

US EPA ARCHIVE DOCUMENT

**ENVIRONMENTAL FATE AND EXPOSURE
ASSESSMENT OF METSULFURON METHYL**

Final Report

**REVIEW AND EVALUATION OF DATA
SUBMITTED SUBSEQUENT TO THE
INITIAL REVIEW**

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Submitted to:
Environmental Protection Agency
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STUDY 1

McFetridge, R.D. and G.E. Cadwgan. 1985. Photodegradation of [triazine-2-¹⁴C]metsulfuron methyl in water. Document No. AMR-451-85. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 074003. Exhibit 1.

CONCLUSIONS:

Degradation - Photodegradation in Water

MMO 153321

1. This study is scientifically valid.
2. Triazine-labeled [¹⁴C]metsulfuron methyl, at 5 ppm, did not photodegrade in aqueous buffer solutions (pH 5, 7, and 9) maintained outdoors in Wilmington, Delaware. At 35 days after treatment, metsulfuron methyl concentrations were similar for irradiated and dark control samples at each pH (~23% at pH 5, ~97-98% at pH 7, and ~90% at pH 9). At pH 5 both the light and dark 35 day samples contained 23 percent metsulfuron methyl.
3. This study fulfills EPA Data Requirements for Registering Pesticides by showing that metsulfuron methyl is stable to photolysis in aqueous buffer solutions at pH 5, 7, and 9.

MATERIALS AND METHODS:

Aqueous buffer solutions were prepared at pH 5, 7, and 9, and sterilized by autoclaving for 30 minutes at 15 psi and 270 F. Then, 150 ml aliquots at each pH were treated with triazine-labeled [¹⁴C]metsulfuron methyl (specific activity 35.4 μ Ci/mg, >99% pure, New England Nuclear) at 5 ppm. Samples at each pH were placed outdoors in water baths (25 C) in Wilmington, Delaware, from August 13, 1985 to September 17, 1985. Solar radiation during the test period, measured using a pyranometer, is shown in Table 1. Additional samples were maintained at 25 C in darkness. Samples at pH 7 were connected to a gas washing bottle containing sodium hydroxide to trap evolved ¹⁴CO₂.

Samples (4 ml) were taken at 0, 1, 7, 14, 21, 28, and 35 days, and aliquots were quantified by LSC to determine total radioactivity. The trapping solution (pH 7 only) was removed at each sampling interval, quantified by LSC, and replaced with fresh solution. Additional aliquots of the pH 7 and 9 test solutions were analyzed by reverse phase HPLC.

REPORTED RESULTS

Total recovery of radioactivity from the test solutions is shown in Table 2. Concentrations of metsulfuron methyl were similar at each pH for irradiated and dark control samples during the test period, indicating that photodegradation of metsulfuron methyl did not occur (Table 3). Metsulfuron methyl degraded in pH 5 solutions with a half-life of 14-21 days, and declined to ~23% of the recovered radioactivity by 35 days after treatment. At pH 7, metsulfuron methyl comprised 95.6-98.4% of the radioactivity recovered by day 35; the remainder was composed of 4-methoxy-6-methyl-1,3,5-triazine-2-amine and two or three minor compounds. Metsulfuron methyl comprised ~90% of the

recovered radioactivity in pH 9 buffer solutions at day 35. 4-Methoxy-6-methyl-1,3,5-triazine-2-amine was present at <1%, and three or four unidentified compounds each accounted for <8% of the recovered.

DISCUSSION:

Although degradates were not characterized in pH 5 solutions, degradate identification (at >10%) is required only for one pH at which hydrolytic degradation is minimized. At pH 5, hydrolysis was apparently responsible for degradation of metsulfuron methyl in aqueous photolysis studies.

Table 1. Sunlight intensity during the test period.

Sampling date	Intensity (watt-hours/m ²)
8/13/85 ^a	5148
8/14/85	5984
8/15/85	6508
8/16/85	5108
8/17/85	5556
8/18/85	1372
8/18/85	4846
8/19/85	4250
8/20/85	3582
8/21/85	5569
8/22/85	5285
8/23/85	5455
8/24/85	1261
8/25/85	4496
8/26/85	5613
8/27/85	6168
8/28/85	5607
8/29/85	4247
8/30/85	3169
9/01/85	4184
9/02/85	5196
9/03/85	5082
9/04/85	5690
9/05/85	5908
9/06/85	4891
9/07/85	5440
9/08/85	3552
9/09/85	3454
9/10/85	4301
9/11/85	5264
9/12/85	5966
9/13/85	4932
9/14/85	6113
9/15/85	6189
9/16/85	5651
9/17/85 ^b	644
Average	4906

a Test day began at 10:00 a.m.

b Test day ended at 10:00 a.m.

Table 2. Total radioactivity (ppm) in pH 5, 7, and 9 buffer solutions treated with [¹⁴C]metsulfuron methyl at 5 ppm.

