

**DPX-M6316**

**Final Report**

**Task 1: Review and Evaluation of  
Individual Studies**

**Task 2: Environmental Fate and  
Exposure Assessment**

**Contract No. 68-02-4250**

**MARCH 23, 1987**

**Submitted to:**  
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## INTRODUCTION

According to the submitted label, DPX-M6316 is an herbicide recommended for selective postemergent control of various broadleaf weeds in wheat and barley. The proposed application rate is 0.33-0.67 oz ai/A (9.4-19 g). DPX-M6316 is formulated as a single active ingredient product (75% G) and applied as a spray by air or ground equipment.

CASE GS -- DPX-M6316 STUDY 1 PM --

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CHEM 128845 DPX-M6316

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT  
-----FICHE/MASTER ID No MRID CONTENT CAT 01  
Rhodes, B.C., M.K. Koeppel, and R.W. Reiser. 1986. Hydrolysis of <sup>14</sup>C-DPX-  
M6316. Document No. AMR-224-84. E.I. du Pont de Nemours and Company, Inc.,  
Wilmington, DE. Acc. No. 263760. Reference 1.  
-----SUBST. CLASS = S.  
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CONCLUSIONS:Degradation - Hydrolysis

1. This study is scientifically valid.
2. Thiophene-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purity >99%), at 0.5 and 5.0 ppm, degraded with half-lives of 3-6 days in sterile aqueous buffered solutions of pH 5 and >30 days in aqueous buffered solutions of pH 7 and 9. 2-Ester-3-sulfonamide was the major degradate at pH 5 (62-64% of the applied at day 30) and the only degradate at pH 7 (9-10% of the applied) and 9 (4-8% of the applied). 2-Ester-3-triuret and O-demethyl DPX-M6313 were detected in pH 5 solutions at maximum concentrations of 8-32% and 4-7% of the applied, respectively. In a related study, triazine amine was the major degradate of triazine-labeled [<sup>14</sup>C]DPX-M6316 at pH 5.
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 at pH 5, 7, and 9.

## MATERIALS AND METHODS:

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%, specific activity 23.1  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) was added at 0.5 and 5.0 ppm to sterile aqueous buffered solutions adjusted to pH 5, 7, and 9. The solutions were incubated in the dark at 25°C. Aliquots of each solution were removed for analysis at intervals up to 30 days posttreatment.

Aliquots of each sample were analyzed for total radioactivity by LSC. The remaining samples were adjusted to pH 3-4 with dilute acetic acid and partitioned three times with methylene chloride. Aliquots of each methylene chloride composite were concentrated, separated using TLC, and identified by comparison to standards. TLC plates were developed in ethylene dichloride:methanol:ammonium hydroxide (145:150:5). The nonradiolabeled standards were located on the developed plates by fluorescence quenching, and radiolabeled DPX-M6316 and degradates were located and quantified using TLC linear analysis and autoradiography. Aliquots of the methylene chloride concentrates were dissolved in acidic water (pH 2):acetonitrile (75:25) and analyzed using HPLC.

In a related study, either thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%, specific activity 23.1  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) or triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%, specific activity 33.9  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) were dissolved at 260 ppm in sterile buffered pH 5 solutions. The solutions were incubated in the dark at 25°C for 31 days. Degradates were separated by TLC as previously described, located on the plates by autoradiography, scraped, extracted with acetone, and purified by HPLC. The purified isolate was analyzed by MS, NMR, and IR.

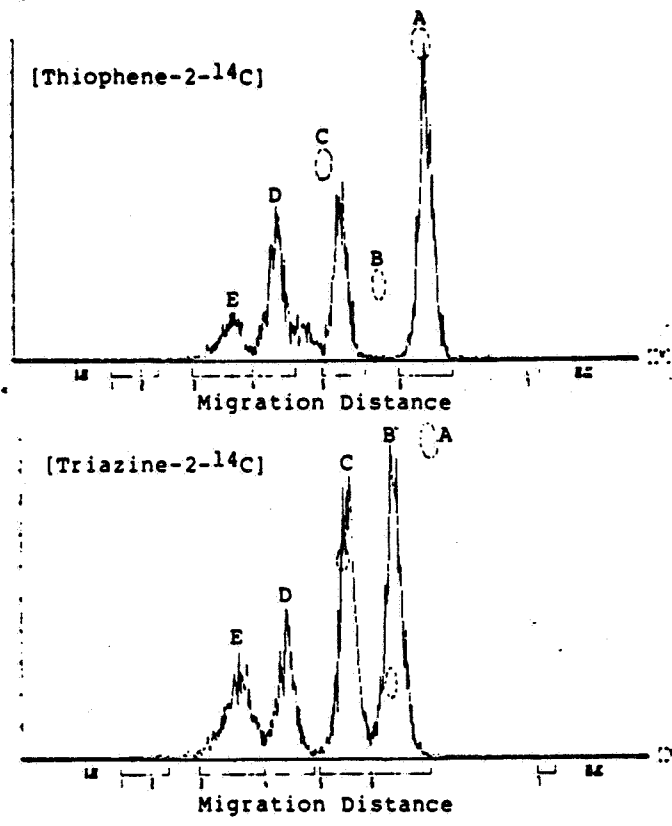
## REPORTED RESULTS:

[ $^{14}\text{C}$ ]DPX-M6316 degraded with half-lives of 3-6 days in aqueous buffered solutions of pH 5 and >30 days in aqueous buffered solutions of pH 7 and 9 (Tables 1 and 2). 2-Ester-3-sulfonamide was the major degradate of [thiophene-2- $^{14}\text{C}$ ]DPX-M6316 at pH 5, 7, and 9 for both 0.5 and 5.0 ppm solutions. 2-Ester-3-sulfonamide comprised 62-64% of the total radioactivity after 30 days in pH 5 solutions, 9-10% in pH 7 solutions, and 4-8% in pH 9 solutions. No other degradates were present at pH 7 and 9. 2-Ester-3-triuret and O-demethyl DPX-M6316 were detected in pH 5 solutions at maximum concentrations of 8-32% and 4-7% of the initial concentration.

Triazine amine was the major radiolabeled degradate of triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 at pH 5 (Figure 1), representing ~36% of the applied radioactivity after 31 days.

## DISCUSSION:

1. The material balance for the 0.5 ppm, pH 5 sample was incomplete.
2. No detection limits for analysis were given.



Hydrolysis Product	
A	2-Ester-3-sulfonamide
B	Triazine amine
C	DPX-M6316
D	2-Ester-3-triuret
E	O-Demethyl DPX-M6316

Figure 1. Comparison of the TLC radiochromatograms of thiophene- and triazine-labeled [14C]DPX-M6316 (31 days, pH 5 solution).

Table 1. Distribution of radioactivity (% of the applied) in sterile aqueous solutions of pH 5, 7, and 9 treated with thiophene-labeled [<sup>14</sup>C]DPX-M6316 at 0.5 ppm and incubated in the dark at 25°C.

Sampling interval (days)	DPX-M6316	2-Ester-3-sulfonamide	2-Ester-3-triuret	O-Demethyl DPX-M6316	Polar <sup>a</sup>	Total
<u>pH 5</u>						
0	112.5	0.9	<0.1	<0.1	0.7	114.1
0.04	109.8	0.3	<0.1	<0.1	0.8	110.9
0.17	102.9	2.0	<0.1	<0.1	1.7	106.6
1	93.0	7.0	0.8	<0.1	2.7	103.5
2	81.3	10.2	0.6	3.6	3.5	99.2
3	68.3	20.7	<0.1	1.3	4.5	94.8
6	50.1	35.5	5.6	2.3	5.4	98.9
8	36.9	37.3	2.1	0.8	5.6	82.7
10	27.8	45.4	<0.1	1.9	5.1	80.2
14	13.6	60.5	<0.1	3.8	4.5	82.4
21	6.0	64.7	5.0	<0.1	3.9	79.6
30	3.0	62.4	8.4	4.4	4.1	82.3
<u>pH 7</u>						
0	103.1	0.7	--	--	1.2	105.0
1	101.2	0.9	--	--	0.2	102.3
2	102.4	1.1	--	--	0.2	103.7
3	99.7	2.2	--	--	0.3	102.2
6	101.7	3.3	--	--	0.4	104.8
8	99.0	3.5	--	--	0.7	103.2
10	100.7	4.0	--	--	0.8	105.5
14	97.3	8.3	--	--	1.0	106.6
21	94.1	11.0	--	--	1.6	106.7
30	92.0	9.7	--	--	2.4	104.1
<u>pH 9</u>						
0	104.5	<0.1	--	--	0.3	104.8
1	89.4	<0.1	--	--	0.7	90.1
2	91.5	<0.1	--	--	1.1	92.6
3	92.0	1.1	--	--	1.3	94.4
6	90.0	2.5	--	--	1.4	94.8
8	91.1	2.7	--	--	1.7	95.5
10	91.8	2.3	--	--	1.9	96.0
14	90.0	5.3	--	--	2.2	97.5
21	85.5	7.6	--	--	3.6	96.7
30	82.3	8.2	--	--	4.8	95.3

<sup>a</sup> Percent of applied radioactivity remaining in the acidified aqueous phase after the methylene chloride extractions.

Table 2. Distribution of radioactivity (% of the applied) in sterile aqueous solutions of pH 5, 7, and 9 treated with thiophene-labeled [<sup>14</sup>C]DPX-M6316 at 5.0 ppm and incubated in the dark at 25°C.

Sampling interval (days)	DPX-M6316	2-Ester-3-sulfonamide	2-Ester-3-triuret	O-Demethyl DPX-M6316	Polar <sup>a</sup>	Total
<u>pH 5</u>						
0	106.1	0.3	<0.1	<0.1	1.5	107.9
0.04	105.7	1.2	<0.1	1.4	1.5	109.8
0.17	100.2	2.9	<0.1	1.5	3.1	107.7
1	82.1	11.7	2.9	2.0	4.3	103.0
2	75.0	18.4	7.3	1.8	5.9	108.4
3	62.6	23.0	8.7	6.9	6.5	107.7
6	36.0	39.0	17.5	8.2	6.4	107.1
8	24.9	48.6	9.2	3.4	6.3	92.4
10	18.2	57.3	24.0	3.4	6.2	103.1
14	8.5	56.8	27.5	4.3	5.2	102.3
21	2.8	62.6	34.8	1.1	5.0	106.3
30	4.0	64.1	32.0	<0.1	5.1	105.2
<u>pH 7</u>						
0	103.6	<0.1	--	--	0.1	103.7
1	98.9	0.9	--	--	0.3	100.1
2	99.9	1.2	--	--	0.3	101.4
3	101.0	1.7	--	--	0.4	103.1
6	102.4	2.8	--	--	0.6	105.8
8	100.1	3.7	--	--	0.9	104.7
10	99.6	4.5	--	--	1.0	105.1
14	97.0	5.7	--	--	1.4	104.1
21	95.3	6.5	--	--	2.2	104.0
30	89.5	9.4	--	--	2.9	101.8
<u>pH 9</u>						
0	110.6	1.0	--	--	0.4	112.0
1	108.8	0.3	--	--	1.6	110.7
2	107.5	0.1	--	--	2.1	109.7
3	104.8	0.8	--	--	3.2	108.8
6	101.6	1.1	--	--	4.5	107.2
8	97.5	1.5	--	--	5.6	104.6
10	94.8	1.7	--	--	5.9	102.4
14	94.6	2.7	--	--	6.7	104.0
21	92.7	3.8	--	--	7.7	104.2
30	87.6	4.9	--	--	9.7	102.2

<sup>a</sup> Percent of applied radioactivity remaining in the acidified aqueous phase after the methylene chloride extractions.



CASE GS --                      DPX-M6316                      STUDY 2                      PM --

CHEM 128845                      DPX-M6316

BRANCH EAB                      DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID                      CONTENT CAT 01  
 Ryan, D.L. 1986. Photodegradation of [thiophene-2-<sup>14</sup>C]DPX-M6316 and [triazine-2-<sup>14</sup>C]DPX-M6313 in water. Document No. AMR-511-86. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 2.

SUBST. CLASS = S.

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.
2. Thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purities >98%), at 10 ppm, degraded with a half-life of 30-72 hours in a pH 5 aqueous buffered solution irradiated with natural sunlight, and a half-life of 72-144 hours in pH 7 and 9 solutions. DPX-M6316 in the dark control degraded with a half-life of >336 hours. In the irradiated pH 7 solution treated with triazine-labeled [<sup>14</sup>C]DPX-M6316, methyl-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl-amino)-3-thiophene-carboxylate (tentative), triazine amine, and triazine urea were the major degradates (0.78, 1.24, and 1.55 ppm, respectively, at 336 hours). In the pH 7 solution treated with thiophene-labeled [<sup>14</sup>C]DPX-M6316, methyl-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl-amino)-3-thiophene-carboxylate was the only major degradate (0.84 ppm at 336 hours).
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 in water.

## MATERIALS AND METHODS:

### Experiment 1

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >98%, specific activity 23.3  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) was added at 10 ppm to sterile buffered solutions of pH 5, 7, and 9. In addition, triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >98%, specific activity 33.9  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) was added at 10 ppm to a sterile buffered pH 7 solution. A portion of each solution was irradiated outdoors under natural sunlight in water-jacketed glass beakers with quartz lids. The remaining solution was incubated in glass flasks in the dark. In the irradiated samples air was passed over the solutions and through a 1 N sodium hydroxide trapping solution. All test solutions were maintained at 25°C throughout the study. Solutions exposed to sunlight were sampled at 4, 8, 30, 72, 144, 240, and 336 hours after initiating exposure. Dark control solutions were sampled at 72, 144, 240, and 336 hours. Sodium hydroxide traps were changed at 144 and 336 hours.

Total radioactivity in aliquots of the samples was determined before analysis using LSC. DPX-M6316 was separated from its degradates using HPLC and quantified by LSC. Additional separation of compounds using TLC was done using the thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 336-hour pH 7 photolysis sample. The sample was extracted three times with methylene chloride, concentrated, resuspended in water, and analyzed by HPLC. Peaks eluting between 2.5 and 5 minutes were collected, combined, reduced in volume, and analyzed by TLC using cellulose plates. Plates were developed in methanol:water:1.0 M ammonium hydroxide (80:20:1). Radioactivity was detected using autoradiography; individual radioactive bands were scraped from the plate, dissolved in water, and analyzed by LSC.

Samples from the irradiated thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 treated solutions were also analyzed by TLC after solid sorbent extraction using C-18 Bond-Elut extraction columns. The sample pH was adjusted to pH 2.6 with 1.0 M HCl and then applied to a Bond Elut column previously conditioned with pH 2.2 HPLC-grade water. The column was eluted with pH 2.2 water, followed by methanol. The aqueous and methanol eluates were collected separately and analyzed for total radioactivity by LSC. The methanol fractions were concentrated and analyzed by TLC on silica gel plates using three developing solvents; toluene:acetone:methanol:ammonium hydroxide (50:50:25:1), methylene chloride:methanol:formic acid (85:15:1), and toluene:ethyl ether:formic acid (25:75:1). Products were detected by autoradiography and fluorescence quenching at 254 nm, and quantitated by LSC.

Total radioactivity in the sodium hydroxide trapping solutions was determined by quantifying total radioactivity by LSC. Aliquots of the sodium hydroxide solutions were mixed with saturated barium chloride solution followed by 2 M potassium carbonate to precipitate the  $\text{CO}_2$ . The mixture was centrifuged and the supernatant was analyzed by LSC.

### Experiment 2

In order to generate sufficient degradates to accurately identify, buf-

ferred pH 7 solutions were treated with either thiophene- or triazine-labeled [<sup>14</sup>C]DPX-M6316 at 320 ppm. The solutions were placed in the photolysis vessels previously described, covered with 0.12-inch thick Pyrex plates, and irradiated for 42 hours at a distance 6 inches below sunlamps (Westinghouse FS20).

Aliquots of the artificial light-irradiated solutions were adjusted to pH 3.5 with 1 M hydrochloric acid and extracted three times with methylene chloride. The methylene chloride extracts were combined, reduced, and resuspended in acetonitrile:pH 2.2 water (20:80). Aliquots were analyzed by HPLC, and peaks eluting between 4-6, 8-10, and 32-33 minutes were collected separately. Acetonitrile was removed from the collected fractions by rotary evaporation, the acidity of the fractions was adjusted to pH 5 with 1.0 M sodium hydroxide, and the solutions were extracted three times with methylene chloride. The methylene chloride was removed by rotary evaporation, and samples were checked for purity using HPLC and TLC as described above. The peak eluting between 4-6 minutes was analyzed by cochromatography using TLC and HPLC. The peak eluting between 8-10 minutes was analyzed by NMR and MS. The peak eluting at 32-33 minutes was not of sufficient purity for spectral identification and was purified using a different method. Samples were extracted three times with diethyl ether. The extracts were combined and concentrated. The concentrated extract was separated by TLC on silica gel plates using a developing solution of toluene:ethyl acetate:formic acid (60:40:1). A band located by ultraviolet fluorescence quenching was scraped from the plate and extracted with ethyl acetate. The ethyl acetate was evaporated to dryness, and the residue was resuspended in a 50% acetonitrile solution. The compound was purified by HPLC, and the acetonitrile was removed from the collected fraction by rotary evaporation. The sample was extracted with ethyl acetate and concentrated. The sample was then analyzed GC/MS using EI and CI and by NMR.

#### REPORTED RESULTS:

DPX-M6316 in irradiated solutions degraded with half-lives of 30-72 hours at pH 5 and 72-144 hours at pH 7 and 9; dark controls degraded with half-lives of >336 hours (Table 1).

In the irradiated pH 7 solution treated with triazine-labeled [<sup>14</sup>C]DPX-M6316, triazine amine (maximum concentration 1.24 ppm) and triazine urea (maximum concentration 1.55 ppm) were major degradates (Table 2). In the irradiated pH 7 solution treated with thiophene-labeled [<sup>14</sup>C]DPX-M6316, methyl-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl-amino)-3-thiophene-carboxylate was the only major degradate identified (0.84 ppm). Carbon dioxide and several unidentified compounds (each <1.15 ppm) were also detected.

#### DISCUSSION:

Degradation data for the pH 9 dark controls do not agree with data from the hydrolysis study.

Table 1. DPX-M6316 (ppm) in aqueous buffered solutions treated with thiophene- or triazine-labeled [<sup>14</sup>C]DPX-M6316 (purities >98%) at 10 ppm, and either irradiated with natural sunlight or incubated in the dark at 25°C.

Sampling interval (hours)	Cumulative watt-hr/m <sup>2</sup>	pH 5a	pH 7a	pH 7b	pH 9a
<u>Irradiated</u>					
0	0	10.1	10.4	9.7	10.5
4	2663	9.1	9.6	9.2	9.3
8	5129	8.4	9.2	8.6	8.6
30	7808	7.4	8.3	8.0	7.6
72	15140	6.2	7.2	6.9	6.0
144	34851	3.4	4.6	4.2	3.3
240	58082	1.7	2.5	2.4	1.6
336	81129	0.9	1.6	1.5	0.9
<u>Dark controls</u>					
0	--	10.1	10.4	9.7	10.5
72	--	9.1	10.0	9.7	9.0
144	--	8.0	10.1	9.4	7.8
240	--	7.5	9.8	9.5	6.7
336	--	6.8	9.8	9.4	5.6

a Thiophene-labeled [<sup>14</sup>C]DPX-M6316 study

b Triazine-labeled [<sup>14</sup>C]DPX-M6316 study.

Table 2. Distribution of radioactivity (ppm) in pH 7 buffered solutions treated with thiophene- or triazine-labeled [<sup>14</sup>C]DPX-M6316 (purities >98%) at 10 ppm and irradiated with natural sunlight.

Sampling interval (hours)	DPX-M6316	Triazine amine	Triazine urea	CO <sub>2</sub>	Unknown <sup>a</sup>	Unidentified <sup>b</sup>	Polar compounds
<u>Thiophene-labeled</u>							
72	7.67	--	--	--	0.44	2.59	0.70
144	5.03	--	--	0.15	0.70	4.14	1.38
240	3.21	--	--	--	0.78	5.23	2.18
336	1.95	--	--	--	0.84	5.38	2.83
<u>Triazine-labeled</u>							
72	7.00	0.38	0.63	--	0.40	2.59	--
144	4.53	0.74	1.01	0.02	0.72	3.99	--
240	2.80	1.08	1.34	--	0.69	4.79	--
336	1.69	1.24	1.55	0.06	0.78	7.37	--

<sup>a</sup> It is proposed that Unknown 1 is methyl-2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl-amino)-3-thiophene-carboxylate.

