.0	0.9	ND
	0.17	99.1	0.9	ND
	1	98.6	1.4	ND
	4	97.2	2.5	0.3
	7	97.5	2.1	0.4
	9	96	2.9	0.7
9	0	97.9	1.8	0.3
	0.17	85.9	12.2	0.9
	1	44.5	44.4	3.6
	4	4.4	79.3	3.8
	7	0.8	71.0	16.1
	9	0.3	61.8	21.1

[a] Total radioactivity recovered ranged from 9.63 to 10.03 ppm out of the 10 ppm applied.

[b] ND, none detected.

Conclusions

Thiodicarb is relatively stable at pH 6, but is hydrolyzed under acidic and alkaline conditions. At pH 6 only 3% of the thiodicarb degraded during the 9-day test period. Thiodicarb degradation of around 50% at pH 3 and 99.7% decomposition at pH 9 were measured during the same period. Half-life values of 8.6 and 0.9 days were obtained at pH 3 and 9, respectively. The principle hydrolysis product of thiodicarb was methomyl. The only other product identified was methomyl oxime. Methomyl was found to be stable at pH 3 and 6, but was hydrolyzed at pH 9.

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Photochemical transformation of UC 51762, Andrawes, R.R., and P.R. College, Union Carbide Corporation, August 18, 1977, File No. 24023, Acc. No. 099602 Tab 2.

Procedure/Methodology

Three aqueous pH 6 buffered solutions containing [^{14}C]thiodicarb (UC 51762, purity >98%) at 5 ppm were prepared; one contained 2% acetone as a sensitizer, one did not, and the third one was kept in dark as the control. These solutions were exposed to a high-pressure mercury-vapor immersion lamp that radiated light at wavelengths >290 nm. The temperature of the reaction solutions was kept within 20-25 C by a continuous flow of water in the cooling jacket of the reaction vessel. Samples were partitioned five times with a mixture of chloroform:acetonitrile. The organic fractions were combined, dried over sodium sulfate, and concentrated. Radioactivity in both the organic fraction and the water phase was determined by liquid scintillation counting (LSC). At each sampling time, aliquots of the reaction solutions were removed and counted for total ^{14}C radioactivity. The concentrated organic extract was analyzed by two-dimensional thin-layer chromatography with various solvent systems. Photolysis products in the organic extracts were identified by radioautography and quantitated by LSC.

Results

Thiodicarb was stable in the dark control solution during the 12-day period, but was photodegraded when exposed to light under the described experimental conditions. The half-life of the compound in the aqueous solution was about 8 days and the reaction rate constant was 8.6×10^{-3}/day, whereas, in the aqueous solution with 2% acetone the half-life was about 19 days and the reaction rate constant was 3.72×10^{-2}/day. The photoproducts of thiodicarb in aqueous solution were monosulfoxide, methomyl, methomyl oxime, methomyl sulfoxide, and methomyl sulfoxide oxime. Methomyl was the major product of photolysis especially in the presence of acetone as a sensitizer. The distribution of radioactivity recovered from thiodicarb and its photoproducts in three reaction solutions is summarized in Table 1. The data showed that water soluble (polar) compounds comprised only 0.4% of the degradation products.

Table 1. Photolysis of radiolabeled thiodicarb in aqueous buffered solutions.

Reaction condition	Sampling time (day)	Recovered radioactivity (%)						
		Thiodicarb	Monosulfoxide	Methomyl	Methomyl sulfoxide	Methomyl oxime	Methomyl sulfoxide oxime	Water solubles
Dark control	0	98.7	0.2	1.0	--[a]	ND[b]	--	T[c]
	0.17	98.5	ND	1.3	--	0.2	--	T
	1	97.5	0.2	2.1	--	ND	--	0.1
	3	97.6	0.2	2.0	--	ND	--	0.1
	6	94.9	ND	3.8	--	0.3	--	0.1
	9	95.0	0.2	4.3	--	0.3	--	0.1
	12	94.9	0.2	4.2	--	0.3	--	0.1
Without acetone	0	98.3	ND	1.5	ND	ND	ND	T
	0.17	98.2	ND	1.3	ND	0.4	ND	0.1
	1	96.1	0.5	2.9	ND	0.3	ND	0.1
	3	94.0	1.3	4.0	ND	ND	ND	0.2
	6	90.3	2.0	5.9	0.2	0.3	ND	0.3
	9	90.1	2.0	5.7	0.2	0.3	ND	0.3
	12	88.7	2.5	7.1	0.3	0.3	0.4	0.4
With 2% acetone	0	97.3	ND	1.9	ND	ND	ND	T
	0.17	95.0	1.0	3.3	ND	ND	ND	0.1
	1	89.3	2.7	5.2	0.2	0.2	0.3	0.3
	3	81.4	5.0	8.4	0.6	0.3	0.5	0.7
	6	72.8	5.3	13.0	1.1	0.3	0.8	1.0
	9	66.6	7.2	14.5	1.4	0.3	0.8	1.2
	12	62.3	5.2	15.9	1.5	0.6	0.9	1.8

[a] --, not measured.
[b] ND, none detected.
[c] T, traces of less than 0.05%.

Conclusions

Thiodicarb is photodegraded in aqueous solution with and without acetone as a sensitizer. Without acetone, a half-life of about 81 days and a reaction rate constant of 8.6×10^{-3}/day were estimated. With acetone, the half-life of thiodicarb was about 19 days and the rate constant was 3.72×10^{-2}/day. Methomyl was the major photolysis product. Other photoproducts were monosulfoxide, methomyl oxime, methomyl sulfoxide, and methomyl sulfoxide oxime.

Soil adsorption and desorption of thiodicarb, Andrawes, N.R., and R.H. Bailey, Union Carbide Corporation, March 10, 1980, Acc. No. 099602, Tab 3.

Procedure

Adsorption. Twenty-five gram samples of Norfolk loamy sand (NLS) (reported as sandy loam), California clay loam (CCL) (reported as silty clay loam), and Texas sandy loam (TSL) soils (see Table 1 for soil characteristics) were air dried and sieved to 12 mesh. The soil samples were treated with 10 ml of solutions of [^{14}C]thiodicarb at 0.1, 1.0, or 10.0 ppm and then mixed on a shaker. Samples were removed from the shaker at 0.5, 1, 3, and 5 hours after treatment, centrifuged, and analyzed for radioactivity.

Desorption. Tests for desorption were conducted on the previously adsorbed samples by replacing the supernatant of the pesticide solution with distilled water. The samples were placed on a shaker and aliquots were removed at 0.5, 1, 2, and 3 hours and analyzed for radioactivity.

Methodology

Supernatant and bound residue (combusted to $^{14}CO_2$) samples were analyzed with a liquid scintillation spectrophotometer. Organo-soluble residues were characterized by thin-layer chromatography (TLC).

Results

The adsorption properties of all three soils were linear (Figure 1). The amount of [^{14}C]thiodicarb residues adsorbed ranged from 18.4 to 65.0% with equilibrium occuring within 1 hour (Table 2).

The four desorptions removed no more than 95.4% and no less than 61.5% of the total thiodicarb residues adsorbed (Table 2).

The Freundlich constants were determined by least squares linear regression analysis. The adsorption K values were 1.34, 0.58, and 1.22 for the CCL, NLS, and TSL soils, respectively. The 1/n values were all less than unity (Table 3). No desorption coefficients were calculated.

TLC characterization data were provided for the adsorption incubation samples, but the organo-soluble extraction efficiency was not provided, thus making "true" characterization impossible.

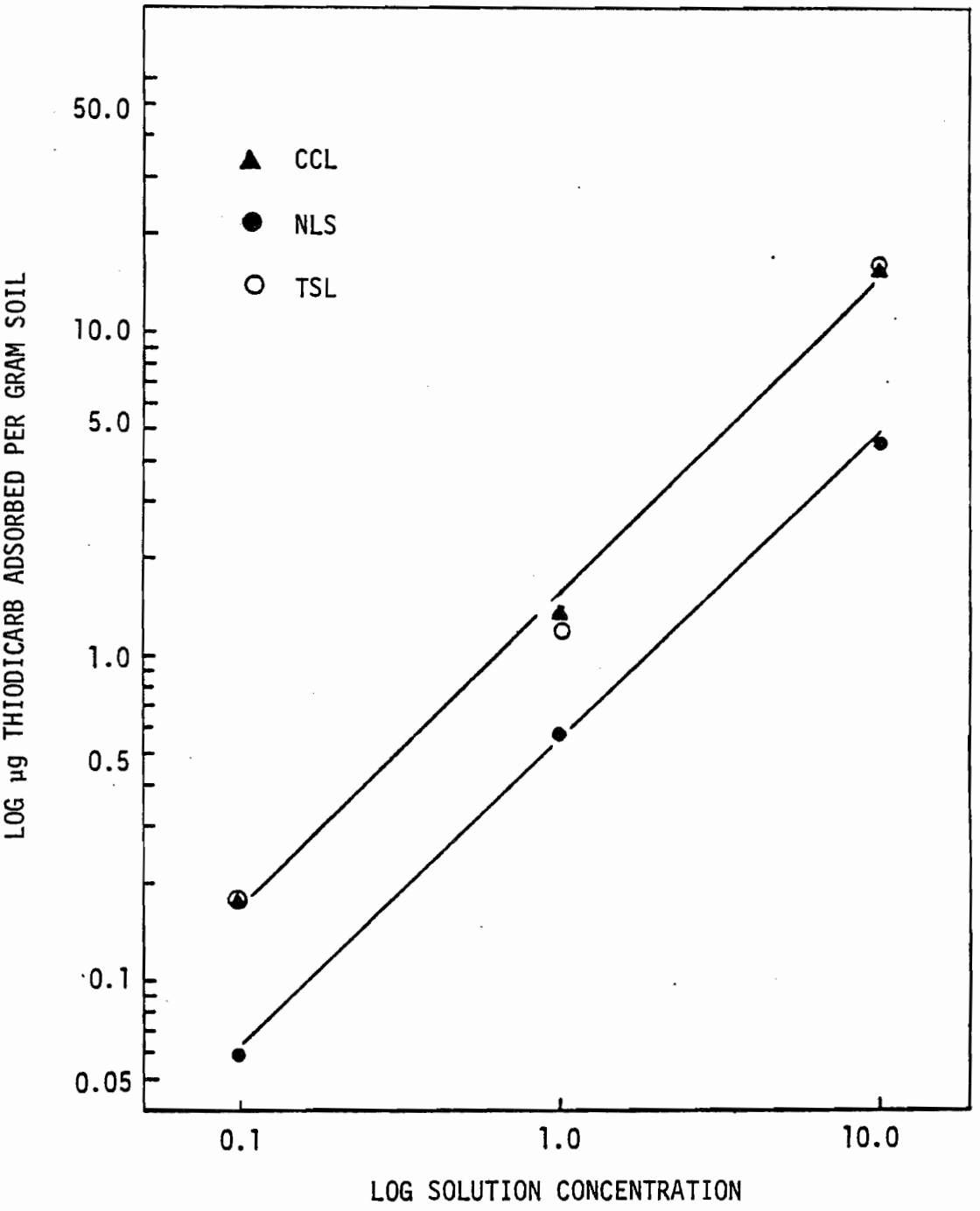

Figure 1. Freundlich adsorption isotherms for [^{14}C]thiodicarb in California clay loam (CCL), Norfolk loamy sand (NLS), and Texas sandy loam (TSL) soils.

