Soil Studies with ^{14}C-Labeled Hexazinone

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The active ingredient in Velpar weed killer is 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione (hexazinone). Under field conditions, the half-life of intact [^{14}C]hexazinone in soil treated at 3.7 kg/ha was ca. 1 month in Delaware, 2 months in Illinois, and 6 months in Mississippi. The time for 50% loss of total radioactive residues was ca. 3–4 months in Delaware, 6–7 months in Illinois, and 10–12 months in Mississippi. The major degradation product at all locations was 3-(4-hydroxycyclohexyl)-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione. Greenhouse soil degradation tests on both silt loam and sandy loam soil showed a half-life of intact hexazinone of less than 4 months. Laboratory biometer flask studies to determine microbial degradation in the dark in two soil types showed that 45–75% of the applied radioactivity was evolved as $^{14}CO_2$ during an 80-day incubation period. Soil thin-layer chromatography data place hexazinone in Class 4 in the mobility classification of Helling and Turner (1968).

Velpar weed killer is a highly effective herbicide when applied to soil or actively growing vegetation for the control of many annual and perennial broadleafed weeds, grasses, herbaceous vines, and woody plants. Hexazinone (formerly DPX-3674), the active component of Velpar, is 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione.

Studies on the metabolism of [^{14}C]hexazinone in the rat (Rhodes and Jewell, 1980) and its fate in water and fish (Rhodes, 1980) have been reported.

This paper describes degradation studies with [^{14}C]-hexazinone in soil under actual field conditions and in the laboratory.

EXPERIMENTAL SECTION

Apparatus and Reagents. Radioactivity in aqueous samples was determined by direct counting using a Nuclear Chicago liquid scintillation spectrometer (Model 6801). Solid samples were analyzed by combustion in a Packard Model 305 sample oxidizer, followed by liquid scintillation counting.

Chromatographic separations were made on thin-layer chromatographic (TLC) plates (250 μm silica gel 60F-254, E. M. Laboratories, Inc.) which were developed in a 9:1 (v/v) mixture of ethyl acetate and methanol or a 9:1 (v/v) mixture of chloroform and methanol. The location of the ^{14}C-labeled materials on the TLC plates was detected using a Varian-Aerograph/Berthold Model 6000-2 automatic integrating TLC radioscanner.

All mass spectra were obtained on a Du Pont Model 21-492 high-resolution mass spectrometer.

[^{14}C]Hexazinone (sp act., 7.11 μCi/mg >99% radiochemical purity) and its metabolites and degradation products were synthesized according to the procedure of Rhodes and Jewell (1980).

Field Soil Studies. Studies to determine the fate of [^{14}C]hexazinone in soil under actual field conditions were conducted on test sites at Newark, DE (Keyport silt loam), Rochelle, IL (Flanagan silt loam), and Scott, MS (Dundee silt loam). The soil characteristics are given in Table I.

The procedure at each location was identical. Eight stainless steel cylinders (10 × 30 cm long in Delaware, 10 × 38 cm at all other locations) were driven into undisturbed soil, leaving about 3 cm of rim protruding above ground level to minimize run-off and splashing. The soil inside each cylinder was treated with [^{14}C]hexazinone (3.65 mg in 1 mL of water) at the rate equivalent to 3.7 kg/ha. Water (10 mL) was added to each cylinder to distribute and settle the compound into the soil. All cylinders were fully exposed to normal weather conditions throughout the indicated test periods. Cylinders from each location were dug up at regularly scheduled intervals and maintained frozen until analyzed.