Sampling interval (days)	pH 5		pH 7		pH 9	
	Irradiated	Dark	Irradiated	Dark	Irradiated	Dark
0	5.20	5.20	5.00	5.00	4.47	4.47
1	5.30	5.15	4.94	4.94	4.49	4.47
2.2	5.41	5.36	--	--	--	--
7	5.39	5.30	5.09	5.09	4.58	4.50
14	5.30	5.29	5.08	5.07	4.54	4.50
21	5.47	5.26	5.09	5.09	4.55	4.50
28	5.30	5.32	5.12	5.08	4.55	4.53
35	5.37	5.31	5.11	5.08	4.55	4.50

^a Total radioactivity recovered as ¹⁴CO₂ was <1 ppb.

Table 3. Concentration of metsulfuron methyl (% of recovered) in pH 5, 7, and 9 buffer solutions treated with [¹⁴C]metsulfuron methyl at 5 ppm.

Sampling interval (days)	pH 5		pH 7		pH 9	
	Irradiated	Dark	Irradiated	Dark	Irradiated	Dark
0	98.1	98.1	98.9	98.9	99.3	99.3
1	93.5	95.0	98.6	100.7	98.8	99.6
2.2	91.2	92.0	--	--	--	--
7	74.9	75.0	99.3	98.5	96.5	96.2
14	56.8	54.8	98.0	99.0	94.0	95.1
21	42.2	41.1	96.3	99.0	92.1	94.8
28	33.3	30.5	97.4	98.3	92.3	90.5
35	23.3	23.1	95.6	98.4	89.1	90.2

STUDY 2

Buchta, R.C. 1985. Photodegradation of [triazine-2-¹⁴C]metsulfuron methyl on soil. Document No. AMR-450-85. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 074003. Exhibit 2.

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is scientifically valid.
2. Triazine-labeled [¹⁴C]metsulfuron methyl, at 0.5 oz ai/A, did not photodegrade on Keyport silt loam soil maintained outdoors in Wilmington, Delaware. At 30 days after treatment, metsulfuron methyl accounted for ~10-11% of the extractable radioactivity in both irradiated and dark control soil samples. Five unidentified degradates accounted for up to 30.8% of the extractable radioactivity at the end of the test period.
3. This study fulfills EPA Data Requirements for Registering Pesticides by showing that metsulfuron methyl is stable to photodegradation on Keyport silt loam soil.

MATERIALS AND METHODS:

Keyport silt loam soil (11% sand, 78% silt, 11% clay, 4.7% organic matter, pH 4.3, CEC 14.1 meq/100 g) was applied as a slurry to glass TLC plates (20 x 20 cm) and was treated with triazine-labeled [¹⁴C]-metsulfuron methyl (specific activity 35.4 μ Ci/mg, >98% pure, New England Nuclear) at 0.5 g ai/A. Soil samples were placed outdoors in Lucite boxes at Wilmington, Delaware from June 26, 1985 to July 26, 1985. Two soil samples were protected from light to serve as dark controls. All soil samples were maintained at 25 C; selected samples were connected to vacuum pumps so that air passing through the boxes was drawn through an impinger containing 1 N NaOH to trap evolved ¹⁴CO₂. Solar radiation during the test period, measured using a pyranometer, is shown in Table 1.

Irradiated soil samples were taken at 0, 2, 4, 7, 15, 22, and 30 days; dark controls were sampled at day 15 and 30. Soil samples were scraped from the plates, the plates were rinsed with the extraction solvent described below, and the plate rinse was quantified by LSC. Soil samples were extracted three times with methylene chloride:methanol:2 M ammonium carbonate (3:4:1, v:v:v), and a portion of the combined extracts was quantified by LSC. A separate portion was reduced in volume, centrifuged, and the supernatant analyzed using reverse-phase HPLC. The extracted soil residue was air dried, combusted, and the evolved ¹⁴CO₂ trapped and quantified by LSC. The NaOH trapping solution was quantified by LSC.

REPORTED RESULTS:

Total recovery of radioactivity from the soil samples is shown in Table 2. Amounts of metsulfuron methyl for irradiated and dark

control soil samples were similar during the test period, indicating that photodegradation of metsulfuron methyl did not occur (Table 3). The half-life for metsulfuron methyl on irradiated soil was 4-7 days; 10.1 and 11.3% of the extractable radioactivity remained as parent compound in irradiated and dark control soil samples, respectively, at 30 days posttreatment. Five unidentified compounds accounted for up to 30.8% of the extractable radioactivity at day 30.

DISCUSSION:

Degradates were not characterized; however, identification is required only for photoproducts occurring at >10%, and the data indicate that photolytic degradation of metsulfuron methyl did not occur. Hydrolysis was apparently responsible for degradation of metsulfuron methyl (in the pH 4.3 Keyport soil) during the soil photolysis study.

Table 1. Sunlight intensity during the test period.

Sampling date	Intensity (watt-hours/m ²)
6/27/85	5522
6/28/85	3783
6/29/85	4491
6/30/85	5583
7/01/85	5449
7/02/85	4929
7/03/85	6625
7/04/85	5997
7/05/85	6459
7/06/85	4308
7/07/85	5072
7/08/85	7378
7/09/85	3553
7/10/85	7011
7/11/85	4231
7/12/85	7350
7/13/85	4693
7/14/85	7164
7/15/85	5883
7/16/85	4531
7/17/85	5577
7/18/85	8133
7/19/85	7464
7/20/85	7141
7/21/85	6075
7/22/85	6274
7/23/85	7011
7/24/85	8230
7/25/85	7379
7/26/85	4793

Table 2. Total radioactivity (% of applied) in Keyport silt loam soil samples treated with [¹⁴C]metsulfuron methyl.

