

US EPA ARCHIVE DOCUMENT

Date Out EFB: NOV 17 1980

TO: Product Manager 25 Taylor
TS-767

From: Dr. Willa Garner
Chief, Review Section No. 1
Environmental Fate Branch

Samuel M. Greger (Acting Chief)

Attached please find the environmental fate review of:

Reg./File No.: 352-EUP-RNL

Chemical: DPX-4189

Type Product: Herbicide

Product Name: Du Pont DPX-4189 DF Weed Killer

Company Name: Du Pont

Submission Purpose: EUP wheat and barley

Action Cod 705

ZBB Code: Section 5

EFB #513

Date in: 6/23/80

Date Completed: NOV 17 1980

Deferrals To:

- ☐ Ecological Effects Branch
- ☐ Residue Chemistry Branch
- ☐ Toxicology

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Introduction

- 1.1 This is a request for an EUP of DuPont's DPX-4189 DF Weed Killer for trial use on wheat, barley and reduced-tillage fallow. This product contains a new active ingredient, DPX-4189, 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl] benzene-sulfonamide

The Environmental Fate data are referenced in the documents submitted under Acc. No. 099459 and 099462, dated June 1980.

- 1.2 The permit will involve using DPX-4189 Dry Flowable as a weed killer for post plant and pre-emergence in wheat, post-emergence use in barley and reduced tillage fallow systems for wheat and barley.

The product is proposed to be tested, in several states including AZ, ND, CA, CO, ID, KS, MN, NE, OK, OR, SD, TX, MT, WA and WY, at rates specified in a temporary label on test plots varying between 1 to 100 acres. A test schedule to cover 3 years of experimentation to test three non-fallow crop cycles and two reduced tillage fallow crop cycles is shown below:

Year	Lbs	Total Acreage*
1981	1000	8000
1982	3000	24000
1983	<u>4000</u>	32000
TOTAL	8000	

*Alternately will not exceed 0.03% of U.S. small grain acreage. Lbs of chemical and acreage proposed to be used. In each state has been listed

1.3

Structures

Active ingredient

2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzene-sulfonamide (DPX-4189)

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Directions for use

- 2.1 The temporary label includes precautions to prevent contamination of the general area(s) of test sites.
- 2.2 Both tractor and aerial spray application modes are suggested.
- 2.3 Application rates

General Guide for Different Soils:

Coarse soil ----- lower rate (low in clay or OM)

Finer soil ----- higher rate (high in clay or OM)

The product for EUP, which contains 75%AI, is applied as follows:
(applied in weight units)

For barley - (Spring and Winter) single application - 1/8 - 1 oz/acre
Apply any time after crop emerges before "boot stage".

For wheat (spring and summer) pre-emergence or shallow postplant,
single treatment followed by post emergence or post emergence only,
apply DPX-4189 DF as follows:

- 1. Pre-emergence ----- 1/4 - 3/4 oz/acre (apply before crop emergence)
- 2. Shallow post plant ----- 1/8 - 1 oz/acre
- 3. Post-emergence ----- 1/8 - 1 oz/acre.

For reduced - tillage fallow - wheat or barley - 1/2 - 2 oz/acre

2.4

Precautions:

Do not graze or feed forage or hay from treated areas to livestock.

Do not replant treated areas to any crop other than wheat or barley within one year of application.

Do not replant sugar beets or any cole crop within 2 years of last application.

Storage and Disposal

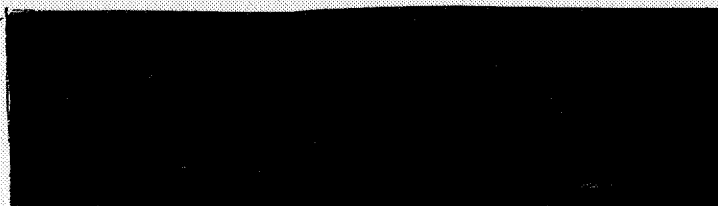
Empty container or product that cannot be used must be kept in a safe place. Open dumping is prohibited. For disposal procedures consult federal, state, or local authorities.

3. Discussion of Data

3.1 Dupont DPX 4189 DF Weed Killer composition is given below.

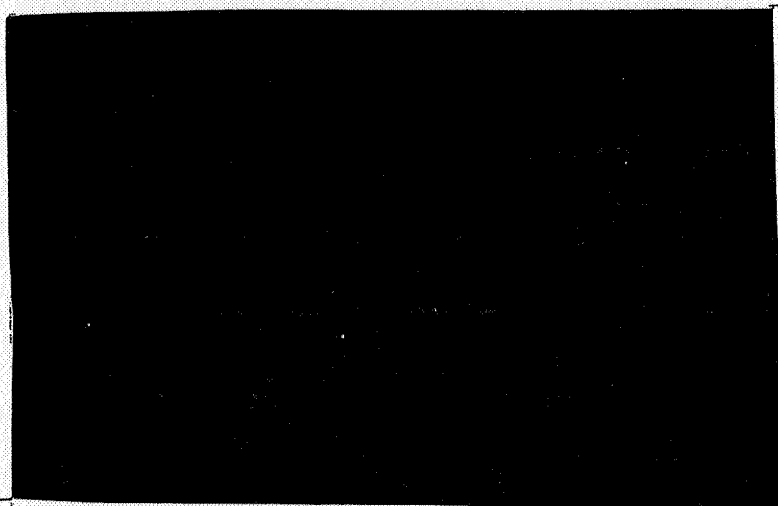
DPX -4189 Technical 82.5%

Other Ingredients



Impurities in Technical DPX-4189

1. DPX -4189 91%



The EUP Product Dupont DPX DF Weed Killer dry flowable product contains 75% of AI.

3.2 Chemical and Physical Properties

Mol. formula ... $C_{12}H_{12}ClN_5O_4S$

Mol. Wt.357.78

Appearance White Crystalline Solid

M.P.....174°C

Solubility

Water @ 25°C	125 ppm
Solubility in organic solvents (wt/wt), at 22 °C	
Toluene	0.3%
Methanol	1.8%
Acetone	7.0%
Methylene chloride	7.7%
N,N-dimethyl formamide	27.3%
hexane	< 10 ppm

K-Values: (Freundlich, isotherm constant)

Keypost silt loam = 0.45

Flunagun silt loam = 0.7

K_{ow} = (octanol/water partition coefficient) measured at 24-26°C

K_{ow} at concentration 895 ppm = 16

K_{ow} at concentration 428 ppm = 10

Comment: The physical properties indicate low solubility and the chemical may not adsorb strongly to fresh soil surfaces. The above information on the properties of the chemical are useful.

3.3

Hydrolysis Ref: 1. "Hydrolysis and photolysis studies with ^{14}C -DPX-4189". By J. C-Y. Han Doc. No. AMR-08-80A. Exhibit 1.