The soil from each cylinder was removed and divided into the following increments, as measured from the soil surface: 0–3, 3–8, 8–13, 13–20, 20–30, and 30–38 cm. All aliquots were air-dried in a hood and ballmilled (dry) for 12 h. Duplicate 1-g aliquots of each increment were analyzed for total ^{14}C by the combustion–liquid scintillation counting method. Aliquots (100 g) of each increment containing 10% or more of the applied ^{14}C were analyzed specifically for [^{14}C]hexazinone and degradation products. Each sample was extracted five times with 150 mL of 10% water in acetone in a blender for 10 min. The extracts were combined, and the volume of the resulting solution was reduced to ca. 2 mL in vacuo at 50 °C. The solution was quantitatively transferred to a 3-mL volumetric flask and made to volume with acetone. A 50-μL aliquot of the solution was added to 15 mL of Aquafluor (New England Nuclear Corp.) scintillation solution in a scintillation vial and counted to determine the total ^{14}C in the extract. A second aliquot (250 μL) of each extract was applied to a TLC plate as a narrow streak, and the appropriate reference standards (ca. 10 μg) were spotted next to the sample. The TLC plate was developed 15 cm in the chloroform–methanol mixture and then air-dried. The location of the radioactive compounds on the plate was determined by scanning the plate with the radioscanner. The area of silica gel containing each ^{14}C compound was scraped into a scintillation vial containing 3.5 mL of water. Scintillation cocktail (11.5 mL) was added to each vial, and the vials were shaken. The resulting suspensions were counted.

Triplicate control soil samples, fortified with 4 ppm [^{14}C]hexazinone, were dried, ballmilled, extracted, and analyzed by the above procedure.

Greenhouse Soil Study. Soil metabolism studies with [^{14}C]hexazinone in the greenhouse were conducted using two soils, Fallsington sandy loam (Glasgow, DE) and Flanagan silt loam (Rochelle, IL). The characteristics of these two soils are given in Table I. The normal moisture capacity of each soil was determined in duplicate using the

Biochemicals Department, Research Division, Experimental Station, E. I. du Pont de Nemours Nemours & Co., Inc., Wilmington, Delaware 19898.

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Table I. Characteristics of Soils Used in Greenhouse and Field Studies[a]

component	Fallsington sandy loam (Glasgow, DE)	Flanagan silt loam (Rochelle, IL)	Keyport silt loam (Newark, DE)	Dundee silt loam (Scott, MS)
sand	56%	5%	21%	15%
silt	29%	64%	62%	67%
clay	15%	31%	17%	18%
organic matter	1.40%	4.02%	2.75%	1.30%
nitrogen	0.085%	0.282%	0.097%	0.049%
pH	5.6	5.0	6.4	5.5
cation-exchange capacity	4.8 mequiv/100 g	23.4 mequiv/100 g	8.2 mequiv/100 g	14.3 mequiv/100 g

[a] Soil analyses were performed by the College of Agricultural Sciences, University of Delaware, Newark, DE.

Table II. Percentage of Applied ^{14}C-Activity Remaining in [^{14}C]Hexazinone Treated Field Soils

A. Keyport silt loam (Newark, DE)

	exposure time (months)					
soil depth, cm	0	1	2	3	4	11
0-3	99.4	26.8	17.2	11.6	4.7	3.6
3-8	<0.1	24.3	17.1	16.8	6.2	6.0
8-13	<0.1	7.4	11.7	18.2	8.0	6.6
13-20	<0.1	5.0	4.2	9.6	10.3	8.6
20-30	<0.1	2.7	3.8	6.2	14.1	7.2
total recov	99.4	66.2	54.0	62.4	43.3	32.0
total rainfall, cm	0.00	21.4	31.2	35.0	48.5	107.2

B. Flanagan silt loam (Rochelle, IL)

	exposure time (months)							
soil depth, cm	0	0.5	1.5	2.5	4.0	8.0	10.0	12.0
0-3	99.0	103.5	22.4	7.9	6.2	1.7	12.4	2.9
3-8	<0.1	0.2	38.6	13.4	15.3	3.8	8.8	3.7
8-13	<0.1	<0.1	17.9	23.0	24.1	3.0	5.8	2.6
13-20	<0.1	<0.1	2.5	19.3	25.6	6.7	3.1	1.7
20-30	<0.1	<0.1	0.5	6.6	3.9	11.7	2.4	2.0
30-38	<0.1	<0.1	<0.1	0.7	0.3	5.0	1.5	1.0
total recov	99.1	103.7	81.9	70.9	75.4	31.9	34.0	13.9
total rainfall, cm	0.00	0.6	17.9	35.1	42.4	68.2	103.3	127.5