Sampling interval (days)	Extractable	Unextractable	¹⁴ C ₀₂	Plate rinse	Total
<u>Irradiated soil</u>					
0	101	0.6	0	0.2	102
2	96.5	2.2	--	0.3	99
4	95.9	3.0	--	0.1	99
7	96.3	3.4	0.003	0.2	100
15	94.8	4.2	0.089	0.4	100
22	96.0	4.5	0.23	0.1	101
30	94.0	3.5	0.42	0.1	98
<u>Dark Control</u>					
15	98.5	2.2	0.048	0.2	101
30	96.2	5.4	0.30	0.1	102

Table 3. Distribution of radioactivity (% of extracted) in Keyport silt loam soil samples treated with [¹⁴C]metsulfuron methyl.

Sampling interval (days)	Peak #1	Peak #2	Peak #3	Peak #4	Peak #5	Metsulfuron methyl
<u>Irradiated soil</u>						
0	0.0	0.0	0.4	0.0	2.0	97.0
2	4.1	0.5	11.9	3.9	11.7	67.3
4	4.2	0.8	9.8	6.0	15.5	62.5
7	16.6	1.8	27.4	9.1	13.6	30.5
15	19.8	2.1	20.9	12.9	19.7	23.5
22	24.6	2.8	21.6	13.9	21.1	15.0
30	29.4	2.2	25.1	14.3	17.8	10.1
<u>Dark control</u>						
15	15.0	1.9	19.4	7.8	25.5	29.6
30	25.5	1.2	21.6	9.0	30.8	11.3

STUDY 3

Chrzanowski, R.L. 1984a. Degradation of ^{14}C -DPX-W4189 in anaerobic aquatic environments. Document No. AMR-38-81. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 260973.

This study was submitted to provide surrogate data for the fate of the triazine moiety of metsulfuron methyl. The triazine moiety of this chemical (chlorsulfuron) is identical to that of metsulfuron methyl.

CONCLUSIONS:

Metabolism - Anaerobic Aquatic

1. This study is scientifically valid.
2. Triazine-labeled [^{14}C]chlorsulfuron (radiochemical purity >99%), at 1 ppm, degraded with a half-life of 16-52 weeks in sterile and >52 weeks in nonsterile silt loam soil incubated under nitrogen gas in the dark at 25 C. The major degradate was 2-amino-4-methoxy-6-methyl-1,3,5-triazine. Phenyl-labeled [^{14}C]chlorsulfuron (radiochemical purity >99%), at 1 ppm, degraded with a half-life of >10 weeks in flooded and nonflooded anaerobic soils. The major degradates were 2-amino-4-methoxy-6-methyl 1,3,5-triazine (21-25% of applied at week 52) in the triazine-labeled treatment and 2-chlorobenzene-sulfonamide (up to 14%) in the phenyl-labeled treatments.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides because no apparent attempt was made to characterize up to 18% of the degradates, the moisture content of the nonflooded soils was not specified, and the phenyl-labeled treatments were not studied long enough to establish a half-life. This study is satisfactory to provide surrogate data for the fate of the triazine moiety of metsulfuron methyl.

MATERIALS AND METHODS:

Samples (50-g) of silt loam soil from Pennsylvania (Table 1) were moistened with 100 ml of pond water (uncharacterized) and amended with ground alfalfa; the flasks were purged with nitrogen gas and incubated in the dark at 25 C for 30 days. Following the anaerobic aging, several samples were sterilized by autoclaving and treated with 100 ml of a 0.1% sodium azide solution (to maintain sterility) to serve as sterile controls for the study. Then, half of the samples (sterile and nonsterile) were treated with phenyl-labeled [^{14}C]chlorsulfuron (radiochemical purity >99%, specific activity 6 $\mu\text{Ci}/\text{mg}$) at 1 ppm. The remaining samples were treated with triazine-labeled [^{14}C]chlorsulfuron (radiochemical purity >99%, specific activity 15 $\mu\text{Ci}/\text{mg}$) at 3 ppm. The flasks were purged with nitrogen gas, resealed, and returned to the dark at 25 C. The phenyl-labeled [^{14}C]chlorsulfuron treatments were sampled 0, 1, 4, and 10 weeks posttreatment. The triazine-labeled treatments were sampled 0, 2, 8, 16, and 52 weeks posttreatment.

The pH and O_2 level in the soils were determined immediately after sampling. The samples were centrifuged to separate the soil and water phases; the soil was mixed with additional water, centrifuged, and the wash water added to the original water from the sample. Aliquots of the water were analyzed for total radioactivity by LSC and for specific compounds using TLC on silica gel plates developed in methylene chloride:methanol:concentrated ammonium hydroxide (144:50:6, v:v:v). Radioactive compounds were located by radioscaner and autoradiography, identified by comparison to standards, and quantified by LSC. The soil was extracted with 5% ammonium carbonate in methanol:water (2:1, v:v) and with methanol. The extracts were combined and analyzed by TLC as described. The extracted soil was analyzed for remaining radioactivity by LSC following combustion.