Hydrolysis of ^{14}C -phenyl labeled DPX-4189 was studied as follows:

Procedure

^{14}C -phenyl labeled DPX-4189 at 1 ppm concentration was added to pH 4, 7 and 9 aqueous buffers. These solutions were kept in dark at a constant temperature of 20 °C for 4 weeks. Small aliquots of each solution were taken for radioactivity count and TLC analysis. Standards of postulated hydrolysis products were chromatographed on the same plates, scanned for radioactivity and visualized under 254 nm UV light. Plate areas corresponding to standards were removed and confirmed by mass spectra.

Results

In all samples the total loss of radioactivity was <5%. At pHs 7 and 9, DPX-4189 was found to be stable for 4 weeks under the above test conditions showing a low <3% decomposition. However at pH 4 the chemical degraded to 2-chlorobenzenesulfonamide and 2-amino-4-methoxy-6-methyl-1,3,5-triazine. 50% of DPX-4189 decomposed after 1 week at pH 4, and complete decomposition occurred after 4 weeks.

Conclusion

DPX-4189 is stable to hydrolysis at pHs 7 and 9 showing <3% degradation in 30 days. At pH 4 the chemical degrades to provide 2-amino-4-methoxy-6-methyl 1,3,5-triazine and 2-chlorobenzenesulfonamide showing a half-life of one week.

For the proposed EUP, the above study sufficiently describes the fate of the chemical under hydrolysis.

It is recommended that at the time of full registration, a revision on the hydrolysis test-protocol be carried out according to existing guide lines for "chemistry requirements-Environmental Fate" under FIFRA 163.627(b)

3.4

Photodegradation

Ref: "Hydrolysis and Photolysis studies with ^{14}C DPX-4189" by C-Y Han. Exhibit #1, pp. 3-7.

Laboratory photodegradation studies with ^{14}C -phenyl labeled DPX-4189 in water.

The photodegradation of ^{14}C -phenyl labeled DPX-4189 in aqueous solutions was studied using artificial light source. The average light intensity (300-400 nm, peak sensitivity ca 365 nm;) of this source was ca 1200 microwatts/cm² indicated to be about 1/2 the intensity of typical sunlight.

Procedure

Two aqueous solutions, 1 ppm and 100 ppm DPX-4189 in distilled water were placed in flasks kept 6 inches under the light source. The temperature of the solutions was about 40°-42°C. The volume of the test solutions was maintained at constant level by adding distilled water periodically (1 to 3 days) during the 4 weeks of exposure. Every week, aliquots of sample were taken out for counting total radioactivity and TLC analysis. In the TLC analysis, 5 ml of sample were dried in nitrogen atmosphere redissolved in methanol and applied to silica gel TLC plates along with standards. The area of silica gel corresponding to each band of radioactivity was scraped, mixed with scintillation solution and counted in a liquid scintillation spectrophotometer. The 4th week samples were also analysed by a liquid chromatograph. The degradation products were identified by HPLC and TLC. Isolated compounds were derivatized with diazomethane and confirmed by comparing their mass spectra with standards.

Results

The results of this study showed that only 10% of intact DPX-4189 had remained after 4 weeks exposure. The loss of radioactivity was 65% in the 1 ppm solution and 36% in the 100 ppm solution.

2-chlorobenzenesulfonamide and 2-amino-4-methoxy-6-methyl-1,3,5-triazine were the major degradates. 2-chlorophenyl sulfonyl area was a minor degradate. An unidentified polar compound was also detected.

Comments:

This is a laboratory study using aqueous solutions exposed to artificial light having about 1/2 the intensity of summer sunlight. Qualitatively, it is found that 90% ¹⁴C-DPX-4189 degrades to the following in 4 weeks: 2-chlorobenzenesulfonamide, 2-amino-4-methoxy-6-methyl-1,3,5-triazine, 2-chlorophenylsulfonylurea and an identified polar compound.

Laboratory Photodecomposition of ¹⁴C-phenyl DPX-4189 as a dryfilm on glass.

Procedure: Using the same light source of the previous study, 5x20cm glass plates coated with ¹⁴C-DPX-4189, (5mg on each plate) were exposed for one week and one month. Same analytical procedures were used as previously described.

Results

After one month, only 5% of DPX-4189 was photodegraded. About 20% of radioactivity was lost after 1 month's exposure. About 1-2% of radioactivity was found to be 2-chlorobenzene sulfonamide.

Comments

This study indicates that, without moisture, the photodegradation of DPX-4189 is low and is about 5%. Low amounts of degradate 2-chlorobenzene-sulfonamide was detected.

This information is useful but not a required study.

Degradation of ^{14}C -DPX-4189 in natural sunlight

Photolysis of the chemical in water was conducted in summer sunlight in Wilmington, Delaware.

Procedure

Studies on photodegradation of DPX-4189 labeled at either ^{14}C -phenyl or 2- ^{14}C -triazine, were conducted with the test solutions containing 0.1 ppm of the radioactive chemical in distilled water. For the purpose of comparison, photolysis tests were conducted with solutions of the labeled compound in a standard reference water containing specific inorganic salts a sample of creek water, and a sample of creek water with bottom sediments.

All of the above aqueous solutions were placed in beakers covered with quartz cover plates and exposed to direct summer sunlight, and kept in a constant temperature bath maintained at 20°C. Weekly analysis of aliquots of samples were conducted for a period of 8 weeks. In the analysis, total ^{14}C was determined. Intact DPX-4189 and photolysis products were determined by TLC.

Results

The TLC analyses of the water solutions during photolysis are summarized in the following tables. (See Page 8)

Conclusion

The TLC analyses indicate that the degradation rate of the chemical, under photolysis using distilled water, is the fastest showing an estimated $t_{1/2}$ of <2 weeks. In the creek water, photolysis occurs at a slower rate showing an estimated $t_{1/2}$ of >4 weeks. Inorganic salts contained in the standard reference water appears to retard photodegradation. DPX-4189 content in this reference water was 60% at 6 weeks exposure.

The photodegradation products produced are the same in all the tested solutions. These photodegradates are identified to be the following:

1. 2-chlorobenzenesulfonamide
2. 2-chlorophenyl sulfonyl urea
3. 2-amino-4-methoxy-6-methyl-1,3,5-triazine

The triazine degradate appears to be the most predominant.