<sup>b</sup> Individual products <1.15 ppm.

CASE GS --                      DPX-M6316                      STUDY 3                      PM --

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 CHEM 128845                      DPX-M6316

BRANCH EAB                      DISC --

FORMULATION 00 - ACTIVE INGREDIENT

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 FICHE/MASTER ID No MRID                      CONTENT CAT 01  
 Ferguson, E.M., 1986a. Photodegradation of [thiophene-2-<sup>14</sup>C]DPX-M6316 and  
 [triazine-2-<sup>14</sup>C]DPX-M6316 on soil. Document No. AMR-505-86. E.I. du Pont  
 de Nemours and Company, Inc. Wilmington, DE. Acc. No. 263760. Reference 3.  
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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is scientifically valid.
2. Thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purities >98%), at 0.83 µg/cm<sup>2</sup>, degraded with a half-life of 7-14 days in sunlight-irradiated silt loam soil; the half-life was 14-21 days in the dark controls. The major degradate of the thiophene-labeled [<sup>14</sup>C]DPX-M6316 was 2-ester-3-sulfonamide (20.4% of the applied at 30 days). The major degradate of the triazine-labeled [<sup>14</sup>C]DPX-M6316 was triazine amine (32.3% of the applied at 30 days). Other degradates included O-demethyl DPX-M6316, DPX-M6316 acid, 2-acid-3-sulfonamide, thiophene-sulfonamide, and triazine urea.
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 on soil.

MATERIALS AND METHODS:

A slurry of Flanagan silt loam soil (2% sand, 81% silt, 17% clay, 4.3%

organic matter, pH 5.4, CEC 21.1 meq/100 g) and water was spread over microscope slides and dried (~1-mm thick, 18-cm<sup>2</sup> surface). Either thiophene-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purity >98%, specific activity 23.3 μCi/mg, New England Nuclear) or triazine-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purity >99%, specific activity 33.9 μCi/mg, New England Nuclear) was applied to each slide at 0.83 μg/cm<sup>2</sup>. All samples were set outdoors and covered with lids containing quartz plates inlaid into Lucite. Half of the samples were exposed to sunlight, and the remainder were kept in the dark. All samples were maintained at 25°C and air was drawn over the samples and through 1 N sodium hydroxide to trap <sup>14</sup>CO<sub>2</sub>. Slides were removed after 0, 2, 7, 14, 21, and 30 days of irradiation. Dark controls were removed after 0, 7, 14, 21, and 30 days. The sodium hydroxide traps were changed when the slides were removed.

Soil from each slide was extracted sequentially three times with acetone:0.1 M ammonium carbonate (90:10), once with 0.1 M ammonium carbonate, and twice with acetone. Combined extracts were analyzed by LSC. Soil residues were further extracted by 0.1 N sodium hydroxide and extracts were analyzed by LSC. Remaining soil residue was combusted and analyzed by LSC. Extracts of soil treated with triazine-labeled [<sup>14</sup>C]DPX-M6316 were filtered and analyzed by HPLC. Extracts of soil treated with thiophene-labeled DPX-M6316 were filtered, concentrated, and then analyzed using HPLC. The original treatment solutions and the acetone/ammonium carbonate composite extracts were also analyzed by TLC on silica gel plates. Plates were developed in methylene chloride:methanol:concentrated ammonium hydroxide (150:50:6). Radioactivity was detected and quantified by TLC linear analysis. Aliquots of the sodium hydroxide trapping solution were analyzed for <sup>14</sup>CO<sub>2</sub> by LSC. This was confirmed by LSC of barium [<sup>14</sup>C]carbonate precipitated by the addition of saturated barium chloride and 1 M potassium carbonate to aliquots of the sodium hydroxide trapping solution.

#### REPORTED RESULTS:

DPX-M6316 degraded with a half-life of 7-14 days when irradiated and 14-21 days in the dark (Tables 1 and 2). The major degradates were 2-ester-3-sulfonamide (maximum concentration 20.4% of applied) and triazine amine (maximum concentration 32.3% of applied). O-Demethyl DPX-M6316, DPX-M6316 acid, 2-acid-3-sulfonamide and triazine urea were also detected.

#### DISCUSSION:

The detection limit and recovery from fortified samples were not reported.

Table 1. DPX-M6316 and its degradates (% of the applied) in soil treated with thiophene-labeled [<sup>14</sup>C]DPX-M6316.

Sampling interval (days)	Acetone extract							NaOH extract	<sup>14</sup> CO <sub>2</sub>	Unextractable	Total
	DPX-M6316	2-Ester-3-sulfonamide	O-Demethyl DPX-M6316	DPX-M6316 acid	2-Acid-3-sulfonamide	Thiophene-sulfonamide	Unidentified				
<u>Irradiated</u>											
0	96.9	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	--	<0.01	1.1	98.0
2	78.9	3.9	1.2	<0.2	<0.2	<0.2	9.2	5.8	1.0	0.6	94.8
7	54.0	10.9	1.3	<0.4	<0.4	<0.4	15.5	11.2	3.7	1.4	86.8
14	41.4	15.7	1.0	0.6	0.4	0.3	13.6	9.2	5.8	1.0	79.4
21	31.1	19.8	0.8	0.9	1.3	1.3	16.9	13.6	7.0	2.5	81.6
30	19.9	20.4	1.6	1.3	0.9	0.3	14.5	7.9	7.6	6.0	72.5
<u>Dark control</u>											
7	57.8	15.2	1.1	<0.4	1.8	<0.4	4.7	8.1	<0.01	1.4	82.0
14	51.2	18.8	1.8	<0.4	<0.4	<0.4	13.1	11.8	<0.01	1.2	86.1
21	43.3	24.6	1.9	0.5	1.2	<0.4	14.4	9.6	<0.01	3.0	88.9
30	32.5	24.4	1.2	<0.4	<0.4	3.6	16.3	11.5	<0.01	4.5	82.5



Table 2. DPX-M6316 and its degradates (% of the applied) in soil treated with ~~triazine~~-labeled [14C]-DPX-M6316.

Sampling interval (days)	Acetone extract					Total in extract	
	DPX-M6316	Triazine amine	O-Demethyl DPX-M6316	DPX-M6316 acid	Triazine urea		Unidentified
<u>Irradiated</u>							
0	98.4	<0.2	<0.2	<0.2	<0.2	0.5	98.9
2	79.6	4.4	0.7	<0.4	1.4	5.6	91.7
7	59.9	12.1	1.2	<0.4	3.3	19.8	96.3
14	43.9	17.5	0.7	1.4	3.5	21.4	88.4
21	35.7	23.7	4.1	3.5	1.3	23.5	91.8
30	29.4	32.3	2.6	1.6	1.6	17.0	84.5
<u>Dark control</u>							
7	63.4	16.7	0.8	1.4	<0.4	7.3	89.6
14	52.1	14.6	0.6	2.2	<0.4	20.9	90.4
21	48.4	17.1	2.8	4.4	<0.4	20.3	93.0
30	41.5	19.4	1.9	2.4	<0.4	15.8	81.0

CASE GS -- DPX-M6316 STUDY 4 PM --

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CHEM 128845 DPX-M6316

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

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FICHE/MASTER ID No MRID CONTENT CAT 01  
Rapisarda, C. Undated. Aerobic soil metabolism of DPX-M6316 [thiophene-2-<sup>14</sup>C]. Document No. AMR-236-84. E.I. du Pont de Nemours and Company, Inc.,  
Wilmington, DE. Acc. No. 263760. Reference 4.

-----  
SUBST. CLASS = S.

-----  
DIRECT RVW TIME = 2 (MH) START-DATE END DATE

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REVIEWED BY: T. Colvin-Snyder  
TITLE: Staff Scientist  
ORG: Dynamac Corp., Rockville, MD  
TEL: 468-2500

-----  
APPROVED BY: T. Dougherty  
TITLE: Chemist  
ORG: EAB/HED/OPP  
TEL: 557-0335

SIGNATURE:

DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

In response to the previous review of this study (EAB; 11/1/84), the registrant has adequately addressed the issue of the loss of volatile compounds. This study fulfills EPA Data Requirements for Registering Pesticides by providing information concerning the aerobic metabolism of thiophene-labeled [<sup>14</sup>C]DPX-M6316 in soil.

Thiophene-labeled [<sup>14</sup>C]DPX-M6316 degraded to <sup>14</sup>CO<sub>2</sub> via several intermediates with a half-life of 2-6 days; 31-44% of the applied radioactivity was mineralized after 20 weeks of incubation.

CASE GS -- DPX-M6316 STUDY 5 PM --  
-----  
CHEM 128845 DPX-M6316  
BRANCH EAB DISC --

## FORMULATION 00 - ACTIVE INGREDIENT

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FICHE/MASTER ID No MRID CONTENT CAT 01  
Lewis, W. and L.G. Carter. 1986. Anaerobic aquatic metabolism of [thio-  
phene-2-<sup>14</sup>C]DPX-M6316. Document No. AMR-540-86. E.I. du Pont de Nemours  
and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 5.  
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SUBST. CLASS = S.

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DIRECT RVW TIME = 8 (MH) START-DATE END DATE  
-----

REVIEWED BY: T. Colvin-Snyder  
TITLE: Staff Scientist  
OPG: Dynamac Corp., Rockville, MD  
TEL: 468-2500  
-----

APPROVED BY: T. Dougherty  
TITLE: Chemist  
ORG: EAB/HED/OPP  
TEL: 557-0335  
-----

SIGNATURE:

DATE:

CONCLUSIONS:Metabolism - Anaerobic Aquatic

1. This study is scientifically valid.
2. Thiophene-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purity >99%), at 52-60 ppb, degraded with half-lives of 7-14 days in anaerobic (flooded) loamy sand sediment and 14-28 days in anaerobic (flooded) sandy loam and silt loam sediments. The major degradates were 2-ester-3-sulfonamide (maximum concentration 13-40% of recovered), 2-acid-3-sulfonamide (maximum concentration 25-43%), and 2-acid-3-sulfonic acid (maximum concentration 16-24%). 2-Ester-3-triuret, O-demethyl DPX-M6316, and DPX-M6316-acid were also detected. In sterile anaerobic sediments, DPX-M6316 degraded with a half-life of 56-112 days.
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the anaerobic metabolism of thiophene-labeled [<sup>14</sup>C]DPX-M6316 in aquatic systems.

## MATERIALS AND METHODS:

Loamy sand, sandy loam, and silt loam sediments and pond water (Table 1) were collected from three sites and maintained under nitrogen for 3-4 weeks to establish anaerobic conditions. Then, sediment and pond water were combined (1:2, w:v) in centrifuge bottles and treated with thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%, specific activity 23.3  $\mu\text{Ci}/\text{mg}$ , E.I. du Pont) at 52-60 ppb. Samples were flushed with nitrogen and incubated at 25°C in the dark. Samples were analyzed at 0 and 4 days, and at 1, 2, 4, 8, 28, 40, and 52 weeks posttreatment.

Additional sediment and water samples were autoclaved and treated with sodium azide, then incubated and sampled as described above.

Samples were extracted with methylene chloride, ethyl acetate, and ammonium carbonate as shown in Figure 1. Water and sediment extracts were analyzed with reference standards by TLC on silica gel plates developed with either diethyl ether:toluene:formic acid (12:8:1) or methylene chloride:methanol:concentrated ammonium hydroxide (150:50:3). Radioactivity was detected and quantified with a TLC linear analyzer. Extracts were also analyzed by radio-HPLC. Radioactivity remaining in the pond water samples after extraction was quantified by LSC. Extracted sediments were air-dried and analyzed for unextractable radioactivity by combustion and LSC.

## REPORTED RESULTS:

In nonsterile samples, DPX-M6316 degraded with half-lives of 7-14 days in loamy sand sediment and 14-28 days in sandy loam and silt loam sediments (Tables 2 and 4). The major degradates were 2-ester-3-sulfonamide (maximum concentration 13-40% of recovered), 2-acid-3-sulfonamide (maximum concentration 25-43%) and 2-acid-3-sulfonic acid (maximum concentration 16-24%). 2-Ester-3-triuret, O-demethyl DPX-M6316, and DPX-M6316 acid were also detected.

In sterile samples, DPX-M6316 degraded with a half-life of 56-112 days (Tables 3 and 5). The major degradates were 2-ester-3-sulfonamide (maximum concentration 33-55% of recovered) and 2-acid-3-sulfonamide (maximum concentration 10-21%). In addition, in sandy loam soil, 2-acid-3-sulfonic acid (maximum concentration 24%) and DPX-M6316 acid (maximum concentration 13%) were also major degradates. 2-Ester-3-triuret and O-demethyl DPX-M6316 were also detected.

## DISCUSSION:

This study fulfills data requirements by providing information on the anaerobic metabolism of thiophene-labeled DPX-M6316 in aquatic systems.

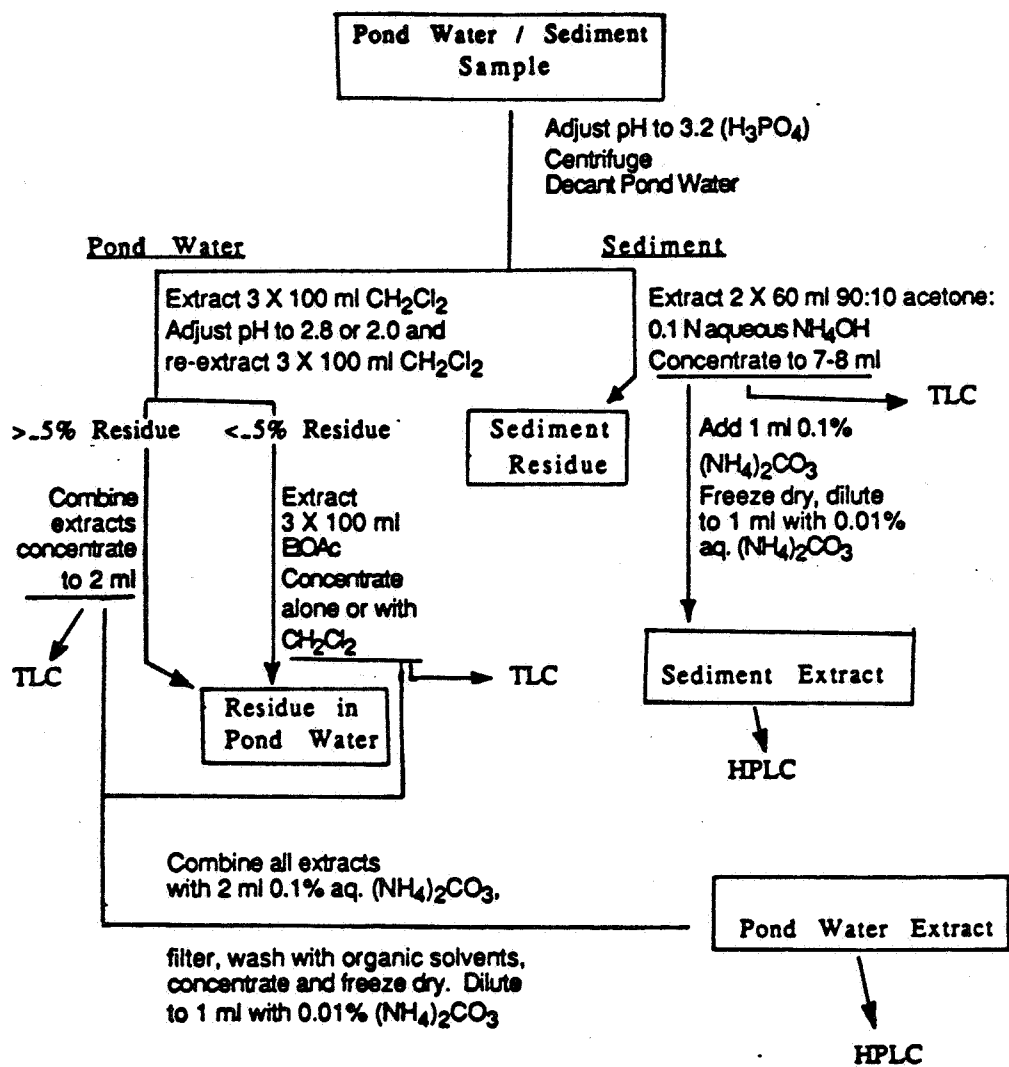


Figure 1. Scheme for the extraction of DPX-M6316 and its degradates from sediment-pond water samples.

Table 1. Sediment and pond water characteristics.

Sediment type	Source	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	Sediment:pond water pH	
								%	Sterile
Loamy sand	Fayetteville, NC	82	15	3	3.9	4.9	2.3	5.8	4.4
Sandy loam	Rochelle, IL	61	26	13	2.2	7.5	15.5	7.2	6.3
Silt loam	Landenberg, PA	9	68	23	2.8	6.5	6.3	6.4	5.5

Table 2. Distribution of radioactivity (ppb) in nonsterile anaerobic sediment:water samples treated with DPX-M6316 and incubated in the dark at 25°C.

Sampling interval (days)	Pond water		Sediment		Total radioactivity recovered (% of applied)
	Extracted	Unextracted	Extracted	Unextracted	
<u>Loamy sand<sup>a</sup></u>					
0	4	0.1	42	3	94.7
4	5	0.3	42	4	--
7	9	0.7	39	4	102.4
14	10	0.6	34	3	91.1
28	10	0.3	30	7	90.4
64	11	0.4	26	11	92.1
78	19	4	6	12	--
112	20	0.7	23	2	88.6
196	17	1	20	5	83.2
280	25	1	17	6	94.0
<u>Sandy loam<sup>b</sup></u>					
0	25	0.3	34	8	112.4
4	47	0.5	20	8	--
7	17	0.7	34	9	100.2
14	15	0.2	23	13	87.0
28	14	1	16	30	102.1
56	31	4	26	15	126.3
112	19	4	19	20	103.6
196	20	6	6	25	93.4
264	32	1	14	0.5	--
280	14	5	8	22	84.6
<u>Silt loam<sup>c</sup></u>					
0	20	0.3	37	4	107.6
7	23	2	17	15	100.0
14	32	0.8	31	6	122.2
28	19	0.4	36	8	109.1
56	21	0.5	22	15	101.6
90	30	4	7	11	105.6
112	18	1	14	27	98.1
196	30	1	17	8	88.3
280	25	4	10	11	62.4
336	2	2	2	29	99.4

a Applied at 52 ppb.

b Applied at 60 ppb.

c Applied at 57 ppb.

Table 3. Distribution of radioactivity (ppb) in sterile anaerobic sediment:water samples treated with DPX-M6316 and incubated in the dark at 25°C.

Sampling interval (days)	Pond water		Sediment		Total radioactivity recovered (% of applied)
	Extracted	Unextracted	Extracted	Unextracted	
<u>Loamy sand<sup>a</sup></u>					
0	38	0.4	13	0.9	98.7
4	22	0.2	33	3	--
7	7	0.2	44	6	110.7
14	7	0.2	38	15	115.4
28	11	0.1	39	12	117.9
64	15	0.1	32	2	95.4
112	18	0.4	30	2	96.8
196	22	0.5	27	2	98.5
280	25	0.6	20	3	92.2
<u>Sandy loam<sup>b</sup></u>					
0	22	0.4	37	8	112.8
7	24	0.4	34	5	104.6
14	15	ND	39	7	101.0
28	21	0.2	27	15	105.8
56	36	0.6	16	3	92.5
112	48	0.5	7	3	96.0
196	46	0.9	14	4	108.6
280	29	0.4	22	1	87.8
<u>Silt loam<sup>c</sup></u>					
0	25	0.3	28	3	97.4
7	14	2	34	7	100.0
14	29	0.6	28	2	105.5
28	25	0.2	38	4	118.6
56	22	0.2	29	7	101.3
112	25	0.2	27	7	106.0
196	31	0.3	14	0.8	80.1
280	33	6	18	2	103.4
336	32	16	15	16	88.1

a Applied at 52 ppb.

b Applied at 60 ppb.

c Applied at 57 ppb.



Table 4. Distribution of radioactivity (% of the recovered) in the extractable fractions of nonsterile anaerobic sediment:water samples treated with DPX-M6316 and incubated in the dark at 25°C.

