Data Evaluation Report on the phototransformation of XDE-742 (pyroxsulam) on soil

PMRA Submission Number 2006-4727; EPA MRID Number {46908328}; APVMA ATS 40362

Data Requirement:	PMRA DATA CODE:	8.2.3.3.1
	EPA DP Barcode:	332118
	OECD Data Point:	IIA 7.1.3
	US EPA Guideline:	Subdivision N, 161-3
Test material:	^{14}C-XDE-742-TP and ^{14}C-XDE-742-PYR Purity: See Figure 1	
Common name:	XDE-742 (pyroxsulam)	
Chemical name:		
IUPAC:	N-(5,7-dimethoxy[1,2,4]triazolo[1,5-α]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide	
CAS name:	N-(5,7-dimethoxy[1,2,4]triazolo[1,5-α]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide	
CAS No:	422556-08-9	
Synonyms:	INV1901 (TP), INV1905 (PYR)	
Smiles string:	c1(c(ccnc1OC)C(F)(F)F)S(Nc2nn3c(n2)nc(cc3OC)OC)(=O)=O	

Primary Reviewer: Barbara Martinovic (PMRA #1193) **Date:** March 8, 2007

Secondary Reviewers: Hemendra Mulye, PhD (PMRA #213) **Date:** March 13, 2007

David McAdam, PhD (AUS DEW) **Date:** 30 May 2007
D. Murphy for David McAdam November 2, 2007

Greg Orrick (USEPA) EBell for **Date:** 31 May 2007
Greg Orrick October 25, 2007

Émilie Larivière (PMRA) Date: 19 October 2007
Émilie Larivière 19 October 2007

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EPA PC Code: 108702

2070877

CITATION: Rutherford, L. A., Meitl, T. J., Balcer, J. L., and Linder, S. J., 2005, Photodegradation of XDE-742 on Soil, Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268-1054, 040014, M. D. Culy, 12-Apr-2005.

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EXECUTIVE SUMMARY

The phototransformation of ^{14}C-XDE-742 (two radiolabels: triazdopyrimidine and pyridine) was studied on a Charentilly silt loam soil (pH 6.2, organic carbon 1.0%) from France at 25 °C and 75% of 1/3 bar moisture using a xenon lamp as a light source. Samples, fortified at approximately 3 mg a.i./kg soil, were irradiated for up to the equivalent of 30 days of spring sunlight at 50° N latitude.

The experiment was conducted in accordance with the EPA Pesticide Registration Guidelines, Subdivision N, § 161-3, and SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 2.0 guidelines, and to meet the Good Laboratory Practices standards, 40 CFR Part 160.

^{14}C-XDE-742 was applied in water on the soil surface by positive displacement pipette. The treated samples were irradiated by continuous irradiation using a 6500 W xenon arc lamp, with an inner CERA filter and an outer Soda Lime filter. Irradiated test vessels were connected to traps containing ascarite for the collection of CO_2 and acidic volatiles. Dark control samples were maintained in a dark incubator set at 25 °C. Samples were taken at 0, 1, 3, 7, 10, and 15 days after treatment for the determination of the parent compound and transformation products. The soil samples were extracted with 90:10 acetonitrile:0.1 N HCl and the ^{14}C-XDE-742 residues were analyzed by HPLC. Soils were not sterilized.

A PNAP/pyridine (p-nitroacetophenone/pyridine) chemical actinometer solution was used to quantitate the amount of light that the samples received. Based on the PNAP/pyridine actinometer data, 15 DAT of irradiation was equivalent to 30 days of irradiation in the spring sun at 50° N latitude.

The mass balance was 97.1 ± 5.7% and 96.2 ± 4.8% in the dark and irradiated samples, respectively. At the test termination, approximately 31% of the applied ^{14}C remained as the parent XDE-742 in the dark samples. The major biotransformation products identified in the dark samples were 5-OH-XDE-742 and 7-OH-XDE-742 formed at approximately 9% and 11% of applied radiocarbon, respectively. The minor biotransformation product identified in the dark samples was the 7-OH-6-Cl-XDE-742 formed at approximately 4% of applied radiocarbon. At study termination, levels of the transformation products 5-OH-XDE-742 and 7-OH-XDE-742 in the dark control samples remained stable at approximately 9% and 11% of applied, respectively, while 6-Cl-7-OH-XDE-742 was increasing.