Table 1. Soil characteristics.

Characteristics	Soil		
	California[a] clay loam	Norfolk[b] loamy sand	Texas sandy loam
% Sand	25	83	65
% Silt	42	15	17
% Clay	33	2	18
% Organic matter	1.3	0.8	1.0
pH	8.1	5.8	7.8
Bulk density	1.32	1.65	1.39

[a]Reported as a silty clay loam soil.

[b]Reported as a sandy loam soil.

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Table 2. Adsorption and desorption of [^{14}C]thiodicarb residues in three soil types.

Soil type	Initial fortification (µg)	Maximum time of adsorption (hours)	Adsorption (µg)	Percent adsorption	Desorption[a] (µg)	Percent desorption[b]
CCL	1.0	1	0.6	65	0.9	64.3
	10.0	1	6.0	60.5	8.3	61.5
	100.0	1	64.4	64.4	96.8	67.5
NLS	1.0	5	0.2	25.0	0.8	88.9
	10.0	5	2.5	24.8	7.5	92.0
	100.0	5	18.4	18.4	65.5	95.4
TSL	1.0	1	0.4	43.0	1.3	87.8
	10.0	1	3.7	37.3	12.2	86.6
	100.0	1	47.2	47.3	123.2	82.5

[a]Values after 3 hours desorption.

[b]Percent desorption = $\frac{\text{µg desorbed}}{\text{µg desorbed + µg in soil}} \times 100$

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Table 3. Freundlich constants[a] for the adsorption of [^{14}C]thiodicarb on three soil types.

Soil type	1/n	log K	K	Q[b]
CCL	0.97	0.127	1.34	103
NLS	0.94	-0.237	0.58	73
TSL	0.97	0.086	1.22	122

[a]Determined by least squares linear regression of the equation:

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K$$

where:

x = weight (µg) of compound
m = weight (g) of soil
c = equilibrium concentration of compound in water (µg/ml)
1/n = slope of line
K = distribution coefficient (y-intercept)

[b]Q, distribution coefficient = $\frac{K \times 100}{\%\ \text{soil organic matter}}$

Conclusions

Thiodicarb residue adsorption rates of the soils were, in increasing order, NLS < TSL < CCL. The desorption rates (based on percent, not coefficient data) were in the order CCL < TSL < NLS.

Freundlich calculations were based on a equilibrium time of 0.5 hour when, in fact, the adsorption rate had not leveled off until 1 hour in all three soil types. The relatively low K values indicate high mobility of thiodicarb residues in all three soil types.

TLC characterization revealed little degradation of thiodicarb in NLS and TSL soils. However, appreciable degradation of thiodicarb to methomyl occurred after 3 hours in the CCL soil. Quantitation of metabolites was not possible, since extraction efficiencies were not provided.

Investigation of the metabolism of UC 51762 by activated sludge: a preliminary report, the effects of UC 51762 on the operating parameter of the activated sludge process, Gezo, T.A., and W.F. Stein, Union Carbide Corporation, August 5, 1980, Project No. 11504-24, Acc. No. 099602, Tab 4.

Procedure/Methodology

A continuous flow bench scale activated sludge process (ASP) system employing gravity sedimentation tank and sludge recycling was used for this study. Activated sludge was obtained from the New York Osceola treatment facility, which treats domestic wastes. Synthetic feed was prepared daily and thiodicarb (dissolved in 99% acetone) was added to the feed at specific concentrations. Four reactors were operated: a blank, a solvent control, one in shock mode, and one in continuous mode. The solvent control reactor was dosed with acetone carrier alone parallel with the continuous reactor. Continuous and shock mode reactors were operated to determine process effects of continuous and shock load of thiodicarb. Mixed liquor characteristics were determined by monitoring total suspended solids (TSS), settleability, specific oxygen uptake rate (SOUR), and protozoan indicator organisms. The effluent parameters monitored were TSS, total organic carbon (TOC), and turbidity. Testing was conducted according to Standard Methods (APHA 14th ed).

Results

The effects of thiodicarb on the continuous activated sludge process are summarized in Tables 1 and 2. The data indicated that thiodicarb at 10 ppm or higher concentrations significantly (significance level not specified) decreased the effluent quality and mixed liquor characteristics as compared to the control. The settleability of mixed liquor was generally poor throughout the study in all reactors. However, solid separation in the clarifier was rapid and presented no operational difficulties when the test unit received feed containing thiodicarb at 10 ppm or less. Thiodicarb solids at 100 ppm did not settle and were lost in the effluent. The control reactor exhibited high activity and protozoan numbers, specifically, stalked ciliates, free swimming ciliates, and rotifers, throughout the study. The continuous mode reactor showed a decrease in protozoan numbers and activity with thiodicarb at 10 ppm and higher filamentous growth than that in the control unit. Shock loading of thiodicarb did not affect the performance of the ASP. Effluent turbidity and TSS of grab samples taken 7 and 24 hours after shock loading did not indicate a decrease in effluent quality. However, thiodicarb at 10, 50, and 100 ppm increased effluent TOC levels in response to shock loading as compared to the control.

Table 1. Effects of thiodicarb on the ASP - continuous loading[1].

Thiodicarb concentration (ppm)	Effluent characteristics								
	Turbidity (NTU)			TSS (mg/l)			TOC (ppm)		
	Control	Solvent control	Continuous mode	Control	Solvent control	Continuous mode	Control	Solvent control	Continuous mode
0.1	3.2[a]	7.9[a]	3.4[a]	12.3[a]	37.4[a]	13.2[a]	8.4[a]	14.7[a]	6.3[a]
1	6.2[a]	5.4[a]	11.1[a]	22.9[a]	17.0[a]	54.5[a]	10.0[a]	15.8[b]	11.1[a]
10	4.3[c]	33.8[a]	69.0[b]	17.4[a]	149.3[b]	258.6[c]	10.6[a]	40.8[b]	32.9[b]

Although not specified in the report, data in the same row with the same effluent parameter and the same superscript are not significantly different.

Table 2. Effects of thiodicarb on the ASP - continuous loading[1].

Thiodicarb concentration (ppm)	Mixed liquor characteristics								
	TSS (mg/liter)			SOUR (mg O_2/liter-hr-g)			OUR (mg O_2/liter-hr)		
	Control	Solvent control	Continuous mode	Control	Solvent control	Continuous mode	Control	Solvent control	Continuous mode
0.1	2368[a]	2256[a]	2565[b]	14.9[a]	14.7[a]	10.9[b]	35.6[a]	33.1[a]	28.1[a]
1.0	2389[a]	2480[a]	2711[a]	16.8[a]	39.1[a]	16.7[a]	39.6[a]	44.1[a]	46.2[a]
10	2924[b]	3803[a]	3554[a]	10.0[a]	27.8[b]	83.7[c]	27.0[a]	100.7[b]	334.6[c]
100	3582[a]	3456[a]	1208[b]	--	--	--	--	--	--

Although not specified in the report, data in the same row with the same effluent parameter and the same superscript are not significantly different.

Conclusions

The performance of the activated sludge process was affected by continuous feeding thiodicarb at 10 ppm or greater. However, the process was not affected by shock loading of thiodicarb up to 100 ppm. Whether thiodciarb was degraded in the system or discharged with the effluent was not determined in this study.

Fate of a single dosage exposure of [^{14}C]acetyl UC 51762 in aquaria bluegill sunfish, Feung, C.S., and E.L. Chancey, Union Carbide Corporation, February 5, 1979, File No. 25960, Acc. No. 099602, Tab 5.

Procedure

Two 10-liter aquariums were treated with [^{14}C]thiodicarb (purity 98.5%) at 0.150 mg/liter (0.15 ppm). Ten bluegill sunfish per tank were exposed for a 4-day period. The fish were then dissected into edible and nonedible tissues.

Methodology

The edible or nonedible tissue was blended with acetonitrile:methanol: water (5:4:1), centrifuged, and filtered. The solids were reblended twice with fresh solvent and filtered. The radioactivity in the filter cake was determined by combustion and liquid scintillation counting (LSC).

The filtrate was partitioned with chloroform:acetonitrile (1:1) to yield two fractions (organo-and water-soluble). The organo-soluble fraction was concentrated and analyzed by thin-layer chromatography (TLC). The water-soluble fraction was incubated with β-glucosidase and β-glucuronidase. The reaction mixture was partitioned three times with chloroform:acetonitrile (1:1) to yield an aglycone and an aqueous fraction. The aglycone fraction was analyzed by TLC.

The aqueous fraction was hydrolyzed with 1 N HCl and partitioned three times with chloroform. The chloroform fraction was concentrated and analyzed by TLC. The aqueous fraction was analyzed by LSC.