Photodegradation of ^{14}C -DPX-4189TLC results with Triazine ^{14}C -label ^{14}C -Compound %

Type of Water	Exposure Time Weeks	Origin	Intact DPX-4189	2-amino-4-methoxy 6-methyl-1,3,5-triazine
Distilled Water	2	30	43	21
	4	24	27	41
	6	29	12	48
	8	26	10	44
STD, Reference Water	2	12	77	8
	4	10	72	13
	6	10	68	14
	8	11	60	17
Creek Water	2	18	68	9
	4	11	68	12
	6	12	58	18
	8	16	52	22
Creek Water with Sediment	2	4	71	5
	4	10	64	7
	6	11	51	13
	8	13	46	17

Photodegradation of ^{14}C -DPX-4189TLC results with Phenyl ^{14}C -label ^{14}C -Compound &

Type of Water	Exposure Time Weeks	Origin	Intact DPX-4189	2-Chlorobenzene Sulfonamide	2-Chlorophenyl sulfonyl urea
Distilled Water	2	25	37	21	0
	4	20	20	6	1
	6	14	13	6	1
	8	13	7	4	2
STD, Reference Water	2	20	66	9	3
	4	13	68	7	3
	6	15	61	5	3
	8	15	58	8	4
Creek Water	2	11	73	6	1
	4	12	45	5	3
	6	18	43	5	4
	8	17	41	8	4
Creek Water with Sediment	2	6	63	7	1
	4	9	55	10	2
	6	14	40	11	2
	8	18	34	15	3

The beakers were not sealed to prevent loss of water and radioactivity.

The above studies are adequate to support photodegradation in water. For terrestrial crop use photolysis in soil and studies in vapor phase as a part of the assessment of reentry hazard may be required for full registration.

3.5 Column Leaching Studies

Ref: "Soil Column Adsorption Studies with ^{14}C -DPX-418H herbicide on Soil" by Robert L. Chrzanowski. Exhibit #3, Document No. AMR-08-80B, Acc. No. 099462.

Column leaching studies with ^{14}C -phenyl-labeled DPX-4189 were conducted using sandy loam and silt loam soil as follows:

Procedure: Fresh soil leaching

18"htx2" dia. glass columns were packed with each soil type and wetted with water. ^{14}C -DPX-4189 (0.09 mg in 1 ml methylene chloride 0.5uCi) equivalent to 0.45 kg active/hectare of soil surface was added to the top of each column. Water was immediately and continuously percolated through the column. The water was collected on 0.2" increments for a period of 24 hours for the sandy loam column. It took 48 hours to do the same for the silt loam column. From both the columns 20" of water was collected. The total radioactivity was measured for each increment of water.

Aged Soil Leaching

100 grams of fresh soil samples of both types were treated with 0.09 mg ^{14}C -DPX-4189. To the above treated samples, water was added to adjust the moisture content to about 70% of normal holding capacity and placed in a green house for 30 days. 100 grams of aged soils were placed over fresh soil packed to 16" depth in 2" column to correspond to a final soil depth of 18". Water was percolated through the columns, and the eluents were collected and analysed.

For all the leached soils, 2" sections were removed and the radioactivity remaining in the soil was determined. The "break-through volume" (V_B) for sodium chloride - ^{36}Cl and the void volume (V_0) for each soil column type was also determined.

Results

The characteristics of the test soils are shown below:

Fallsington Sandy Loam:

Sand = 56%, Silt = 29%, Clay = 15%, OM = 1.4%
pH = 5.6, and CEC = 4.8 meg/100g.

Flanagan Silt Loam:

Sand = 5%, Silt = 64%, Clay = 31% OM 4.02%
pH = 5.0, CEC = 23.4 meg/100g

Analyses of 2" sections of the soil column after the leaching are given in the following table:

<u>Soil Section</u>	<u>%14-C recovered</u>	
	<u>Fallingston Soil</u>	<u>Flanagan Soil</u>
0-2	62	25
2-4	8	16
4-6	4	8
6-8	4	9
8-10	5	8
10-12	6	9
12-14	5	6
14-16	3	7
16-18	3	11

Leachate Composition in ppm DPX-4189 are given below:

<u>Increment of Eluent*</u>	<u>Fallingston Soil</u>		<u>Flanagan Soil</u>	
	<u>Fresh Soil</u>	<u>Aged Soil</u>	<u>Fresh Soil</u>	<u>Aged Soil</u>
4"	0	0	0	0
10"	0.19	0.12	0.34	0.09
15"	0.075	0.05	0.07	0.07
20"	0.04	0.03	0.01	0.03

* taken every 0.2"

With the Fallsington and Flanagan soils, , 84% and 99% of the unaged residues were found in 20 inches of leachate.

For the sandy loam column, $V_B = 1.6 V_0$ and for the silt loam column $V_B = 0.89 V_0$. The highest concentrations of ai in the percolation water occurred at $0.88 V_B$ and $0.84 V_B$, respectively, for the freshly treated and aged Fallsington soils ($V_B = 9.8$ inches), and occurred at $1.56 V_B$ and $1.73 V_B$, respectively for the freshly treated and aged, Flanagan soils ($V_B = 6.8$ inches).

Leaching characteristics of the chemical are discernable. The parent compound leaches more than aged parent.

- 3.6 Aerobic Soil Metabolism: Ref: "Aerobic Soil Metabolism of ^{14}C -Phenyl labeled DPX-4189" by J. Gy. Han, Document No. AMR 08-80C; Exhibit #4 Acc. No. 099462

Soil degradation studies in a greenhouse, using ^{14}C -phenyl labeled DPX-4189 and two types of soils (Keyport silt loam and Fallsington Sandy loam) are presented.

Procedure.

200 grams each of air dried fresh soil samples were placed in 13 (16oz) paper cups. Each soil sample was then treated with 20 ul of a methanolic solution containing 20 ug ^{14}C -phenyl labeled DPX-4189. This treatment rate was equivalent to 0.1 ppm (100 g active/ha assuming incorporation to 0-10 cm depth). Water was added to each sample to adjust moisture level to 80% and the contents were mixed. These samples were then placed in a greenhouse in November and tested for a period of 9 months. The test soil samples were taken periodically and analysed for the total radioactivity remaining in the soil for DPX-4189 and the degradation products by the combustion -LSC technique.

Sample of test soils were also extracted with methanol, partitioned with water and ethyl acetate and analysed by TLC and LSC techniques.

Results:

The soil characteristics are shown in Table 1. The aerobic soil degradation data are summarized in Table 2.