In the irradiated samples, concentration of the parent XDE-742 decreased from 98.5% at day 0 to 60.7% of the applied amount at test termination. Since the transformation products formed in the irradiated samples were less than 6% of applied, they were not conclusively identified. In irradiated samples, at the end of the study, less than 1% of the applied radioactivity was present in the ascarite traps as evolved CO_2 and acid gases.

Extractable ^{14}C residues decreased from 98.9% of the applied amount at day 0 to 56.9% and 75.6% of the applied amount at termination in the dark and irradiated samples, respectively. In the

irradiated samples, non-extractable ^{14}C residues increased from 0.3% of the applied amount at day 0 to 16.2% of the applied at study termination. Non-extractable residues in the dark samples were 0.3% of the applied amount at day 0, and 39.0% of the applied amount at test termination. XDE-742 transformed into non-extractable residues and volatiles when irradiated. Characterization of these residues from irradiated samples showed that 68% of ^{14}C non-extractable residues are associated with the fulvic acid fraction. Approximately 6% and 18% are associated with the humic and acid humin fraction, respectively. For the dark control, 45%, 14% and 41% of the ^{14}C non-extractable residues were associated with the fulvic acid, humic acid and humin fraction, respectively. Unidentified radioactivity increased to 14.8% in the irradiated samples, however, no single transformation product was >6% in any single sample.

The transformation rate constants of XDE-742 in the dark and irradiated samples were 0.079 and 0.017 $days^{-1}$, respectively. The transformation rate in the dark was greater than the total (phototransformation + non-phototransformation) rate; therefore, a $k_{photolysis}$ could not be calculated. Reviewer-calculated first order kinetic half-life values were 23 (r^2=>0.92) and 9 (r^2=>0.92) days for the light and dark samples, respectively. Since the soil samples were not sterilized, other possible routes of transformation such as biotransformation might have contributed to the transformation rates in this study.

Results Synopsis

Soil type: Charentilly silt loam
Source of irradiation: Xenon lamp
Half-life/DT_{50} for dark: 9 days (r^2=>0.92)
Half-life/DT_{50} for irradiated: 23 days (r^2=>0.92)
Half-life/DT_{50} for phototransformation: Stable. (The metabolism rate in the dark was greater than the total (phototransformation + metabolism) rate; therefore, a $k_{photolysis}$ couldn't be calculated.)
Major phototransformation products: None.
Minor phototransformation products: None.

Study Acceptability: This study is classified as acceptable and fulfills the guideline requirement for a study on phototransformation on soil.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was designed and conducted to meet data requirements for photodegradation studies in soil as outlined in EPA Pesticide Registration Guidelines, Subdivision N, § 161-3, and SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 2.0 guidelines.

Experimental design of study was based on EPA Pesticide Registration Guidelines, Subdivision N, § 161-3 guidelines; therefore, the design deviated slightly from the SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 2.0 guidelines. The SETAC guidelines suggest an air-dried soil be irradiated or

incubated at 20 ± 3 °C. The EPA guidelines suggest the soil be maintained at 75% of 1/3 bar and an experimental temperature between 18 and 30 °C. The experimental design for this study maintained the soil at 75% of 1/3 bar with a temperature of 25 °C.

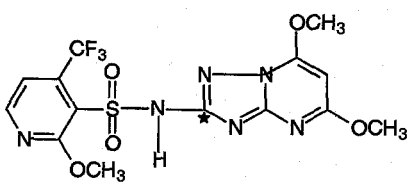
COMPLIANCE: All aspects of this study were conducted to meet Good Laboratory Practices standards, 40 CFR Part 160. Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided.

A. MATERIALS:

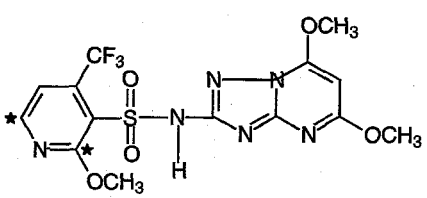
1. **Test Material** ^{14}C-XDE-742-TP and ^{14}C-XDE-742-PYR; XDE-742 contains two separate ring systems so two radiolabeled test substances, each labeled in a separate ring system, were used in this study.