The TLC spots were scraped and the radioactivity was quantitated by LSC.

The water samples were analyzed using a referenced method.

Results

Thiodicarb was present in edible tissue and methomyl and methomyl oxime were present in both edible and nonedible tissue. Methomyl and methomyl oxime each accounted for approximately 20% of the ^{14}C residues in the fish. Thiodicarb residues accounted for 0.29% of the extracted ^{14}C residues (Table 1). Nonextractable residues and volatile products lost during the extraction procedure represented 51.9% of the radioactivity in the fish tissue.

Methomyl and methomyl oxime residues (90.1 and 5.1%, respectively) were present in the water samples at 4 days after treatment. Thiodicarb residues were not detected in the water samples (Table 2).

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Table 1. Thiodicarb residues in bluegill sunfish after 4 days exposure to thiodicarb at 0.15 ppm.

Residue	Residue levels (% of radioactivity in fish)		
	Total	Edible tissue	Nonedible tissue
Thiodicarb	0.18	0.18	--
Methomyl	20.14	4.52	15.62
Methomyl oxime	20.25	3.76	16.49
Unknown	7.65	2.78	4.87
Water-soluble fraction	23.24	--	23.24
Unextractable residue	23.37	4.39	18.98
Volatile, lost during preparation	5.27	5.27	--
Total	100.10	20.90	79.20

Table 2. Thiodicarb residues present in treated water after 4 days.

Residue	Radioactivity (%)
Methomyl	90.11
Methomyl oxime	5.14
Unknown	1.75
Water soluble	3.00
Total	100.00

Conclusions

Thiodicarb, methomyl, and methomyl oxime residues will be present in sunfish tissues 4 days after the initial exposure to [^{14}C]thiodicarb and most (79%) of the residues will be present in the nonedible tissues.

Metabolite characterization was poor because greater than 50% of the total ^{14}C in fish was not identified. Whole fish samples were not analyzed.

Fate of a single dose exposure of [^{14}C]acetyl UC 51762 in aquaria catfish, Feung, C.S., and E.L. Chancey, Union Carbide Corporation, August 24, 1979, File No. 26708, Acc. No. 099602, Tab 6.

Procedure/Methodology

[^{14}C] Thiodicarb (purity 98.5%) at 0.073 ppm was introduced into two aquariums filled with well water. Ten catfish were introduced into each tank for a 4-day exposure period. The fish were then dissected into edible and nonedible tissues.

Tissues (edible or nonedible) were blended with acetonitrile:methanol: water (5:4:1), centrifuged, and filtered. The solid material was reblended twice with fresh solvent and filtered. An aliquot of the filter cake was combusted and the radioactivity determined by liquid scintillation counting (LSC). The filtrate was partitioned with chloroform:acetonitrile (1:1) and the organo-soluble fraction was concentrated (volatile components were trapped in acetone), characterized by thin-layer chromatography, and quantitated by LSC. Radioactivity in the water-soluble fraction and acetone traps was also analyzed by LSC.

Results

Mehtomyl oxime was the only compound identified in the fish tissues, accounting for 63% of total ^{14}C residues (Table 1). Methomyl and methomyl oxime were present in the water samples and accounted for 96 and 0.9% of the ^{14}C residues in water, respectively. Unidentified water-soluble, unextractable, and volatile residues represented 36.8% of the ^{14}C residues in the fish.

Table 1. [^{14}C]Thiodicarb residues in catfish tissue and treated water (thiodicarb application 0.073 ppm).

Residue	Residue levels in fish			
	Total	Edible tissue	Nonedible tissue	Treated water (%)
Thiodicarb	--	--	--	--
Methomyl	--	--	--	95.64
Methomyl oxime	63.2	19.3	43.9	0.86
Water soluble	15.7	2.6	13.1	3.50
Unextractable	14.0	1.5	12.5	--
Volatile[a]	7.1	3.7	3.4	--
Total	100.0	27.1	72.9	100.00

[a]Volatile products lost during extraction procedure.

Conclusions

Methomyl oxime residues will be present in catfish tissues 4 days after the beginning of exposure to [^{14}C]thiodicarb. Most of the radioactivity (73%) will be in the nonedible tissues.

The extraction procedure was poor because 14% of the radioactivity was unextractable and 16% remained in the water-soluble fraction. Whole fish samples were not run.

Thiodicarb residues study in subsequent crops, Feung, C.S., and E.L. Chancey, Union Carbide Corporation, February 1, 1980, File No. 27292, Acc. No. 099602, Tab 7.

Procedure

Loamy sand soil, reported as sandy loam soil (82% sand, 8% silt, 10% clay, pH 5.7, organic matter content 1.1%, CEC 4.0 meq/100 g, and 1/3 bar moisture content 20.5%), was sieved (2 mm) and treated with unlabeled thiodicarb and [^{14}C]thiodicarb.

Untreated soil was added to plastic containers to a depth of 9 inches. Three inches of treated soil was then added and 1 cm of untreated soil was placed on top. The treatment represented a nominal application of 12 ppm (8.7 ppm recovered immediately after treatment).

The containers were maintained in a greenhouse and weeds were removed periodically. Thirty days after treatment lettuce seeds were sown and 77 days after treatment (47 days after planting) the lettuce foliage was harvested.

At 120 days after treatment, corn and soybeans were planted (2 containers of each) in the same soil used for the lettuce. The corn was harvested at 246 days after treatment and the soybeans at 275 days after treatment (126 and 155 days after planting, respectively).

One year after treatment the third crops, lettuce and mustard, were planted in the containers and 3-week-old white radish plants were transplanted into the same containers along with the lettuce and mustard. At 395 days after treatment the crop foliage and radish roots were harvested. Soil samples were collected 30, 77, 104, 258, 365, and 395 days after treatment. All crop samples were stored in a freezer until analyzed.

Methodology

Portions of the crop and (air-dried) soil samples were combusted, and their radioactivity was determined by liquid scintillation counting (LSC).

The frozen crop samples were blended with acetonitrile:acetone:water (9:1:1) and filtered. Extracted plant material was air dried, combusted, and radioactivity determined by LSC. The aqueous metabolite phase was partitioned with acetonitrile:chloroform (1.5:1), which yielded organo and glycone fractions. Each fraction was concentrated and analyzed by thin-layer chromatography (TLC).

The glycone fraction was incubated with β-glucosidase and/or glusidase. After enzymolysis the mixture was extracted with acetonitrile:chloroform (1:1), which yielded aglycone and aqueous fractions. The aglycone fraction was analyzed by cochromatographic TLC.

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Soil samples were air dried and then extracted three times with acetone: water (9:1). The filtrates were combined, concentrated, and partitioned with chloroform to yield two fractions (organic and aqueous). The organic fraction was concentrated and analyzed by cochromatographic TLC. The extracted filter cake was air dried, combusted, and radioactivity determined by LSC.

Results

Radioactive residues were present in rotational crops planted 30, 120, and 365 days after treatment. The highest residue level (0.618 ppm) was found in lettuce planted 30 days after treatment. Lower residue levels were found in crops planted 120 and 365 days after treatment. (Table 1).

Methomyl, methomyl methylol, and methomyl oxime residues were identified in the lettuce (30-day crop) samples. Methomyl was the only degradation product found in the corn foliage (120-day crop).

About 69% of the ^{14}C residues in lettuce were extractable, and of these, 79.7% were found in the water-soluble fraction and 20.3% in the organo-soluble fraction. Only 31.4% of the ^{14}C residues in corn leaves were extractable, with 40.6% of this being found in water-soluble fraction and 59.4% in the organo-soluble fraction. (Table 2).

^{14}C residue levels in soil were 4.28 and 0.48 ppm at 30 and 395 days after treatment, respectively (Table 3). Thiodicarb and methomyl were the only identifiable products present in the soil extract. Approximately 64-74% of the ^{14}C residues in the treated soil were unextractable.

Table 1. Distribution of ^{14}C residues in rotational crops at harvest.

Component	Treatment-to-planting interval (days)	Radioactivity at harvest	
		ppm[a]	dpm/g
Lettuce foliage	30	0.618	15,935
	365	0.012	299
Soybean foliage	120	0.003	85
seed	120	0.046	1,186
pod	120	0.054	1,387
Corn foliage	120	0.005	132
grain	120	0.034	877
silk	120	0.026	670
cob	120	0.032	825
shuck	120	0.056	1,444
Mustard foliage	365	0.013	334
Radish foliage	365	0.076	1,966
	365	0.006	153

[a]Calculated by reviewer: $\text{ppm} = \frac{\text{Radioactivity (dpm/g)}}{25{,}784 \text{ dpm/}\mu\text{g thiodicarb}}$

Table 2. Thiodicarb metabolites in corn foliage at harvest (120-day crop).

Metabolite	^{14}C residue levels: Organo fraction ppm	Organo fraction dpm/g	Aglycone fraction ppm	Aglycone fraction dpm/g
Methomyl	0.022	567[a]	--	--
Unknown	0.020[a]	514	0.002[a]	63
Glycones	--	--	0.086[a]	2,213
Unextracted plant residue	0.351[a]	9,052	--	--

Total (organo-soluble & aglycone fractions) 0.481 ppm.

[a]Calculated by reviewer: $\text{ppm} = \frac{\text{Radioactivity (dpm/g)}}{25{,}784 \text{ dpm/}\mu\text{g thiodicarb}}$

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Table 3. ^{14}C residues remaining in soil treated with thiodicarb.