In a related study, soil samples (50 g) were treated with phenyl-labeled [^{14}C]chlorsulfuron and flooded with distilled water. The flasks were purged with nitrogen gas and incubated in the dark at 25 C. Samples were analyzed 0 and 3 days and 1, 2, 3, 4, 5, and 8 weeks posttreatment. The samples were analyzed using LSC and TLC as described.

REPORTED RESULTS:

In the anaerobically aged soil treated with phenyl-labeled [^{14}C]chlorsulfuron, >66% of the chlorsulfuron remained undegraded after 10 weeks of incubation (Table 2). At 52 weeks, 37% of the triazine labeled [^{14}C]chlorsulfuron remained in the sterilized soil and 54% in the unsterilized soil (Table 3). The major radioactive degradates were 2-chlorobenzene-sulfonamide in the phenyl-labeled treatment and 2-amino-4-methoxy-6-methyl-1,3,5-triazine in the triazine labeled treatment.

In the unaged flooded soils, phenyl-labeled [^{14}C]chlorsulfuron degraded with a half-life of >8 weeks, 2-chlorophenylsulfonamide and 2-chlorobenzene-sulfonamide were the major degradates (Table 4).

DISCUSSION:

1. With the exception of the study using triazine labeled [^{14}C]chlorsulfuron, the experiments were of insufficient duration.
2. In the nonflooded soils, the moisture content of the soils was not specified.
3. No attempt was made to characterize the unidentified residues, although these comprised up to 18% of the applied.

Table 1. Soil characteristics.

Soil type	Source	Sand	Silt	Clay %	Organic matter	pH	CEC (meq/100 g)
Silt loam	Pennsylvania	25.0	74.0	1.0	3.7	5.6	11.0
Silt loam	Canada	35.5	51.5	13.0	7.6	8.4	24.9
Loam	Nebraska	40.0	47.0	13.0	6.5	8.3	23.6
Silty clay loam	Illinois	5.0	64.0	31.0	4.0	5.0	23.4

a Used in the anaerobically aged (30-day) study.

b Used in the unaged flooded soil study.

Table 2. Phenyl-labeled [¹⁴C]chlorsulfuron and its degradates (% of applied) in sterile and nonsterile silt loam soil treated at 1 ppm with [¹⁴C]chlorsulfuron (radiochemical purity >99%) and incubated under anaerobic conditions in the dark at 25 C.

Compound	Sampling interval (weeks)			
	0	1	4	10
<u>Nonsterile</u>				
2-Chlorobenzene-sulfonamide	ND ^a	1.5	6.1	14
Chlorsulfuron	100	96	83	75
2-Chlorophenylsulfonylurea	ND	3.1	0.5	2.1
2-Chloro-5-hydroxy-benzene-sulfonamide	ND	ND	ND	ND
Unidentified	ND	1.5	2.8	11
Nonextractable	0.1	1.0	1.9	1.0
<u>Sterile</u>				
2-Chlorobenzene-sulfonamide	ND	2.1	5.4	13
Chlorsulfuron	100	102	83	66
2-Chlorophenylsulfonylurea	ND	0.5	0.3	2.2
2-Chloro-5-hydroxy-benzene-sulfonamide	ND	ND	ND	ND
Unidentified	ND	1.6	5.6	9
Nonextractable	ND	1.1	1.0	1.3

^a Not detected; detection limit was 0.1% of the applied.

Table 4. Phenyl-labeled [¹⁴C]chlorsulfuron and its degradates (% of applied) in flooded soils treated at 1 ppm and incubated under anaerobic conditions in the dark at 25 C.

Sampling interval (weeks)	2-Chlorobenzene sulfonamide	Chlor-sulfuron	2-Chlorophenyl-sulfonurea	2-Chloro-5-hydroxy-benzene-sulfonamide	Un-identified	Unextractable
<u>Silt loam</u>						
0	ND ^a	90	ND	ND	ND	10
1	ND	92	ND	ND	ND	5
2	4.1	84	4.1	ND	ND	10
4	1.0	88	8.2	ND	ND	5.1
8	11	50	14	ND	18	14
<u>Loam</u>						
0	ND	92	ND	ND	ND	8
0.5	ND	94	ND	ND	ND	12
3	17	49	7	ND	ND	14
5	3.2	82	12	ND	ND	9.6
<u>Silty clay loam</u>						
0	ND	98	ND	ND	ND	2
1	ND	89	ND	ND	1.4	8.5
2	13	67	11	ND	ND	9.0
4	13	66	9.1	ND	ND	13

^a Not detected; the detection limit was 0.1% of the applied.

STUDY 4

NR10 86817

Han, J.C.-Y. 1984a. ¹⁴C-DPX-W4189 soil disappearance studies in the field. Document No. AMR-54-81. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 260974.

This study was submitted to provide surrogate data for the fate of the triazine moiety of metsulfuron methyl. The triazine moiety of this chemical (chlorsulfuron) is identical to that of metsulfuron methyl.