C. Dundee silt loam (Scott, MS)

	exposure time (months)							
soil depth, cm	0	0.5	1.5	2.5	3.5	6.0	9.0	12.0
0-1	96.1	87.9	58.0	33.5	24.3	22.6	16.5	7.8
3-8	1.7	1.2	24.4	37.6	35.9	31.7	19.2	10.1
8-13	<0.1	<0.1	0.2	8.1	13.6	11.5	17.7	12.7
13-20	<0.1	0.5	1.4	2.0	6.0	10.6	12.4	10.4
20-30	<0.1	<0.1	<0.1	0.2	0.9	0.5	2.0	1.4
30-38	<0.1	<0.1	<0.1	0.2	0.1	0.1	0.3	0.1
total recov	97.8	89.6	84.0	81.6	80.7	76.9	68.1	42.5
total rainfall, cm	0.00	4.4	18.6	31.2	43.5	92.4	155.4	191.0

procedure described by Puri (1949). The normal moisture capacities are 16 and 31% (by weight) for Fallsington sandy loam and Flanagan silt loam, respectively.

Each soil was partially air-dried and passed through a 4-mm screen prior to treatment. The soils were stored in a refrigerator while 200-g aliquots of each soil were air-dried in a hood for 72 h to determine the moisture contents. Several fresh samples of both soils were then prepared using the following procedure: Soil, equivalent to 50-g air-dry weight, was weighed into 475-mL paper cups, [^{14}C]hexazinone (0.200 mg, 1.43 μCi) in 1 mL of water was added, and the soil was thoroughly mixed with a spatula. A second portion of soil (50-g dry weight) and [^{14}C]hexazinone (0.200 mg in 1 mL of water) were added, and the entire mixture was again thoroughly mixed with a spatula, giving a total of 0.4 mg (2.86 μCi) of hexazinone in 100 g of soil for each sample or 4 ppm. Finally, water was added to each sample to adjust the moisture contents to 75% for Fallsington sandy loam and 65% for Flanagan silt loam (percent of normal holding capacities). All samples were placed in the greenhouse in Delaware starting in April, and water was added as needed to maintain the moisture levels.

Entire individual samples were taken periodically and analyzed to determine the total ^{14}C remaining in the soil and specifically for hexazinone and degradation products. Each sample was extracted as previously described and a 50-μL aliquot was counted to determine the ^{14}C in the extract. A second aliquot of each extract was analyzed by the TLC–liquid scintillation counting procedure previously described using a mixture of ethyl acetate and methanol (9:1, v/v) as the developing solvent. The extracted soil was air-dried in a hood, and duplicate 1-g samples were analyzed for unextracted ^{14}C by combustion–liquid scintillation counting.

One sample (17 weeks) of each soil extract was analyzed using two solvent systems to separate the possible mixtures. An aliquot of each was subjected to TLC as described above. The area of gel corresponding to each ^{14}C location was removed from the plate, and the ^{14}C materials were washed from the gel with three 20-mL portions of

methanol. The washings were each reapplied to silica gel TLC plates and developed 15 cm with a mixture of chloroform and methanol (9:1, v/v). All ^{14}C areas on these plates were removed and counted as previously described.

Anaerobic Soil Test. Two samples each of the treated soils from the greenhouse soil test were removed after a 30-day exposure period in the greenhouse and immmediately placed under anaerobic conditions. The samples were placed in an enclosed Lucite box under a nitrogen atmosphere in the dark at ca. 21 °C. The nitrogen atmosphere was maintained with a continuous nitrogen purge (25 cm^3/min). One sample from each soil type was removed and analyzed by the procedure previously described for the greenhouse soil test after 30 and 60 days under anaerobic conditions.

Effect of Soil Microorganisms on the Degradation of Hexazinone. Laboratory studies to determine the effects of soil microorganisms on the degradation of hexazinone were performed using the procedure and apparatus described by Bartha and Pramer (1965).

Duplicate samples of two soil types (Fallsington sandy loam and Flanagan silt loam) were used with each of the following treatments: control, sterile soil plus 4 ppm [^{14}C]hexazinone, nonsterile soil plus 4 ppm [^{14}C]hexazinone, and nonsterile soil plus 20 ppm [^{14}C]hexazinone.

Sterile samples were obtained by autoclaving the soils in the biometer flask three times for 15 min at a steam pressure of 15 psi.