Table 1. Soil Characteristics

	<u>Keyport silt loam</u>	<u>Fallsington sandy loam</u>
Sand %	16.2	48.8
Silt %	72.8	42.5
Clay %	11.0	8.7
OM %	1.4	1.0
CEC (Me/100g)	7.7	5.8
pH	6.0	6.4

Table 2: DEGRADATION ¹⁴C-DPX-4189
GREENHOUSE SOIL STUDIES

% Radioactivity in Keyport Silt Loam/Fallsington Sandy Loam

Extracted portion

Time Days	% in Solvent Phase	% in Water Phase	% Unextracted activity	% DPX-4189	% 2-chlorobenzene sulfonamide
0 day	69/70	15/17	16/13	75/85	8/3
1 day	62/67	20/19	17/13	78/66	4/14
3 day	60/61	24/23	17/14	58/58	22/19
7 day	56/60	24/25	18/14	61/51	19/22
14 day	52/61	26/25	18/14	46/50	25/28
21 day	47/56	29/26	19/14	51/48	24/30
1 month	47/60	30/26	20/13	49/39	26/34
2 month	42/45	31/30	21/13	36/34	30/36
6 month	23/32	39/46	22/12	17/16	19/20
9 month	23/20	40/39	22/16	12/11	13/12

Conclusion:

Under the test conditions ¹⁴C-DPX-4189 had a half-life soil of about 1 month.

The major degradate, 2-chlorobenzene sulfonamide, reached 30-35% of the residual radioactivity at 2 months and then declined to 12-13% at 9 months. 2-chlorophenyl sulfonyl urea was detected but the mass spectra was inconclusive.

Recovery studies with soils fortified with ¹⁴C-phenyl labeled DPX-4189 at the 0.1 ppm level and aged for 2-3 hours showed that 80-85% of the DPX-4189 was recovered by the test procedure used for the soil experiments.

Aerobic soil metabolism of the chemical is discernible. The data submitted is adequate for EUP requirements.

3.7 Soil Dissipation

"Field soil disappearance Studies with ^{14}C - labeled DPX-4189" by J. C-Y-Han, Exhibit #5. Document No. AMR-08-80D, Acc. No. 099462.

Introduction: DPX-4189 is intended for field and vegetable crop use. The test protocol for field dissipation studies requires that soil samples be taken up to a depth of 30 cm from application sites in 4 agricultural use areas for a maximum period of 18 months. The registrant has stated that soil dissipation studies are scheduled for 18 months. Nearly 90% degradation of the chemical is reported within 26 weeks in this study

Procedure:

Several stainless steel cylinders (10-cm dia x 38 cm) were driven into soil at known field locations in Delaware, Illinois, Nebraska and North Dakota. The soil in each cylinder was treated with ^{14}C -DPX-4189 equivalent to a rate of 100 g/ha.

At known intervals these soil cylinders were removed for analysis. Specific sections of the soil cores removed from the cylinders- 0-5, 5-10 10-20 and 20-38 CM were analysed for total radioactivity. The sections containing 3% or more of applied radioactivity were analysed for DPX-4189 and its degradates by ammonium carbonate-water-methanol extraction and TLC.

Results:

The characteristics of the test soils are shown in the following table.

	Newark, Delaware	Stanton, Delaware	Corrington, North Dakota	Claycenter Nebraska*	Rochelle, Illinois
<u>Texture (USDA)</u>	<u>Silt Loam</u>	<u>Sandy Loam</u>	<u>Laom</u>	<u>Silt Loam</u>	<u>Silt Loam</u>
% Sand	16	49	41	0	20
% Silt	73	42	49	76	68
% Clay	11	9	10	24	12
CAC (ME/100g)	7.73	5.8	22	23.4	43.6
OM	1.4	1.0	4.4	3.8	7.4
pH	6	6.4	6.6	5.6	6.7

The radioactive materials at different depths of soil at different test intervals between 0-26 weeks are shown in the following tables 1, 2A, 2B, and 2D.

*The data contained conflicting sand, silt and clay percentages.

TABLE I

Percentage of Original ^{14}C -activity Remaining in ^{14}C -phenyl-DPX-4189

Exposure Time Weeks	Soil Depth, cm		Newark Delaware		Total Recovery	Total Rainfall mm
	0-5	5-10	10-20	20-end		
0	99.8	<0.1	<0.1	<0.1	99.8	0
2	65.6	26.6	8.7	<0.1	99.9	42
4	31.7	27.8	20.1	<0.1	79.6	86
8	33	18.5	27.3	19.3	98.1	199
16	21	15.6	14.8	10.7	62.1	346
26	20.1	11.1	13.3	10.0	54.5	670

Corrington, N.D.

0	102.3	<0.1	<0.1	<0.1	102.3	0
2	37.5	37.3	16.1	3.1	88	108
4	27.3	16.1	29.5	19.0	91.9	150
8	10.8	18.2	28.6	32.1	89.7	202
16	17.6	7.1	14.6	16.2	55.5	231

Clay Center, Neb.

0	96.1	<0.1	<0.1	<0.1	96.1	0
2	92.9	<0.1	<0.1	<0.1	92.9	20
4	82.6	3.6	<0.1	<0.1	86.2	20
8	69.6	1.9	3.4	<0.1	74.9	117
16	52.1	10.2	3.7	1.9	67.9	184
26	39.2	12.2	14.2	2.2	67.9	373

Rochelle, Illinois

0	98.2	<0.1	<0.1	<0.1	98.2	0
2	80.9	6.0	<0.1	<0.1	86.9	45
4	85.2	8.7	<0.1	<0.1	93.9	64
6	77.2	13.5	4.6	<0.1	95.3	92
8	46.5	17.7	6.5	1.4	72.1	170
20	44.1	22.9	7.4	1.3	75.4	461

Analyses of Treated Soils

Delaware Soil - % Radioactivity Distribution

Exposure Time (Wk)	Soil Increment cm	(NH ₄) ₂ CO ₂ -H ₂ O -Methanol Extract		% Unextracted Residue	% DPX-4189	% 2-chloro- benzene Sulfonamide
		Ethyl- acetate Phase	Water Phase			
0	0-5	72	11.3	16.5	70.7	1.3
2	0-5	36.9	12.5	8.2	36.9	8.8
	5-10	17.5	7.3	4.1	16.8	5.6
	10-2	<u>7.3</u>	<u>3.8</u>	<u>2.4</u>	<u>7.3</u>	<u>2.5</u>
	TOTAL	61.7	23.6	14.7	61.0	16.9
4	0-5	18.6	7.7	5.3	14.1	8.0
	5-10	15.8	7.6	4.5	11.6	7.4
	10-20	<u>14.3</u>	<u>3.9</u>	<u>1.9</u>	<u>10.0</u>	<u>5.9</u>
	TOTAL	48.7	19.2	11.7	35.7	21.3
8	0-5	15.5	12.1	5.3	4.3	10.5
	5-10	9.8	7.1	1.8	3.1	6.5
	10-20	15.2	8.3	3.7	4.2	10.6
	20-end	<u>10.4</u>	<u>7.1</u>	<u>1.8</u>	<u>3.6</u>	<u>6.5</u>
	TOTAL	50.9	34.6	12.6	15.2	34.1
16	0-5	4.8	10.0	5.8	2.0	4.9
	5-10	4.3	6.8	4.1	1.9	3.6
	10-20	4.8	6.5	2.9	1.9	3.9
	20-end	<u>2.7</u>	<u>5.4</u>	<u>2.6</u>	<u>1.2</u>	<u>2.6</u>
	TOTAL	16.6	28.7	15.4	7.0	15.0
26	0-5	4.5	10.0	5.7	1.6	3.2
	5-10	3.5	3.7	3.1	0.7	1.2
	10-20	2.9	2.9	5.7	0.4	0.9
	20-end	<u>4.2</u>	<u>3.3</u>	<u>2.5</u>	<u>0.9</u>	<u>1.5</u>
	TOTAL	15.1	19.9	17.0	3.6	6.8

TABLE 2B.