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.
2. Triazine-labeled [¹⁴C]chlorsulfuron (radiochemical purity >99%) degraded with a half-life of 2-4 weeks in silt loam soil treated at 100 g ai/A. The degradate, 2-amino-4-methoxy-6-methyl-1,3,5-triazine, reached maximum levels of ~40-48% of the applied 2-4 weeks after treatment.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the fate of the triazine moiety in field studies.

MATERIALS AND METHODS:

Stainless steel cylinders (11.5 cm diameter x 38 cm height) were driven into field plots of silt loam soil (16.2% sand, 72.8% silt, 11.0% clay, 1.4% organic matter, pH 6.0, CEC 7.73 meq/100 g) located at Newark, Delaware. To minimize runoff and splashing, ~2.5 cm of rim was left above the soil surface. The soil surface was then treated with triazine-labeled [¹⁴C]chlorsulfuron (specific activity 12.0 μ Ci/mg, radiochemical purity >99%, New England Nuclear) at 100 g ai/ha. at 0, 2, 4, 8, 16, 26, 52, and 77 weeks after treatment, soil cylinders were sampled and divided into 0-5, 5-10, 10-20, and 20-38 cm segments.

Soil samples (50 g) were refluxed with 150 ml of 5% ammonium carbonate in methanol:water (2:1, v:v), cooled, and centrifuged. The supernatant was decanted, and the soil was washed with methanol. The supernatant and methanol solutions were combined, concentrated, and partitioned between distilled water and ethyl acetate. After phase separation, the two solutions were concentrated and analyzed by TLC. The extracted soil residues were analyzed by combustion.

REPORTED RESULTS:

Rainfall during the test period totalled 1102 mm. Total radioactivity dissipated from the soil cylinders with a half-life >77 weeks (Table 1). Leaching into lower soil depths was evident; <20% of the applied radioactivity remained in the 0-5 cm soil depth by the end of the test period. Parent chlorsulfuron was present at ~76% of the applied at time 0, and reached a half-life within 4 weeks (Table 2). The degradate, 2-amino-4-methoxy-6-methyl-1,3,5-triazine, reached maximum levels of ~40-48% of the applied at 2-4 weeks after treatment.

DISCUSSION:

The steel cylinder procedures for evaluating terrestrial field dissipation have been approved for this study.

Table 1. Total radioactivity (% of applied) in silt loam soil cylinders treated with [¹⁴C]chlorsulfuron at 100 g ai/ha.

Sampling depth (cm)	Sampling interval: (weeks)							
	0	2	4	8	16	26	52	77
0-5	105.1	66.0	54.0	59.3	23.8	22.0	31.3	18.8
5-10	<0.1	23.0	29.4	16.7	19.0	16.5	13.2	14.5
10-20	<0.1	4.1	19.5	13.8	13.9	17.7	10.5	21.2
20-38	<0.1	<0.1	3.4	10.4	10.5	7.0	4.3	5.2
Total	105.1	93.1	104.3	100.2	67.2	63.2	59.3	59.7

Table 2. Distribution of radioactivity (% of applied) in silt loam soil cylinders treated with [¹⁴C]chlorsulfuron at 100 g ai/ha.

Sampling interval (weeks)	Sampling depth (cm)	Unextractable	Chlorsulfuron	2-Amino-4-methoxy-6-methyl-1,3,5-triazine
0	0-5	17.2	76.4	6.2
2	0-5	10.7	40.3	10.5
2	5-10	2.9	13.3	5.3
2	10-20	0.5	2.2	1.0
4	0-5	4.2	15.3	24.9
4	5-10	1.2	8.9	14.3
4	10-20	0.9	6.0	7.7
4	20-38	0.3	1.2	1.1
8	0-5	7.4	9.5	23.5
8	5-10	1.3	3.2	6.8
8	10-20	1.0	1.7	5.0
8	20-38	0.6	2.4	4.5
16	0-5	4.7	2.5	4.5
16	5-10	4.1	1.7	4.3
16	10-20	3.3	1.4	1.2
16	20-38	2.4	3.5	2.3
26	0-5	4.6	1.8	2.7
26	5-10	3.7	1.3	2.9
26	10-20	3.4	1.2	1.9
26	20-38	1.8	0.5	1.0
52	0-5	9.3	1.1	6.0
52	5-10	3.2	0.7	3.4
52	10-20	3.0	0.5	1.9
52	20-38	1.3	0.3	0.9
77	0-5	9.1	0.5	4.1
77	5-10	6.3	0.3	3.4
77	10-20	10.7	0.4	4.3
77	20-38	2.5	0.1	1.4

STUDY 5

Han, J.C-Y. 1984b. Crop rotation study with ^{14}C -DPX-W4189 in the field. Document No. AMR-46-81. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 260975.

This study was submitted to provide surrogate data for the fate of the triazine moiety of metsulfuron methyl. The triazine moiety of this chemical (Chlorsulfuron) is identical to that of metsulfuron methyl.

CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. This study is scientifically valid.
2. Neither [^{14}C]chlorsulfuron nor 2-amino-4-methoxy-6-methyl-1,3,5-triazine were detected (<1 ppb) in soybeans and rape plant in soil containing 1 ppb of chlorsulfuron and 4 ppb of 2-amino-4-methoxy-6-methyl-1,3,5-triazine; the plants did contain 1-7 ppb of uncharacterized [^{14}C]residues in various tissues.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the test substance was incompletely characterized and soil data were not provided from the time of treatment to confirm the application rate. However, this study is satisfactory to provide surrogate data for the fate of the triazine moiety of metsulfuron methyl.