Days after treatment	Residue levels[a] (ppm)	Radioactivity (dpm/g)	Percent of applied dosage
0	8.69	224,124	100.0
30	4.28	110,377	49.2
104	1.60	41,162	18.4
258	0.60	15,385	6.9
365	0.52	13,396	6.0
395	0.48	12,409	5.5

[a]Calculated by reviewer: $ppm = \frac{\text{Radioactivity (dpm/g)}}{25{,}784 \text{ dpm/}\mu g \text{ thiodicarb}}$

Conclusions

In this study, the results for residues in plant tissues appear to have been reported on a wet weight basis, which would make the residue levels appear artificially low. Thiodicarb residue levels of 0.6, 0.003-0.056, and 0.006-0.076 ppm may be present in rotational crops planted 30, 120, and 365 days after treatment, respectively. Grain, seed, pod, and/or shuck will have higher residue levels than the foliage, and root residue levels will generally be lower than those in foliage. Degradation products that may be found include methomyl, methomyl methylol, and methomyl oxime in crops planted 30 days after treatment. Methomyl and thiodicarb are likely to be found in plants that are sown 120-365 days after treatment.

It is not possible to determine all of the degradation products present or the concentration of any products because only the organo-soluble fraction was characterized. Approximately 30 and 69% of the ^{14}C residues in lettuce and corn, respectively, were unextractable and therefore were not characterized. Recovery rates were not presented and controls were not run. Only lettuce and corn foliage ^{14}C residues were characterized, and conflicting data were reported for corn foliage (Tables 1 and 2). Residue levels in corn foliage were reported as 0.005 ppm in one table and 0.48 ppm in another.

Since most of the soil residues (64-72%) were unextractable, the character of the soil residues could not be determined. Total ^{14}C residue levels ranged from 8.7 ppm at day zero to 0.48 ppm after 395 days. Since treated soil was placed on top of untreated soil, and only the treated soil layer was analyzed, an appreciable amount of the residues may have leached into the unanalyzed untreated soil as shown in the leaching study (Tab 10). Therefore no accurate data on residue decline in the soil can be extrapolated.

UC 51762 pesticide mobility on soil thin-layer chromatograms, Khasawinah, A.M., Union Carbide Corporation, November 1, 1976, File No. 22754, Acc. No. 099602, Tab 10.

Procedure

The leachability of thiodicarb (UC 51762), its metabolites, and three standard pesticides was examined using soil thin-layer chromatography (TLC). Four soils (Table 1) were air dried, passed through 0.5-1 mm sieves, and spread as aqueous slurries on glass TLC plates.

Methodology

Approximately 1 µg of each compound was spotted on the prepared TLC plates and allowed to develop with water by ascending chromatography. After chromatographic development, the plates were air dried and placed in contact with X-ray film for 3 days. R_f values were measured from the autoradiogram as the front of a streak or a spot.

Results

The leaching R_f values of thiodicarb are presented in Table 2.

Table 1. Characteristics of four soils used in thiodicarb leaching study.

Characteristic	Soil type (texture)			
	California[a] clay loam	N. Carolina[b] loamy sand	Texas sandy loam	Ohio[c] loam
% Sand	25	83	65	38
% Silt	42	15	17	42
% Clay	33	2	18	20
pH	8.1	5.8	7.8	5.4
% Organic matter	1.3	0.8	1.0	1.3
Bulk density	1.32	1.65	1.39	--

[a] Reported as a silty clay loam soil.
[b] Reported as a sandy loam soil.
[c] Reported as a silt loam soil.

Table 2. Mobility of thiodicarb and its soil metabolites in four soil types.

Compound	R_f values[1]			
	N. Carolina loamy sand	California clay loam	Texas sandy loam	Ohio loam
Thiodicarb	0.21 ± 0.01	0.12 ± 0.01	0.12 ± 0.02	0.08 ± 0.00
Methomyl oxime	0.89 ± 0.01	0.86 ± 0.09	0.93 ± 0.02	0.88 ± 0.04
Methomyl	0.77 ± 0.01	0.64 ± 0.04	0.79 ± 0.02	0.73 ± 0.03

[1]Frontal R_f values used.

Conclusions

Thiodicarb exhibits a comparatively low leaching potential (R_f 0.08-0.21, class 2) in soil. However, the metabolites tested, methomyl oxime (R_f 0.86-0.93, class 5) and methomyl (R_f 0.64-0.79, class 4), are leached much more readily. Therefore, the relative leachability of thiodicarb residues in soil depends on the rate of metabolism of the parent structure, which was shown to be rapid in Tab 11.

Fate of UC 51762 in soils, Khasawinah, A.M., Union Carbide Corporation, August 3, 1977, File No. 23940, Acc. No. 099602, Tab 11.

Procedure

Air-dried soil was treated with an acetonitrile solution of [acetaldehyde-1-^{14}C]thiodicarb (purity 98%) at 1 ppm. The treated soils were moistened to 75% of the field capacity for aerobic conditions. The flasks were wrapped completely with aluminum foil to shield them from light. For anaerobic conditions, treated soils in the flasks were flooded with a 2-cm layer of water. The flasks were then placed in Gas Pak anaerobic jars filled with CO_2. The jar unit was wrapped completely with aluminum foil.

The Texas sandy loam soil (65% sand, 17% silt, 18% clay, pH 7.8, and organic matter content 1.0%) was incubated under aerobic conditions at room temperature (25 C) or 15 C and under anaerobic conditions at 25 C. Sterile soil controls under aerobic conditions at room temperature were included. Each system contained a 1 N NaOH trap for volatile thiodicarb products. The other two soils, Norfolk loamy sand (reported as a sandy loam; 83% sand, 15% silt, 2% clay, pH 5.8, and organic matter content 0.8%) and the California clay loam (reported as a silt clay loam; 25% sand, 42% silt, 33% clay, pH 8.1, and organic matter content 1.3%) were only investigated under aerobic conditions at 25 C and 15 C. Some soils were maintained in an active state by growing grass and beans in the greenhouse; these soils were referred to as "greenhouse activated soils."

Methodology

At specific intervals, the soils were sampled to estimate the rate of degradation and to characterize the metabolites. Each soil sample was mixed with water and extracted with acetone or acetonitrile. After centrifugation, the soil extract was partitioned with chloroform. The organic phase was concentrated and analyzed by thin-layer chromatography (TLC). The soil solids were subjected to further extraction such as boiling in water or acid treatment. After exhaustive extraction, the solids were fractionated into fulvic acid, humic acid, and humin by a standard procedure.

Degradation products were identified on TLC chromatograms, located by radioautography. Radioactivity in each spot was determined by scraping and liquid scintillation counting (LSC). The radioactivity in the soil extract, liquid and organic phases, and soil solids was counted by LSC.

$^{14}CO_2$ in the NaOH trap was determined by neutralizing the solution with HCl and then passing the evolved gases through an HCl scrubber and retrapping it in an organic base (carbosorb). The neutralized solution, HCl scrubber, and the carbosorb were all counted for radioactivity. For the anaerobic studies, more than 80% of the radioactivity recovered in the organo-soluble extract was lost through evaporation. To identify this volatile material, an alternate

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extraction procedure was used. The anaerobic soil sample was extracted with water and partitioned with chloroform. Radioactivity was determined in each fraction. A measured volume of unlabeled acetonitrile was added to the chloroform fraction, and then the mixture was distilled, collecting the chloroform and acetonitrile fractions separately. The acetonitrile fraction was mixed with N, N-dimethylformmaide, and distilled. The radioactivity of the distilled acetonitrile was then quantitated.

Results

Recovered radioactivity from treated soils under aerobic and anaerobic conditions is shown in Tables 1 and 2. Under aerobic nonsterile conditions, the extractable radioactivity soils rapidly decreased, whereas volatile radioactivity rapidly increased and extractable radioactivity remained relatively constant (8-31% of the applied radioactivity). In the sterile soil, there was no volatile loss of the radioactivity and most of the radioactivity was extractable even after prolonged incubation. The pattern under anaerobic conditions was similar to that of aerobic conditions.

Under aerobic conditions, the half-life of thiodicarb in fresh field soil was less than 1 week, irrespective of the soil type and experimental conditions (sterile vs. nonsterile). The half-life value of thiodicarb in Texas sandy loam soil under anaerobic conditions was estimated to be about 1 week (estimated from the decline of organo-soluble residue levels). Methomyl and methomyl oxime were identified as degradation products under both aerobic and anaerobic conditions. Polar material and water-soluble products were prevalent but unidentified in anaerobic samples. Methomyl also degraded fairly rapidly in nonsterile soils, forming CO_2 and acetonitrile under aerobic and anaerobic conditions, respectively. These volatile products accounted for more than 70% of the applied radioactivity after 14 days in most cases.

Higher temperature, lighter soil texture, and fresh soil enhanced the overall degradation rate of thiodicarb in soils under aerobic conditions. In sterile soil, thiodicarb did not degrade beyond methomyl except for slight hydrolysis to the oxime. No attempt was made to identify degradation products other than acetonitrile in the organo-soluble fraction and water-soluble fractions of soil extracts under anaerobic conditions.

Table 1. Decomposition of [^{14}C]thiodicarb in soils under aerobic and anaerobic conditions at 25 ± 1 C after an application of 1 ppm.

Experimental conditions	Incubation period (days)	% Distribution of ^{14}C			TLC analysis of extractable radioactivity (% of the applied ^{14}C)		
		Extractable	Unextractable	Volatile[a]	Thiodicarb	Methomyl	Methomyl oxime
Aerobic, Texas sandy loam	0	95	--[b]	--	72	20	2
	7	32	26	42	1.0	1.3	25
	9	15	31	54	1.1	1.2	8
	14	4	26	70	0.6	0.6	2
	20	2	19	79	--[b]	--	--
	57	1	18	81	--	--	--
Aerobic, Norfolk sandy loam	0	90	--	--	60	25	2
	7	9	18	73	4	4	0.7
	12	5	15	80	3	1	0.2
	15	4	12	85	3	4	0.2
	22	3	9	88	2	4	0.2
	28	3	18	79	2	0.9	0.1
	35	2	8	90	1	0.7	0.1
Aerobic, California silt clay loam	0	100	--	--	83	13	1
	7	32	24	44	3	27	3.2
	15	21	28	51	1.5	18	0.4
	20	12	25	63	1.3	10	0.1
	29	14	25	61	0.7	12	0.3
	36	8	24	69	0.5	7	0.2
	44	9	27	64	0.9	8	0.1
Anaerobic, Texas sandy loam	7	81	9	10	NR[c]	NR	NR
	20	46	15	40	NR	NR	NR
	27	44	15	41	NR	NR	NR
	28	39	15	47	NR	NR	NR
	40	19	10	72	NR	NR	NR
Aerobic, Texas sandy loam, sterile	8	100	--	0	11	87	3
	17	98	11	0	39	52	7
	27	98	8	0	2	83	12
	36	88	14	0	3	72	11
	57	97	10	0	3	75	17
	62	85	22	0	12	67	5

[a] Presumably $^{14}CO_2$ for aerobic soils and [^{14}C]acetonitrile for anaerobic soils.