Soil, equivalent to 50-g air-dry weight, was weighed into the 250-mL Erlenmeyer flask side of a biometer flask. [^{14}C]Hexazinone in 1 mL of water was added to produce the above treatment levels (4 and 20 ppm) and then water was added to adjust the moisture content to 70% of the normal holding capacity of each soil type. The biometer flasks, with 10 mL of 0.1 N sodium hydroxide in the 50-mL side tube, were closed and stored in the dark at 22 °C for the duration of the test. The NaOH in the side tubes was changed periodically and analyzed for $^{14}CO_2$ by counting a 1-mL aliquot in Aquoafluor scintillation solution. With several samples, a second 1-mL aliquot was treated with 5% barium chloride solution to precipitate ^{14}C-labeled carbonate. The resulting suspensions were centrifuged for 10 min at 2000 rpm, and the aqueous solution was decanted into a scintillation vial and counted as before. Carbon dioxide free fresh air was added to the system every third day through an ascarite filter fitted to the apparatus with a stopper and stopcock.

Freundlich Isotherm Constants and Soil TLC. Soil TLC data were obtained on four different soils using the techniques described by Helling and Turner (1968), Rhodes et al. (1970), and Helling (1971b). Terbacil and diuron were used in this work as comparative standards since soil TLC data have been reported for these compounds. Freundlich isotherm constants (K value) for [^{14}C]hexazinone were determined on Fallsington sandy loam and Flanagan silt loam by the procedure described by Rhodes et al. (1970).

RESULTS AND DISCUSSION

The results of analyses for total ^{14}C remaining in the field soils are given in Table II, and the results of analyses for hexazinone and its soil metabolites are listed in Table III. The time for 50% loss of hexazinone was about 1 month in the Delaware test, ca. 2 months in Illinois and ca. 6 months in Mississippi. The time for 50% loss of ^{14}C residues was ca. 3–4 months in Delaware, 6–7 months in Illinois, and 10–12 months in Mississippi.

The major routes of degradation of hexazinone in soil involve both demethylation and hydroxylation of the 4 position of the cyclohexyl ring. The major metabolite at each location was metabolite C (Figure 1). Other soil metabolites present in significant amounts at each location were metabolites A, B, and G. Extraction efficiencies for the final soil analyses were 70% (11 months Delaware), 77% (10 months Illinois), and 76% (12 months Mississippi). The identities of all the major soil metabolites were confirmed by comparing the mass spectra of the isolated compounds and reference standards (Reiser et al., 1979). The soil metabolites were all previously shown to be degradation products of hexazinone in the rat (Rhodes and Jewell, 1980) and in water (Rhodes, 1980).

Table III. Analysis for [^{14}C]Hexazinone and Metabolites[a] in Treated Field Soils

A. Keyport silt loam (Newark, DE)

	percent of ^{14}C recov from TLC plate, exposure time (months)						
compd	0	1	2	3	4	11	R_f
hexazinone	100	29	7	4	3	1	0.80
A	<1	6	30	16	5	<1	0.57
B	<1	11	12	11	7	8	0.70
C	<1	36	46	59	70	79	0.27
G	<1	14	3	4	5	6	0.60
at origin	<1	4	2	6	10	6	

B. Flanagan silt loam (Rochelle, IL)

	percent of ^{14}C recov from TLC plate, exposure time (months)							
compd	0	0.5	1.5	2.5	4	8	10	R_f
hexazinone	100	94	62	36	20	32	22	0.80
A	<1	<1	2	2	<1	<1	<1	0.57
B	<1	2	4	10	7	9	7	0.70
C	<1	4	17	34	49	38	63	0.27
D	<1	<1	3	4	2	5	<1	0.77
G	<1	<1	10	6	11	10	8	0.60
at origin	<1	<1	2	8	11	6	<1	

C. Dundee silt loam (Scott, MI)

	percent of ^{14}C recov from TLC plate, exposure time (months)								
compd	0	0.5	1.5	2.5	3.5	6	9	12	R_f
hexazinone	97	90	76	68	74	69	40	19	0.80
A	<1	<1	1	<1	1	1	3	4	0.57
B	<1	3	7	9	6	8	10	19	0.70
C	1	1	3	4	4	4	20	29	0.27
D	1	3	2	2	3	4	1	4	0.77
G	1	2	9	17	8	14	23	21	0.60
at origin	<1	1	2	<1	4	<1	3	4	

[a] See Figure 1 for structures.