Sampling interval (days)	DPX-M6316	2-Ester-3-sulfonamide	2-Acid-3-sulfonamide	2-Acid-3-sulfonic acid	2-Ester-3-triuret	O-Demethyl DPX-M6316	DPX-M6316 acid	Un-knowns
<u>Loamy sand</u>								
0	93	ND	ND	ND	ND	ND	ND	ND
7	72	14	ND	ND	2	ND	1	ND
14	41	28	3	7	10	3	2	ND
28	37	34	4	4	6	ND	ND	ND
64	17	27	14	11	3	ND	2	4
112	ND	40	26	22	ND	ND	ND	7
196	ND	20	37	24	ND	ND	ND	6
<u>Sandy loam</u>								
0	87	ND	ND	ND	ND	ND	ND	ND
7	66	13	ND	ND	ND	2	ND	3
14	59	7	ND	ND	ND	1	7	1
28	24	2	10	ND	ND	2	11	ND
56	19	4	12	8	ND	ND	30	2
112	2	3	25	16	ND	ND	13	2
280	ND	ND	24	16	ND	ND	5	ND
<u>Silt loam</u>								
0	92	1	ND	ND	ND	ND	ND	ND
7	63	7	ND	ND	ND	ND	ND	ND
14	67	15	ND	1	ND	3	4	ND
28	39	20	9	3	2	6	7	2
56	26	31	1	2	3	5	4	4
196	ND	13	43	22	ND	ND	2	4
280	ND	1	41	16	ND	ND	8	4
336	ND	4	ND	2	ND	ND	3	2

Table 5. Distribution of radioactivity (% of the recovered) in the extractable fractions of sterile anaerobic sediment:water samples treated with DPX-M6316 and incubated in the dark at 25°C.

Sampling interval (days)	DPX-M6316	2-Ester-3-sulfonamide	2-Acid-3-sulfonamide	2-Acid-3-sulfonic acid	2-Ester-3-triuret	O-Demethyl DPX-M6316	DPX-M6316 acid	Un-knowns
<u>Loamy sand</u>								
0	98	ND	ND	ND	ND	ND	ND	ND
7	88	1	ND	ND	ND	1	ND	ND
14	67	4	ND	ND	2	2	ND	ND
28	71	6	1	ND	1	1	2	ND
64	59	24	5	ND	2	ND	5	ND
112	32	55	2	ND	5	1	ND	ND
196	15	52	7	ND	6	ND	ND	ND
280	12	42	21	7	9	3	ND	ND
<u>Sandy loam</u>								
0	87	ND	ND	ND	ND	ND	ND	ND
7	88	3	ND	ND	ND	ND	1	ND
14	82	2	ND	ND	ND	ND	3	ND
28	71	1	ND	ND	ND	ND	1	2
56	60	17	7	3	4	ND	4	ND
112	46	21	18	ND	2	ND	8	ND
196	37	17	8	16	3	ND	13	ND
280	16	33	12	24	6	ND	6	ND
<u>Silt loam</u>								
0	95	ND	ND	ND	ND	ND	ND	ND
7	81	3	ND	ND	ND	1	ND	ND
14	89	3	ND	ND	ND	1	3	ND
28	87	3	ND	ND	2	ND	ND	ND
56	70	10	2	ND	1	2	4	ND
112	42	20	10	1	2	5	5	4
196	29	54	2	6	5	1	1	1
280	17	54	3	2	7	ND	ND	3

[<sup>14</sup>C]Residues that were not leached from the soils were distributed throughout the columns (Figure 1).

The aged (6 days) thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 residues were mobile in columns of silt loam soil; 72% of the thiophene-labeled [<sup>14</sup>C]residues and 69% of the triazine-labeled [<sup>14</sup>C]residues were recovered in the leachate (Table 2). DPX-M6316 acid comprised 35-44% of the [<sup>14</sup>C]residues in the leachate. [<sup>14</sup>C]Residues that did not leach were distributed throughout the columns (Figure 2).

#### DISCUSSION:

In the aged study, [<sup>14</sup>C]DPX-M6316 and its degradates were not characterized in the soil prior to leaching. However, residues in the soil and leachate were adequately characterized after leaching and little degradation is expected to have occurred during leaching.

CASE GS -- DPX-M6316 STUDY 6 PM --

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CHEM 128845 DPX-M6316

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

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FICHE/MASTER ID No MRID CONTENT CAT 01  
Ferguson, E.M. 1986b. Soil column leaching behavior of [thiophene-2-<sup>14</sup>C]-  
DPX-M6316 and [triazine-2-<sup>14</sup>C]DPX-M6316. Document No. AMR 454-85. E.I. du  
Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760.  
Reference 6.-----  
SUBST. CLASS = S.-----  
DIRECT RVW TIME = 8 (MH) START-DATE END DATE-----  
REVIEWED BY: T. Colvin-Snyder  
TITLE: Staff Scientist  
ORG: Dynamac Corp., Rockville, MD  
TEL: 468-2500-----  
APPROVED BY: T. Dougherty  
TITLE: Chemist  
ORG: EAR/HED/OPP  
TEL: 557-0335

SIGNATURE:

DATE:

CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Unaged thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purities >98%) was very mobile in columns of sandy loam, loamy sand, silt, and silt loam soils; 72-97% of the recovered radioactivity was leached from the columns.  $K_d$  values were 0, 0.01, 0.86, and 0.15-0.16 for sandy loam, loamy sand, silt, and silt loam soils, respectively. DPX-M6316 was the major [<sup>14</sup>C]compound in the leachate from the unaged soil. Aged (6 days) thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 residues were very mobile in columns of silt loam soil; 69-72% of the thiophene- and triazine-labeled [<sup>14</sup>C]residues were recovered in the leachate. DPX-M6316 acid comprised 35-44% of the residues in the leachate from the aged soil.
3. This study contributes toward the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the mobility of unaged and aged thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 in soils.

## MATERIALS AND METHODS:

Column chromatograph tubes (2-inch diameter) were packed with either sandy loam, silt loam, silt, or loamy sand soil to a depth of ~13 inches (Table 1), and treated with thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >98%, specific activity 23.3  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) at 0.016 mg/column (~1.1 oz ai/A). Additional columns of silt loam soil were treated with triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%, specific activity 33.9  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) at 0.011 mg/column (~0.8 oz ai/A). Soil columns were leached with 20 inches of water, and 20-mL fractions of the leachate were collected.

To determine the leaching potential of aged residues, moistened silt loam soil was placed in glass jars and treated with either 0.016 mg of thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 or 0.011 mg of triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316. The samples were incubated in the dark at 25°C for 6 days. The soils were then transferred to the top of 10-inch columns of silt loam soil. The soil columns were leached and leachate was collected as described above.

Leachate fractions were collected and analyzed for total radioactivity using LSC. Fractions containing the highest [ $^{14}\text{C}$ ]residue concentrations were pooled, and composite samples were analyzed for DPX-M6316 and its degradates by HPLC.

Leachate from the silt loam soil columns treated with aged or unaged DPX-M6316 were also analyzed by TLC. Composite samples were filtered using C-18 Sep-Pak cartridges. Samples were eluted with acetonitrile and concentrated. Concentrated samples and standards were applied to silica gel TLC plates and developed in methylene chloride:methanol:concentrated ammonium hydroxide (150:50:6). Areas of radioactivity were detected and quantified using TLC linear analysis. Standards were located by fluorescence quenching.

After leaching, the soil columns were divided into 2-inch segments. The soils from each segment were analyzed for total radioactivity by LSC following combustion. Soil segments from columns of silt soil treated with thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 and from columns of silt loam soil treated with aged thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 that contained significant amounts of radioactivity were extracted ultrasonically three times with acetone:0.1 M ammonium carbonate (90:10). The extracts were combined and aliquots were analyzed for total radioactivity by LSC. Additional aliquots were concentrated, filtered, and analyzed by HPLC. Extracted soils were analyzed for unextractable radioactivity by LSC following combustion.

## REPORTED RESULTS:

Unaged DPX-M6316 was very mobile in columns of sandy loam soil (96% of the recovered radioactivity in leachate), loamy sand soil (97% in leachate), silt soil (72% in leachate), and silt loam soil (93% in leachate) (Table 2).  $K_d$  values were 0, 0.01, 0.86, and 0.15-0.16 for sandy loam, loamy sand, silt, and silt loam soils, respectively. DPX-M6316 comprised >83% of the [ $^{14}\text{C}$ ]residues in the leachate (Table 3).

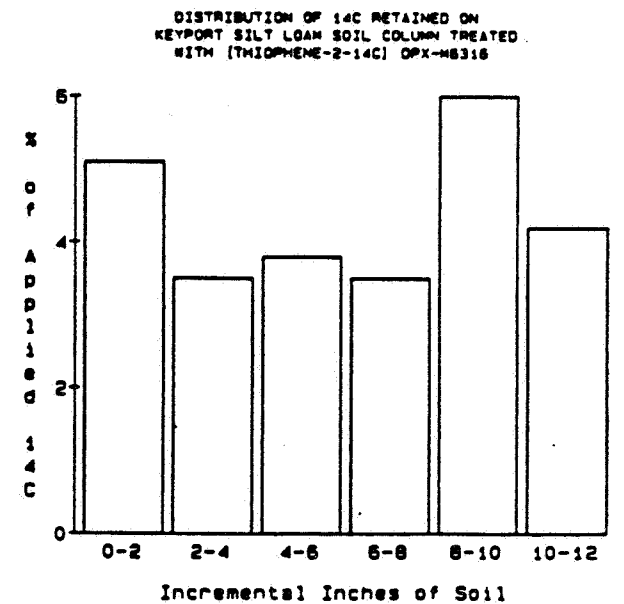
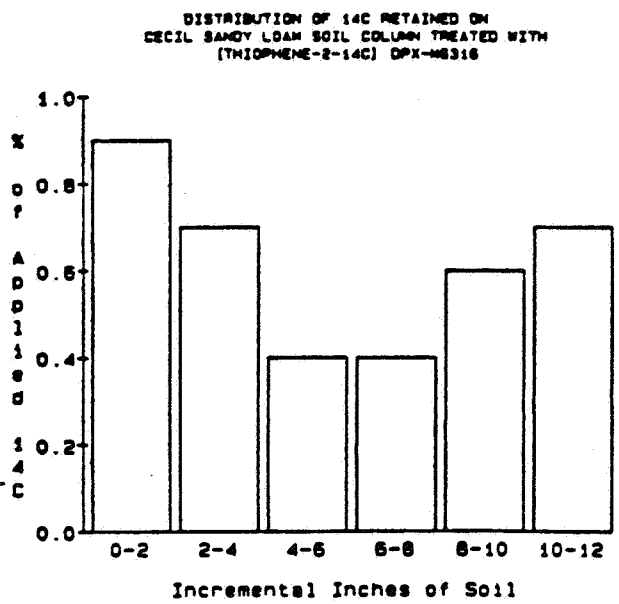
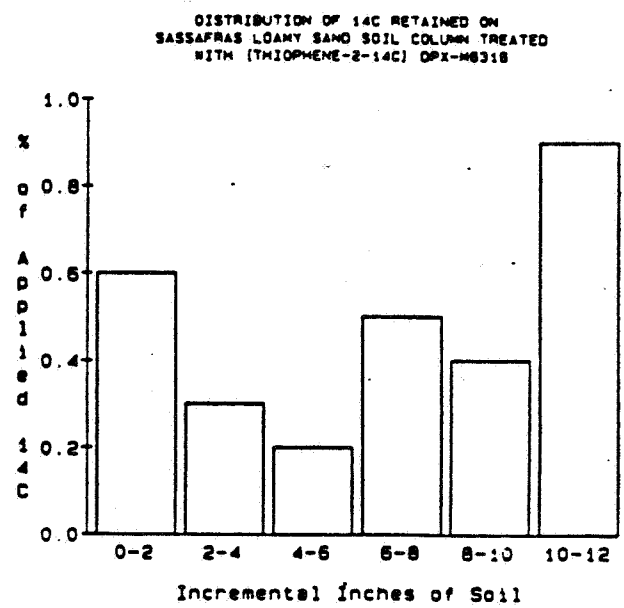
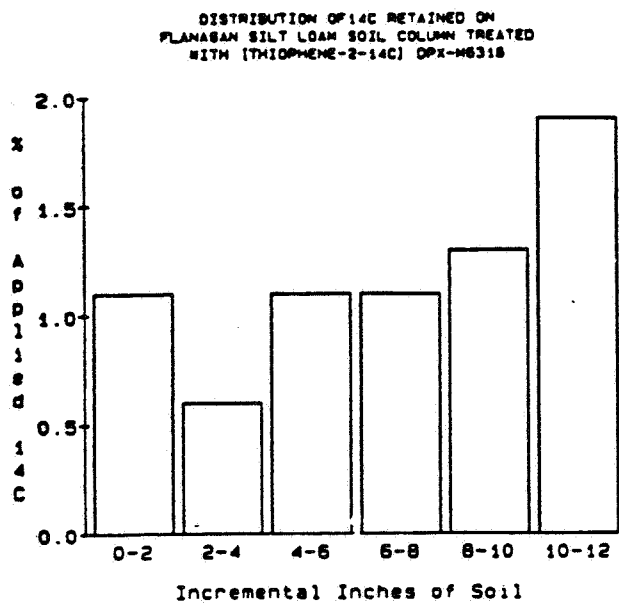
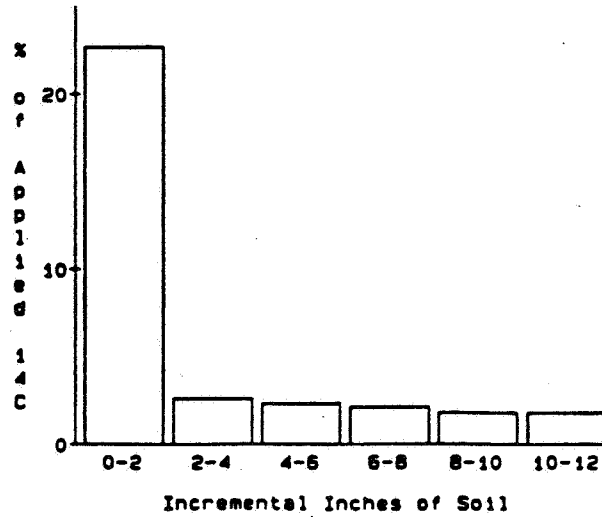


Figure 1. Distribution of radioactivity (% of the applied) in columns of sandy loam, silt loam, silt, and loamy sand soils treated with unaged thiophene-labeled [<sup>14</sup>C]DPX-M6316.

DISTRIBUTION OF <sup>14</sup>C RETAINED ON AGED  
 FLANAGAN SILT LOAM SOIL COLUMN TREATED  
 WITH (THIOPHENE-2-<sup>14</sup>C) DPX-M6316



DISTRIBUTION OF <sup>14</sup>C RETAINED ON AGED  
 FLANAGAN SILT LOAM SOIL COLUMN TREATED  
 WITH (TRIAZINE-2-<sup>14</sup>C) DPX-M6316

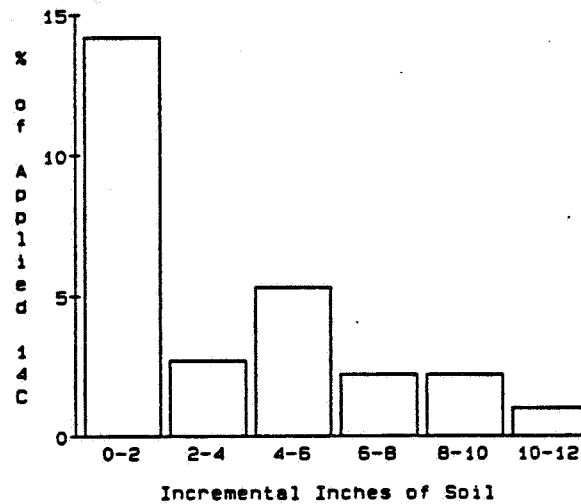


Figure 2. Distribution of radioactivity in columns of silt loam soil treated with aged (6 days) thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Cecil sandy loam	61	21	18	2.1	6.5	6.6
Flanagan silt loam	2	81	17	4.3	5.4	21.1
Silt <sup>a</sup>	12	83	5	7.5	5.2	15.5
Sassafras loamy sand	75	20	5	0.8	6.9	3.4

<sup>a</sup> This soil was classified as a Keyport silt loam by the author; however, this soil is a silt according to the USDA Soil Textural Classification System.



Table 2. Distribution of radioactivity (% of applied) in the leachate and soil from columns of sandy loam, silt, loamy sand, and silt loam soils treated with [<sup>14</sup>C]DPX-M6316 and leached with 20 inches of water.

Soil type	Leachate	Soil	Total
<u>Thiophene-labeled</u>			
Sandy loam	96	4	102
Silt	72	28	93
Loamy sand	97	3	96
Silt loam (unaged)	93	7	98
Silt loam (aged)	72	28	116
<u>Triazine-labeled</u>			
Silt loam (unaged)	93	7	99
Silt loam (aged)	69	31	87

Table 3. Distribution of radioactivity (% of the applied) in leachate and soil from soil columns treated with [<sup>14</sup>C]DPX-M6316.

Soil type	Fraction	Segment (inches)	DPX-M6316	DPX-M6316 acid	O-Demethyl DPX-M6316	2-Ester-3-sulfonamide	2-Acid-3-sulfonamide	Triazine amine	Polar compounds
<u>Thiophene-labeled</u>									
Sandy loam	Leachate		92	3	ND <sup>a</sup>	ND	ND	--	ND
Silt	Leachate		60	5	ND	1	ND	--	ND
	Soil	0-2	4	ND	ND	ND	ND	--	ND
		8-12	5	ND	ND	3	ND	--	ND
Loamy sand	Leachate		75	3	ND	ND	ND	--	14
Silt loam, unaged	Leachate		76	4	ND	ND	ND	--	10
Silt loam, aged	Leachate		35	29	2	2	5	--	5
	Soil	0-2	2	ND	ND	3	ND	--	ND
<u>Triazine-labeled</u>									
Silt loam, unaged	Leachate		85	2	1	--	--	ND	5
Silt loam, aged	Leachate		24	26	2	--	--	ND	1
	Soil	0-2	2	ND	ND	--	--	2	ND
		4-6	ND	ND	ND	--	--	4	ND

<sup>a</sup> Not detected; the detection limit was 1% of the applied.

CASE GS -- DPX-M6316 STUDY 7 PM --

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 CHEM 128845 DPX-M6316

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FORMULATION 00 - ACTIVE INGREDIENT

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 FICHE/MASTER ID No MRID CONTENT CAT 01  
 Priester, T.M. 1986. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with [thiophene-2-<sup>14</sup>C]DPX-M6316. Document No. AMR-286-84. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 7.

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 SUBST. CLASS = S.

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 DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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 REVIEWED BY: T. Colvin-Snyder  
 TITLE: Staff Scientist  
 ORG: Dynamac Corp., Rockville, MD  
 TEL: 468-2500

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 APPROVED BY: T. Dougherty  
 TITLE: Chemist  
 ORG: EAB/HED/OPP  
 TEL: 557-0335

SIGNATURE:

DATE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Thiophene-labeled [<sup>14</sup>C]DPX-M6316 was very mobile in two sandy loam soils, a silt loam soil, and a silt soil ( $K_{ads}$  0.19-1.38,  $K_{des}$  0.27-1.67) based on batch equilibrium studies. Based on soil TLC studies, DPX-M6316 was very mobile in two sandy loam soils ( $R_f$  0.73-0.92) and was mobile in silt loam and silt soils ( $R_f$  0.44-0.49).
3. This study contributes toward the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the mobility (batch equilibrium and soil TLC) of unaged DPX-M6316 in four soils.

MATERIALS AND METHODS:

Experiment 1

Four soils (a silt, a silt loam, and two sandy loam soils; Table 1) were

treated with a 0.01 N calcium sulfate solution containing thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >98%, specific activity 10.7  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) at 0.2-6.0 ppm; the soil: water ratio was 1:1 (w:v). The solutions were shaken for 24 hours at 25°C, centrifuged, and the supernatant was analyzed for radioactivity by LSC.