[b] --, none detected.

[c] NR, not reported.

Table 2. Decomposition of [^{14}C]thiodicarb in greenhouse activated soils under aerobic conditions at 15 C.

Soil type	Incubation period (days)	Distribution of ^{14}C (%)			TLC analysis (% of applied)		
		Extractable	Unextractable	$^{14}CO_2$	Thiodicarb	Methomyl	Methomyl oxime
Texas sandy	2	69	9	22	10.4	55.8	2.1
loam	4	68	19	14	3.4	58.5	3.4
	6	66	21	11	1.3	53.5	9.9
	9	4	31	65	--	--	--
	14	3	22	75	--	--	--
Norfolk	1	99	3	0	26	73	--
loamy sand	3	83	5	12	7.5	73.9	--
	6	75	8	17	6.8	66.8	--
	8	78	11	11	8.6	67.9	1.6
	20	55	17	28	5.5	48.4	--
California	3	100	6	0	22	76	2
clay loam	7	81	15	4	8.1	69.7	1.6
	10	54	23	23	4.9	47.0	1.1
	13	48	25	27	4.8	41.3	0.5
	16	48	24	28	2.9	44.2	0.5

Conclusions

Thiodicarb degraded rapidly in soils under both aerobic and anaerobic conditions. Half-life values of thiodicarb were less than 1 week and about 1 week under aerobic and anaerobic conditions, respectively. The primary degradation product was identified as methomyl, which was further degraded to CO_2 under aerobic conditions or acetonitrile under anaerobic conditions. The amount of methomyl oxime formed was highly variable, (2-25% of the applied radioactivity in the Texas soil, 0.1-3.2% in the other two soils). Physico-chemical factors can produce the degradation to methomyl and methomyl oxime, but microbial metabolism is responsible for the production of the volatile products, CO_2 and acetonitrile.

UC 51762 Photodegradation on soil surfaces, Khasawinah, A.M., and P.R. College, Union Carbide Corporation, August 29, 1978, File No. 25451, Acc. No. 099602, Tab 12.

Procedure/Methodology

Soils used were: California clay loam (reported as silty clay loam; pH 8.1, 1.3% organic matter), North Carolina Norfolk loamy sand (reported as sandy loam; pH 5.8, 0.8% organic matter, and Texas sandy loam (pH 7.8, 1.0% organic matter). All soils were obtained from a 0-10 cm profile, air dried, ground, and passed through a 2-mm sieve. Soil slides, prepared for each soil type, were air dried and treated with [^{14}C]thiodicarb (purity 98%) at a rate of 1 lb ai/A. The treated soil slides were subjected to a high-pressure mercury immersion lamp that irradiated incandescent light at >290 nm. A dark control was also included in the study. At intervals, soil was scraped from the slides, extracted in methanol, and then centrifuged. The extractable fraction was concentrated on a rotary evaporator and analyzed by thin-layer chromatography (TLC). Photolysis products were identified by radioautography and quantitated by liquid scintillation counting (LSC). After the soil was combusted, unextractable soil radioactivity was determined by LSC.

Results

The distribution of recovered radioactivity and the distribution of extracted radioactivity from thiodicarb and its degradation products for the three soil types are summarized in Tables 1-3. The data showed that the unextractable radioactivity never exceeded 3% in any of the three soils tested. In the irradiated soils, particularly in the Norfolk loamy sand, considerable ^{14}C radioactivity was lost through volatilization; presumably, acetonitrile was the volatile product. The half-life of the applied thiodicarb in the Norfolk loamy sand soil was less than 8 hours, as compared to approximately 21 days and >28 days for Texas and California soils, respectively. TLC analysis showed that thiodicarb declined steadily indicating conversion to other products. Methomyl was the major degradation product. The concentration of methomyl increased slowly with irradiation and then plateaued toward the end of experiment. Methomyl oxime was found only in small concentrations in all irradiated soils. Some polar material was also detected at the origin of the TLC plates; however, it was not identified.

Table 1. Photolysis of [^{14}C]thiodicarb in a Texas sandy loam soil.

Photolysis (days)	Distribution of ^{14}C (%)			Distribution of extractable ^{14}C (% of applied radioactivity)			
	Extracted	Unextracted	Volatile	Origin	Thiodicarb	Methomyl	Methomyl oxime
Light reaction							
0	100	--	--	ND[a]	81	7	4
1	98	2	--	1	26	37	16
7	86	2	12	3	50	25	3
14	79	3	18	3	45	26	1
21	74	3	23	3	41	21	1
28	70	2	28	6	26	30	2
Dark reaction							
0	100	--	--	ND	81	7	4
7	100	--	--	ND	74	12	5
28	100	--	--	ND	74	13	3

[a]ND, nondetectable.

Table 2. Photolysis of [^{14}C]thiodicarb in a California clay loam soil.

Photolysis (days)	Distribution of ^{14}C (%)			Distribution of extractable ^{14}C (% of applied radioactivity)			
	Extracted	Unextracted	Volatile	Origin	Thiodicarb	Methomyl	Methomyl oxime
Light reaction							
0	100	--	--	<1	80	9	4
1	95	1	4	<1	60	14	7
7	88	1	11	<1	72	11	2
14	82	1	17	<1	73	7	<1
21	85	2	13	<1	70	8	<1
28	85	2	13	<1	69	11	2
Dark reaction							
0	100	--	--	ND[a]	80	10	3
7	100	--	--	ND	80	11	2
28	100	--	--	<1	81	9	3

[a]ND, nondetectable.

Table 3. Photolysis of [^{14}C]thiodicarb in Norfolk loamy sand soil.

Photolysis (days)	Distribution of ^{14}C (%)			Distribution of extractable ^{14}C (% of applied radioactivity)			
	Extracted	Unextracted	Volatile	Origin	Thiodicarb	Methomyl	Methomyl oxime
Light reaction							
0	100	--	--	<1	87	6	<1
4	54	1	45	1	47	4	<1
8	38	1	61	2	29	4	<1
12	37	1	62	1	30	4	<1
16	21	1	78	<1	15	3	ND[a]
20	22	1	77	1	16	3	ND
24	16	1	83	<1	12	2	ND
Dark reaction							
0	100	--	--	--	87	6	<1
12	99	1	--	<1	86	8	<1
24	89	1	10	<1	77	7	<1

[a]ND, nondetectable.

Conclusions

Thiodicarb will photodegrade rapidly on the surface of light-textured soils. A half-life of 8 hours was obtained for thiodicarb in an irradiated Norfolk loamy sand. In a Texas sandy loam and a California clay loam half-lives of 21 days and >28 days were obtained, respectively. The major photolysis product of thiodicarb was identified as methomyl. The other identified product was methomyl oxime. No attempt was made to trap and identify the volatile compounds, but 28-83% of the applied radioactivity was lost after 28 days, presumably as acetonitrile.

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^{14}C - UC 51762, bluegill sunfish, *Lepomis macrochirus*, bioconcentration study, Kuc, W.J., Union Carbide Corporation, February 20, 1979, Project No. 11504-20, Acc. No. 099602, Tab 13.

Procedure

Acclimated bluegill sunfish (Lepomis macrochirus) were exposed for 30 days to [^{14}C]thiodicarb at 0.136 ± 0.015 ppm in a flow-through system. The treated tank and a solvent (acetone) control tank were maintained under a 16-hour photoperiod. Physical and chemical parameters of the aerated sterilized tank water were: 25 C, pH 8, flow rate of 2.8 liters/6 minutes, and approximately 8 ppm dissolved oxygen. Water and thirteen fish were sampled from each tank at 1, 3, 7, 10, 14, 22, and 30 days of the uptake period. A 14-day depuration period (untreated water, parameters as decribed above) followed and fish (13) from the treated tank were sampled on days 1, 3, 7, 10, and 14.

Methodology

Water samples were radioassayed directly by liquid scintillation counting (LSC). Three fish were assayed whole (control and treated tanks) and ten fish (treated tank only) were divided into edible and nonedible portions for analysis. The tissue samples were combusted and the $^{14}CO_2$ was collected. Radioactivity was determined by LSC. The method sensitivity was 0.05 ppm in fish samples and 0.005 ppm in the water.

Results

Mortality in control fish was about 3% over the duration of the experiment, whereas exposed fish mortality was about 5%. In water samples, thiodicarb concentrations ranged from 0.116-0.157 ppm during the uptake phase. Thiodicarb concentrations in whole tissues reached a maximum of 0.62 ppm on day 30 of uptake (Table 1). A minimum concentration of 0.11 ppm was determined on day 1 of uptake. Thiodicarb concentrations in nonedible tissues peaked on day 30 of uptake at 0.65 ppm. In edible tissue, the maximum concentration of 0.39 ppm (3.1 bioaccumulation factor) occurred on day 30 of uptake.

Depuration of thiodicarb residues from whole, edible, and nonedible tissues occurred with a half-life of about 10 days, with concentrations declining to 0.29, 0.18, and 0.25 ppm, respectively, after 17 days (Table 1).

Table 1. Thiodicarb residue levels in bluegill sunfish and water samples (flow-through system).