Recovery studies with three replicate soil samples (Flanagan silt loam) fortified with 4 ppm [^{14}C]hexazinone, dried, ballmilled, extracted, and analyzed by TLC using the described procedure, show that an average of 94% of the added hexazinone was recovered.

The degradation of hexazinone in greenhouse-treated soils was similar to the degradation in field-treated soils. The time required for 50% degradation was less than 4 months in both soil types (Table IV). The half-life for total radioactive resudies was greater than 6 months; 65% and 68% of the applied ^{14}C was present in Fallsington sandy loam and Flanagan silt loam soils, respectively, after a 6-month greenhouse exposure. The major metabolites in the greenhouse soils were compounds A, B, and D (Figure 1, Table IV) in contrast to the field studies, where compound C was the major metabolite.

No degradation of hexazinone or loss of radioactivity occurred when Fallsington sandy loam and Flanagan silt

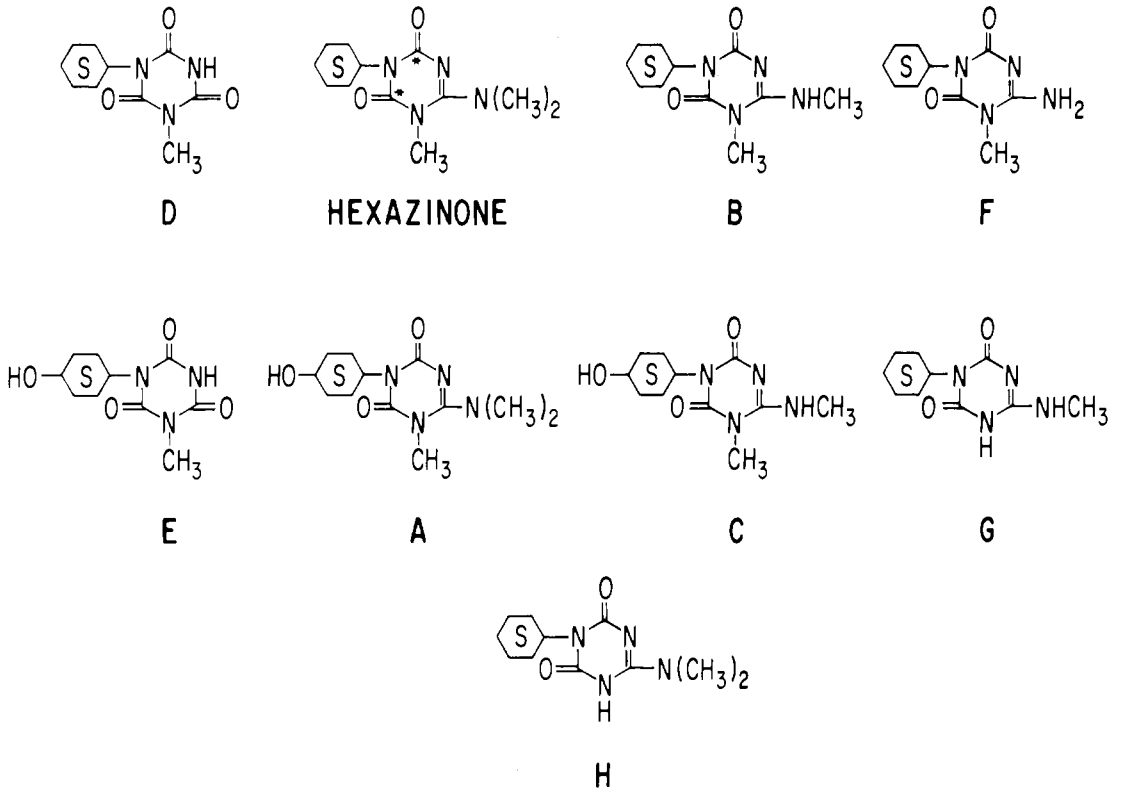

Figure 1. Structures of hexazinone degradation products. Metabolite A, 3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione; metabolite B, 3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione; metabolite C, 3-(4-hydroxycyclohexyl)-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione; metabolite D, 3-cyclohexyl-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione; metabolite E, 3-(4-hydroxycyclohexyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione; metabolite F, 3-cyclohexyl-6-amino-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione; metabolite G, 3-cyclohexyl-6-(methylamino)-1,3,5-triazine-2,4(1*H*,3*H*)-dione; and metabolite H, 3-cyclohexyl-6-(dimethylamino)-1,3,5-triazine-2,4(1*H*,3*H*)-dione. (*) Denotes position of label.