Desorption of DPX-M6316 was studied using the 6.0 ppm soil solutions from the adsorption study. After a known volume of supernatant was discarded, untreated 0.01 N calcium sulfate solution was added to reestablish the 1:1 soil:water ratio. The samples were shaken for 24 hours at 25°C and then centrifuged. The supernatant from each solution was analyzed by LSC. This procedure was repeated five additional times. The supernatants of the final desorptions were analyzed by HPLC. Soils from the final desorption were extracted three times with acetone:0.1 M ammonium carbonate. The extracts were combined and analyzed for total radioactivity by LSC. The extracted soil was further extracted with 0.1 M ammonium carbonate, and then twice by acetone. These extracts were combined and analyzed for total radioactivity by LSC. All soil extracts were combined, filtered, concentrated, and analyzed by reverse-phase HPLC.

The extracted soil was again extracted with 0.1 M sodium hydroxide for 1 hour at 50°C, and then washed twice with acetone. Each extract was analyzed separately for radioactivity by LSC, and then the three extracts were combined and analyzed by LSC. The combined extract was concentrated, filtered, and analyzed by reverse-phase HPLC.

Extracted soil samples were analyzed for unextractable radioactivity by combustion and LSC.

## Experiment 2

The silt, silt loam, and sandy loam soils were hammer-milled to 1-5  $\mu\text{m}$  and used to prepare soil TLC plates (400  $\mu\text{m}$  thickness). Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316, terbacil (purity 99%), and carbonyl-labeled [ $^{14}\text{C}$ ]diuron (purity 95.2%) were spotted onto the lower 0.5 cm of the soil TLC plates. The plates were developed in water to a distance of 10 cm. Plates were air-dried and then analyzed by autoradiography.

## REPORTED RESULTS:

### Experiment 1

DPX-M6316 was very mobile in all four soils. Freundlich  $K_{\text{ads}}$  values were 0.19-1.38 and  $K_{\text{des}}$  values were 0.27-1.67 (Table 2). Following the final desorption DPX-M6316 and DPX-M6316 acid were the major [ $^{14}\text{C}$ ]-residues (Tables 3 and 4).

### Experiment 2

DPX-M6316 was very mobile in Woodstown sandy loam ( $R_f = 0.92$ ) and Cecil sandy loam ( $R_f = 0.73$ ) soils (Table 3). DPX-M6316 was mobile in Flanagan silt loam ( $R_f = 0.44$ ) and silt ( $R_f = 0.49$ ) soils.

## DISCUSSION:

1. For the soil TLC study, soils were hammer-milled to a 1-5  $\mu\text{m}$  particle size. Since sand and silt particles are larger than 5  $\mu\text{m}$ , this procedure would break down sand and silt particles into smaller particles than naturally occur in the soil.
2. The determined mobility classifications for Flanagan silt loam and silt soils differed in the batch equilibrium and soil TLC studies, possibly because the soils were hammer-milled in the TLC study.
3. The silt soil was classified as a Keyport silt loam soil by the study author; however, the Keyport soil is classified as a silt according to the USDA Soil Textural Classification System and is referred to as silt in this review.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Woodstown sandy loam	60	33	7	1.1	6.6	5.3
Cecil sandy loam	61	21	18	2.1	6.5	6.6
Flanagan silt loam	2	81	17	4.3	5.4	21.1
Silt a	12	83	5	7.5	5.2	15.5

<sup>a</sup> This soil was classified as Keyport silt loam soil by the author; however, this soil is a silt according to the USDA Soil Textural Classification System.

Table 2. Freundlich K and 1/n values for the adsorption and desorption of DPX-M6316 on four soils.

Soil type	Adsorption			Desorption		
	K <sub>ads</sub>	K <sub>oc</sub>	1/n	K <sub>ads</sub>	K <sub>oc</sub>	1/n
Woodstown sandy loam	0.081	7.4	0.79	0.27	19	0.16
Cecil sandy loam	0.19	9.1	1.0	0.72	34	0.18
Flanagan silt loam	1.38	32	0.87	1.67	39	0.64
Silt	1.25	17	0.90	1.39	19	0.67

Table 3. DPX-M6316 and its degradates (% of the recovered in the aqueous phase) after the final desorption at 25°C.

Compound	Woodstown sandy loam	Cecil sandy loam	Flanagan silt loam	Silt
2-Acid-3-sulfonamide	4	9	9	13
Thiophene sulfonamide	ND	ND	ND	1
Unknown III	ND	ND	1	9
2-Ester-3-sulfonamide	6	ND	2	ND
O-Demethyl DPX-M6316	ND	ND	4	1
DPX-M6316 acid	8	35	25	65
DPX-M6316	71	49	53	6



Table 4. DPX-M6316 and its degradates (% of the recovered in the soil) after the final desorption at 25°C.

Compound	Woodstown sandy loam	Cecil sandy loam	Flanagan silt loam	Silt
Unknown polar I	11	3	ND	ND
Unknown polar II	1	ND	ND	ND
2-Acid-3-sulfonamide	ND	3	4	10
Thiophene sulfonamide	ND	ND	ND	1
Unknown III	ND	5	3	6
2-Ester-3-sulfonamide	6	5	3	1
O-Demethyl DPX-M6316	ND	2	4	2
DPX-M6316 acid	10	23	17	50
Unknown IV	1	1	ND	ND
DPX-M6316	61	52	55	15
Unextracted	11	6	13	16

Table 5. Soil thin-layer chromatography  $R_f$  values for DPX-M6316 on four soils.

Soil type	$R_f$ value
Woodstown sandy loam	0.92
Cecil sandy loam	0.73
Flanagan silt loam	0.44
Silt	0.49

CASE GS -- DPX-M6316 STUDY 8 PM --

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CHEM 128845 DPX-M6316

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FORMULATION 00 - ACTIVE INGREDIENT

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FICHE/MASTER ID No MRID CONTENT CAT 01  
Rapisarda, C. and M.T. Scott. 1985. Field dissipation studies with [thio-  
phene-2-<sup>14</sup>C]DPX-M6316 in U.S. and Canadian soils. Document No. AMR-460-85.  
E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760.  
Reference 8.-----  
SUBST. CLASS = S.-----  
DIRECT RVW TIME = 7 (MH) START-DATE END DATE-----  
REVIEWED BY: T. Colvin-Snyder  
TITLE: Staff Scientist  
ORG: Dynamac Corp., Rockville, MD  
TEL: 468-2500-----  
APPROVED BY: T. Dougherty  
TITLE: Chemist  
ORG: EAB/HED/OPP  
TEL: 557-0335

SIGNATURE:

DATE:

CONCLUSIONS:Field Dissipation - Terrestrial

1. This study is scientifically valid.
2. Thiophene-labeled DPX-M6316 (radiochemical purity >98%), at ~80 g ai/ha, degraded with a half-life of 3-21 days in field plots of silt loam soil near Moscow, Idaho, loam soil near Akron, Colorado, silty clay loam soil near Fargo, North Dakota, and silty clay loam soil near Manitoba, Canada. The degradates 0-demethyl DPX-M6316 and 2-ester-3-sulfonamide were recovered in the soil at all four test sites. Most [<sup>14</sup>C]residues remained in the upper 5 inches of the soils throughout the 60- to 80-week study at all four test sites.
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the dissipation of DPX-M6316 in field plots of silt loam, loam, and silty clay loam soil.

## MATERIALS AND METHODS:

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >98%, specific activity 23.3  $\mu\text{Ci}/\text{mg}$ , New England Nuclear) was applied at ~80 g ai/A to the surface of soil inside stainless steel cylinders (4-inch diameter x 15-inch length, extending ~1 inch above the soil surface) that had been driven into field plots located near Moscow, Idaho (treatment date April 23, 1984); Akron, Colorado (treatment date May 17, 1984); Fargo, North Dakota (treatment date June 6, 1984); and Fisher Branch, Manitoba, Canada (treatment date June 7, 1984) (Table 1). Soil samples (0- to 2-, 2- to 5-, 5- to 9-, and 9- to 14-inch depths) were collected from inside one stainless steel cylinder at each test site at intervals up to 80 weeks posttreatment. Samples were frozen at  $-25^\circ\text{C}$  until analysis.

The soil samples were thawed, air-dried for 3-4 days, and homogenized by grinding. A portion of each sample was analyzed for total radioactivity by LSC following combustion. Soil samples containing more than 5% of the applied radioactivity were analyzed for DPX-M6316 and its degradates. The soil samples were extracted sequentially once with acetone:0.1 M ammonium carbonate (90:10), once with 0.1 M ammonium carbonate, and twice with acetone. The two acetone extracts and the ammonium carbonate extract were combined. Aliquots of the acetone: ammonium carbonate extract (first extraction) and the combined extract were analyzed for total radioactivity by LSC. The two solutions were then combined, concentrated, applied to silica gel plates, and analyzed by TLC. The plates were developed in methylene chloride:methanol:1 M ammonium hydroxide (170:27:3). [ $^{14}\text{C}$ ]Residues were visualized using autoradiography. Radioactive zones were scraped from the plates and quantified by LSC. The nonradiolabeled reference compounds were visualized under ultraviolet light.

A portion of each extracted soil was analyzed for remaining radioactivity by LSC following combustion. Soils that contained a high concentration of unextracted [ $^{14}\text{C}$ ]residues were further extracted with 0.1 N sodium hydroxide at  $70^\circ\text{C}$ . The samples were cooled and diluted with distilled water, centrifuged, and the supernatant was decanted. The extracted soil was twice washed with distilled water. The sodium hydroxide extract and the two aqueous washes were combined, and aliquots were analyzed for total radioactivity by LSC.

## REPORTED RESULTS:

DPX-M6316 degraded with a half-life of 3-21 days at all four test sites (Table 5). O-Demethyl DPX-M6316 was a major degradate at the Idaho and Colorado sites. O-Demethyl DPX-M6316 and 2-ester-3-sulfonamide were recovered in the soil at all four test sites. Up to 35% of the applied [ $^{14}\text{C}$ ]residues were unextractable at the final sampling interval; alkaline hydrolysis of the extracted soils failed to extract more than ~20% additional radioactivity (2.5-7.1% of the applied). The unextractable radioactivity was assumed to be incorporated into the soil.

Total radioactivity in the upper 14 inches of the plots declined to ~48% of the applied at 72-80 weeks at the Idaho and Colorado sites,

and to 69-70% of the applied at 60-72 weeks at the North Dakota and Canada sites (Table 3). Evolution of CO<sub>2</sub> was assumed to explain the decrease in recovered radioactivity with time. Most [<sup>14</sup>C]residues remained in the upper 5 inches of soil at all four test sites.

DISCUSSION:

1. The test plots were too small to be representative of actual use conditions.
2. All degradates were not characterized. The TLC band between R<sub>f</sub> 0.10-0.24, which included 2-acid-3-sulfonamide, DPX-M6316 acid, and thiophene sulfonamide, was not separated; however, this band contained up to 48.9 ppb of the [<sup>14</sup>C]residues.
3. The test substance was not a typical end-use product.
4. Half-lives were calculated by the registrant and not the reviewer.

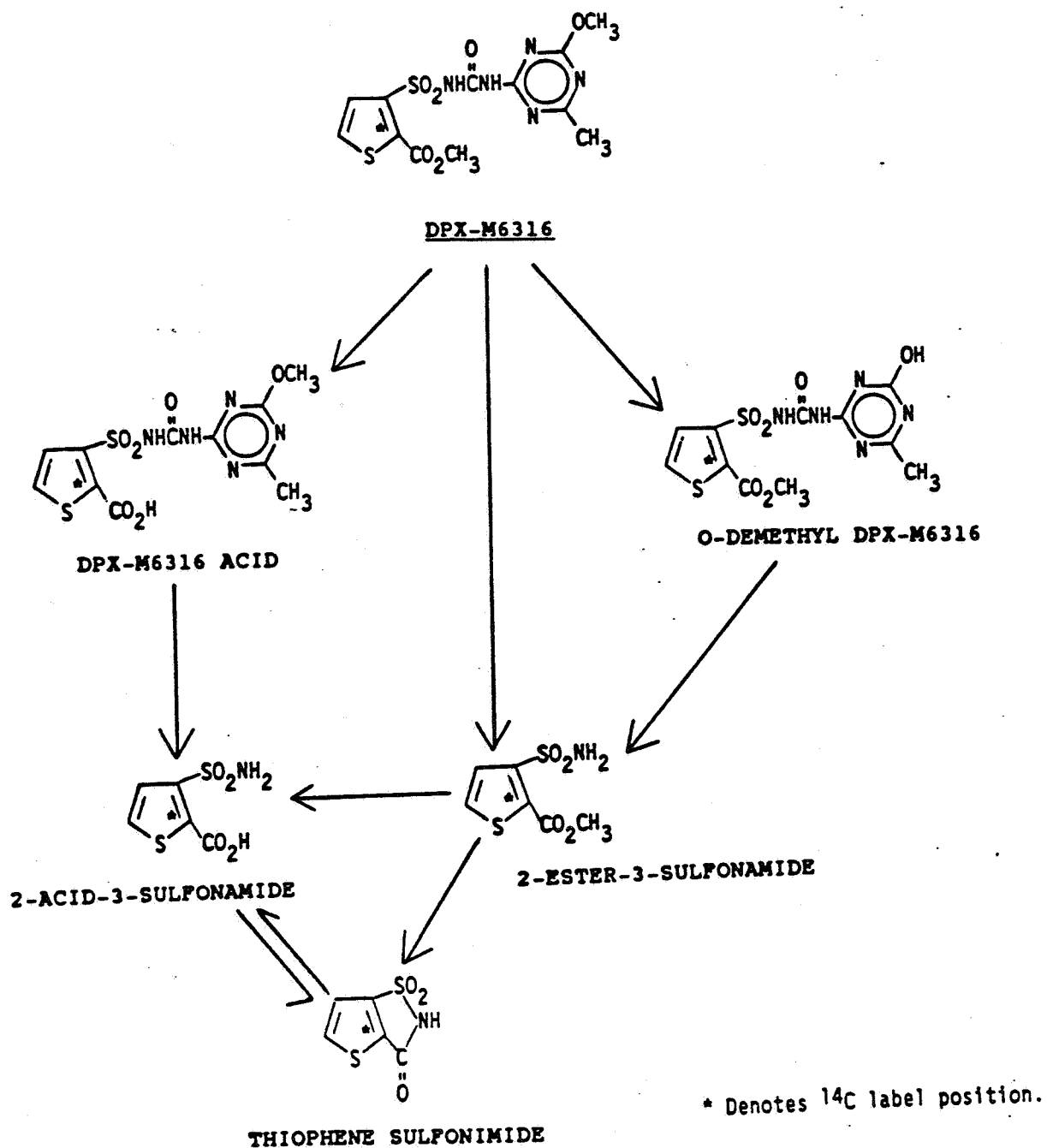


Figure 1. Proposed metabolic pathway of [thiophene-2-<sup>14</sup>C]DPX-M6316 in field soil dissipation studies.

Table 1. Soil characteristics.

Site	Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
		%					
Akron, Colorado	Loam	40	43	17	1.2	6.5	10.8
Moscow, Idaho	Silt loam	2	75	23	2.1	6.4	20.2
Fargo, North Dakota	Silty clay loam	0	67	33	5.3	7.3	46.2
Fisher Branch, Manitoba, Canada	Silty clay loam	1	59	40	6.4	7.9	41.8

Table 2. DPX-M6316 and its degradates in soil treated with [<sup>14</sup>C]DPX-M6316 at ~80 g ai/A.

Sampling interval (weeks)	Soil depth (inches)	Extractable [ <sup>14</sup> C] (ppb as DPX-M6316 equivalents)					Unextractable (% of applied)
		DPX-M6316	O-Demethyl DPX-M6316	2-Ester-3-sulfonamide	Rand 1 <sup>a</sup>	Polar	
<u>Moscow, Idaho - silt loam</u>							
1	0-2	117.8	17.3	5.2	15.6	ND	12.0
2	0-5	50.1	43.5	2.2	28.6	ND	18.5
4	0-5	36.3	47.6	6.2	25.0	ND	23.1
10	0-5	4.7	8.7	3.3	5.0	5	35.4
24	0-5	1.3	3.1	1.3	5.0	1.2	33.2
53	0-9	0.6	<0.3	<0.3	0.6	<0.3	28.1
65	0-9	<0.5	<0.5	<0.5	<0.5	<0.5	24.3
80	0-9	<0.5	<0.5	<0.5	<0.5	<0.5	24.5
<u>Akron, Colorado - loam</u>							
0	0-2	131.5	0.7	2.8	2.8	ND	--
1	0-5	<1.2	ND	<1.2	2.4	ND	--
2	0-5	<1.1	ND	<1.1	4.4	ND	47.7
4	0-5	1.7	ND	3.6	4.9	ND	42.5
10	0-5	2.9	ND	1.1	5.4	ND	44.5
24	0-9	<0.1	--	--	--	ND	29.2
50	0-5	<0.3	<0.3	<0.3	<0.3	<0.3	29.8
61	0-5	<0.2	<0.2	<0.2	<0.2	0.9	22.6
72	0-9	<0.1	<0.1	<0.1	0.2	<0.1	22.8
<u>Fargo, North Dakota - silty clay loam</u>							
0	0-2	124.6	1.5	9.2	9.2	ND	7.0
1	0-5	49.8	3.6	2.8	42.5	ND	13.2
2	0-5	50.4	27.5	4.1	5.9	ND	19.0
4	0-5	10.7	30.6	<1.5	10.7	ND	29.0
10	0-9	0.7	--	--	--	--	10.2
20	0-14	0.8	--	--	--	--	13.2
48	0-9	0.9	<0.2	0.2	2.7	44	17.5
60	0-9	0.9	0.3	<0.2	0.9	0.3	21.8
<u>Fisher Branch, Manitoba, Canada - silty clay loam</u>							
0	0-2	134.0	3.4	6.7	13.4	ND	8.0
1	0-5	15.0	3.8	<1.4	11.8	ND	4.4
2	0-5	19.9	2.6	<1.7	48.9	ND	17.2
4	0-9	1.0	0.5	<0.3	10.4	ND	10.4
10	0-9	3.1	8.0	<2.1	17.7	ND	36.3
20	0-9	1.6	--	--	--	--	18.0
48	0-9	<0.2	<0.2	<0.2	2.6	0.4	26.1
60	0-5	0.6	0.6	<0.3	1.8	<0.3	35.7
72	0-9	<0.2	0.2	<0.2	0.9	<0.2	ND

<sup>a</sup> Includes 2-acid-3-sulfonamide, DPX-M6316 acid, and thiophene sulfonimide.



Table 3. Total [<sup>14</sup>C]residues (% of the applied) in soil treated with [<sup>14</sup>C]DPX-M6316 at ~80 g ai/A.

Soil depth (inches)	Sampling interval (weeks)														
	0	1	2	4	10	20	24	48	50	53	60	61	65	72	80
<u>Moscow, Idaho - silt loam</u>															
0-2	100.2	100.2	91.8	84.3	74.4	--	59.0	--	--	42.2	--	--	35.8	--	34.8
2-5	ND	2.0	8.0	4.5	7.4	--	12.1	--	--	12.9	--	--	22.7	--	12.1
5-9	ND	ND	ND	ND	ND	--	0.1	--	--	2.9	--	--	2.8	--	1.1
9-14	ND	ND	ND	ND	ND	--	ND	--	--	0.6	--	--	0.4	--	0.2
<u>Akron, Colorado - loam</u>															
0-2	103.5	22.1	27.6	32.3	40.9	--	29.4	--	32.8	--	--	29.3	--	30.4	--
2-5	0.2	37.9	30.5	18.9	11.4	--	38.5	--	16.9	--	--	21.0	--	16.5	--
5-9	ND	3.2	1.8	1.1	1.7	--	2.1	--	1.5	--	--	2.1	--	1.3	--
9-14	ND	ND	ND	1.6	0.5	--	ND	--	ND	--	--	ND	--	0.2	--
<u>Fargo, North Dakota - silty clay loam</u>															
0-2	102.5	60.7	67.1	54.4	39.4	41.1	--	39.8	--	--	33.0	--	--	--	--
2-5	ND	18.1	17.0	27.7	28.7	24.1	--	29.1	--	--	29.6	--	--	--	--
5-9	ND	2.5	0.8	4.3	13.9	17.9	--	6.9	--	--	6.1	--	--	--	--
9-14	ND	0.8	ND	ND	ND	6.3	--	0.7	--	--	0.1	--	--	--	--
<u>Fisher Branch, Manitoba, Canada - silty clay loam</u>															
0-2	102.8	24.0	56.0	45.7	34.3	31.6	--	43.1	--	--	49.2	--	--	38.7	--
2-5	0.4	4.2	7.8	26.3	24.1	23.5	--	28.2	--	--	24.6	--	--	27.7	--
5-9	ND	0.3	0.6	12.6	13.1	16.9	--	5.5	--	--	2.3	--	--	3.4	--
9-14	ND	1.5	ND	0.1	1.5	1.4	--	1.6	--	--	0.7	--	--	0.4	--

Table 4. Meteorological data for the study sites.