Experimental phase	Day	Water (ppm)	Edible tissue (ppm)	Bioaccumulation factor in edible tissues	Nonedible tissue (ppm)	Bioaccumulation factor in nonedible tissues	Whole fish (ppm)	Bioaccumulation factor in whole fish tissue
Uptake	1	0.157	0.17	1.18	0.15	0.965	0.11	0.72
	3	0.137	0.08	0.55	0.21	1.52	0.14	1.03
	7	0.122	0.19	1.52	0.32	2.64	0.28	2.28
	10	0.116	0.27	2.37	0.39	3.39	0.31	2.65
	14	0.145	0.38	2.62	0.56	3.87	0.43	3.00
	22	0.147	0.38	2.57	0.65	4.43	0.58	3.96
	30	0.125	0.39	3.09	0.61	4.88	0.62	4.94
Depuration	1	Tr[a]	0.25	--	0.50	--	0.49	--
	3	0.001	0.32	--	0.45	--	0.43	--
	7	0.001	0.22	--	0.37	--	0.37	--
	10	0.003	0.19	--	0.30	--	0.26	--
	14	0.003	0.18	--	0.25	--	0.29	--

[a] Tr, trace.

Conclusions

The bioaccumulation factors of 3 and 5 for edible and whole fish tissues, respectively, after 30 days, demonstrate a low accumulation potential for thiodicarb. Residue levels reached a plateau at 14 days in edible tissue (0.38 ppm) and between 22 and 30 days in the nonedible tissue (0.65 ppm). The rate of depuration was moderately slow, indicating that exposure of fish to high levels of thiodicarb could result in persistent residues in fish tissues. The ^{14}C metabolites in the fish were not characterized.

^{14}C - UC 51762, channel catfish, *Ictalurus punctatus*, bioconcentration study, Kuc, W.J., Union Carbide Corporation, March 27, 1979, Project No. 11504-20, Acc. No. 099602, Tab 14.

Procedure

Sandy loam soil (60% sand, 27% silt, 13% clay; buffered to pH 7) was treated with [^{14}C]thiodicarb at 2 lb ai/A and aged aerobically for 14 days. Untreated control soil was similarly aged. Both treated and untreated containers were then flooded to a depth of 0.45 m (1, 950 liters) with sterilized well water (Tarrytown, N.Y., pH 7.6-8.3, 6.9 mg/liter dissolved O_2, total hardness 260 mg/liter $CaCO_3$) and aged in this flooded state for 14 days under an artifically controlled 16-hour photoperiod at 25 C. Channel catfish (Ictalurus punctatus), acclimated at 30 C, were then added to the aged tanks (250 fish per tank). Fish were kept under the described conditions for a 30-day static exposure period. For the depuration phase, 75 fish were transferred to a clean tank having a constant flow system (10 tank volumes/24 hours) of fresh well water (pH 7.7-7.9, 8.6 mg/liter dissolved O_2, total hardness 199 mg/liter $CaCO_3$, mean temperature 23 C) for a period of 14 days.

During the soil aging period, soil samples were collected; during the soil-water aging period, soil and water were sampled. Soil, water, and fish (8 treated, 8 control) were sampled on days 1, 3, 7, 10, 14, 22, and 30 of the uptake period; water and fish (8 treated) were sampled on days 1, 3, 7, 10, and 14 of depuration.

Methodology

Water samples were assayed directly by liquid scintillation counting (LSC). No soil extraction or assay protocol was given. Whole fish samples (3) were blended and combusted, and $^{14}CO_2$ was counted by LSC. The remaining (5) fish were separated into edible and nonedible portions and analyzed as above. The method sensitivity was 0.03 ppm for fish tissues and soil, and 0.003 ppm for water.

Results

Data on [^{14}C]thiodicarb residues in soil, water, and fish tissues are summarized in Table 1. Levels of [^{14}C]thiodicarb residues in whole fish tissues peaked on day 14 (0.44 ppm); however, bioaccumulation factors continued to increase through day 30 of uptake (9.0 to 13.7 during days 14 through 30). Maximum bioaccumulation factors for edible and nonedible tissues were 9.6 and 16.3, respectively, occurring on day 22 of uptake. In general, [^{14}C]thiodicarb residue levels increased in catfish tissues during the first 2 weeks of uptake and then stabilized. Dissipation of residues was slow in catfish tissues with over half of the whole fish residues (0.28 ppm) remaining at the end of the 14-day depuration period. Mortality was <1% in the control tank and no deaths occurred in the treated tank.

Table 1. [^{14}C]thiodicarb residue levels in catfish, soil, and water (static system).

Experimental phase	Day	Water (ppm)	Soil (ppm)	Edible tissue (ppm)	Bioaccumulation factor in edible tissue	Nonedible tissue (ppm)	Bioaccumulation factor in nonedible tissue	Whole fish (ppm)	Bioaccumulation factor in whole fish
Soil aging									
	1	--	5.58	--	--	--	--	--	--
	7	--	4.11	--	--	--	--	--	--
	14	--	4.03	--	--	--	--	--	--
Soil-water aging									
	1	0.014	3.87	--	--	--	--	--	--
	7	0.085	1.73	--	--	--	--	--	--
	14	0.109	1.45	--	--	--	--	--	--
Uptake									
	1	0.101	2.76	0.07	0.73	0.13	1.29	0.13	1.24
	3	0.091	2.61	0.12	1.27	0.30	3.27	0.27	2.93
	7	0.078	2.27	0.21	2.69	0.39	4.95	0.42	5.36
	10	0.067	1.12	0.27	4.04	0.53	7.88	0.28	4.09
	14	0.050	1.43	0.27	5.48	0.52	10.5	0.44	8.95
	22	0.034	1.35	0.32	9.6	0.55	16.3	0.37	11.2
	30	0.029	1.34	0.31	10.7	0.51	17.4	0.49	13.7
Depuration									
	1	Tr[a]	--	0.27	--	0.44	--	0.29	--
	3	0.001	--	0.33	--	0.48	--	0.20	--
	7	0.001	--	0.23	--	0.37	--	0.42	--
	10	Tr	--	0.28	--	0.41	--	0.35	--
	14	Tr	--	0.22	--	0.30	--	0.28	--

[a] Tr, trace.

Conclusions

The bioconcentration factors for whole fish tissues (9-14) indicate a low accumulation potential for thiodicarb in catfish. Depuration of thiodicarb residues in catfish tissues is slow, indicating that as tissue residue concentrations build up over an extended period of time, persistance of residues in the tissues could occur. Radioactive residues in fish, soil, and water are not identified.

Effects of UC 51762 on soil microbes, Moffitt, R.B., Union Carbide Corporation, February 21, 1980, Project No. 11504-23, Acc. No. 099602, Tab 15.

Procedure/Methodology

Samples of pasture (Norfolk sandy loam) and forest (gravelly clay) soils were obtained from Clayton, North Carolina. The soils were sieved retaining the fractions between 0.5-2.0 mm and the pH was adjusted to near neutrality. For all experiments, thiodicarb was dissolved in acetone and then applied to soil samples at 1 ppm (the prescribed field application rate) and 10 ppm. Acetone without thiodicarb was added to control samples. The soil samples were flushed with CO_2-free air and moistened to 40% of saturation by adding sterilized distilled water. Three microbial functions in the soil were studied: biopolymer degradation, nitrogen fixation, and nitrification.

Biopolymer degradation. ^{14}C substrates (100 mg/sample) were applied to soil samples simultaneously with the thiodicarb application or at 2, 4, or 8 weeks after the thiodicarb application. ^{14}C-Protein, ^{14}C-starch, and ^{14}C-pectin were applied as solutions and ^{14}C-cellulose was added in suspension. After 24 hours of incubation at 22 C with ^{14}C-substrate, samples were removed for analysis. The $^{14}CO_2$ was removed by flushing with CO_2-free air and trapped in Oxifluor. The amount of $^{14}CO_2$ was determined by liquid scintillation counting. The analysis was repeated at 48 hours and at 1 week after the ^{14}C-substrate addition.

Nitrogen fixation. Two sets of soil samples were incubated at 22 C and 80% relative humidity in an environmental chamber. Immediately after thiodicarb application, one set of soil samples was flushed with N_2 gas for use in the anaerobic nitrogen fixation assay. The other set of soil samples was flushed with CO_2-free air three times each week in the aerobic nitrogen fixation assay. Aqueous dextrose solution (2% by weight in soil) was added to the sample simultaneously with thiodicarb application, or at 2, 4, 6, or 8 weeks after thiodicarb application to stimulate microbial activity prior to analysis. Seven days after dextrose amendment, acetylene was added to each sample. After 24 and 48 hours of incubation with acetylene the samples were analyzed for ethylene formation by gas chromatography.

Nitrification. Ammonia was added to the appropriate sample sets at 100 ppm (as $(NH_4)_2SO_4$, based on dry soil weight) simultaneously with thiodicarb application, or at 2, 4, or 8 weeks after thiodicarb application and incubated at 22 C until analyzed. The soil samples were extracted with sterilized deionized water and centrifuged. The concentrations of NO_3^-, NO_2^-, and NH_4^+ in the extracting supernatant were determined using specific ion electrodes and a specific ion meter.

Microbial populations were counted at the beginning and the conclusion of the study using a modified dilution plate procedure to ensure that a large microbial population was present and that no one population had predominated.

Results

Biopolymer degradation. The mean total percent of ^{14}C-substrate degraded to $^{14}CO_2$ for each treatment level and each substrate is presented in Table 1. Thiodicarb stimulated protein degradation 17 and 19% over controls at time zero in pasture soil treated with thiodicarb at 1 and 10 ppm, respectively. Subsequent assays exhibited no further effects of thiodicarb on protein degradation in pasture soil. At time zero, thiodicarb at 10 ppm increased protein degradation 18% over controls in the forest soil. Thiodicarb at 1 and 10 ppm did not affect starch degradation in pasture soil, whereas an initial slight stimulation (5.2% increase) was observed in the forest soil. In pasture soil, thiodicarb at 1 and 10 ppm increased cellulose degradation 28.7 and 44.2% over controls, respectively, at 4 weeks after application. However, thiodicarb at 1 and 10 ppm did not affect cellulose degradation in forest soil. Thiodicarb at 1 and 10 ppm did not retard pectin degradation in the pasture or forest soils.