Table IV. Analysis of [^{14}C]Hexazinone Treated Soils (Greenhouse)[a]

compd	percent of extracted radioactivity[b]	
	Fallsington sandy loam	Flanagan silt loam
hexazinone	39	48
A	20	6
B	20	14
C	5	1
D	3	18
E	1	6
at origin	12	7

[a] Samples taken 4 months after treatment. [b] Both samples contained 76% of the original added radioactivity.

loam, treated with 4 ppm [^{14}C]hexazinone, were maintained under anaerobic conditions for a 60-day period.

Laboratory studies in biometer flasks (Bartha and Pramer, 1965) with the two soil types treated with [^{14}C]-hexazinone indicate that hexazinone is degraded by microbial action (Figures 2 and 3). The results show that after an initial lag period of 10–20 days, the rate of $^{14}CO_2$ evolution increased rapidly. After 80 days, 45–75% of the applied radioactivity had been evolved as $^{14}CO_2$. All radioactivity in the caustic traps was precipitated with $BaCl_2$, indicating that the trapped radioactivity was [^{14}C]-carbonate from evolved CO_2. These data suggest that the triazine ring is totally degraded to liberate $^{14}CO_2$. No $^{14}CO_2$ was detected in the treated sterile Fallsington sandy loam, and only trace amounts were found from the treated sterile Flanagan silt loam.

The soil TLC R_f values (Table V) place hexazinone in Class 4 of the mobility classification scheme of Helling and

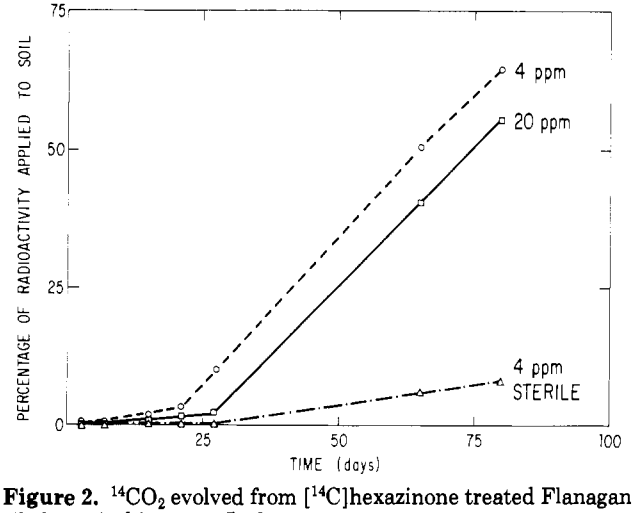

Figure 2. $^{14}CO_2$ evolved from [^{14}C]hexazinone treated Flanagan silt loam in biometer flasks.

Table V. Soil TLC of DPX-3674

	soil TLC R_f values		
	hexazinone	terbacil	diuron
Flanagan silt loam	0.68	0.47	0.20
Fallsington sandy loam	0.85	0.72	0.35
Keyport silt loam	0.75	0.58	0.24
Cecil loamy sand	0.90	0.85	0.42

Turner (1968) and show that it is somewhat more mobile than terbacil in this type of laboratory comparison test. Soil TLC data for the comparison standards, diuron and terbacil, have been reported by Rhodes et al. (1970), Helling (1971a,b,c,), and Helling et al. (1971). The soil K