Analysis of Treated Soil

Nebraska Soil - % Radioactivity Distribution

Exposure Time (wk)	Soil Increment	(NH ₄) ₂ CO ₃ /H ₂ O/ MeOH Extract		% Unextracted Residue	% DPX-4189	% 2-chloro- benzene Sulfonamide
		<u>ETOAC</u>	<u>H₂O</u>			
0	0-5	84.8	8.7	2.4	78.8	18.3
2	0-5	78.9	10.1	4.3	55.2	29.5
4	5-10	62.4	9.7	9.8	34.0	33.3
	10-20	<u>2.6</u>	<u>0.3</u>	<u>0.3</u>	<u>1.9</u>	<u>0.9</u>
	TOTAL	65.0	10.0	10.1	35.9	34.2
8	0-5	28.9	32.1	7.7	18.7	17.3
	5-10	0.8	0.6	0.3	0.4	0.4
	10-20	<u>1.0</u>	<u>1.9</u>	<u>0.4</u>	<u>0.6</u>	<u>0.6</u>
	TOTAL	30.7	34.6	8.4	19.7	18.3
16	0-5	22.8	21.8	7.1	9.8	17.6
	5-10	3.1	5.8	0.6	1.3	2.7
	10-20	<u>1.2</u>	<u>2.0</u>	<u>0.4</u>	<u>0.4</u>	<u>0.9</u>
	TOTAL	27.1	29.6	8.1	11.5	21.2
20	0-5	22.0	13.0	6.0	1.7	8.2
	5-10	5.3	4.8	2.1	0.6	1.5
	10-20	4.9	5.9	3.5	0.5	1.6
	20-end	<u>0.7</u>	<u>1.0</u>	<u>0.5</u>	<u>0.2</u>	<u>0.4</u>
	TOTAL	32.9	24.9	12.1	3.0	11.9

TABLE 2C

Analyses of Treated Soil

North Dakota Soil - % Radioactivity Distribution

Exposure Time (Wk)	Soil Increment	(NH ₄) ₂ CO ₂ -H ₂ O- Methanol Extract		% Unextracted Residue	% DPX-4189	% -2-chloro- benzene Sulfonamide
		ETOAC Phase	H ₂ O Phase			
0	0-5	57.9	38.9	33.9	76.9	16.9
	5-10	17.9	17.1	2.6	23.1	5.7
	10-20	17.8	11.1	2.9	21.3	4.6
	20-end	7.0	7.1	1.7	10.0	2.2
		<u>1.3</u>	<u>1.5</u>	<u>0.2</u>	<u>1.9</u>	<u>0.4</u>
	TOTAL	43.6	36.8	7.4	56.3	12.9
4	0-5	8.0	13.8	4.7	9.4	3.5
	5-10	4.3	9.7	2.7	6..	2.3
	10-20	7.5	16.8	4.8	9.8	3.7
	20-end	<u>5.8</u>	<u>9.8</u>	<u>3.1</u>	<u>6.9</u>	<u>2.4</u>
	TOTAL	25.6	50.1	15.3	32.2	11.9
8	0-5	1.8	6.4	3.3	1.8	3.0
	5-10	8.1	5.6	4.5	4.3	4.6
	10-20	11.8	10.1	6.7	6.1	9.0
	20-end	<u>13.5</u>	<u>11.7</u>	<u>6.9</u>	<u>7.5</u>	<u>8.9</u>
	TOTAL	35.2	33.8	21.4	19.7	25.5
16	0-5	4.0	8.7	4.0	1.6	2.1
	5-10	2.4	2.9	1.8	1.2	1.6
	10-20	5.2	5.7	3.7	2.0	2.5
	20-end	<u>6.5</u>	<u>5.6</u>	<u>4.1</u>	<u>2.4</u>	<u>2.5</u>
	TOTAL	18.1	22.9	13.6	7.2	8.7

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TABLE 20

Analyses of Treated Soil

Illinois Soil - % Radioactivity Distribution

Exposure Time (Wk)	Soil Increment (cm)	(NH ₄) ₂ CO ₃ / H ₂ O/MeOH Extract		Unextracted Residue	% DPX-4189	% 2-Chlorobenzene sulfonamide
		EtOAc Phase	H ₂ O Phase			
0	0-5	53.2	39.3	5.7	74.3	27.2
2	0-5	51.2	18.5	11.2	48.1	18.6
	5-10	3.1	2.0	0.9	4.5	0.6
	TOTAL	54.3	20.5	12.1	52.6	19.2
4	0-5	45.0	22.1	18.1	26.1	32.8
	5-10	4.2	3.3	1.2	4.4	1.7
	TOTAL	49.2	25.4	19.3	30.5	34.5
6	0-5	35.7	24.9	16.6	17.1	29.3
	5-10	6.9	4.0	3.6	3.5	5.1
	10-20	2.4	1.3	0.9	1.5	1.2
	TOTAL	45.0	30.2	21.1	22.1	35.6
8	0-5	11.7	24.5	11.1	8.2	2.0
	5-10	4.7	8.8	4.4	3.7	2.8
	10-20	1.4	2.5	1.6	1.2	1.1
	TOTAL	17.8	35.8	17.1	13.1	11.9
20	0-5	10.8	19.8	12.8	2.3	8.7
	5-10	6.8	8.6	7.5	1.2	3.8
	10-20	2.4	2.6	2.4	0.7	1.2
	20-end	0.4	0.5	0.4	0.1	0.2
	TOTAL	20.4	31.5	23.1	4.3	13.9

Conclusion

The data indicate that the chemical, regardless of the soil type and climatic condition, remains concentrated in the upper part of the soil cores between 0-10 cm. Some losses occur at the top portion of the soil as a result of volatility, rain-splash and photolysis and it is deduced to be 10-20%.