Figure 1. Test Material Information

	Test Substance	Structure
Common Name	XDE-742-TP	
Synonyms	INV1901	
Molecular Weight	434.4 g/mole	
Inventory #	INV1901	
FA & PC Reference #	034003	
SPS Reference #	F0981-185A	
Description	Technical, solid	
Specific Activity	36.6 mCi/mmol	
Radiochemical Purity	100% on 3/12/04	
Storage Stability	Stable in frozen storage	



	Test Substance	Structure
Common Name	XDE-742-PYR	
Synonyms	INV1905	
	XDE-742-pyridine-2,6-^{14}C	
Molecular Weight	434.4 g/mole	
Inventory #	INV1905	
FA & PC Reference #	034005	
SPS Reference #	GHD-7035-64B	
Description	Technical, solid	
Specific Activity	43.7 mCi/mmol	
Radiochemical Purity	100% on 3/12/04	
Storage Stability	Stable in frozen storage	

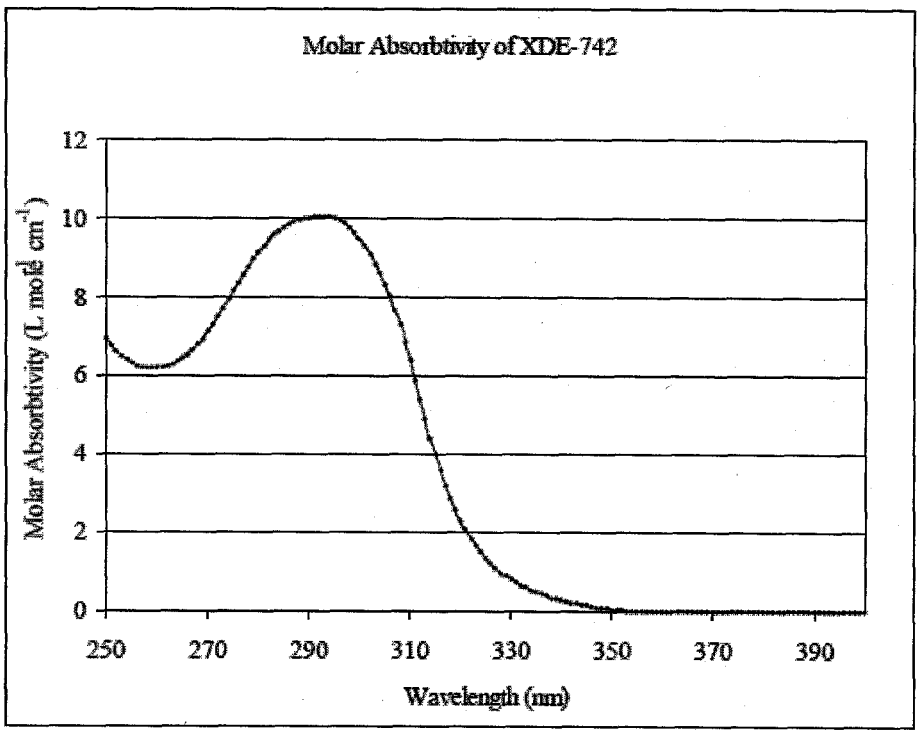


* indicates position of radiolabel

Physico-chemical properties of XDE-742

Parameter	Values	Comments

Parameter	Values	Comments
Water solubility	16.4 mg/L at pH 4 and 20 °C 3.20 x 10^3 mg/L at pH 7 and 20 °C 1.37 x 10^4 mg/L pH 9 and 20 °C 62.6 mg/L at 20 °C (unbuffered)	Very soluble in water Turner, B. J. "Determination of Water Solubility for XDE-742" NAFST806, unpublished report of Dow AgroSciences LLC, 22-December-2004.
Vapour pressure/ volatility	< 10^{-7} Pa (<10^{-9} torr)	Low volatility Madsen, S. "Determination of the Surface Tension, Density, and Vapour Pressure of the Pure Active Ingredient XDE-742," DERBI 144723, unpublished report of Dow AgroSciences LLC, 09-October-2003.
UV absorption	See below	
pKa	4.51 (25 °C)	Probe data: Sheets, J. J., Gast, R. E., Hanley, T. R., Krieger, M., Mayes, M. A. "Early Stage Registration Assessment of X666742: Phase I Weed Management Sulfonamide for European and Canadian Cereal Markets," DERBI No 79155, unpublished report of Dow AgroSciences LLC, 28 September 2000.
Kow	pH 4: 1.080 pH 7: -1.010 pH 9: -1.600	Low potential for bioaccumulation
Log D	1.080 at pH 4 -1.010 at pH 7 -1.600 at pH 9	Sheets, J. J., Gast, R. E., Hanley, T. R., Krieger, M., Mayes, M. A. "Early Stage Registration Assessment of X666742: Phase I Weed Management Sulfonamide for European and Canadian Cereal Markets," DERBI No 79155, unpublished report of Dow AgroSciences LLC, 28 September 2000.
Stability of compound at room temperature, if provided	Not available	



2. Soil Characteristics:

Table 1: Field information and handling procedures.