Sampling interval (weeks)	Cumulative rainfall (inches)	Air temperatures (°F)	Soil temperatures (4-inch depth)
<u>Moscow, Idaho</u>			
1	0.41	31-82	41-69
2	1.32	29-69	43-68
4	2.13	33-74	50-72
10	6.40	35-105	52-90
24	9.05	18-99	34-89
53	22.58	-12-81	31-66
65	26.78	33-99	43-87
80	--	-20-78	32-86
<u>Akron, Colorado</u>			
0	--	--	--
1	0.90	50-76	61 <sup>a</sup>
2	1.21	50-76	61
4	2.18	51-81	72
10	4.17	59-89	80
24	13.64	24-88	48-78
50	17.67	23-59 <sup>a</sup>	30-53
65	23.86	65-74 <sup>a</sup>	65-79
80	--	29-59 <sup>a</sup>	51-77
<u>Fargo, North Dakota</u>			
0	--	--	--
1	2.10	50-76 <sup>a</sup>	59-68 <sup>a</sup>
2	2.57	50-81	62-76
4	2.70	51-88	63-81
10	3.44	53-102	65-84
20	11.51	13-100	37-81
48	16.91	-26-66	17-44
60	27.29	26-98	35-84
<u>Fisher Branch, Manitoba, Canada</u>			
0	--	--	--
1	2.40	49-73 <sup>a</sup>	--
2	5.00	49-73	--
4	6.05	53-78	--
10	10.70	53-81	--
20	18.40	12-59	--
48	20.16	-13-66	--
60	27.72	45-75	--
72	--	1-57	--

<sup>a</sup> Average monthly temperature for interval; all other data are range of daily temperatures for interval.

Table 5. First order rate constants and calculated half-lives of DPX-M6316 in soil treated with [<sup>14</sup>C]DPX-M6316 at ~80 g ai/A.

Site	Soil type	First order rate constant, K (weeks <sup>-1</sup> ) <sup>a</sup>	Half-life (days) <sup>b</sup>
Akron, Colorado	Loam	--	3
Moscow, Idaho	Silt loam	-0.244	20
Fargo, North Dakota	Silty clay loam	-0.341	14
Fisher Branch, Manitoba, Canada	Silty clay loam	-0.824	6

<sup>a</sup> K values were determined from linear least squares best fitting lines to the first order kinetic equation:

$$\text{LN} (\% \text{ of DPX-M6316}) = Kt + \text{LN} (\% \text{ DPX-M6316})_{t=0}$$

where t = time in weeks

<sup>b</sup> Half-life values were determined by the following equation:

$$\text{Half-life} = \frac{0.693}{K} \times \frac{7 \text{ days}}{\text{week}}$$

## EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report but do not fulfill data requirements unless noted in the Recommendations section of this report.

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%), at 0.5 and 5.0 ppm, degraded with half-lives of 3-6 days in sterile aqueous buffered solutions of pH 5, but was relatively stable to hydrolysis at pH 7 and 9, with ~10% degradation of parent occurring within thirty days. (Rhodes et al., Account #263760). 2-Ester-3-sulfonamide was the major degradate at pH 5 (62-64% of the applied at day 30) and the only degradate at pH 7 (9-10% of the applied) and pH 9 (4-8% of the applied). 2-Ester-3-triuret and O-demethyl DPX-M6316 were detected in pH 5 solutions at maximum concentrations of 8-32% and 4-7% of the applied, respectively. In a related study, triazine amine was the major degradate of triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 at pH 5, representing 36% of the applied radioactivity at 31 days.

Radiolabeled [ $^{14}\text{C}$ ]triazine amine (radiochemical purity 99%), at 0.5 and 5 ppm, was stable to hydrolysis at pH 5, 7, and 9 for 30 days (Friedman, Acc. No. 252492).

Thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purities >98%), at 10 ppm, degraded with a half-life of 30-72 hours in a pH 5 aqueous buffered solution irradiated with natural sunlight, and a half-life of 72-144 hours in pH 7 and 9 solutions (Ryan, Acc. No. 263760). DPX-M6316 in the dark control degraded with a half-life of >336 hours. In the irradiated pH 7 solution treated with triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316, methyl-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl-amino)-3-thiophene-carboxylate (tentative), triazine amine, and triazine urea were the major degradates (0.78, 1.24, and 1.55 ppm, respectively, at 336 hours). In the pH 7 solution treated with thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316, methyl-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl-amino)-3-thiophene-carboxylate was the only major degradate (0.84 ppm at 336 hours).

Thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purities >98%), at 0.83 g/cm<sup>2</sup>, degraded with a half-life of 7-14 days in sunlight-irradiated silt loam soil; the half-life was 14-21 days in the dark controls (Ferguson, Acc. No. 263760). The major degradate of the thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 was 2-ester-3-sulfonamide (20.4% of the applied at 30 days). The major degradate of the triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 was triazine amine (32.3% of the applied at 30 days). Other degradates included O-demethyl DPX-M6316, DPX-M6316 acid, 2-acid-3-sulfonamide, thiophene-sulfonamide, and triazine urea.

Under aerobic conditions in soil, thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 degraded to  $^{14}\text{CO}_2$  via several intermediates with a half-life of 2-6 days; 31-44% of the applied radioactivity was mineralized after 20 weeks of incubation (Rapisarda, Acc. No. 263760). DPX-M6316 acid, 2-acid-3-sulfonamide, 2-ester-3-sulfonamide, O-demethyl DPX-M6316, and thiophene sulfonimide each comprised up to 30% of the recovered radioactivity. Unextractable residues comprised up to 46% of the recovered radioactivity.

Surrogate data for the triazine moiety was obtained from studies on DPX-4189. Under aerobic conditions in soil, DPX-4189, at 0.1 and 1 ppm, degraded with a half-life of 4-10 days (Rapisarda, Acc. No. 072846). Triazine amine was isolated at up to 25% of the recovered at one month, then plateaued at about 15% of the recovered during the 4-7 months remaining incubation period.

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purity >99%), at 52-60 ppb, degraded with half-lives of 7-14 days in anaerobic (flooded) loamy sand sediment and 14-28 days in anaerobic (flooded) sandy loam and silt loam sediments (Lewis and Carter, Acc. No. 263760). The major degradates were 2-ester-3-sulfonamide (maximum concentration 13-40% of recovered), 2-acid-3-sulfonamide (maximum concentration 25-43%), and 2-acid-3-sulfonic acid (maximum concentration 16-24%). 2-Ester-3-triuret, O-demethyl DPX-M6316, and DPX-M6316 acid were also detected. In sterile anaerobic sediments, DPX-M6316 degraded with a half-life of 56-112 days.

Triazine-labeled [ $^{14}\text{C}$ ]chlorsulfuron (radiochemical purity >99%), at 1 ppm, degraded with a half-life of >52 weeks in silt loam soil incubated under anaerobic conditions (Chrzanowski, Acc. No. 260973). Chlorsulfuron and DPX-M6316 have the same triazine moiety. The major degradate, triazine amine, increased over time with a maximum concentration of 21% at 52 weeks.

Unaged thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 (radiochemical purities >98%) was very mobile in columns of sandy loam, loamy sand, silt, and silt loam soils; 72-97% of the recovered radioactivity was leached from the columns (Ferguson, Acc. No. 263760).  $K_d$  values were 0, 0.01, 0.86, and 0.15-0.16 for sandy loam, loamy sand, silt, and silt loam soils, respectively. DPX-M6316 was the major [ $^{14}\text{C}$ ]compound in the leachate from the unaged soil. Aged (6 days) thiophene- and triazine-labeled [ $^{14}\text{C}$ ]DPX-M6316 residues were very mobile in columns of silt loam soil; 69-72% of the thiophene and triazine-labeled [ $^{14}\text{C}$ ]-residues were recovered in the leachate. DPX-M6316 acid comprised 35-44% of the residues in the leachate from the aged soil.

Thiophene-labeled [ $^{14}\text{C}$ ]DPX-M6316 was very mobile in two sandy loam soils, a silt loam soil, and a silt soil ( $K_{ads}$  0.19-1.38,  $K_{des}$  0.27-1.67) based on batch equilibrium studies (Priester, Acc. No. 263760). Based on soil TLC studies, DPX-M6316 was very mobile in two sandy loam soils ( $R_f$  0.73-0.92) and was mobile in silt loam and silt soils ( $R_f$  0.44-0.49).

Thiophene-labeled DPX-M6316 (radiochemical purity >98%), at 80 g ai/ha, degraded with a half-life of 3-20 days in field plots of silt loam soil near Moscow, Idaho, loam soil near Akron, Colorado, silty clay loam soil near Fargo, North Dakota, and silty clay loam soil near Manitoba, Canada (Rapisarda and Scott, Acc. No. 263760). The degradates O-demethyl DPX-M6316 and 2-ester-3-sulfonamide were recovered in the soil at all four test sites. Most [ $^{14}\text{C}$ ]-residues remained in the upper 5 inches of soil throughout the 60- to 80-week study at all four test sites; however, some leaching of residues was evident.

In soil field studies, triazine-labeled [ $^{14}\text{C}$ ]chlorsulfuron (radiochemical purity >99%), applied at 100 g ai/A, degraded with a half-life of 2-4 weeks (Han,

Acc. No. 260974). The metabolite, triazine amine, reached maximum levels of 48% of the applied at 4-8 weeks, then declined to 13% at 16 weeks, and plateaued at that level for the 77-week study period. Some leaching of the triazine amine at the lowest depth sampled (20-38 cm) was evident.

Thiophene-labeled [<sup>14</sup>C]DPX-M6316, at 4-5 ppm, did not bioaccumulate in bluegill sunfish during 28 days exposure (Larkin, Acc. No. 072646). Also, since the octanol/water partition coefficient for DPX-M6316 is 0.027, residues would not be expected to accumulate in fish.

For 30-day crop (beets, peas, sunflowers) rotation intervals following soil application of thiophene-labeled [<sup>14</sup>C]DPX-M6316 (radiochemical purity >98%) at 34.8 g ai/A (1.8 x maximum proposed use rate), residues at maturity were detected in beet and sunflower foliage at up to 22 ppb and 17 ppb, respectively (Hardesty, Acc. No. 254641).

Soil was treated with triazine-labeled [<sup>14</sup>C]chlorsulfuron at 28.3 g ai/A and then planted to soybeans, rape, and sugar beets 1 year posttreatment (Han, Acc. No. 260975). Sugar beets died after one month. Residues were detected at 1-7 ppb in seeds and foliage of both rape and soybeans.

#### RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of and the exposure of humans and nontarget organisms to DPX-M6316. The submission of data relevant to registration requirements (Subdivision N) for terrestrial food crop use sites is summarized below:

Hydrolysis studies: Two studies (Rhodes et al., Acc. No. 263760 and Friedman, Acc. No. 252492) were reviewed and fulfill data requirements by providing information on the hydrolysis of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 at pH 5, 7, and 9.

Photodegradation studies in water: One study (Ryan, Acc. No. 263760) was reviewed and fulfills data requirements by providing information on the photodegradation of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 in water.

Photodegradation studies on soil: One study (Ferguson, Acc. No. 263760) was reviewed and fulfills data requirements by providing information on the photodegradation of thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 on soil.

Photodegradation studies in air: No data were reviewed. However, no data are required.

Aerobic soil metabolism studies: Based on previously reviewed data (Rapisarda, Acc. No. 072846 and Rapisarda, Acc. No. 245878) and the response to the review of the former study, no additional data are required.

Anaerobic soil metabolism studies: No data were included in the current submission; however, two studies were previously reviewed. The first study (Lewis and Carter, Acc. No. 263760), a satisfactory anaerobic aquatic metabolism study using thiophene-labeled [<sup>14</sup>C]DPX-M6316 fulfills anaerobic soil metabolism

data requirements for the thiophene label only. The second study (Chrzanowski, Acc. No. 260973), an acceptable anaerobic aquatic metabolism study using triazine-labeled [<sup>14</sup>C]DPX-W4189, fulfills data requirements by providing surrogate data for the triazine moiety of DPX-M6316.

Anaerobic aquatic metabolism studies: One study (Lewis and Carter, Acc. No. 263760) was reviewed and fulfills data requirements by providing information on the anaerobic metabolism of thiophene-labeled [<sup>14</sup>C]DPX-M6316 in aquatic systems. No data are required because DPX-M6316 has no aquatic or aquatic impact uses.

Aerobic aquatic metabolism studies: No data were reviewed; however, no data are required because DPX-M6316 has no aquatic or aquatic impact uses.

Leaching and adsorption/desorption studies: Two studies (Ferguson, Acc. No. 263760; Priester, Acc. No. 263760) were reviewed. The studies fulfill data requirements by providing information on the mobility of unaged (column leaching, batch equilibrium, and soil TLC) [<sup>14</sup>C]DPX-M6316 in four soils and aged (column leaching) thiophene- and triazine-labeled [<sup>14</sup>C]DPX-M6316 in one soil.

Laboratory volatility studies: No data were reviewed. However, no data are required because of low vapor pressure.

Field volatility studies: No data were reviewed. However, no data are required.

Terrestrial field dissipation studies: One study (Rapisarda and Scott, Acc. No. 263760) was reviewed and fulfills data requirements by providing information on the dissipation of DPX-M6316 in field plots of silt loam, loam, and silty clay loam soil.

Aquatic field dissipation studies: No data were reviewed; however, no data are required because DPX-M6316 has no aquatic or aquatic impact uses.

Forestry dissipation studies: No data were reviewed; however, no data are required because DPX-M6316 has no forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed. However, all data may be required pending decision by Toxicology Branch concerning residues of DPX-M6316 acid and the triazine amine.

Confined accumulation studies on rotational crops: No data were included in the current submission; however, two studies were previously reviewed. The first study (Han, Acc. No. 260975) did not fulfill data requirements. The second study (Hardesty, Acc. No. 254641) will fulfill data requirements for the thiophene label only. An acceptable confined rotational crop study using triazine-labeled [<sup>14</sup>C]DPX-M6316 is needed.

Field accumulation studies on rotational crops: No data were reviewed. The data requirement is deferred pending the results of additional confined rotational crop studies.

Accumulation studies on irrigated crops: No data were reviewed; however, no data are required because DPX-M6316 does not have an aquatic food crop or aquatic noncrop use, is not used in and around holding ponds used for irrigation purposes, and has no use involving effluents or discharges to water used for crop irrigation.

Laboratory studies of pesticide accumulation in fish: Based on previously reviewed data (Larkin, Acc. No. 072646), no additional data are required.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed; however, no data are required because DPX-M6316 has no forestry, aquatic nonfood, or aquatic impact uses.

Reentry studies: No data were reviewed. The data requirement is deferred pending evaluation of toxicity data.

#### REFERENCES

The following studies are new submittals reviewed in this report:

Ferguson, F.M. 1986a. Photodegradation of [thiophene-2-<sup>14</sup>C]DPX-M6316 and [triazine-2-<sup>14</sup>C]DPX-M6316 on soil. Document No. AMR-505-86. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 3.

Ferguson, E.M. 1986b. Soil column leaching behavior of [thiophene-2-<sup>14</sup>C]-DPX-M6316 and [triazine-2-<sup>14</sup>C]DPX-M6316. Document No. AMR 454-85. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 6.

Lewis, W. and L.G. Carter. 1986. Anaerobic aquatic metabolism of [thiophene-2-<sup>14</sup>C]DPX-M6316. Document No. AMR-540-86. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 5.

Priester, T.M. 1986. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with [thiophene-2-<sup>14</sup>C]DPX-M6316. Document No. AMR-286-84. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 7.

Rapisarda, C. Undated. Aerobic soil metabolism of DPX-M6316 [thiophene-2-<sup>14</sup>C]. Document No. AMR-236-84. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 4.

Rapisarda, C. and M.T. Scott. 1985. Field dissipation studies with [thiophene-2-<sup>14</sup>C]DPX-M6316 in U.S. and Canadian soils. Document No. AMR-460-85. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 8.

Rhodes, B.C., M.K. Koeppel, and R.W. Reiser. 1986. Hydrolysis of <sup>14</sup>C-DPX-M6316. Document No. AMR-221-84. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 1.



Ryan, D.L. 1986. Photodegradation of [thiophene-2-<sup>14</sup>C]DPX-M6316 and [triazine-2-<sup>14</sup>C]DPX-M6313 in water. Document No. AMR-511-86. E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acc. No. 263760. Reference 2.

The following studies were previously reviewed by EAB:

Anderson, J.J. Undated. Crop rotation study with <sup>14</sup>C-metsulfuron methyl in the field. Document No. AMR-190-84. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Friedman, P.L. Undated. Hydrolysis of <sup>14</sup>C-4-methoxy-6-methyl-1,3,5-triazine-2-amine. Document No. AMR-136-83. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Han, J. C-Y. Undated. Crop rotation study with <sup>14</sup>C-DPX-W4189. Document No. AMR-46-81. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Hardesty, P.T. Undated. Crop rotation studies with DPX-M6316 [thiophene-<sup>14</sup>C] in the greenhouse. Document No. AMR-256-84. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 254641.

Harvey, J., Jr. Undated. Crop rotation study with <sup>14</sup>C-DPX-T6376 in the greenhouse. Document No. AMR-120-83. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Koeppe, M.K. and B.C. Rhodes. Undated. Hydrolysis of DPX-M6316 [thiophene-2-<sup>14</sup>C]. Document No. AMR-224-84. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Larkin, J.C. 1984. DPX-M6316 [thiophene-2-<sup>14</sup>C] flow-through bioconcentration study with bluegill sunfish. Document No. AMR-182-84. Prepared by Biospherics Incorporated, MD, and submitted by E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

Rapisarda, C. Undated. Microbial degradation of <sup>14</sup>C-DPX-4189 in soil. Document No. AMR-43-81. E.I. du Pont de Nemours and Co., Inc., Wilmington, DE. Acc. No. 072846.