Water soluble residues may be subject to leaching. The major metabolites were 2-chlorobenzenesulfonamide from ¹⁴Cphenyl DPX-4189 and 2-amino-4-methoxy-6-methyl-1, 3, 5-triazine from ¹⁴C-triazine labeled DPX-4189. There are some polar materials in bound unextractable residues, in amounts less than 10% of applied rate except where the %OM in the soil is high as indicated in the case of Illinois soil. Under the test conditions, the half-life of DPX-4189 is shown to be 1 month in all the soils tested.

3.8 Microbial - Soil Degradation

Ref: "Microbial degradation of ¹⁴C-phenyl labeled DPX-4189 in Soil" by C. Rapisardi Exhibit #6. Document No. AMR-08-80E, ACC. No. 99462 (6-16-1980)

Studies have been conducted on sterile and non-sterile soil to determine biodegradation of ¹⁴C-DPX-4189 according to procedure described by Bartha and Pramer [Soil Science 100 68 (1965)].

Procedure

Samples of sterile and non sterile Keyport silt loam soil, treated with ¹⁴C-DPX-4189 at 0.1, 1, and 10 ppm, were placed in the dark for 6 months.

By TLC analysis of radioactive residues extracted from the treated soil, several metabolites were indentified at specific intervals during the 6 months. The sterile soils were extracted and analysed after 6 months.

Results

Characteristics of test soil

The Keyport silt loam from Newark, Delaware used in this study contained sand 21%, silt 62% clay 17%, OM 2.75%. Soil pH and CEC were 6.4 and 8.2 meg/100g, respectively.

¹⁴C-phenyl-DPX-4189 degradation, in terms of % recovered radioactivity in CO₂, extractable portion of the tested soil and the unextracted soil residue, has shown good material balance, >97% of applied ¹⁴C.

The TLC analytical data on extract material (total of different extracts) are summerized in the following Table:

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Summary Table: Extract Composition Based on % Radioactivity in Soil and $^{14}\text{CO}_2$

Values at 0.1 ppm/ 1ppm of Treatment

Time Interval Months	$^{14}\text{CO}_2$	<u>Nonsterile Soil</u>				Highly Polar Materials*
		<u>Unextracted</u>	<u>DPX-4189</u>	<u>2-Chloro Sulfonamide</u>	<u>Metabolites A, B, C*</u>	
0			96.2/96.5	1.2/1.6	1.4/1.4	0/0
0.25	0.3/0.2	2.5/2.5	69.5/70.1	15.4/12.3	9.4/12.8	2.9/2.1
0.5	0.5/0.4	5.4/3.4	28.1/31.5	38.5/34.8	26.0/27.2	1.5/2.7
1	1/0.8	1.8/2	31.3/15.2	35.1/41.4	25.6/20.3	5/20
2	1.7/1.7	3.2/2.5	12.1/5.5	52.3/57.7	30.0/29.6	0.7/3.0
3	2.4/2.4	6.8/5.7	2.8/4.9	47.1/47.5	22.2/30.8	18.7/8.7
4	3.5/3.1	9/6.7	3.2/2.7	46.5/51.3	29.3/24.6	8.5/11.6
6	4.9/4.5	5.3/5.7	6.7/7.4	52.9/59.4	18.5/11.5	11.7/11.5
<hr/>						
			<u>Sterile Soil</u>			
1	0.2/0.1	9/0				
6	0.8/0.2	0.9/1.2	8.9/14.6	62.5/65.8	24.3/17.6	2.6/0.6

* A, B, C = Polar materials (Rf = 0.15 - 0.3) that have not been identified.

** Highly polar materials have A, B, and C and some that have not been identified.

Conclusion:

For sterile soils, analytical data for the % of recovered radioactivity at different rates at the 6 month, show the presence of 7% DPX-4189, 65% 2-chlorobenzenesulfonamide, and 25% of total polar (unidentified) materials. This degradation is attributed to hydrolysis probably catalysed by the soil components. The rate of degradation under sterile conditions is comparable to non-sterile data during the 2 and 3 month. In the non-sterile soil, after the 3rd month and up to the 6th month, the rate of degradation slows down. Regardless of the time period, about 40% of total radioactivity in the non-sterile soil is attributed to unidentified polar materials.

Analysis of extractable materials show two major metabolites- 2-chlorobenzenesulfonamide and 4-methoxy-6-methyl-1,3,5 triazine. Comparison of data between the sterile soil study and non-sterile study has established that microbial degradation does occur. The soil binding polar materials have not been indentified. The half-life of the chemical seems to be less than 2 weeks in non-sterile soils. The adequacy of this data on any need of the identification for metabolites in the unextractable portion will be judged at a later time, in conjunction with crop data to understand the influence if any on residue uptake.

- 3.9 Effects of Pesticide on Nitrifying Bateria: Ref: "Evaluation of Possible Effects of DPX-4189 2-chloro-N-[4-methoxy-6-methyl-1,3,5-triazine-2-yl) Animo Carboxyl] Benzenesulfonamide, on Nitrifying Bacteria in Two Soil Types" by G.A. Smith and C-Y Han Exhibit #7, AMR-14-80. Acc, No.99462 (6-16-80)

Procedure

The change of NH_4^+ ions to nitrate ions in the soil occurs due to nitrifying autotropic bacteria. The influence of DPX-4189 on nitrification was studied on two soils. Keport silt loam and Fallsington sandy loam treated with 0.1 ppm and 1.0 ppm of the chemical were studied under laboratory conditions. As controls, soil samples treated with $(\text{NH}_4)_2 \text{SO}_4$ (without-DPX-4189) and untreated soils were used.

The Test Soils were prepared as follows:

- 1) 200 ppm of nitrogen, as $(\text{NH}_4)_2 \text{SO}_4$, was added to soil samples and, 0.1 and 1.0 ppm of the DPX-4189 was added to both the soils.
- 2) Ammonium Sulfate alone was added to a separate soil series (no pesticide added)
- 3) A third series without $(\text{NH}_4)_2 \text{SO}_4$ or the pesticide was tested to observe any normal nitrification which might occur in the test soils.

All of the above soil samples were placed in flasks and incubated at 35°C for a period up to 10 weeks. During that period, at known time

intervals, soil samples were extracted with water and analysed for NO_3^- concentration. This was accomplished by taking potentiometric measurements using nitrate ion activity electrode.

Results

Soil Characteristics:

Keyport silt loam: Sand % = 21%, silt = 62% clay = 17%
OM = 2.75%, N_2 = 1%, PH = 6.4, CEC = 8.2 mg/100g

Fallsington sandy loam: Sand = 5%, silt = 64%, clay = 31%
OM = 1.4%, N_2 = 0.9%, PH = 5.6, CEC = 4.8 mg/100g

The effect of pesticide in terms of NO_3^- at 0.1 and 1.0 ppm level is shown in the following table for both the test soils.