Nitrogen fixation. The results of the nitrogen fixation assay for pasture and forest soils are summarized in Table 2. The data indicated that no nitrogen fixation was observed in many aerobic control samples. The effects of thiodicarb on aerobic nitrogen fixation in pasture soil oscillated from stimulatory to inhibitory at each assay point. In forest soil, thiodicarb at 1 and 10 ppm inhibited aerobic nitrogen fixation significantly at 6 weeks after thiodicarb application in the 24-hour assay. Anaerobic nitrogen fixation was not affected by thiodicarb at 1 and 10 ppm in either soil type. High coefficients of variation were observed in both the aerobic and anaerobic assays.

Nitrification. The effects of thiodicarb on nitrification in pasture and forest soils are presented in Table 2. Data showed a slight inhibition of the ammonia-to-nitrite transformation in the pasture soil samples at 2 and 4 weeks after thiodicarb application. In forest soil, the nitrification was inhibited by thiodicarb at 1 ppm after 4 weeks, but slightly stimulated in soil samples treated with thiodicarb at 10 ppm after 8 weeks.

Table 1. Biopolymer degradation to CO_2.

Assay	Soil	Thiodicarb application (ppm)	Percent of applied radioactivity[a]			
			Time from application (weeks)			
			0	2	4	8
Protein degradation	Pasture	Control	35.26[b]	40.70	41.07	42.11
		1	41.37[b]	41.31	37.32	41.89
		10	41.97[b]	39.79	40.47	41.43
	Forest	Control	37.07	40.52	43.94	49.06
		1	36.97	40.82	44.43	46.24
		10	43.74[b]	41.36	43.27	49.13
Starch degradation	Pasture	Control	37.55	33.06	37.86	41.87
		1	37.50	33.33	37.75	45.57
		10	39.05	33.04	35.85	44.07
	Forest	Control	41.03	32.01	43.63	47.69
		1	40.38[b]	33.70	43.10	46.72
		10	43.18[b]	40.11	42.27	46.84
Cellulose degradation	Pasture	Control	17.33	12.13	13.24[b]	20.43
		1	17.69	12.82	17.04[b]	23.33
		10	17.30	13.76	19.09[b]	22.68
	Forest	Control	26.19	15.75	16.73	17.58
		1	26.53	16.97	17.70	17.01
		10	26.80	16.91	17.46	17.18
Pectin degradation	Pasture	Control	26.77	26.05	29.87	29.74
		1	27.55	26.36	30.64	30.47
		10	26.09	26.70	30.56	29.67
	Forest	Control	30.57	32.63	38.22	37.10
		1	36.09	32.04	39.16	37.25
		10	36.19	32.42	37.89	34.96

[a] Mean of three replicates.
[b] Significantly different from controls (95% or greater significance level, Duncan's multiple range test).

Table 2. Effects of thiodicarb at 1 and 10 ppm on microbial functions.

Assay	Sample	Effects of thiodicarb (2 treatment levels) at intervals after application									
		0 weeks		2 weeks		4 weeks		6 weeks		8 weeks	
		1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm
Biopolymer degradation	Protein pasture	+	+	o	o	o	o	--	--	o	o
	Protein forest	o	+	o	o	o	o	--	--	o	o
	Starch pasture	o	o	o	o	o	o	--	--	o	o
	Starch forest	o	+	o	o	o	o	--	--	o	o
	Cellulose pasture	o	o	o	o	+	+	--	--	o	o
	Cellulose forest	o	o	o	o	o	o	--	--	o	o
	Pectin pasture	o	o	o	o	o	o	--	--	o	o
	Pectin forest	o	o	o	o	o	o	--	--	o	o
Nitrification	Pasture - NH_4+	o	o	o	+	+	o	--	--	o	o
	- NO_3-	o	o	o	o	o	o	--	--	o	o
	- NO_2-	o	o	o	o	o	o	--	--	o	o
	Forest - NH_4+	o	o	o	o	o	o	--	--	o	o
	- NO_3-	o	o	o	o	o	o	--	--	o	+
	- NO_2-	o	o	o	o	+	o	--	--	o	o
Nitrogen fixation	Pasture 24 hrs	+	+	x	x	x	x	o	o	-	-
	aerobic 48 hrs	o	o	-	-	+	+	o	o	o	o
	Forest 24 hrs	x	x	x	x	o	o	-	-	o	o
	aerobic 48 hrs	o	o	o	o	o	o	x	x	o	o
	Pasture 24 hrs	o	o	o	o	o	o	o	o	o	o
	anaerobic 48 hrs	o	o	o	o	o	o	o	o	o	o
	Forest 24 hrs	o	o	o	o	o	o	o	o	o	o
	anaerobic 48 hrs	o	o	o	o	o	o	o	o	o	o

Significance according to Duncan's multiple range test, 95% confidence level.

Key: o No significant effect.
+ Levels significantly higher than control.
- Levels significantly lower than control.
x No fixation in control samples.
-- No assay conducted.

Conclusions

Thiodicarb at 1 and 10 ppm generally had no effect or slightly stimulated degradation of protein, starch, cellulose, and pectin in pasture and forest soils. The effects of thiodicarb on aerobic nitrogen fixation in pasture and forest soils are not conclusive: the effect varied from stimulatory to inhibitory over the course of study, and aerobic nitrogen fixation was low or undetectable in many control samples. The anaerobic nitrogen fixation was not affected by thiodicarb at 1 or 10 ppm in either forest or pasture soil. Thiodicarb at 1 or 10 ppm had no prolonged effects on the nitrification in pasture or forest soil.

Soils from treated field corn, soybeans and cotton fields, Myers, W.R., Union Carbide Residue Laboratory, W. Va. (Cooperators: Ag-TX, Ag-NC, Chemonics, Todd, Multa Chem), December 10, 1979, Acc. No. 099602, Tab 16.

Procedure

Field plots in Texas, Arizona, North Carolina, Georgia, and Louisiana were treated with 1-12 applications of thiodicarb (75% WP or 500 g ai/liter F) at 0.375-4.0 lb ai/A per application. Soil samples were collected to various depths at various time intervals for up to 257 days after the last application (Tables 1 and 2).

Methodology

The soil samples were reportedly analyzed using the Thiodicarb-FPD-Soil method. No information was provided concerning this method.

Results

Results were highly irregular as shown in Tables 1 and 2. In particular, the 1977 and 1978 samples often showed increasing residue levels with time (as much as 10-fold) even though no further thiodicarb was added. The number and rate of applications correlated poorly with the initial amount of thiodicarb residues. Many control plots were useless because they were first sampled 56-112 days after the last application. In general, residue levels were undetectable (<0.02 ppm) 42-98 days after the last thiodicarb application.

Table 1. Thiodicarb residue levels in soil samples; 1979 data. Sampling depth was reported as "top of soil" except in Arizona where it was 0-3 inches.

Plot location	Treatment			Thiodicarb equivalents (ppm)								
				Days after last application								
	Formulation	No. of applications	Rate (lb ai/A)	1	3	7	14	21	28	42	56	84
Texas	75 WP	3	1.0	NR[c]	--	NR	<0.02	<0.02	--	<0.02	--	<0.02
Texas	75 WP	3	2.0	NR	--	NR	<0.02	<0.02	--	<0.02	--	<0.02
Texas	500[a]	3	1.0	NR	--	NR	<0.02	<0.02	--	20.02	--	<0.02
Texas	500	3	2.0	NR	--	NR	<0.02	<0.02	--	<0.02	--	<0.02
Texas	--	Control	--	--	--	--	--	--	--	--	--	--[d]
Texas	75 WP	1	1.0	0.05	0.05	<0.02	0.04	<0.02	--	<0.02	--	--
Texas	75 WP	1	2.0	0.29	0.23	0.13	0.26	0.03	--	<0.02	--	--
Texas	500	1	1.0	0.35	0.07	0.26	0.30	0.03	--	<0.02	--	--
Texas	500	1	2.0	0.43	0.40	0.19	0.34	0.03	--	<0.02	--	--
Texas	--	Control	--	2.39	0.20	1.36	--	--	--	--	--	--
Arizona	75 WP	Multi[b]	Multi	0.19	0.22	0.12	0.86	--	0.94	--	--	--
N. Carolina	500	3	4.0	--	--	--	--	--	--	--	0.06	--
N. Carolina	--	Control	--	--	--	--	--	--	--	--	<0.02	--

[a] Larvin 500.
[b] Six treatments - 2 x 0.375, 2 x 0.45, and 2 x 0.9.
[c] No results; samples thawed in shipment.
[d] Sampled 105 days after application, residue level <0.02 ppm.

Table 2. Thiodicarb residue levels in soil samples; 1976-1978 data. Sampling depth was top 2-4 inches except in the Texas soil that received 12 applications where sampling depth was 6 inches.

Plot location	Year	Treatment: Formulation	Treatment: No. of applications	Treatment: Rate (l b ai/A)	Thiodicarb equivalents (ppm): Days after last application: 0	1	3	7	14	21	28	38	42
Texas	1978	75 WP	5	2.0	--	0.08	--	0.68	1.2	--	2.0	--	--
Texas	1978	75 WP	5	4.0	--	1.7	--	2.5	6.1	--	4.7	--	--
Texas	1978	500[a]	5	2.0	--	1.5	--	1.1	2.3	--	5.7	--	--
Texas	1978	500	5	4.0	--	1.6	--	0.92	9.1	--	5.6	--	--[b]
Texas	1978	--	Control	--	--	--	--	--	--	--	--	--	--
Texas	1978	75 WP	8	2.0	--	7.5	--	1.6	6.6	--	--	0.03	--
Texas	1978	75 WP	8	4.0	--	17.0	--	4.6	11.0	--	--	0.03	--
Texas	1978	500	8	2.0	--	4.7	--	8.2	5.6	--	--	0.19	--
Texas	1978	500	8	4.0	--	16.0	--	5.8	--	--	--	0.03	--
Texas	1978	75 WP	12	2.0	--	1.1	--	0.71	8.4	--	--	--	<0.02
Texas	1978	75 WP	12	4.0	--	4.5	--	2.0	23.0	--	--	--	0.04
Texas	1978	500	12	2.0	--	1.3	--	4.8	2.6	--	--	--	<0.02
Texas	1978	500	12	4.0	--	7.1	--	12.0	10.0	--	--	--	0.05
Georgia	1978	75 WP	1	0.45	--	0.3	0.04	0.03	<0.02	--	--	<0.02	--
Georgia	1978	--	Control	--	--	--	--	--	--	--	--	--	--
Texas	1977	75 WP	11	0.75	0.11	--	--	0.20	--	<0.02	--	--	0.05
Texas	1977	75 WP	11	1.0	0.12	--	--	0.97	--	0.02	--	--	0.04
N. Carolina	1977	75 WP	1	0.75	--	0.06	0.12	0.04	<0.02	<0.02	--	--	<0.02
N. Carolina	1977	75 WP	1	1.0	--	0.04	0.10	0.06	0.03	<0.02	--	--	<0.02
N. Carolina	1977	--	Control	--	--	--	--	--	--	<0.02	--	--	--
Louisiana	1976	75 WP	1	1.0	1.2	1.2	1.4	1.1	0.60	--	0.37	--	--
Louisiana	1976	--	Control	--	<0.02	--	--	--	--	--	--	--	--

[a] Larvin 500.
[b] Sampled 112 days post application, residue level <0.02 ppm.

