

Shaughnessy No.: 1228845

Date Out EAB: 30 NOV 1984

TO: Taylor/Wallers
Product Manager # 25
Registration Division
TS-767

5735



FROM: Samuel M. Creeger, Chief
Environmental Chemistry Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

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

Chemical: DPX-M6316

Type Product: Herbicide

Product Name: _____

Company Name: Du Pont

Submission Purpose: Review rotational crop study

ZBB Code: other

Action Code: 711

Date In: 9/28/84

EAB # 4581

Date Completed: 11/28/84

TAIS (Level II)

Days

61

1.5

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

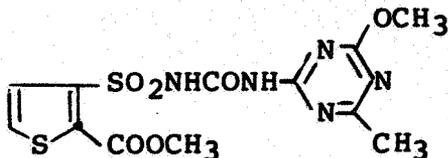
_____ Toxicology Branch

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



• [¹⁴C-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-¹⁴C] 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 ft², volume 0.75 ft³) 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-¹⁴C] (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 ¹⁴C-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}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}C AND 14 -DPX-M6316 IN SOIL
IN PLANTING OF THE ROTATIONAL CROP

Aging Period (day)	Appl. rate (g/ha)	^{14}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}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}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}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}C accumulated in the foliages.

4.0 CONCLUSION

4.1 The following environmental fate data requirements have been satisfied for DPX-M6316:

- o Aerobic soil metabolism
- o Fish accumulation
- o Hydrolysis (for EUP only: see section 5.1 of EAB review 11/1/84)
- o Rotational crop

4.2 EAB considers the data requirements for an EUP as satisfied. However, the following questions stated in 11/1/84 review concerning the aerobic soil metabolism study need to be answered:

- o How long were the flasks open to let in O_2 ?
- o Why was there not any loss of volatile ^{14}C ?

4

Soobok Hong

Soobok Hong, Ph.D.

November 28, 1984

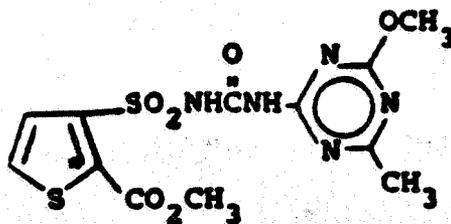
Environmental Chemistry Review Section #1

Exposure Assessment Branch/HED

5

PROPOSED METABOLIC PATHWAY OF DPX-M6316 [THIOPHENE-2-¹⁴C] IN

AEROBIC SOILS

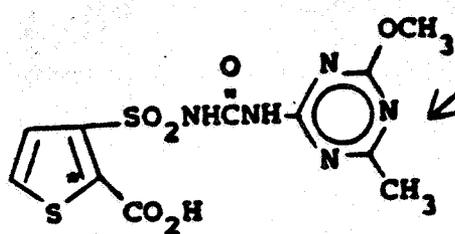


Photocopied as per OPP Security Procedures Manual

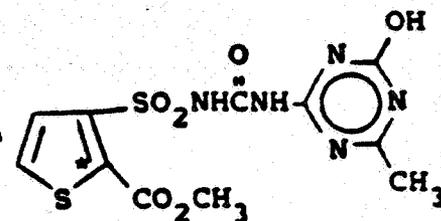
Date: 11/1/78 Rev: S.H. Company: DuPont

Activity #: 872946

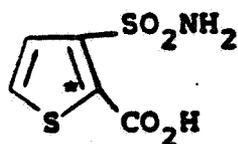
¹⁴C-DPX-M6316



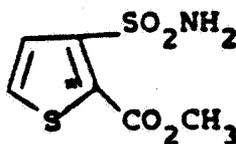
Metabolite A



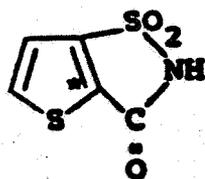
Metabolite D



Metabolite B



Metabolite C



Metabolite E

¹⁴CO₂

"Bound"

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

Met. E: thieno[2,3-d]isothiazole-3(2H)-one, 1,1-dioxide

* Denotes location of ¹⁴C label.

TABLE 2

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

<u>Crop</u> <u>Fraction</u>	<u>30-Day Aging Period</u>		<u>120-Day Aging Period</u>	
	<u>Days After</u> <u>Planting</u>	<u>Total Radiolabeled</u> <u>Residues, ppb^a</u>	<u>Days After</u> <u>Planting</u>	<u>Total Radiolabeled</u> <u>Residues, ppb^a</u>
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

^a ppb reported as ng DPX-M6316 per gram of fresh weight.

Photocopied as per GPP Security Procedures Manual
 Date: 11/2/88 Rev'n: SH Company: Du Pont
 Accession #: 254641 Tab: 3 Page: 7

TABLE 3

LEVELS OF INTACT [¹⁴C]-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^a</u>	<u>Extractable Percentage of Total Residue</u>	<u>PPB of Intact [¹⁴C]-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

Photocopied as per OPR Security Procedures Manual
 Date: 1-7-78 Rev: 5-4 Company: DuPont
 Accession #: 2560 Tab: 4 Page: _____