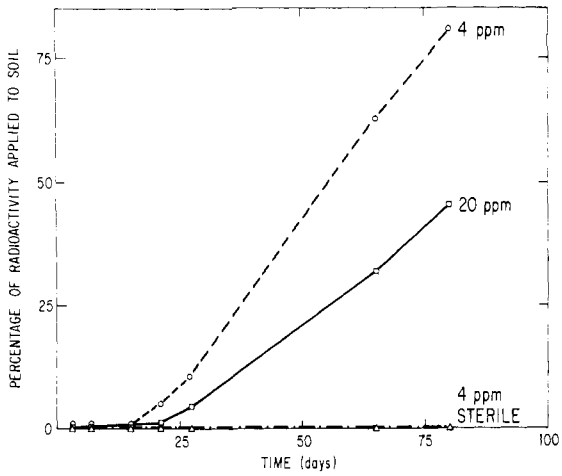

Figure 3. $^{14}CO_2$ evolved from [^{14}C]hexazinone treated Fallsington sandy loam in biometer flasks.

values for hexazinone on Fallsington sandy loam and Flanagan silt loam were 0.2 (slope 0.95) and 1.0 (slope 1.05), respectively. These K values are consistent with data for mobile (Class IV) compounds.

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Photolysis of *N*-Nitrosodi-*n*-propylamine in Water

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The photolysis of the dialkyl nitrosamine *N*-nitrosodi-*n*-propylamine (NDPA) has been studied in lake water and several other aqueous systems. In lake water sunlight photolysis experiments, dissipation of NDPA was significant but variable. Other laboratory studies demonstrated NDPA photodegraded readily in neutral solution and the photodegradation rate was not pH dependent in the 3 to 9 range. The major photoproduct was found to be *n*-propylamine, but the formation of di-*n*-propylamine was also observed.

N-Nitroso-di-*n*-propylamine (NDPA) has been found as a trace contaminant in the herbicide trifluralin (Ross et al., 1977) (TREFLAN, Elanco Products Co., Indianapolis, IN. Trace amounts of NDPA could enter the environment by application of the herbicide to soil. NDPA is readily water soluble [solubility, 10 000 ppm; Mirvish et al. (1976)] and has been shown to move with soil moisture (Saunders et al., 1979), suggesting the chemical might enter natural waters with rainfall runoff.

Though the possibility of water contamination by trace amounts of NDPA exists, no measurable amounts of NDPA in natural waters have been reported. Ross et al. (1978) was unable to detect NDPA in irrigation water taken from a trifluralin-treated field. In work reported by West and Day (1978), no NDPA was found in water samples taken from ponds in areas treated annually with trifluralin for several years. However, because of the potential hazards associated with dialkyl nitrosamines such as NDPA, a study was undertaken to determine the fate of NDPA in water.

Though dialkyl nitrosamines are readily degraded by light under laboratory conditions (Burns and Alliston, 1971; Polo and Chow, 1976), only limited information on their stability in natural waters is available (Tate and Alexander, 1975). This report is concerned with the stability of NDPA in lake water under natural conditions. Additional laboratory studies were conducted to determine factors affecting the photolysis rate in water as well as to identify and quantify NDPA photolysis products.

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EXPERIMENTAL SECTION

Chemicals. NDPA was prepared by nitrosation of the amine and purified by vacuum distillation (bp 81 °C at 5 torr). [1-^{14}C]NDPA was obtained from New England Nuclear (Boston, MA). The radiochemical purity was determined to be greater than 98% by thin-layer chromatography and radioautography, and the specific activity was 28.0 μCi/mg.

Di-*n*-propylamine (DPA) (Aldrich Chemical Co., Inc., Milwaukee, WI) and *n*-propylamine (NPA) (MC/B, Norwood, OH) were redistilled prior to use. 2,6-Dinitrofluorobenzene (DNFB) (Eastman Organic Chemicals, Rochester, NY) was used as received. Di-*n*-propyl-2,6-dinitroaniline (DPA-DNFB) and *n*-propyl-2,6-dinitroaniline (NPA-DNFB) were synthesized by the method of Day et al. (1966). Potassium ferrioxalate was prepared according to the method of Hatchard and Parker (1956). *N'*-Hydroxy-*N*-propylpropanimidamide was prepared by reaction of hydroxamoyl chloride with *n*-propylamine.

All samples containing NDPA were handled with extreme care. Undiluted NDPA was stored and handled in a glovebox equipped with a charcoal filter and maintained under negative pressure. All laboratory work with dilute

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