MATERIALS AND METHODS:

A field plot (12 x 12 feet) of Keyport silt loam soil (16.2% sand, 72.8% silt, 11.0% clay, pH 6.0, 1.4% organic matter, CEC 7.73 meq/100 g), located near Newark, Delaware, was treated with triazine-labeled [^{14}C]chlorsulfuron (test substance uncharacterized) at 70 g ai/ha. One year after treatment, sugar beets (Mono Hy-A1), rape (Dwarf Essen), and soybeans (Kent) were planted. The sugar beets died within a month after germination. Soybeans were sampled at maturity, ~6 months after planting. Rape foliage was sampled at ~6 months, and rape seeds and foliage were sampled at maturity, ~13 months after planting. Soil samples (12-inch depth) were taken at the time of planting, and at both crop sampling intervals.

Plant tissue and seed samples were air-dried, homogenized, and extracted with acetone:water (80:20). The extract was centrifuged and the supernatant evaporated to a small volume. After adjusting the pH to 3.0 with 1N H_2SO_4 , the concentrated extract was reextracted twice with ethyl ether. The ether extracts were combined and evaporated to dryness. The remaining aqueous layer was extracted twice with n-butyl alcohol, and the combined extracts were evaporated to dryness. The ether and n-butanol fractions were analyzed by TLC along with known standards. The plates were developed in toluene:acetone (1:1, v:v) and acetonitrile:ethyl acetate:formic acid (150:50:1.5, v:v:v).

Soil samples (50 g) were refluxed with 150 ml of 5% ammonium carbonate in methanol:water (2:1, v:v), cooled, and centrifuged. The supernatant was decanted, and the soil was washed with methanol.

The supernatant and methanol solutions were combined, concentrated, and partitioned between distilled water and ethyl acetate. After phase separation, the two solutions were concentrated and analyzed by TLC using toluene:acetone (1:1, v:v) as the developing solvent. The extracted soil residues were analyzed by combustion.

REPORTED RESULTS:

Rainfall at the test site totalled ~28 inches from the time of treatment to planting.

Radioactive residues in soil samples are shown in Table 1. Total radioactivity in crop samples were: dry soybean foliage (7 ppb), edible soybean (2 ppb), rape foliage at ~6 months (4 ppb), mature rape foliage (2 ppb), rape seed (1 ppb). No parent compound or the degradate 2-amino-4-methoxy-6-methyl-1,3,5-triazine were detected (<1 ppb) in any crop sample.

DISCUSSION:

1. Residues in the soil were not determined at the time of treatment in order to confirm the application rate.
2. The specific activity and purity of the test substance was not reported.

Table 1. Radioactive residues (ppb) in soil samples from confined field plot treated with triazine-labeled [¹⁴C]chlorsulfuron, at 70 g ai/ha.

Months after treatment	Chlorsulfuron	2-Amino-4-methoxy-6-methyl-1,3,5-triazine	Total ¹⁴ C
12	1	4	29
18	ND ^a	1	15
25	ND	ND	10

^a Not detected; detection limit is 1 ppb.

EXECUTIVE SUMMARY

A previously reviewed study demonstrated that metsulfuron methyl was stable to hydrolysis at pH 7 and 9 at both 15 C and 25 C. Estimated half-lives of the parent at pH 5 were 3 weeks (25 C) and >30 days (15 C). The primary degradate was methyl 2-(aminosulfonyl)-benzoate. The hydrolytic stability of the triazine moiety was addressed in a study that showed 4-methoxy-6-methyl-1,3,5-triazine-2-amine was stable at pH 5, 7, and 9.

Triazine-labeled [¹⁴C]metsulfuron methyl did not photodegrade in aqueous buffer solutions (pH 5, 7, and 9) or on Keyport silt loam soil maintained outdoors in Wilmington, Delaware.

Triazine-labeled [¹⁴C]metsulfuron methyl, at 0.12 ppm in silt loam soil, degraded with a half-life of 120-180 days. The parent compound declined from 93.8% of the applied at day 0 to 41% of the applied by day 180. At day 180, 16.9% of the applied radioactivity consisted of unidentified polar compounds, 9.4% was unextractable, and 22.5% was evolved as ¹⁴CO₂.

Metsulfuron methyl degraded under anaerobic conditions in three simulated pond/sediment systems with calculated half-lives of ~4-11 weeks, based on first-order kinetics. Saccharin was a major but transient degradate while 2-(aminosulfonyl)-benzoic acid, the other major degradate, gradually accumulated during the 54-week study. The field dissipation data confirm that metsulfuron methyl dissipated within 2 to 4 weeks of application and leached through silt loam and sand soils confined in stainless steel cylinders.

Radioactivity from phenyl-labeled [¹⁴C]metsulfuron methyl (unaged) was largely (>87%) eluted from 12-inch columns of sandy loam, sand, silty clay loam, and silt loam soils by 20 inches of water.