The various submissions in Acc. No. 263751 (Pesticide petition for tolerances for DPX-M6316 in or on wheat grain and barley grain and application for registration of Du Pont "Harmony" herbicide, Volume I of X) were not reviewed because:

#### Reference

- 1 Tolerance petition letter
- 2 Tolerance petition fees letter
- 3 Application for pesticide registration

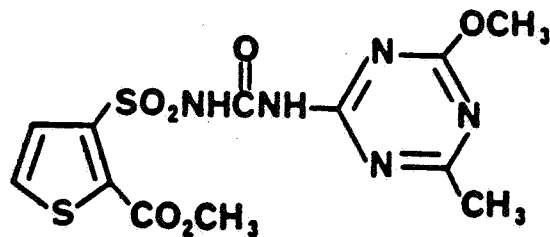
- 4 Certification with respect to citation of data
- 5 Label technical data
- 6 Response to EPA letter requesting additional data
- 7 Analytical methodology and physical/chemical properties of DPX-M6316
- 8 Letter concerning submittal of samples
- 9 Letter concerning submittal of technical grade DPX-M6316
- 10 Proposed label for Du Pont "Harmony" herbicide
- 11-12 Residue chemistry studies
- 13 Analytical methodology
- 14 Freezer storage stability summary data
- 15-29 Residue chemistry data
- 30 Statement of reasonable grounds in support of the petition
- 31 Wheat and barley straw usage study

The various submissions in Acc. No. 263752 (Pesticide petition for tolerances for DPX-M6316 in or on wheat grain and barley grain and application for registration of Du Pont "Harmony" herbicide, Volume II of X) were not reviewed because:

Reference

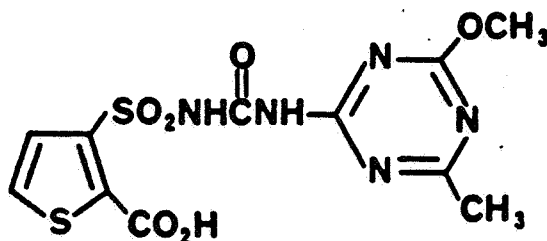
- 1 Statement of formula for technical grade DPX-M6316
- 2 Statement of formula for Du Pont "Harmony" herbicide
- 3 Statement on purity of beginning materials for DPX-M6316
- 4 Statement on purity of beginning materials for "Harmony" 75DF
- 5-6 Manufacturing processes
- 7 DPX-M6316 impurity profiles
- 8 Batch analyses data of "Harmony" 75DF
- 9 Product chemistry data for DPX-M6316
- 10-13 Analytical methodology

APPENDIX  
DPX-M6316 AND ITS DEGRADATES



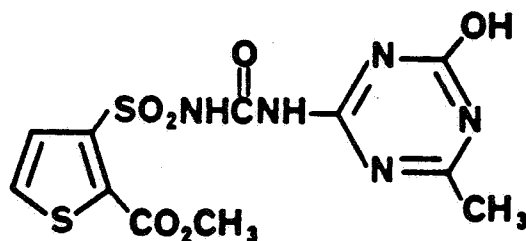
Methyl 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate

(DPX-M6316)



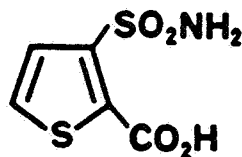
3-[[[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid

(DPX-M6316 acid)



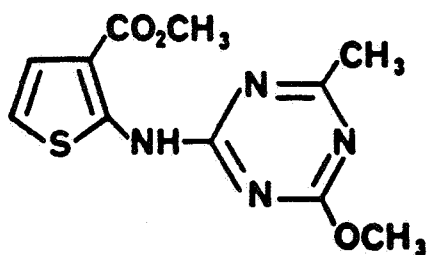
Methyl 3-[[[[(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate

(O-Demethyl DPX-M6316)



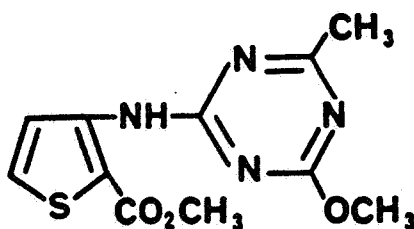
(3-Aminosulfonyl)-2-thiophenecarboxylic acid

(2-Acid-3-sulfonamide)



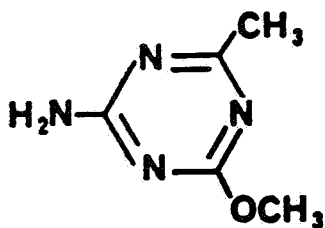
Methyl-2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl-amino)-3-thiophenecarboxylate

(Proposed photoproduct)



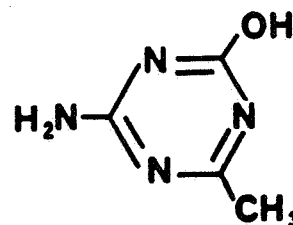
Methyl 3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl-amino)-2-thiophenecarboxylate

(Synthesized photoproduct isomer)



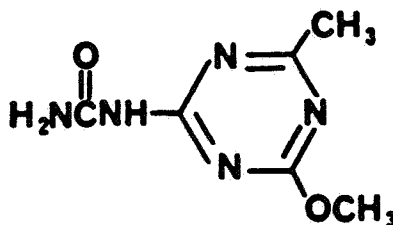
4-Methoxy-6-methyl-1,3,5-triazin-2-amine

(Triazine amine)



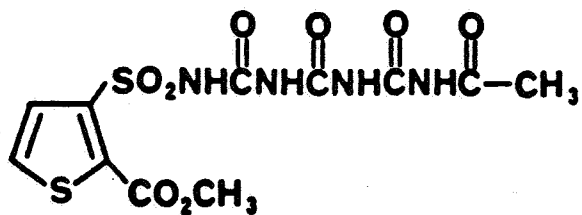
4-Hydroxy-6-methyl-1,3,5-triazin-2-amine

(O-demethyl triazine amine)



N-(4-Methoxy-6-methyl-1,3,5-triazin-2-yl) urea

(Triazine urea)



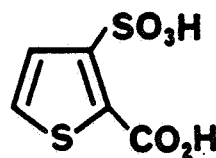
Methyl 3-[[[(acetylamino)carbonylamino]carbonylamino]carbonylamino]sulfonyl]-2-thiophenecarboxylate

(2-Ester-3-triuret)



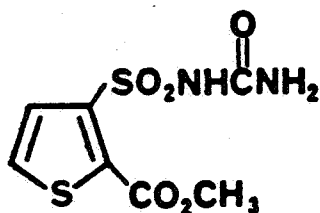
Thieno[2,3-d]isothiazol-3(2H)-one-1,1-dioxide

(Thiophene sulfonimide)



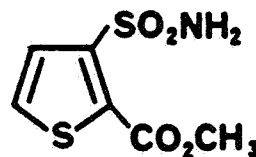
3-Sulfo-2-thiophenecarboxylic acid

(2-Acid-3-sulfonic acid)



Methyl 3-[[[(amino)carbonyl]sulfonyl]-2-thiophenecarboxylate

(2-Ester-3-urea)



Methyl 3-(aminosulfonyl)-2-thiophenecarboxylate

(2-Ester-3-sulfonamide)

Friedman, P.L. Undated. Hydrolysis of  $^{14}\text{C}$ -4-methoxy-6-methyl-1,3,5-triazin-2-amine. Document No. AMR-136-83. (company confidential) E.I. DuPont de Nemours and Co. Experimental Station. Wilmington, DE. 9 pages, 4 figures. No references

### Introduction

The hydrolysis of  $^{14}\text{C}$ -4-methoxy-6-methyl-1,3,5-triazin-2-amine was studied at 25°C, in sterile buffer solutions of pH 5, 7 and 9.

### Experimental

$^{14}\text{C}$ -4-methoxy-6-methyl-1,3,5-triazin-2-amine was prepared, and found to be 99% radiopure with a specific activity of 35.4 uCi/mg. Stock solutions at 0.5 and 5.0 ppm were prepared in pHydrion Buffer Solutions of pH 5, 7 and 9, which had been previously autoclaved for 1 hour on 3 consecutive days. All glassware had been similarly autoclaved.

Solutions were stored in glass stoppered Erlenmeyer flasks in a dark autoclave at a constant 25°C, with 20 ml aliquots being taken on days 0, 1, 2, 5, 7, 14, 21 and 30.

Analysis for total radioactivity was by LSC counting. Component separation was attempted by HPLC using acetonitrile/water mobile phase (5/95, v/v) on a PRP column. Structures for the two peaks detected are appended to this review. Confirmation was by co-chromatography with unlabeled compounds, as well as by TLC separation using pre-coated silica gel 60 F-254 plates and a methylene chloride/methanol/ammonium hydroxide (144/50/8, v/v/v) mobile phase. Peak quantification was by fluorescence quenching (unlabeled compounds) and by Automatic TLC-Linear Analyzer for the radiolabeled compounds.

### Results and Discussion

The 4-methoxy-6-methyl-1,3,5-triazin-2-amine was found to be very stable to hydrolysis at all pH's, with between 96 and 100% of the original material found unchanged at the end of the experiment. A minor (<2%) component (the 4-amino-6-methyl-1,3,5-triazin-2-ol) was detected in the high concentration test.

### Conclusion

This study was scientifically valid, and is acceptable to EAB. Neither sample chromatograms nor copies of TLC plates were included with this study.

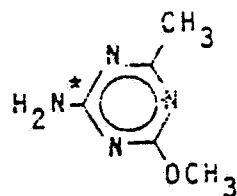
This study satisfactorily addresses EAB concerns raised in the 5/20/83 review.

EAB therefore considers the hydrolysis data requirement satisfied.

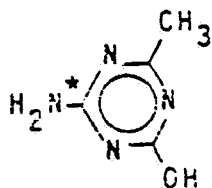
A-2

FIGURE 1

STRUCTURE OF TEST COMPOUND AND HYDROLYSIS PRODUCT



4-methoxy-6-methyl-1,3,5-triazin-2-amine



4-amino-6-methyl-1,3,5-triazin-2-ol

\* denotes the position of the  $^{14}\text{C}$  label which is the carbon atom adjacent to the amine group.



### 3.2 Aerobic Soil Metabolism

#### 3.2.1 Aerobic Soil Metabolism of DPX-M6316 [Thiophene-2-<sup>14</sup>C]. C. Rapisarda, Updated, Du Pont Document No. AMR-236-84.

Duplicate of non-sterile and sterilized soil samples (soil characteristics are described on p.14), equivalent to 50 g oven-dry weight, were weighed into the 250-ml E-meyer flask side of biometers and 10 ml of 0.1 N NaOH were added to the side arms. All soils were treated with 2.53 ug-(0.058 uCi) of <sup>14</sup>C-DPX-M6316 (80 g ai/ha) and moistened to 70% of field maximum moisture capacity. After the samples were thoroughly mixed and oxygen and introduced, the flasks were closed and incubated at 25°C in the dark. Duplicate non-sterile controls without <sup>14</sup>C-DPX-M6316 were also done under the same conditions. The soil metabolism of <sup>14</sup>C-glucose at 2 ppm was checked under the same experimental conditions. All flasks were opened weekly to add oxygen to the system (see recommendation for discussion on the opening of the flask).

The caustic solutions were radioassayed by LSC. After the trapped CO<sub>2</sub> we precipitated with BaCO<sub>3</sub>, the supernatants were also assayed for unprecipitated radioactivity.

The test soil samples were taken after 0, 0.5, 1, 2, 3, 4, 6, 8, 11, 14 and 20 weeks of aging and the sterile control samples were taken after 2, 4, 6, 8 and 20 weeks.

Each soil was extracted and analyzed according to the scheme in the following page.

To identify metabolites, non-sterile Gardena silt loam soil (60 g) was treated with  $^{14}\text{C}$ -DPX-M6316 at 10 ug/g and incubated at 30°C for 7 days. The soil was extracted with methanol/2M  $(\text{NH}_4)_2\text{CO}_3$  (3/1), and the solvent evaporated to dryness. The residue was resuspended in water, acidified with HCl to pH 3 and extracted with  $\text{CH}_2\text{Cl}_2$ . The methylene chloride extract was radioassayed and evaporated to dryness. The residue, dissolved in water, was analyzed by HPLC and then MS.

### Results

The soil characteristics are shown in the following table.

Component	Keyport Silt Loam (Newark, DE)	Flanagan Silt Loam (Rochelle, IL)	Gardena Silt Loam (Rodger, ND)
Sand (2000-50 um) %	12	2	43
Silt (50-2 um) %	83	81	51
Clay (<2 um) %	5	17	6
Organic matter %	7.5	4.3	5.0
Nitrogen %	0.30	0.26	ND
pH	5.2	5.4	8.1
Cation Exchange capacity (mec/100 g)	15.5	21.2	ND

Overall distribution of radioactivity is summarized in tables 1 - 4.

In the non-sterile studies, the percent extractables decreased rapidly with subsequent increase in the percent  $^{14}\text{CO}_2$  and unextractables.

In the sterilized soil studies, no  $\text{CO}_2$  was evolved and extractables decreased slowly with a corresponding increase in unextractables.

After 20 weeks of aging, 44 % of the applied  $^{14}\text{C}$  was recovered as  $\text{CO}_2$  from the Keyport soil and 31 % from the Flanagan soil.

The estimated half-lives were less than 2 days in Keyport soil (24 days in sterile soil) and 6 days in Flanagan soil (32 days in sterile soil).

Five metabolites were identified and the proposed metabolic pathway of DPX-M6316[thiophene-2- $^{14}\text{C}$ ] is shown in figure 1.

#### 4.2 Aerobic Soil Metabolism

DPX-M6316 was mineralized to CO<sub>2</sub> in soil. Both thiazole and triazine moieties are susceptible to mineralization.

Five intermediate metabolites were found (figure 1 in section 3.2.1) from thiazole-labeled parent compound. The half-life was estimated to be 2-6 days. After 20 weeks of incubation, 31-44 % of the applied <sup>14</sup>C was mineralized and 23-38 % was bound to soil.

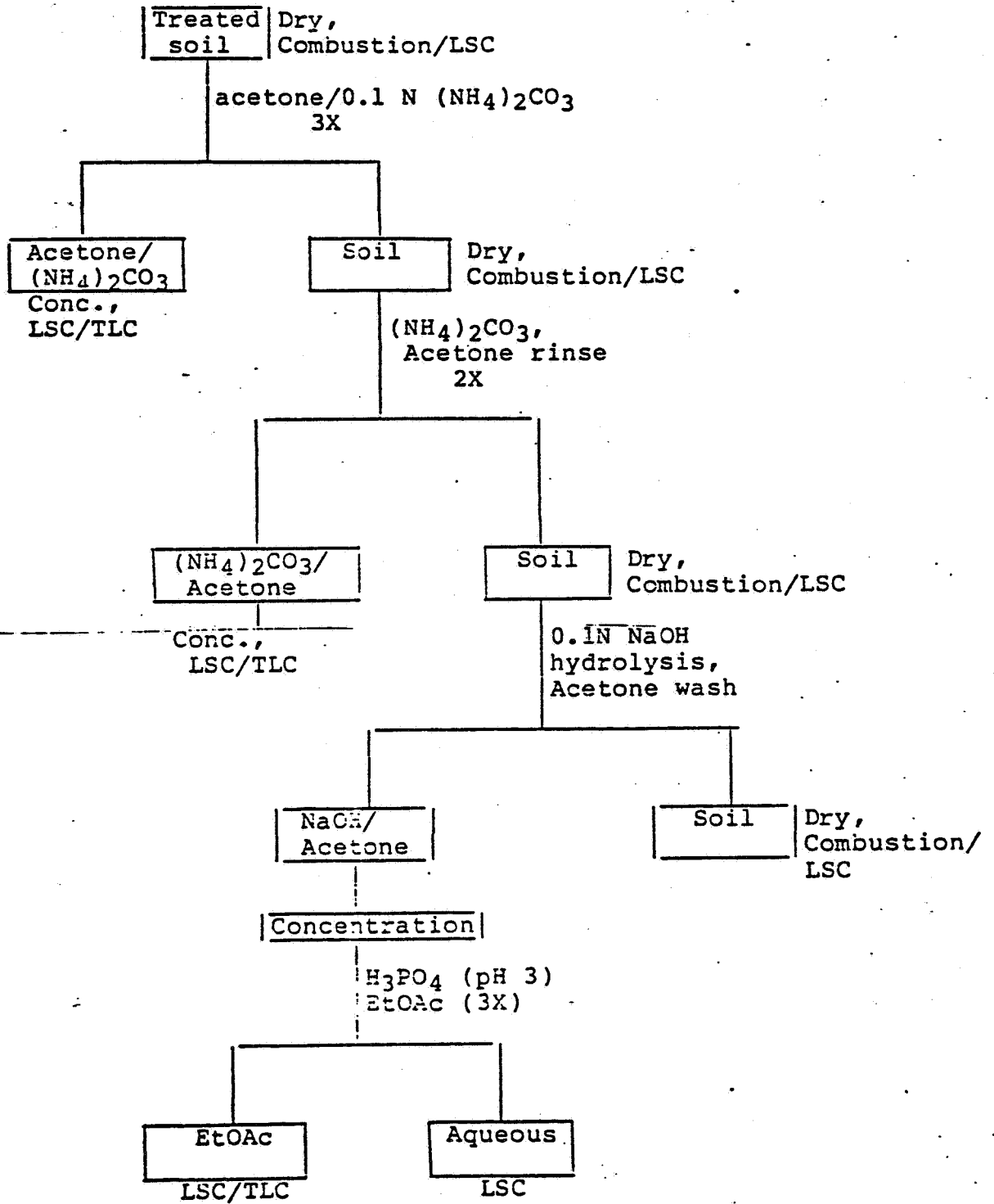
5.3 In the aerobic metabolism study discussed in section 3.2.1, the report says that "all flasks were opened weekly to add oxygen to the system". We would like the following questions answered:

- o How long were the flasks open to let in O<sub>2</sub>?
- o Why was there not any loss of volatile <sup>14</sup>C?

*Soobok Hong*  
Soobok Hong, Ph.D.

November 1, 1984

Environmental Chemistry Review Section 1  
Exposure Assessment Branch/HED



Section 3.2.1

TABLE 1

DISTRIBUTION OF RADIOACTIVITY IN KEYPORT SILT LOAM TREATED WITH  
DPX-46316 [THIOPHENE-2-<sup>14</sup>C]<sup>a</sup>

Photocopied as per CPP Security Procedures Manual  
Date: 11/1/86 Rev: S.H. Company: DuPont  
Accession #: 272246 Tab: Page:

Incubation Time (weeks)	% of Recovered Radioactivity <sup>b</sup>					
	Non-sterile			Sterilized		
	<sup>14</sup> CO <sub>2</sub>	Extracted <sup>c</sup>	Unextracted <sup>d</sup>	<sup>14</sup> CO <sub>2</sub>	Extracted <sup>c</sup>	Unextracted <sup>d</sup>
0	--	99.9	0.1			
0.5	11.7	80.0	8.3			
1	23.4	65.4	11.2			
2	28.7	46.3	25.0	0.0	99.1	0.9
3	30.8	50.3	18.9			
4	31.9	41.7	26.4	0.0	99.1	0.9
6	34.7	23.1	42.2	0.0	97.8	2.2
9	35.3	29.1	35.5	0.0	97.7	2.3
11	38.8	15.2	46.0			
14	39.6	23.4	37.0			
20	43.6	18.3	38.1	0.0	93.9	6.1

<sup>a</sup> Keyport soil was treated with 51 ppb of DPX-46316 [thiophene-2-<sup>14</sup>C] and maintained at 70% of its moisture holding capacity during the incubation at 25 °C in the dark.

<sup>b</sup> On an average, ≥99% of the calculated applied radioactivity was recovered.

<sup>c</sup> Extracted portion, sum of the extracts.

<sup>d</sup> Unextracted portion, consisting of bound material, possibly incorporated <sup>14</sup>C, and caustic hydrolyzable <sup>14</sup>C of high polarity.

## Section 3.2.1

TABLE 2

Photocopyed as per OPP Security Procedures Manual  
 Date: 11/1/76 Rev: 54 Company: DuPont  
 Accession # 47246 Tab: Page:

DISTRIBUTION OF RADIOACTIVITY IN FLANAGAN SILT LOAM TREATED WITH  
 DPX-46316 [THIOPHENE-2-<sup>14</sup>C]<sup>a</sup>

Incubation Time (weeks)	% of Recovered Radioactivity <sup>a</sup>					
	Non-sterile			Sterilized		
	<sup>14</sup> CO <sub>2</sub>	Extracted <sup>c</sup>	Unextracted <sup>d</sup>	<sup>14</sup> CO <sub>2</sub>	Extracted <sup>c</sup>	Unextracted <sup>d</sup>
0	-	99.8	0.2			
0.5	0.7	98.0	1.3			
1	2.5	94.4	3.1			
2	5.5	92.6	1.9	0.0	99.5	0.4
3	8.1	89.2	2.7			
4	10.9	85.7	3.4	0.0	99.2	0.8
6	13.9	66.2	19.9	0.0	96.4	3.6
8	16.9	66.7	16.4	0.0	95.3	4.7
11	21.7	54.9	23.4			
14	26.7	43.5	29.3			
20	31.0	46.5	22.5	0.0	87.2	12.8

<sup>a</sup> Flanagan soil was treated with 51 ppb of DPX-46316 [thiophene-2-<sup>14</sup>C] and maintained at 70% of its moisture holding capacity during the incubation at 25°C in the dark.

<sup>b</sup> On an average, ≥99% of the calculated applied radioactivity was recovered.

<sup>c</sup> Extracted portion, sum of the extracts.

<sup>d</sup> Unextracted portion, consisting of bound material, possibly incorporated <sup>14</sup>C, and caustic hydrolyzable <sup>14</sup>C of high polarity.