Table: Total NO_3^- content in different test series

NO_3^- mg in soil controls and DPX-4189 Treated Soil

Keyport silt loam / Fallsington sandy loam

<u>Time Day</u>	<u>Check Soil (no treatment)</u>	<u>Control Soils</u>	<u>Treated Soil</u>	
			<u>0.1 ppm</u>	<u>1.0 ppm</u>
0	3.7/18	3.8/18	3.7/18	3.7/20
3	1.1/16.7	5.9/20	5.7/20	2.2/18
8	8/13.2	12.4/20	8/16	5/17
15	3.6/11.8	12.4/21	20/24	13/21
24	11/11.8	21.2/35	22/35	29/35
54	20/24.7	51/62	60/73	60/87
66	27/22.9	58.5/76	66/104	66/111

Conclusion:

The data indicate that NO_3^- yield in the Fallsington soil fortified with $(\text{NH}_4)_2\text{SO}_4$ was 95% of theoretical, after correcting for NO_3^- produced by normal nitrification. The yields for Keyport silt loam were lower (45% of theoretical). However, there were no differences between the control samples and the DPX-4189 treated samples at both (0.1 and 1 ppm) concentration levels. For a period of 66 days, there was no observable influence of the DPX-4189 on nitrifying bacteria or the nitrification process.

The above study is acceptable for the requirements of full registration since the effect of the chemical on bacterial nitrification is adequately demonstrated.

3.10

Effect of Pesticide on Microbes.

Ref: "The Effects of DPX-4189 on Microorganisms of Soils" by A. Jay Julius, Exhibit #8, Document No. AMR-13-80 Acc. No. 099462 (6-16-80)

The effect of DPX-4189 on soil microbial population has been studied.

Experimental

Three fresh agricultural soil types varying in texture and characteristics, obtained from Delaware, Kansas and Colorado were treated with DPX-4189 at 0.1, 1.0, 10 and 100 ug/g of soil. These tests soils, kept at 25 °C and maintained 50% moisture level, were examined at intervals of 2, 4, 6 and 8 weeks to study the effects of the chemical on soil borne fungi, bacteria and actinomycetes. Monoxenic culture assay was conducted for the soil borne fungi.

Results

The test soils used were as follows:

Harney silt loam Hays, <u>Kansas</u>	Sand 23%, silt 69%, clay 8% pH = 7.5
Keport silt loam Newark, <u>Delaware</u>	Sand 2%, silt 84%, clay 15% pH = 6.4
Renohill clay loam Platteville, <u>Colorado</u>	Sand 69%, silt 18%, clay 13% pH = 5.9

The populations of fungi at 10^{-2} grams of dry soil and actinomycetes and bacteria at 10^{-4} grams of dry soil, for the above three types of soil with and without DPX-4189 treatment has been tabulated. Microbial counts at DPX-4189 at concentration of (ug/ml) 0.1, 1, 10, and 100 were recorded. At these levels of treatment, the distribution of fungus type, after 2 weeks and 8 weeks of incubation has been recorded.

A comparison of % growth inhibition in chlorneb, thiram and DPX-4189 treated agar, for selected soil-borne fungi, at all levels of 1, 10, 100, 1000 ug/ml has been recorded. Bactericidal activity of DPX-4189 to selected soil-borne bacteria and nitrosomonas europa has also been recorded.

Conclusion:

The data show that the populations of actinomycetes, bacteria and fungi from the three agricultural soils were unaffected during the 8 week period after treatment with DPX-4189. At the test rates no significant differences were detectable between the controls and the treated soils or among the three soil types. Variation occurred in the genera of fungi recovered from the three soil type, and this is attributed to the diversity of geographic origin of the soils.

No fungitoxic effect of DPX-4189 has been noticed, at test concentration (1 to 100 μ g/ml) in monoxenic culture tests, on representative soil borne saprophytic or plant pathogenic fungi.

The chemical showed no bactericidal effect in monoxenic culture tests at rates of 1 to 100 μ g/ml.

4.1

Executive summary and conclusions.

A request for EUP has been made for the product, Dupont DPX-4189 DF weed killer, for trial use on wheat, barley and reduced-tillage fallow. This product contains 75% of a

2-chloro-N [(4-methoxy-6-methyl-1,3,5 triazine-2-yl) aminocarbonyl] benzene - sulfonamide.

The EUP request specifies the geographical locations, the acreage and quantity of pesticide proposed to be used at each location and the rate of application.

The environmental fate data requirements to support the above EUP use included the following studies.

Hydrolysis, aerobic soil metabolism and rotational crop studies. The rotational crop studies are not required for EUP because a rotational crop restriction has been proposed stating that the same crops (wheat and barley) are to be replanted in succeeding seasons during the test.

The EUP required studies submitted are summarized below:

Hydrolysis

The submitted study shows that the active ingredient DPX-4189 is hydrolytically stable in darkness at pHs 7 and 9 showing a decomposition rate of <3% in 30 days. The chemical is however hydrolysed in acidic pH 4 buffer solution, showing a half-life of 7 days and complete decomposition in 4 weeks. Under acidic conditions, the main hydrolytic degradation products are shown to be 2-chloro-benzenesulfonamide and 2-amino-4-methoxy-6-methyl-1,3,5 triazine.

This study is acceptable for the data requirements for EUP.

Aerobic Soil Metabolism:

Experimental studies on the metabolism in soil under aerobic conditions were conducted for 14 C-Phenyl labeled DPX-4189. Two types of soils were used - silt loam and sandy loam. Under the test conditions 14C-DPX-4189 showed a half-life of 1 month in both soils.

2-chlorobenzenesulfonamide has been shown to be the major degradate in both the soils. This metabolite reached 30-35% in terms of residual radioactivity in soil after 2 months and after about 9 months the residual radioactivity declined to 13%. 2-chlorophenyl sulfonyl urea was detected but the mass spectral analysis was not conclusive to evaluate the level of this degradate.

The submitted information is adequate for EUP.

4.2

The submitted document Acc. No 099462 (6/16/80) contains other usefull information and studies.

Review summaries for the same are the following:

Photodegradation.

Studies have been submitted on photolysis under direct sunlight of 14C-phenyl labeled and 2-14C-triazine labeled DPX-4189 at 0.1 ppm concentration in distilled water. Identical experiments were also conducted, using the same radio labeled DPX-4189 materials solublized in a standard reference water and a natural creek water. The studies in distilled water conducted for an 8 week period indicated that 2 amino-4-methoxy-6-methyl-1, 3, 5-triazine is a predominant degradate. At the end of 8 week exposure, only 10% of intact DPx 4189 remained in the test solution. The miner degradates, 2-chlorobenzenesulfonamide and 2-chlorophenyl-sulfonyl urea were found to present to an extent of about <4% after 8 weeks of exposure. In the other waters the results were different. The decomposition rate was 40% in the standard reference water and 30-55% in the creek water respectively.