A confined crop study indicates that residues may be taken up by sugarbeet, rape, oats, and soybeans planted in sandy loam soil 120 days after treatment. Residues are also taken up by oats, soybeans, rape, and sorghum planted in silt loam soil 362 days after treatment at 30 g ai/ha. Total residues were generally 3-9 ppb, but rape seed contained 31 ppb.

A fish accumulation study was not required because of the low (<1000) octanol/water coefficient.

RECOMMENDATIONS

Available data are sufficient to fully assess the environmental fate of metsulfuron methyl as well as the potential for exposure of humans and non-target organisms to metsulfuron methyl. The submission of data to fulfill registration requirements (Subparts N and K) is summarized below:

Hydrolysis studies: Two previously submitted and reviewed studies were cited in this submission. One study (Friedman, 1982, Document AMR-62-82, Acc. No. 071434) was scientifically valid and partially fulfilled data requirements, but did not address the fate of the triazine moiety. The second study (Friedman, 1982, Acc. No. 252492) supplied the appropriate information. Data requirements are satisfied; no further hydrolysis data are required.

Photodegradation studies in water: Two studies have been submitted and reviewed. One previously reviewed study (Friedman, 1984, Document No. AMR-102-82, Acc. No. 072767) does not fulfill data requirements because it was not conducted at a constant pH under sterile conditions. A second study (McFetridge and Cadgwan, 1985, Document No. AMR-451-85, Acc. No. 074003) fulfills data requirements by showing that metsulfuron methyl is stable to photolysis in aqueous buffer solutions at pH 5, 7, and 9.

Photodegradation studies on soil: Two studies have been submitted and reviewed. One previously reviewed study (Friedman, 1984, Document No. AMR-134-83, Acc. No. 072767) was reviewed but does not fulfill data requirements because the incubation temperature was too high. A second study (Buchta, 1985, Document No. AMR-450-85, Acc. No. 074003) fulfills data requirements by showing that metsulfuron methyl is stable to photodegradation on Keyport silt loam soil.

Photodegradation studies in air: No studies were submitted, but no data are required because of the low vapor pressure of metsulfuron methyl.

Aerobic soil metabolism studies: Three studies have been submitted and reviewed. One previously submitted study (Rapisarda, 1981, Acc. No. 250928) was not considered because it has been withdrawn by the registrant. The second study (Friedman, 1982, Document AMR-62-82, Acc. No. 071434) partially satisfies data requirements by providing information on the aerobic metabolism of phenyl-labeled [¹⁴C]metsulfuron methyl. The third study (Rhodes, 1985, Acc. No. 258879) partially satisfies data requirements by providing information on the metabolism of the triazine moiety of metsulfuron methyl in silt loam soil. Taken together, these studies fulfill data requirements for aerobic soil metabolism.

Anaerobic soil metabolism studies: No data were provided; however, this data requirement is waived because a valid anaerobic aquatic metabolism study has been submitted.

Anaerobic aquatic metabolism studies: One study (Friedman, 1984, Document No. AMR-134-83, Acc. No. 072767) partially fulfills data requirements by providing information on the anaerobic aquatic metabolism of phenyl-labeled [¹⁴C]metsulfuron methyl. A second study (Chrzanowski, 1984a, Acc. No. 260973) provides information on the fate of the triazine moiety. No additional data are required.

Aerobic aquatic metabolism studies: No data were submitted, but no data are required because metsulfuron methyl does not have an aquatic or aquatic impact use.

Leaching and adsorption/desorption studies: Based on previously submitted data (Friedman, 1984, Acc. No. 072767; Chrzanowski, 1984, Acc. No. 072767), all data requirements for leaching and adsorption/desorption studies have been fulfilled.

Laboratory and field volatility studies: No data were submitted, but no data are required because of the low vapor pressure of metsulfuron methyl.

Terrestrial dissipation studies: One study (Anderson and Harvey, 1984, Document No. AMR-117-83, Acc. No. 072767) was submitted and reviewed. EAB accepted the metsulfuron steel cylinder method for this study but requested

side-by-side comparison of conventional vs steel cylinder data for consideration before giving general approval of the cylinder protocol. DuPont indicated that Linuron comparison data are available and this was acceptable with EAB. On 11/8/85, du Pont indicated that a new comparison study was being initiated and new data will be generated for comparison of steel cylinders vs the conventional procedure.

In the future, for low application rate chemicals, EAB indicated that du Pont should review groundwater data screening criteria, e.g., k_d , mobility/solubility, hydrolysis, photodegradation, metabolism and field dissipation data before initiating steel cylinder studies.

If the screening criteria data do not trigger the groundwater flag, then do the cylinder studies. If the groundwater data do trigger the groundwater flag then ask EAB if:

- a) the studies can proceed or
- b) is there a need to use longer steel cylinders for estimating leaching potential?

Aquatic field dissipation studies: No data were submitted, but no data are required because metsulfuron methyl does not have an aquatic or an aquatic impact use.

Forestry dissipation studies: No data were submitted, but no data are required because metsulfuron methyl does not have a forestry use.

Long-term field dissipation studies: No data were submitted. Requirements for these data depend upon the results from the terrestrial field dissipation data. No data required.