## Section 3.2.1

Photocopied as per OPP Security Procedures Manual  
 Date: 11/1/84 Rev: SH Company: Dupont  
 Accession #: 572-106 Tab: Page:

TABLE 3

COMPOSITION OF RADIOACTIVITY IN KEYPORT SOIL EXTRACTS<sup>a</sup>

<sup>14</sup> C-Compounds <sup>b</sup>	Percent of the Recovered Radioactivity <sup>c</sup> , at Weeks										
	0	0.5	1	2	3	4	5	8	11	14	20
<u>Non-sterile Soils</u>											
DPX-M6316	97.1	15.5	7.5	7.9	3.1	2.4	1.6	2.5	1.4	2.2	1.6
Metabolites A+B	0.3	15.1	17.7	16.1	20.1	10.6	6.1	8.5	4.8	7.1	6.6
Metabolite C	1.2	3.3	2.3	1.9	2.1	5.8	2.6	4.0	1.6	1.7	0.5
Metabolite D	0.8	18.5	8.0	2.8	2.0	3.6	3.9	4.2	1.2	3.2	2.8
Metabolite E	0.3	24.5	29.6	16.6	20.5	17.4	7.0	8.3	2.5	6.6	4.1
Polar Material	0.2	3.1	0.3	1.0	2.5	1.9	3.4	1.6	3.5	2.6	2.7
Total extracted	99.9	80.0	65.4	46.3	50.3	41.7	23.1	29.1	15.2	23.4	18.3
<u>Sterile Soils</u>											
DPX-M6316				66.0		41.4	35.3	25.5			7.7
Metabolites A+B				2.4		2.1	2.2	2.5			6.5
Metabolite C				13.7		31.1	35.5	43.1			41.8
Metabolite D				5.0		14.5	15.5	15.7			25.0
Metabolite E				4.1		7.9	8.5	10.5			12.1
Polar Material				2.9		2.1	0.8	0.4			0.8
Total extracted				99.1		99.1	97.8	97.7			93.9

<sup>a</sup> The Keyport silt loam soils were treated with 51 ppb of DPX-M6316 [thiophene-2-<sup>14</sup>C] and maintained at 70% of its moisture holding capacity during the incubation at 25°C in the dark.

<sup>b</sup> Structures and Chemical Abstracts names of these compounds are shown in Figure 1.

<sup>c</sup> On the average, ≥99% of the calculated applied radioactivity was recovered.

## Section 3.2.1

TABLE 4

Photocopied as per ODP Security Procedures Manual  
 Date: 4.1.1991 Rev: S.H. Category: Report  
 Approved #: 022846

COMPOSITION OF RADIOACTIVITY IN FLANAGAN SOIL EXTRACTS<sup>a</sup>

<sup>14</sup> C-Compounds <sup>b</sup>	Percent of the Recovered Radioactivity <sup>c</sup> , at Weeks										
	0	0.5	1	2	3	4	6	8	11	14	20
<u>Non-sterile Soils</u>											
DPX-16316	93.5	74.0	53.8	15.1	13.5	11.2	8.1	7.6	3.2	2.5	2.6
Metabolites A+B	1.3	5.5	11.5	23.7	27.8	22.9	16.2	18.2	15.3	14.3	18.1
Metabolite C	1.4	4.7	4.2	10.5	5.7	5.3	2.9	2.3	1.9	2.3	0.8
Metabolite D	2.1	3.5	7.2	12.8	11.5	13.5	10.5	15.5	6.0	3.8	5.8
Metabolite E	1.3	8.8	15.0	25.7	26.1	23.6	24.7	21.1	22.9	13.3	11.4
Polar Material	0.2	1.5	2.7	3.8	4.6	4.2	3.8	1.9	5.6	7.3	7.3
Total Extracted	99.8	99.0	94.4	92.6	89.2	85.7	66.2	66.7	54.9	43.5	46.5
<u>Sterile Soils</u>											
DPX-16316				72.8		51.1	40.9	47.7			11.5
Metabolites A+B				3.2		3.5	4.5	8.1			12.9
Metabolite C				10.6		21.1	25.5	12.7			22.6
Metabolite D				8.3		15.2	15.1	15.3			21.1
Metabolite E				3.7		6.5	6.8	11.0			14.1
Polar Material				0.5		1.6	3.5	0.5			4.8
Total Extracted				99.6		99.2	96.4	95.3			87.2

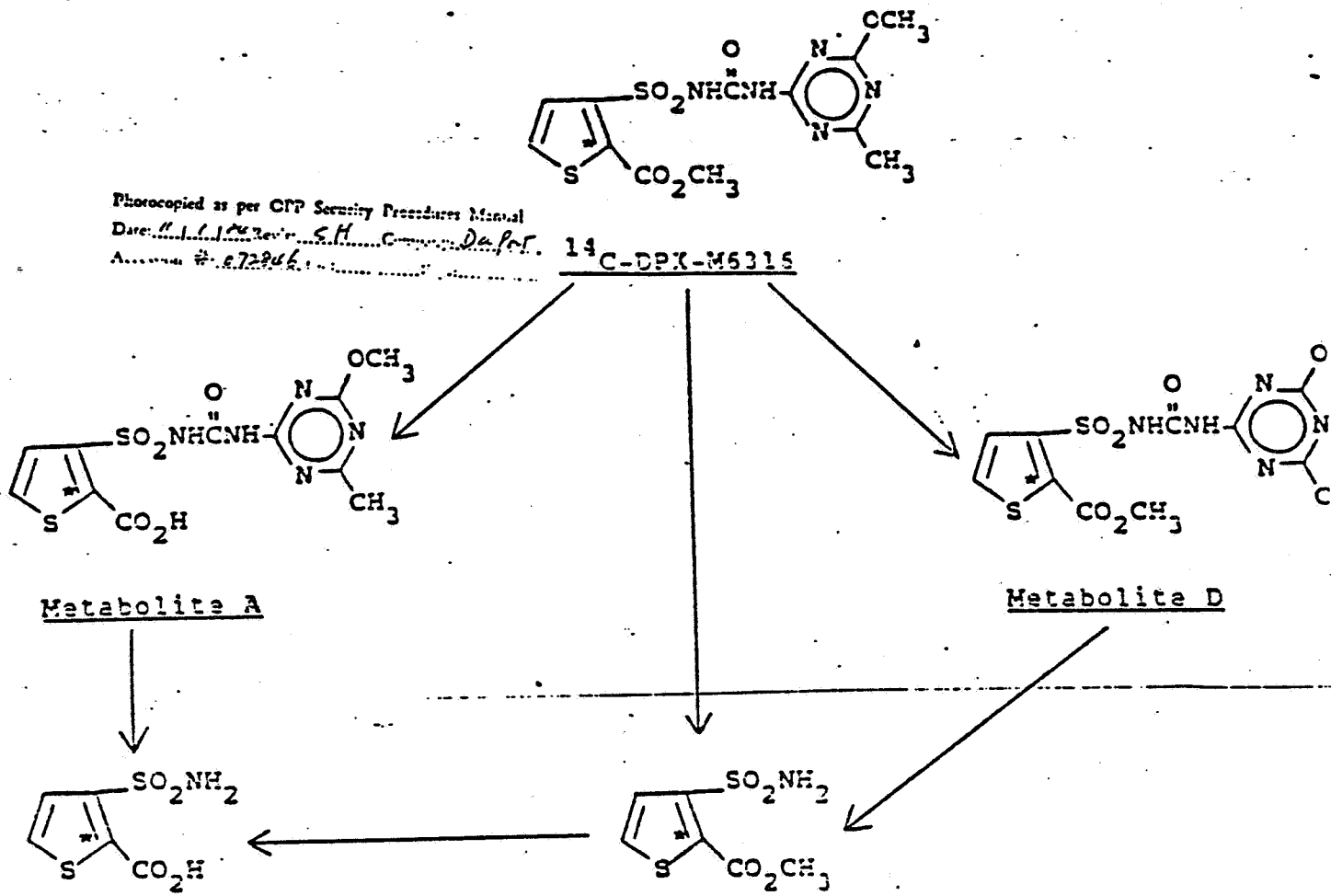
<sup>a</sup> The Flanagan silt loam soils were treated with 51 ppb of DPX-16316 [thiophene-2-<sup>14</sup>C] and maintained at 70% of its moisture holding capacity during the incubation at 25°C in the dark.

<sup>b</sup> Structures and Chemical Abstracts names of these compounds are shown in Figure 1.

<sup>c</sup> On the average, ≥99% of the applied radioactivity was recovered.



PROPOSED METABOLIC PATHWAY OF DPX-M6316 [THIOPHENE-2-<sup>14</sup>C] IN AEROBIC SOILS



Photocopied as per GPP Security Procedures Manual  
 Date: 11/1/74 Rev: S.H. C. Dept. 14C-DPX-M6316  
 Accession #: 672946

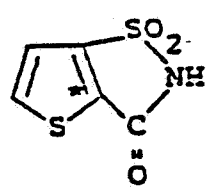
<sup>14</sup>C-DPX-M6316

Metabolite A

Metabolite D

Metabolite B

Metabolite C



Metabolite E

- Met. A: 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid
- Met. B: (3-aminosulfonyl)-2-thiophenecarboxylic acid
- Met. C: methyl 3-(aminosulfonyl)-2-thiophenecarboxylic acid
- Met. D: methyl 3-[[[[(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid methyl ester
- Met. E: thieno[2,3-d]isothiazole-3(2H)-one, 1,2-dioxane

<sup>14</sup>CO<sub>2</sub>

"Bound"

\* Denotes location of <sup>14</sup>C label.

Reviewed By: Emil Regelman  
Date: July 12, 1984  
Shaughnessy No. 122010

- 3.2 Rapisarda, C. Undated. Microbial Degradation of  $^{14}\text{C}$  DPX-4189 in Soil. Document No. AMR-43-81. (company confidential) E.I. DuPont de Nemours and Co. Experimental Station. Wilmington, Delaware. 15 pages, 7 tables, 8 figures. 3 references

#### Introduction

This study, of the rate of degradation of DPX-W4189 (chlorsulfuron, 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino carbonyl]benzenesulfonamide) (Shaughnessy #118601) in two soil types, was submitted in support of an EUP on barley and wheat, and was reviewed on 11/17/80.

Its inclusion in the current submission stems from the 6/8/83 meeting between the registrant and EAB concerning the fate of the triazine moiety of DPX T6376. At the meeting EAB agreed that both aerobic metabolism and field dissipation studies of chlorsulfuron would be adequate to delineate the rate of formation and decline of that moiety, which is identical to that in DPX T6376.

#### Discussion

This study was found acceptable in support of the proposed EUP in the 11/17/80 review.

A reevaluation of the report data (see table 7, appended) indicates the concentration of the aminotriazine moiety peaked about 1 month, then declined slowly. Estimated half-lives were 6 months ( $r^2=0.98$ ) and 10.3 months ( $r^2=0.52$ ) for the 0.1 and 1.0 ppm solution, respectively. The latter data are too unreliable to use in estimating the rate of dissipation.

#### Conclusion

This study adequately addresses one of the earlier EAB concerns (the triazine moiety).

TLC ANALYSES OF THE EXTRACTABLE a) <sup>14</sup>C

% of Recovered Radioactivity b) nt

Rf	Identification	Days			Months			Sterile			
		0	4	10	17	1	2		4	6	7
0.00	Aminotriazine	4.9	12.0	15.2	19.9	23.2	21.8	17.6	13.7	11.6	30.6
0.55	DPX-4189	92.7	62.6	40.7	34.0	23.3	8.8	4.4	3.0	2.2	10.1
<0.3	Polar Metabolites c)	1.7	5.1	6.7	8.7	8.7	13.2	6.3	4.0	5.8	29.7
0.0	Polar Material	0.3	6.9	29.7	24.0	25.1	23.0	29.3	39.4	37.1	25.0
		99.6	86.6	92.3	87.6	80.3	66.8	57.6	60.9	56.7	95.6

1 DPX

Rf Identification

0.00	Aminotriazine	4.7	13.8	18.3	26.3	24.6	19.0	14.0	13.9	16.9	30.6
0.55	DPX-4189	93.3	60.9	37.6	29.8	17.4	6.1	3.1	2.2	2.2	13.0
<0.3	Polar Metabolites c)	1.7	5.7	7.3	9.4	9.6	12.7	9.7	3.8	3.8	26.6
0.0	Polar Material	0.1	7.5	20.3	20.4	29.0	34.1	41.9	38.1	26.4	25.5
		99.8	87.9	91.3	83.9	81.4	71.9	68.7	58.0	49.3	95.7

a) Sum of the different extracts.  
 b) Average of 297% of the calculated applied <sup>14</sup>C was recovered.  
 c) Summation of all compounds with Rf < 0.3 except polar material.

## STUDY 3

Chrzanowski, R.L. 1984a. Degradation of  $^{14}\text{C}$ -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 [ $^{14}\text{C}$ ]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 [ $^{14}\text{C}$ ]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 [ $^{14}\text{C}$ ]chlorsulfuron (radiochemical purity >99%, specific activity 6  $\mu\text{Ci}/\text{mg}$ ) at 1 ppm. The remaining samples were treated with triazine-labeled [ $^{14}\text{C}$ ]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 [ $^{14}\text{C}$ ]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-chlorophenylsulfonylurea 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 [ $^{14}\text{C}$ ]chlorsulfuron and its degradates (% of applied) in sterile and nonsterile silt loam soil treated at 1 ppm with [ $^{14}\text{C}$ ]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 <sup>a</sup>	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

<sup>a</sup> Not detected; detection limit was 0.1% of the applied.

Table 3. Triazine-labeled [ $^{14}\text{C}$ ]chlorsulfuron and its degradates (% of applied) in sterile and nonsterile silt loam soil treated at 1 ppm with [ $^{14}\text{C}$ ]chlorsulfuron (radiochemical purity >99%) and incubated under anaerobic conditions in the dark at 25 C.

Compound	Sampling interval (weeks)				
	0	2	8	16	52
	<u>Nonsterile</u>				
2-Amino-4-methoxy-6-methyl-1,3,5-triazine	4.3	5.1	4.7	11	21
Chlorsulfuron	94	94	89	83	54
Unidentified	1.5	2.0	10	5.6	18.3
2-Amino-4-hydroxy-6-methyl-1,3,5-triazine	ND <sup>a</sup>	ND	ND	ND	ND
Nonextractable	0.3	1.0	2.3	1.5	3.7
	<u>Sterile</u>				
2-Amino-4-methoxy-6-methyl-1,3,5-triazine	4.1	5.2	4.0	16	25
Chlorsulfuron	93	97	84	57	37
Unidentified	2.6	1.7	12	23	31
2-Amino-4-hydroxy-6-methyl-1,3,5-triazine	ND	ND	ND	ND	ND
None extractable	0.3	0.4	1.0	1.0	2.3

<sup>a</sup> Not detected; detection limit was 0.1% of the applied.



Table 4. Phenyl-labeled [<sup>14</sup>C]chlorsulfuron and its degradates (% of applied) in flooded soil 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	Unex-tractabl
<u>Silt loam</u>						
0	ND <sup>a</sup>	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

<sup>a</sup> Not detected; the detection limit was 0.1% of the applied.

## STUDY 4

Han, J.C-Y. 1984a. <sup>14</sup>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.

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 [<sup>14</sup>C]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 [<sup>14</sup>C]chlorsulfuron (specific activity 12.0  $\mu$ 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 [ $^{14}\text{C}$ ]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 [<sup>14</sup>C]chlorsulfuron at 100 g ai/ha.

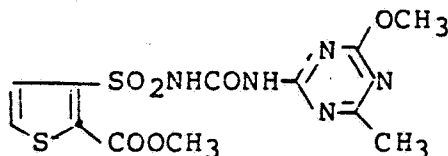
Sampling interval (weeks)	Sampling depth (cm)	Unextractable	Chlorsulfuron	2-Amino-4-methoxy-6-methyl-1,3,5-triazine
0	0-5	17.2	76.4	6.2
2	0-5	10.7	40.3	10.5
2	5-10	2.9	13.3	5.3
2	10-20	0.5	2.2	1.0
4	0-5	4.2	15.3	24.9
4	5-10	1.2	8.9	14.3
4	10-20	0.9	6.0	7.7
4	20-38	0.3	1.2	1.1
8	0-5	7.4	9.5	23.5
8	5-10	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

## 1.0 INTRODUCTION

Du Pont has submitted environmental fate data on its herbicide, DPX-M6316, to support registration for an EUP. EAB review of November 1, 1984 revealed a data gap (rotational crop studies) for the proposed use.

## 1.1 Chemical

DPX-M6316: Methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate



• [<sup>14</sup>C-thiophene]-DPX-M6316

## 2.0 DIRECTIONS FOR USE

Refer to the EAB review of November 1, 1984.

## 3.0 DISCUSSION OF DATA

3.1 Crop Rotation Studies with DPX-M6316[Thiophene-<sup>14</sup>C] in the Greenhouse. P. T. Hardesty, Du Pont Doc. No. AMR-256-84, EPA Acc. No. 254641.

Experimental

Nine clay pots (16 inches i.d., surface area 1.22 ft<sup>2</sup>, volume 0.75 ft<sup>3</sup>) were filled with Sassafras loamy sand (USDA sand 79 %, silt 15 %, clay 6 %, CEC 3.4 %, O.M. 0.6 %, pH 6.6). The surface of the soil of four pots was treated with a solution of DPX-M6316[thiophene-<sup>14</sup>C] (23.3 uCi/mg, >98 % pure) at 1.0 mg (23.3 uCi) per pot (equivalent to 86 g/ha) for 30-day aging studies. Another four pots were treated at 1.1 mg (25.7 uCi) per pot (equivalent to 94 g/ha) for 120-day aging studies. The ninth pot served as a control.

At the end of the aging period, one pot from each of the four groups (30-day and 120-day) was lightly cultivated and planted with peas, one with beets, one with sunflowers, and one with about one-third of each crop. The ninth pot, not treated with <sup>14</sup>C-DPX-M6316, was also planted with one-third of each crop.

During both aging and growing periods, pots were maintained under lights in a greenhouse with a 16-hour photo period at 65-75°C and 30 % relative humidity.

Soil samples were taken and pooled from each of the four pots

from each aging period at planting time.

Plant samples were taken at 16, 29, and 43 days after planting and mature crops were harvested at 65 days (pea), 86 days (beet) and 100 days (sunflower) for the 30-day aging period. For the 120-day aging period, samples from all crops were taken at 13 and 27 days after planting, and mature crops were harvested at 49 days (pea) and 101 days (beet and sunflower).

Plant samples were freeze-dried, homogenized and aliquots analyzed by combustion/LSC. Soils were air-dried, homogenized and radioassayed.

To characterize the residues in soil, soil samples were extracted with acetone/0.1 M  $(\text{NH}_4)_2\text{CO}_3$  (90/10, v/v) (3x). The extracted soil was ultrasonically reextracted with 0.1 M  $(\text{NH}_4)_2\text{CO}_3$  (2x). This was followed by acetone rinse (2x). Aliquots of the acetone/ammonium carbonate, ammonium carbonate, and acetone rinse were separately radioassayed. After all the extracts and rinses were combined and concentrated to dryness, the residues were redissolved in acetone/water. Undissolved solids were removed by centrifugation. Aliquots of the supernatant were subjected to TLC/autoradiography/LSC (silica plate Taperplate®,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{NH}_4\text{OH}$  200/50/3).

Plant samples that contained more than 10 ppb (as DPX-M6316) total  $^{14}\text{C}$ -residue were extracted with acetone/water (8/2) once in a Tekma Tissuemizer® and twice in a wrist-action shaker. Aliquots of the combined extracts were concentrated to about one-tenth of the original volume, adjusted pH to about 8.5 with 0.1 M  $(\text{NH}_4)_2\text{CO}_3$ , and extracted with n-hexane. The aqueous phase was analyzed by HPLC on a Zorbax®-C8 column using  $\text{CH}_3\text{CN}/\text{water}$  (pH 2.2) as the mobile phase.

### Results

No crop injury was noted in all pots.

Results from the soil analyses are shown in table 1.

Table 1

#### LEVELS OF TOTAL $^{14}\text{C}$ AND $^{14}$ -DPX-M6316 IN SOIL IN PLANTING OF THE ROTATIONAL CROP

Aging Period (day)	Appl. rate (g/ha)	$^{14}\text{C}$ -Conc. as DPX-M6316 (ppb)			
		Total	Ext.	Unext.	DPX-M6316
30	94	17.9	14.8	3.1	1.5
120	86	9.2	6.1	2.1	0.2

Total soil residue levels at planting were 17.9 and 9.2 ppb for the 30- and 120-day aging periods, respectively, but intact DPX-M6316 accounted for only 1.5 and 0.2 ppb at these respective periods. Individual degradation products could not be identified because of low levels of activity in the extracts. [From the aerobic soil metabolism study (EAB review 11/1/84), five degradation products were identified (see attachment).]