Information	Details
Geographic location	Charentilly, Loire Valley, France
Site Description	Fallow
Pesticide use history at the collection site	Glyphosate only for past two years
Collection procedures	Hand trowel, 10-12 sites within a 50' x 50' plot, into plastic, 5-gal bucket
Sampling depth (cm)	Approximately 18
Storage conditions at facility	4 °C
Storage length prior to use	1 year
Soil preparation (eg: 2 mm	Sieved, 2 mm

Information	Details
sieved; air dried etc.)	

Following sampling, the soil was handled at all times in accordance with ISO/DIS 10381-6

Table 2: Properties of the soil.

Property	Details	
Soil texture (USDA)	Silt loam	
% sand	17	
% silt	56	
% clay	27	
pH	6.2	
Organic carbon (%)	1.0	
CEC (meq/100 g)	17.0	
Moisture at 1/3 atm (%)	20.6	
Bulk density (g/cm^3) (distrubed)	1.10	
Microbial biomass/microbial population (unit)	Initial	Final
	86.8	N/A
Soil Taxonomic classification	N/A	N/A
Soil mapping unit (for EPA)	N/A	N/A

N/A = Not applicable

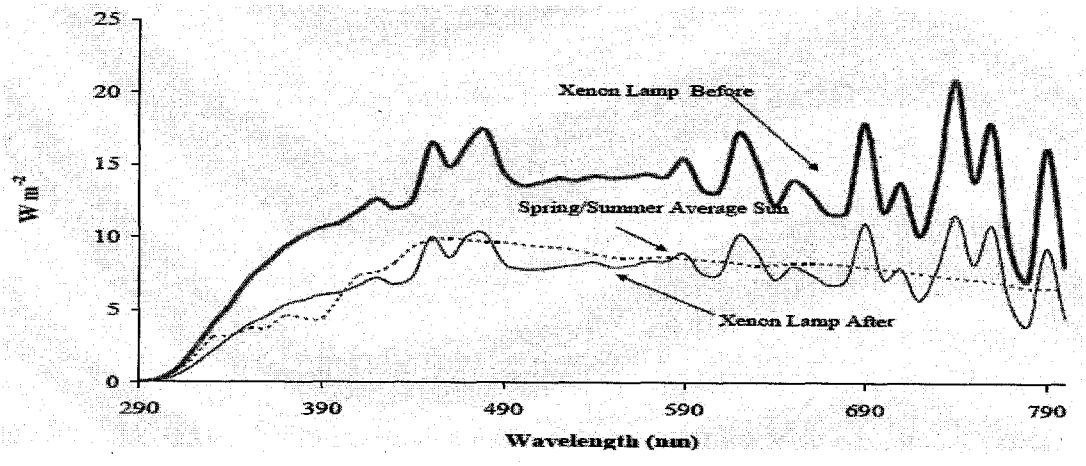
3) Details of light source:

Table 3: Artificial light source.

Property	Details
Type of lamp used	Xenon
Emission wavelength spectrum	See Figure 2
Light intensity	See Figure 2, 1 DAT (days after treatment) of continuous exposure was equivalent to approximately 2 days of spring sunlight at 50° N latitude
Filters used	Inner filter: CIRA filter Outer filter: Soda Lime filter
Relationship to natural sunlight	See Figure 2

A chemical actinometer was used to determine the overall light intensity of the xenon lamp and to compare the light-energy emitted by the lamp with sunlight. An actinometer is a chemical that has a known quantum yield (Φ), independent of wavelength. The actinometer used in conjunction with this study was *p*-nitroacetophenone (PNAP) and pyridine (pyr) in HPLC-grade water.