Conclusions

The half-life and dissipation rate of thiodicarb cannot be determined from the data because the extraction and analysis procedures and recovery data were not presented.

No soil characteristics were reported for any location nor were the size of the plots. The sampling depth was inconsistent and often vaguely reported or not given at all. Controls were lacking at three field plots and duplicate samples were not run for some of the field plots.

The time of sampling was inadequate in many ways. Residue levels immediately after treatment were not reported in all but three experimental units. In some cases the time interval between the first application and the collection of the first sample was more than 2 months. In all instances, samples were not collected until after the last of a series of thiodicarb applications.

Because nothing is known of the method, it is not known whether the residue levels reported include the residue levels of thiodicarb degradation products. Residue levels of 2.39, 0.20, and 1.36 ppm were found in one of the Texas control plots at 1, 3, and 7 days after treatment, respectively. This indicates either that some of the thiodicarb drifted onto the control plot or that the analytical recovery capabilities of the method were inadequate.

ENVIRONMENTAL FATE ANALYSIS

In buffered, weakly acidic aqueous solution (pH 6), thiodicarb is fairly stable to hydrolysis (a 3% loss occurred over 9 days). However, hydrolysis occurs in alkaline and strongly acidic solutions and is most rapid under alkaline conditions (half-life of 0.9 days at pH 9; 8.6 days at pH 3). The major hydrolysis product is methomyl (Figure 1). In alkaline solutions, methomyl residue levels peaked after about 4 days and declined thereafter as the levels of methomyl oxime (Figure 1) increased.

Thiodicarb photodegrades in aqueous solution, and more rapidly with acetone as a sensitizer. The half-lives are 19 and 81 days, with and without acetone, respectively. Methomyl is the major product; minor products include the monosulfoxide, methomyl oxime, methomyl sulfoxide, and methomyl sulfoxide oxime (structures given in Figure 1). Photolysis of thiodicarb also occurs on the surface of soil. The rate correlates with soil texture, with faster degradation occurring on lighter soils. The initial photolysis product is methomyl; lesser amounts of methomyl oxime are formed and high volatile losses occur (28-83%). Reported half-lives range from 8 hours to >28 days for the three soils studied.

Thiodicarb is degraded rapidly with a half-life of <7 days when incubated aerobically in soil. Methomyl, methomyl oxime, and CO_2 are the major products formed. At 25 C the concentration of methomyl reaches a maximum (20-27% of applied radioactivity) 7 days after treatment and declines to half that amount 20 days after treatment. At 15 C, methomyl reaches a maximum concentration (58-74% of applied radioactivity) 4 days after treatment but it declines more slowly at the lower temperature. $^{14}CO_2$ losses from the acetaldehyde-1 position are rapid at 25 C (50-85% in 2 weeks) but may only occur slowly at 15 C. Under anaerobic conditions, the half-life of thiodicarb is about 7 days, but the degradation follows a different pathway from that found in the aerobic soil. The anaerobic end product formed is acetonitrile (72% at 40 days after treatment), and there is an increased amount of unidentified polar and water-soluble products.

The half-life of thiodicarb in sterile soil is less than 8 days; methomyl is the major degradation product. This suggests that the first degradation step could be entirely due to physico-chemical processes. Further degradation to methomyl oxime occurs slowly (17% maximum over 62 days) and no volatile degrada-

tion products are formed. Thus the formation of degradation products beyond methomyl is at least partially microbially mediated. Thiodicarb at 1 or 10 ppm has either no effect or a slight stimulatory effect on the following soil microbial processes: nitrification; anaerobic nitrogen fixation; and protein, starch, cellulose, and pectin degradation.

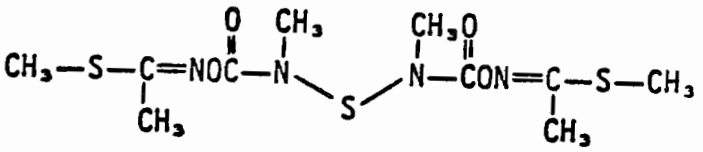
The continuous addition of thiodicarb at 10 ppm or more to an activated sludge reactor significantly increases the effluent turbidity, total organic carbon, and total suspended solids, thus reducing the quality of the effluent produced. The settleability of the mixed liquor is reduced at thiodicarb levels of 0.1, 1.0, and 10 ppm and fails completely at 100 ppm. Shock loading with thiodicarb at 100 ppm does not reduce the effluent quality or affect the activated sludge process.

As shown on soil thin-layer plates, thiodicarb is generally immobile in soil (R_f <0.2). Its degradation products, methomyl and methomyl oxime, are mobile (R_f values of 0.6-0.8 and >0.8, respectively). Similarly, thiodicarb is not volatile under normal field conditions (VP = 4.3×10^{-5}mmHg at 20 C), but some of its degradation products do volatilize (acetonitrile and CO_2). Soil adsorption of thiodicarb residues is fairly low (Freundlich K values of 0.6-1.3) and rapidly reaches an equilibrium level (within 1 hour). The low adsorption coefficients indicate that degradation was occurring in the adsorption study, because thiodicarb itself is immobile and would be expected to adsorb more strongly. Heavier textured soils have higher adsorption coefficents than lighter textured soils; the effect of organic matter content on adsorption was not investigated. Desorption of the residues is fairly rapid and complete, with 80-95% desorbed after 3 hours.

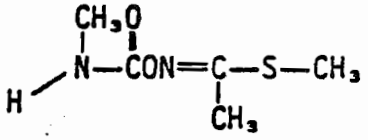
The only rotational crop study submitted was conducted in a greenhouse. [^{14}C]Thiodicarb residue levels of around 0.6 ppm (presumably given on a wet weight basis) may be present in leafy vegetables at harvest when planted 30 days after a 9-ppm application. Planting in the same soil 120 days postapplication will result in ^{14}C residue levels of 0.03-0.4 ppm in grain foliage. Leafy green and root crops planted 365 days after the application may contain ^{14}C residue levels of 0.01-0.08 ppm at harvest. The degradation products present in rotationally planted crops include methomyl, methomyl methylol (Figure 1), and methomyl oxime.

More than 30 days exposure to thiodicarb is required to obtain an equilibrium between accumulation and elimination of thiodicarb residues in catfish and bluegill sunfish. However, the bioconcentration factors (5 and 14 for sunfish and catfish, respectively) for whole fish tissues after 30 days exposure indicate a low uptake rate of thiodicarb residues. Equivalent bioconcentration factors are found in edible and nonedible tissues in both fish species. Thin-layer chromatography studies reveal that methomyl oxime and methomyl are present in fish tissues. Depuration of thiodicarb residues in catfish and bluegill sunfish is relatively slow (half-life $\geq$14 days), indicating possible persistance of residues in fish exposed to constant thiodicarb levels.

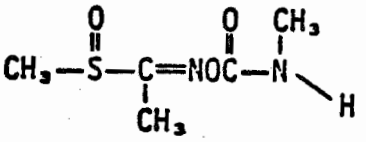
In summary, degradation of thiodicarb in the environment begins with hydrolysis to methomyl, which will occur more rapidly in alkaline aqueous solution. The reaction is also common in soils and acidic aqueous solutions and can be caused by photolysis and possibly by microbial action. Methomyl is fairly mobile in soils. Methomyl oxime is the next product identified in hydrolysis, photolysis, and metabolism studies. It is generally present at <10%. Under aerobic nonsterile conditions, microbial degradation produces CO_2 from the radiolabeled acetaldehyde-1 position; under anaerobic conditions, acetonitrile forms and volatilizes (b.p. 8.16 C) from the acetaldehyde-1 position. The effluent quality and mixed liquor characteristics of the activated sludge process are effected by thiodicarb concentrations of 10 ppm or greater when added by continuous loading. Bioconcentration factors in fish exposed to thiodicarb-contaminated water are low, but depuration is slow.



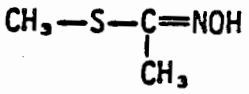
Thiodicarb



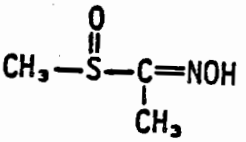
Methomyl



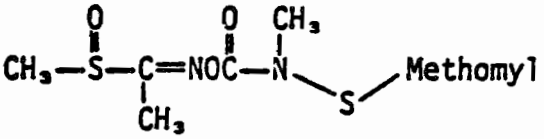
Methomyl Sulfoxide



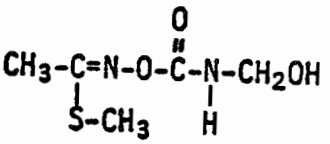
Methomyl oxime



Methomyl Sulfoxide Oxime



Monosulfoxide



Methomyl methylol

Figure 1. Thiodicarb and its major degradation products.

65