Results from the total  $^{14}\text{C}$  analysis of plant tissues are shown in table 2. Edible beet root, pea and sunflower seed contained <1 to 2 ppb in the 120-day study and 1-5 ppb in the 30-day study. Residues accumulated in beet and sunflower foliages in the 30-day study (22 and 54 ppb, respectively). However, results from the residue characterization showed that intact  $^{14}\text{C}$ -DPX-M6316 accounted for only 2 ppb in the 43-day old sunflower-foilage and less than 1 ppb in the mature beet- and sunflower-foiliages (table 3).

#### Comments

- o Recoveries/material balances were not reported.
- o Soil analysis right after application was not done, and the method how the soil was sampled was not described.

#### Conclusion

DPX-M6316[thiophene- $^{14}\text{C}$ ] residues appear not to accumulate in edible parts of the rotational crops (pea, beet, sunflower seed) planted 30 and 120 days after treatment at 86 g/ha (1.7x maximum label rate). Residues accumulated most in foliages, especially in the 30-day studies, but intact DPX-M6316 accounted for less than 4 % of the total  $^{14}\text{C}$  accumulated in the foliages.



TABLE 2

LEVELS OF TOTAL RADIOLABELED RESIDUES IN ROTATIONAL CROPS GROWN IN SOILS  
TREATED WITH [<sup>14</sup>C]-DPX-M6316

Crop Fraction	30-Day Aging Period		120-Day Aging Period	
	Days After Planting	Total Radiolabeled Residues, ppb <sup>a</sup>	Days After Planting	Total Radiolabeled Residues, ppb <sup>a</sup>
beet foliage	16	6	13	<1
"	29	2	27	1
"	43	2	49	1
"	86	22	101	<1
beet root	86	1	101	<1
pea foliage	16	3	13	1
"	29	3	27	1
"	43	9		
"	65	8	49	5
pea pod	65	6	49	2
pea seed	65	5	49	1
sunflower foliage	16	4	13	<1
"	29	4	27	1
"	43	54		
"	100	17	101	12
sunflower seed	100	3	101	2

<sup>a</sup> ppb reported as ng DPX-M6316 per gram of fresh weight.

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TABLE 3

LEVELS OF INTACT [<sup>14</sup>C]-DPX-M6316 IN ROTATIONAL CROP SAMPLES THAT  
CONTAINED GREATER THAN 10 PARTS PER BILLION OF TOTAL RADIOLABELED RESIDUES

<u>Aging Period</u>	<u>Days After Planting</u>	<u>Crop</u>	<u>Total Radiolabeled Residues, ppb<sup>a</sup></u>	<u>Extractable Percentage of Total Residue</u>	<u>PPB of Intact [<sup>14</sup>C]-DPX-M6316</u>
30	43	sunflower	54	85	2.0
30	86	beet-foilage	22	76	<1
30	100	sunflower-foilage	17	84	<1
120	101	sunflower-foilage	12	79	<1

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Reviewed by: Soobok Hong, Ph.D.  
Date: November 1, 1984  
Shaughnessy No. 128845

### 3.3 Residue Accumulation in Rotational Crops

#### 3.3.1 Crop Rotation Study with $^{14}\text{C}$ -DPX-W4189. J. C-Y. Han, Undated, Du Pont Document No. AMR-46-81.

This study has EPA Accession No. 070470 from the previous submission, but EAB file revealed no record of the review of the study.

#### Experimental

Spring wheat was planted (2nd week of April, 1979) on two Keyport silt loam plots (12 ft<sup>2</sup> each, soil characteristics, table 1). When the seedlings were about 8-10" high with fourth leaf fully expanded, one plot was uniformly treated with [ $^{14}\text{C}$ -phenyl]DPX-W4189 at 70 g/ha and the other was treated with [ $^{14}\text{C}$ -triazine]DPX-W4189 (figure 1). Mature wheat was harvested in July 1979.

Next spring, sugar beets, rape and soybeans were planted on both  $^{14}\text{C}$ -treated plots (5/30/80).

Sugar beets died within a month after germination. Rape and soybeans were also slightly injured, but both of these crops recovered after 3 weeks.

Mature soybeans (beans and foliage) and rape foliage were harvested in November 1980. After winter dormancy, rape resumed growth in 1981 and seeds and foliage at maturity (6/30/81) were collected for analysis.

Soil core samples (3/4 x 12") were taken at planting and every harvest.

The total  $^{14}\text{C}$  was measured by combustion analysis after soil and seeds were air-dried and homogenized and after foliage was chopped into small pieces.

Plant tissue samples were extracted in a blender with acetone/water (8/2), centrifuged, and the supernatant was reduced to a small volume. The concentrated extract was adjusted to pH 3 with 1 N  $\text{H}_2\text{SO}_4$  and extracted with ether (2x). The ether extract was evaporated to dryness under nitrogen. The remaining aqueous layer was reextracted with n-butanol (2x) and the n-butanol evaporated. Then ether and n-butanol fractions were analysed by TLC in toluene/acetone (1/1) and  $\text{CH}_3\text{CN}/\text{EtOAc}/\text{HCOOH}$  (150/50/1.5) with standard compounds.

An aliquot of soil samples was refluxed with 5 %  $(\text{NH}_4)_2\text{CO}_3$  in methanol/water (2:1) and then cooled and centrifuged. The supernatant and methanol wash of the soil residue were combined and boiled gently on a hot plate to evaporate and decompose ammonium carbonate. The concentrate was partitioned with a mixture of water and ethyl acetate. After radioassay, both phases were concentrated and analyzed by TLC in toluene/acetone (1:1).

### Results

In all soil analyses parent compound was found to be 1 ppb or less (table 2).  $^{14}\text{C}$ -2-Chlorobenzenesulfonamide and  $^{14}\text{C}$ -2-amino-4-methoxy-6-methyl-1,3,5-triazine were found to be 3 ppb and 4 ppb, respectively after 1 year of aging but these were found to be 1 ppb after 1.5 years and less than 1 ppb after 2 years.

$^{14}\text{C}$ -Residues in plant tissues of rotational crops are shown in table 3. Dry soybean foliage had a total  $^{14}\text{C}$ -residue of between 7 and 9 ppb, calculated as intact DPX-W4189. Beans had a total residue of 2-3 ppb. After the first growing season, 3-4 ppb was found in dry rape foliage and  $^{14}\text{C}$ -residue decreased to 2 ppb at maturity in the second growing season. Rape seeds had 1 ppb from both labeled treatments. Extraction analyses showed that less than 1 ppb was found in all fractions from all tissue samples except in water phase from the soybean foliage where 3 ppb was found from both treatments.

### Comments

A number of deficiencies found in this study include:

- o Rotational crops should include those expected to be representative of roots, small grains, and leafy vegetables. No studies with small grain <sup>leafy vegetables</sup> or root were done.
- o Residue analysis in the soil at the time of treatment was not done.

- o The treatment rate used in this study, 70 g/ha, is only one-half of the maximum treatment rate (2 oz/a, 140 g/ha) in the label: Even after one-year of aging with one-half of the maximum application rate, DPX-4189 residues (27 ppb among which only 1 ppb was parent compound) showed fatal toxicity to sugar beet seedlings. Also, it produced slight injury in soybeans and rape. If the maximum rate had been used, all of the crops might have died. Also, the soil concentration and the tissue concentration would have been higher.
- o No rainfall data, temperature monitoring data and general climatic conditions were reported for the test period.

Section 3.3.1

Table 2

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Residues in Soil From Treatment of <sup>14</sup>C-Labeled DPX-W4189

(Treatment Rate 70 g/ha)

Label tion	Crop	Months After Treatment	Aging Period At Planting	Total <sup>14</sup> C In Soil	Radioactive Residue (Calculated as <sup>14</sup> C-DPX-W4189		14C-2-amino-4-methoxy- 6-methyl-1,3,5-triazine
					14C-DPX-W4189	14C-2-chloro- benzenesulfonamide	
Triazine	None (Soil)	12		27 ppb	1 ppb	3 ppb	---
Triazine	None (Soil)	12		29 ppb	1 ppb	---	4 ppb
Triazine	Soybean	18	Aging Period At Harvest	18 ppb	<1 ppb	1 ppb	---
Triazine	Soybean	18		15 ppb	<1 ppb	---	1 ppb
Triazine	Rape	25		10 ppb	<1 ppb	<1 ppb	---
Triazine	Rape	25		10 ppb	<1 ppb	---	<1 ppb

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Table 3

14C-Residues in Rotational Crops Grown on Soil

Previously Treated With 14C-DPX-W4189

ppb 14C-Residue (Calc'd. as DPX-W4189)

14C-Phenyl-Labeled DPX-W4189

Treatment	Total	Ether Phase	n-butanol Phase	Water Phase
Dry Soybean Foliage	9	<1	<1	3
Edible Soybean	3	<1	<1	<1
Rape Foliage (End of the 1st Growing Season)	3	<1	<1	1
Rape Foliage (Mature Stage)	2	<1	<1	<1
Rape Seed	1	<1	<1	<1

14C-Triazine-Labeled DPX-W4189

Treatment	Total	Ether Phase	n-butanol Phase	Water Phase
Dry Soybean Foliage	7	<1	<1	3
Edible Soybean	2	<1	<1	<1
Rape Foliage (End of the 1st Growing Season)	4	<1	<1	1
Rape Foliage (Mature Stage)	2	<1	<1	<1
Rape Seed	1	<1	<1	<1

## Section 3.3.1

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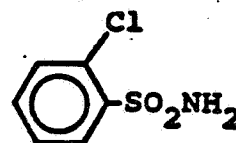
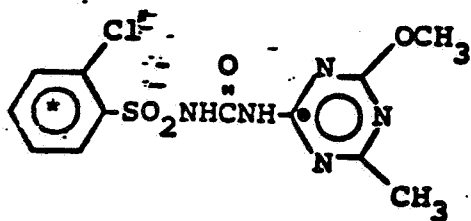
Table ICharacteristics of Keyport Silt Loam

(Analyzed by Soil Testing Laboratory, University of Delaware)

pH	6.0
Mg	105
P <sub>2</sub> O <sub>5</sub>	46
K <sub>2</sub> O	39
Ca	104
Sand USDA (2.0-0.05 mm)	16.2
ISSS (2.0-0.02 mm)	40.3
Silt USDA (0.05-0.002 mm)	72.8
ISSS (0.02-0.002 mm)	48.7
Clay (<0.002 mm)	11.0
Textural Class, USDA	Silt loam
ISSS	Loam
Cation Exchange Capacity (meq/100 g)	7.73
Organic Matter	1.4%

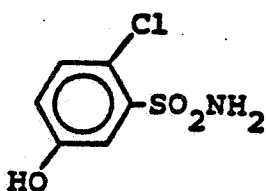


Chemical Structures Of DPX-W4189 And  
Possible Metabolites/Degradation Products

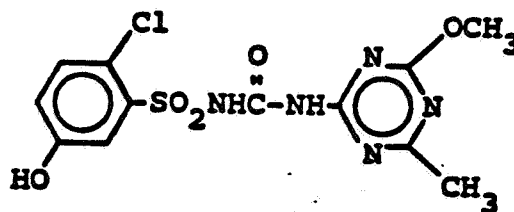


DPX-W4189  
2-chloro-N-[(4-methoxy-6-methyl-  
1,3,5-triazin-2-yl)aminocarbonyl]-  
benzenesulfonamide

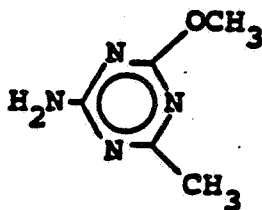
2-chlorobenzenesulfonamide  
(I)



2-chloro-5-hydroxy-  
benzenesulfonamide  
(II)



2-chloro-5-hydroxy-N-[(4-methoxy-6-  
methyl-1,3,5-triazin-2-yl)aminocarbonyl]-  
benzenesulfonamide  
(III)



2-amino-4-methoxy-6-methyl-  
1,3,5-triazine

(IV)

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- \* denotes position of label in phenyl labeled DPX-W4189
- denotes position of label in triazine labeled DPX-W4189

### 3.4 Fish Accumulation

- 3.4.1 DPX-M6316[Thiophene-2-<sup>14</sup>C] Flow-Through Bioconcentration Study with Bluegill Sunfish. J. C. Larkin, Biospherics Incorporated for Du Pont, July 1984, Du Pont Document No. AMR-182-84.

#### Experimental

Bluegill sunfish (average weight 1.67 g, 0.6-3.76 g) were introduced into three glass aquaria (90 x 30 x 40 cm, 108 liter capacity) holding 72.9 liters of water. Two of the aquaria were fortified with DPX-M6316[thiophene-2-<sup>14</sup>C] at a nominal concentration of 5 ppm by delivering a diluted radioactive stock solution into the system using monostat injector system. The diluted radioactive solution was made by mixing 8 ml of radioactive stock solution (5 mg/ml, 23.1 uCi/mg) with 992 ml of non-labeled DPX-M6316 solution (5 g/L). For each cycle of the diluter system, 4 ml of the diluted radioactive solution was ultimately diluted to 4 liters. A third aquarium served as a control. Water was delivered to both control and test chambers by a diluter system as diagrammed schematically in figure 1. A summary of test parameters is presented in table 1.

A total of 80 fish were added to each tank with removal of 4 fish (2 for dissection and 2 for whole fish analysis) and 5 ml water on days 0, 1, 3, 10, 14, 21 and 28. Control fish were sampled on days 0, 1, 14 and 28. During depuration, fish were sampled on days 1, 3, 7, 10 and 14. Control fish were sampled on day 14.

Water samples (5 ml) were analyzed by LSC. Tissue samples were analyzed by combustion analysis.

The estimated sensitivity of detection with a 1.17 g tissue sample was about 3.7 ppm and the minimum detectable concentration for 5.0 ml water sample was about 0.9 ppm.

#### Results

No mortality was observed during the entire study period from both test and control chambers.

Results from the analysis of water samples are shown in table 2. The average water concentration of DPX-M6316 [thiophene-2-<sup>14</sup>C] was 4.4 ppm during the exposure phase and < 0.9 ppm during the depuration phase.

Results from the analysis of fish samples are shown in tables 3 and 4. Throughout the study, no bioaccumulation of <sup>14</sup>C residues from DPX-M6316[thiophene-2-<sup>14</sup>C] occurred in bluegill sunfish.

Conclusion

DPX-M6316 appears not to bioaccumulate in bluegill sunfish under flow-through conditions.

This study was well done and satisfies the fish accumulation data requirement.

DPX-M6316 [thiophene-2-<sup>14</sup>C] Bluegill Sunfish Bioconcentration Study  
Summary of Test Parameters

<u>Parameter</u>	<u>Measurement, Setting or Condition</u>
1. Test material & source.	1. DPX-M6316 [thiophene-2- <sup>14</sup> C] (Specific Activity = 23.1 $\mu$ Ci/mg) was synthesized at New England Nuclear and supplied by the DuPont Agricultural Chemicals Department under the code <sup>14</sup> C-H-15,150.
2. Test type.	2. Flow-through, bluegill sunfish bioconcentration.
3. Test phases & durations	3. Uptake (28 days) and depuration (14 days).
4. Physical test apparatus.	4. Colenoid Activated Diluter System, Aquatic Toxicology Flow-through Bioconcentration Apparatus, (Figure 1).
5. Test compound stock solution concentration.	5. 5.0 mg/mL in well water (pH adjusted to 11).
6. Nominal concentration of test compound in the exposure well water.	6. 4.4 parts per million.
7. Test chambers.	7. Three, 90 cm x 30 cm x 40 cm all-glass aquaria, maximum volume 108 liters, water volume 72.9 liters.
8. Exposure and depuration water.	8. Biospherics Laboratory well water, 2 liter/tank/cycle. Total hardness 108 mg/L as CaCO <sub>3</sub> , total alkalinity 152 mg/L as CaCO <sub>3</sub> , pH 7.0-7.4, temperature 21 $\pm$ 1°C, O <sub>2</sub> concentration 7.2 $\pm$ 0.2 (1s) mg/L, specific conductance 360 $\mu$ mhos/cm.
9. Photoperiod.	9. 16 hrs light/24-hr cycle during both the exposure and depuration phases.
10. Bioassay organism.	10. Bluegill sunfish, <u>Lepomis macrochirus</u> , average weight 1.67 g, initial no./tank 80. Static loading rate 1.83 g/L.
11. Mortality determinations.	11. Direct visual observations.
12. Radiometric analyses	12. <sup>14</sup> C determinations in water and fish tissues.

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## Section 3.4.1

TABLE 2

DPX-M6316 [thiophene-2-<sup>14</sup>C] Bluegill Sunfish Bioconcentration Study  
Concentration of <sup>14</sup>C (Expressed as ppm DPX-M6316)  
in Exposure Water

Concentration in ppm and Standard Deviation

	Sampling Date		Replicate 1		Replicate 2		Average		
	I.D. <sup>a</sup>		ppm	Std. Dev.	ppm	Std. Dev.	ppm	Std. Dev.	
Exposure	0	0	3.2	0.1	3.2	0.1	3.2	0.1	
	1	1	3.2	0.1	3.4	0.2	3.3	0.2	
	3	3	5.0	0.1	5.0	0.1	5.0	0.1	
	7	7	5.4	0.6	5.5	0.2	5.4	0.4	
	10	10	4.8	0.1	4.8	0.1	4.8	0.1	
	14	14	4.4	0.3	4.5	0.2	4.4	0.2	
	21	21	4.8	0.1	4.4	0.5	4.6	0.4	
	28	28	4.4	0.2	4.6	0.2	4.5	0.2	
	Depuration	29	01	<0.9		<0.9		<0.9	
		31	03	<0.9		<0.9		<0.9	
35		07	<0.9		<0.9		<0.9		
38		010	<0.9		<0.9		<0.9		
42		014	<0.9		<0.9		<0.9		

<sup>a</sup>I.D. - consists of 2 columns

First Column - the total number of days that the study had been running since test initiation.

Second Column - the number of days of fish exposure or depuration.

Maximum Percent Counting Error = 5.2 %

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Concentration of <sup>14</sup>C (Expressed as ppm DPX-M6316) and Bioconcentration Factors in Edible and Nonedible Tissues

I.D. b	Exposure	Edible Fish Tissue			Nonedible Fish Tissue			Bioconcentration Factor (BCF)(c)		
		ppm	ppm	ppm	ppm	ppm	ppm	Rep. 1	Rep. 2	Avg
0		Rep. 1	Rep. 2	Avg	Rep. 1	Rep. 2	Avg	Rep. 1	Rep. 2	Avg
1		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<0.8
3		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	5.3	<3.7	4.5
7		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
10		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
14		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
21		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
28		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
29		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
31		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
35		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
38		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7
42		<3.7	<3.7	<3.7	<0.8	<0.8	<0.8	<3.7	<3.7	<3.7

a All data from nonedible tissue combustions were less than the detection limit of 3.7 ppm except day 1 (4.5 ppm). Mean water concentration in the treated aquaria for the 28-day exposure period was 4.4 ppm.

b I.D. consists of 2 columns:  
 First Column - the total number of days the study has been running since test initiation.  
 Second Column - the number of days of fish exposure or depuration.

c BCF Detection limit = 0.8  
 Maximum Percent Counting error = 5.57 %

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## Section 3.4.1

Table 4

Concentration of  $^{14}\text{C}$  (Expressed as ppm DPX-M6316)  
and Bioconcentration Factors in Whole Fish TissueWhole Fish<sup>a</sup>

Depuration Exposure	Sampling Date		ppm			Bioconcentration Factor (BCF) <sup>c</sup>		
	I.D. <sup>b</sup>		Rep 1	Rep 2	Avg	Rep 1	Rep 2	Avg
	0	0	<3.7	4.2	4.0	<0.8 <sup>c</sup>	1.0	0.9
	1	1	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	3	3	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	7	7	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	10	10	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	14	14	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	21	21	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	28	28	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	29	1	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	31	3	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	35	7	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	38	10	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8
	42	14	<3.7	<3.7	<3.7	<0.8	<0.8	<0.8

<sup>a</sup> All data from whole fish combustions were less than the detection limit of 3.7 ppm except day 0 (4.0 ppm). The mean water concentration of DPX-M6316 treated aquaria water for the 28 day uptake period was 4.4 ppm.

<sup>b</sup> I.D. consists of 2 columns:

First Column - the total number of days the study has been running since test initiation.

Second Column - the number of days of fish exposure or depuration.

<sup>c</sup>BCF Detection Limit = 0.8