Studies of photodegradation of 14-C-phenyl labeled DPX-4189 in distilled water exposed to artificial light source, representing half of the typical intensity of summer sunlight, show the same decomposition products.

¹⁴C-phenyl labeled compound applied as dry film on glass upon exposure to the same artificial light source indicated that , 95% of parent compound, about 1 to 2 % of 2-chlorobenzenesulfonamide was recovered after 9 months.

The above studies provide useful information and are acceptable as part of data requirement of full registration. Photolysis studies in soil, performed on preferably the same soils used in aerobic soil metabolism study will be needed to complete the requirement.

Soil Leaching.

The soil leaching studies are adequate. Aged residues do not leach as much as the parent which leaches readily.

Field dissipation.

Experimental studies on field dissipation characteristics of the chemical is shown in the submission under "field soil disappearance studies with 100g/ha of ¹⁴C-DPX-4189." 4 representative soils, silt loam and sandy loam types having different characteristics and different geographical field locations, were treated with the chemical and exposed to natural climatic conditions.

The result of these studies indicate, that regardless of the soil type and climatic conditions, the chemical does not penetrate below 0-4" depth from the soil surface. About 10-20% of loss occurs due to volatility, rain splash and photolysis.

The major field soil metabolites are shown to be 2-chlorobenzene sulfonamide and 2-amino-4-methoxy-6-methyl- 1,3,5 - triazine. Under the test conditions the t-1/2 of DPX-4189 is shown to be one month.

This study is acceptable for full registration.

Metabolism:

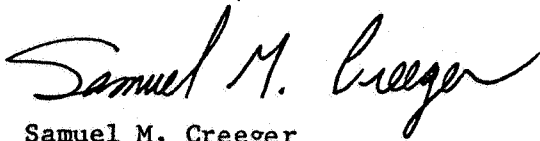
Soil microbes present in natural soils appear to have some action on DPX-4189. DPX-4189 does not influence the growth of soil microbes including nitrification bacteria. Studies on the effect of DPX-4189 on soil borne fung, bacteria and actinomycetes, at dosage rates exceeding the proposed EUP use rate, show that the growth of these microbes are not effected.

These studies are acceptable for full registration.

5.0 Recommendation:

5.1 The data are adequate to support the proposed permit.

5.2 For registration, all environmental fate data, as given in the Proposed Guidelines (July 10, 1978) will have to be submitted.

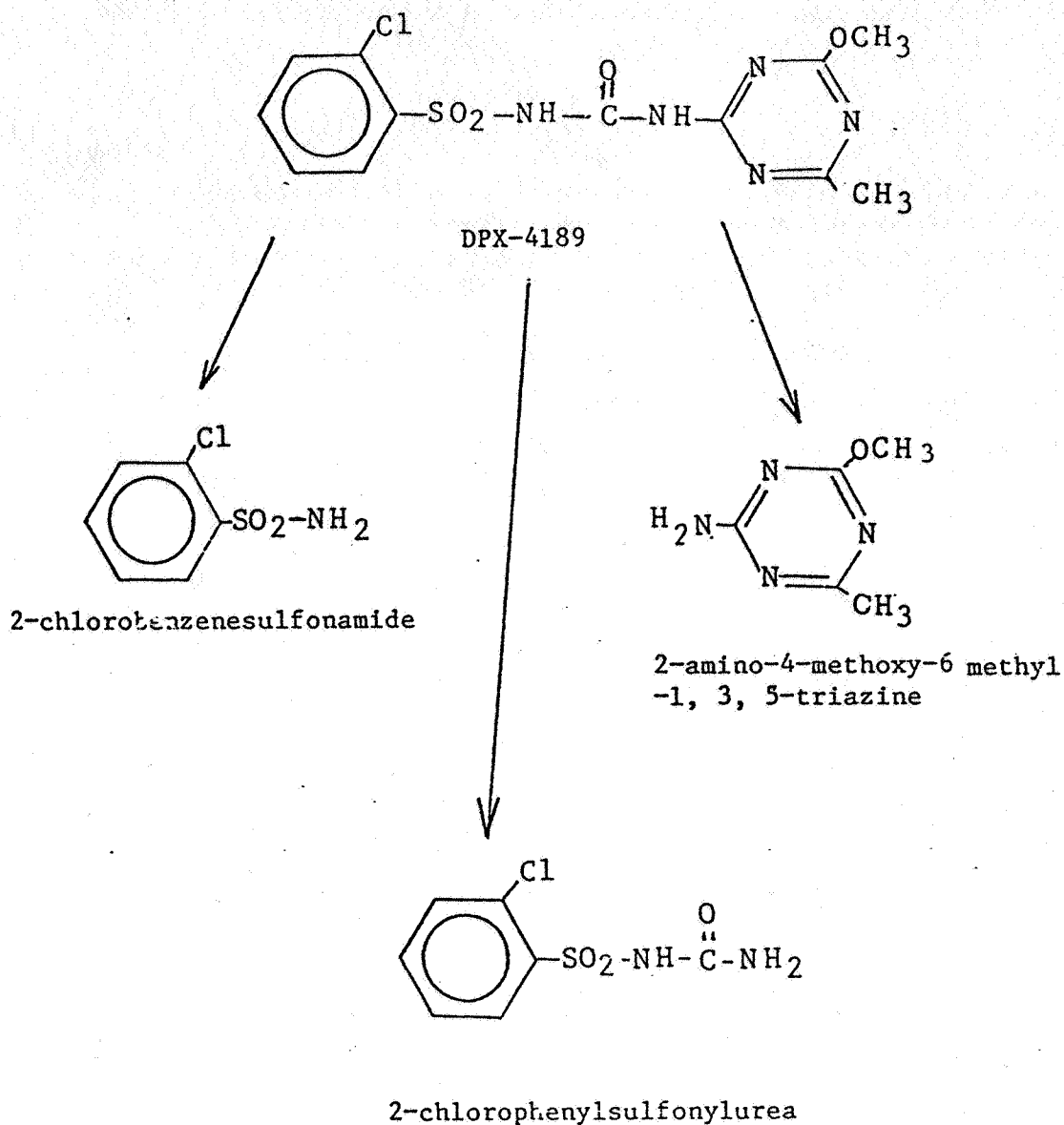


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Samuel M. Creeger

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EFB/HED



1. 2-chlorobenzenesulfonamide and 2-amino-4-methoxy-6 methyl-1, 3, 5-triazine are formed during hydrolysis, photolysis, aerobic soil metabolism, and microbial soil metabolism.
2. 2-chlorophenylsulfonylurea has been found to occur in all of the above processes except hydrolysis.