Confined accumulation studies on rotational crops: Two studies were reviewed. One study (Harvey, 1984, Document No. AMR-120-83, Acc. No. 072767) partially fulfills data requirements by providing information on the uptake of phenyl-labeled [^{14}C] metsulfuron methyl by soybeans, rape, oats, and sugarbeets planted 120 days after treatment. The second study (Anderson, 1984, Document No. AMR-190-84, Acc. No. 072767) does not fulfill data requirements because climatic data were not reported. No additional data are required.

Field accumulation studies on rotational crops: No data were submitted. Data requirements are dependent upon confined accumulation studies on rotational crops. No data required.

Accumulation studies on irrigated crops: No data were submitted; however, data are not required because metsulfuron methyl has no aquatic food crop or aquatic noncrop use, is not used in and around holding ponds used for irrigation purposes, and has no uses involving effluents or discharges to water used for crop irrigation.

Laboratory studies of accumulation in fish: No additional data were submitted; however, no data are required because the octanol/water coefficient is <1000 .

Field accumulation studies on nontarget organisms: No data were submitted; requirements for these studies depend upon the results from laboratory studies of accumulation in fish and toxicological data. No data are required because of low potential for residue accumulation in fish.

References

Anderson, J.J. 1984. Crop rotation study with ^{14}C metsulfuron methyl in the field. Document No. AMR-190-84. Acc. No. 072767. (Included by reference not reviewed here).

Anderson, J.J. and J. Harvey. 1984. Field dissipation study of DPX-T6376 in Delaware, North Carolina, Florida and Mississippi. Document No. AMR-117-83. Acc. No. 072767. (Included by reference not reviewed here).

Buchta, R.C. 1985. Photodegradation of [triazine-2- ^{14}C]metsulfuron methyl on soil. Document No. AMR-450-85. Acc. No. 074003.

Chrzanowski, R.L. 1984a. Degradation of ^{14}C -DPX-W4189 in anaerobic aquatic environments. Document No. AMR-38-81. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 260973.

Chrzanowski, R.L. 1984b. Soil column leaching studies with [^{14}C]-DPX-T6376. Document No. AMR-82-82. Acc. No. 072767. (Included by reference not reviewed here).

Friedman, P. 1982. Aerobic soil metabolism of [^{14}C]phenyl-labeled-DPX-T6376. Document No. AMR-75-82. Acc. No. 071434. (Included by reference not reviewed here).

Friedman, P. 1982. Hydrolysis of ^{14}C -phenyl-DPX-T6376. Document No. AMR-62-82. Acc. No. 071434. (Included by reference not reviewed here).

Friedman, P. 1983. Hydrolysis of ^{14}C -4-methoxy-6-methyl-1,3,5-triazine-2-amine. Document No. AMR-136-83. Acc. No. 25492. (Included by reference not reviewed here).

Friedman, P. 1984. Aqueous photolysis of ^{14}C -DPX-T6376. Document No. AMR-102-82. Acc. No. 072767. (Included by reference not reviewed here).

Friedman, P. 1984. Photodegradation of ^{14}C -phenyl-DPX-T6376 on soil. Document No. AMR-77-82. Acc. No. 072767. (Included by reference not reviewed here).

Friedman, P.L. 1984. Anaerobic aquatic metabolism of [^{14}C -phenyl]-metsulfuron methyl. Document No. AMR-134-83. Acc. No. 072767. (Included by reference not reviewed here).

Friedman, P.L. 1984. Adsorption of ^{14}C -DPX-T6376 on soil. Document No. AMR-82-82. Acc. No. 072767. (Included by reference not reviewed here).

Han, J. C-Y. 1981. ^{14}C -DPX-W4189. Soil disappearance studies in the field. Document No. AMR-54-81. Acc. No. 250928. (Included by reference not reviewed here).

Han, J.C-Y. 1984a. ^{14}C -DPX-W4189 soil disappearance studies in the field. Document No. AMR-54-81. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 260974.

Han, J.C-Y. 1984b. Crop rotation study with ^{14}C -DPX-W4189 in the field. Document No. AMR-46-81. E.I. du Pont de Nemours and Company, Wilmington, DE. Acc. No. 260975.

Han, J. C-Y. 1982. Residue studies with [^{14}C]-DPX-T6376 in bluegill sunfish. Document No. AMR-81-81. Acc. No. 252492. (Included by reference not reviewed here).

Harvey, J. 1984. Crop rotation study with ^{14}C -DPX-T6376 in the greenhouse. Document No. AMR-120-83. Acc. No. 072767. (Included by reference not reviewed here).

McFetridge, R.D. and G.E. Cadwgan. 1985. Photodegradation of [triazine-2- ^{14}C]metsulfuron methyl in water. Document No. AMR-451-85. Acc. No. 074003.

Rapisarda, C. 1981. Microbial degradation of ^{14}C -DPX-4189 in soil. Report No. AMR-43-81. Acc. No. 250928. (Included by reference not reviewed here).

Rhodes, B.C. 1985. Aerobic soil metabolism of [2- ^{14}C]4-methoxy-6-methyl-1,3,5-triazine-2-amine (Interim Report). Acc. No. 258879. (Included by reference not reviewed here).