Figure 2: Comparative Irradiance Spectrum of Xenon Lamp to Natural Sunlight (Light Source Characterization)



B. EXPERIMENTAL DESIGN

1) Preliminary Study: No preliminary studies were conducted.

2) Experimental Design

The maximum application rate for XDE-742 may be 25 g a.i./ha, depending on application timing, weed targets, and the crop. Assuming an 11.4 cm^2 soil surface area, this maximum application rate of XDE-742 translates to approximately 3 µg/sample.

$$\frac{25\,\text{g a.i.}}{\text{ha}} \times \frac{1\,\text{ha}}{10^4\,\text{m}^2} \times \frac{1\,\text{m}^2}{10^4\,\text{cm}^2} \times \frac{11.4\,\text{cm}^2}{\text{sample}} \times \frac{10^6\,\mu\text{g}}{\text{g}} = \frac{2.85\,\mu\text{g}}{\text{sample}}$$

Regardless, 7.1 to 7.2 µg a.i. were added to each sample (p. 23), which corresponds to an application rate of 62-63 g a.i./ha, 3.5x the maximum application rate proposed on labels in the U.S. (18g a.i./ha).

Table 4: Experimental design.

Parameter		**Details**
Duration of the test		15 DAT, equivalent to 30 days of spring sunlight at 50° N latitude
Condition of soil:	Air dried/fresh:	Fresh, moisture maintained at approximately 75% of 1/3 bar moisture content
	Sterile/Non-sterile:	Non-sterile
Soil sample weight (g)		2.98 (moist), 2.5 (dry weight)
Test concentrations (mg a.i/kg soil) dark irradiated		 2.82 for TP-label, 2.86 for PY-label 2.82 for TP-label, 2.86 for PY-label
Dark controls used (Yes/No) Is it foil wrapped and kept in darkness		Yes Kept in darkness
Replications	Dark control:	Duplicates
	Irradiated:	Duplicates
Identity and concentration of co-solvent:		Water
Pesticide application	Volume of test solution used/treatment:	0.050 mL of TP-label, 0.055 mL of PY-label

Parameter		Details
	Method of application:	Positive displacement pipette
	Is the co-solvent evaporated:	No
Test apparatus: Type/Material/Volume		Quartz boiling flask with a flat bottom for light-exposed samples; 45-mL Pyrex amber vial for dark samples
Details of traps for volatile, if any		Trap contained a layer of Silica Gel, 10-18 mesh and a layer of glass wool, followed by Ascarite II, 20-30 mesh, followed by another layer of glass wool and silica gel. Tops of traps were sealed with vacuum grease. Entire trap wrapped in aluminum foil.
If no traps were used, is the system closed/open		Traps were opened to atmosphere for passive trapping. Systems opened for moisture adjustment.
Any indication of the test material adsorbing to the walls of the test apparatus		None
Experimental Conditions	Temperature: Temperature maintenance method:	25±1 °C Waterbath/constant temperature room
	Moisture content: Moisture maintenance method	75% of 1/3 bar moisture Gravimetric
	Duration of light/darkness:	Continuous irradiation for light, continuous darkness for control
Other details, if any		N/A

The irradiated samples were placed under the xenon lamp in a temperature-controlled water bath in a temperature-controlled room. A thermocouple probe was submerged in untreated soil in a quartz flask. A circulating water bath attached to the probe was used to adjust the temperature of the soil. The probe was set to keep the soil temperature at 25°C. The soil temperature was checked each work day. The entire system was maintained in a temperature-controlled room, also set at 25°C.

3) Supplementary experiments: No supplementary experiments were conducted.

4) Sampling:

Table 5: Sampling details.

Criteria	Details
Sampling intervals of soil samples	0, 1, 3, 7, 10 and 15 DAT, equivalent to 0, 2, 6, 14, 20 and 30 days of spring sunlight at 50° N latitude
Sampling method	Transfer soil from flask to centrifuge tube (dark controls already in tubes for extraction). Extract 3 times with 5 mL 90:10 Acetonitrile:0.1N HCl. Analyze aliquots by LSC and HPLC.
Method of sampling CO_2 and volatile organic compounds, if any	Separate silica gel and ascarite. Extract ascarite with water. Analyze aliquots by LSC.
Sampling intervals/times for: sterility check, if any moisture content	 N/A 3 and 11 DAT (irradiated samples only)
Sample storage before analysis	Sample extracts were analyzed by LSC on the day of sampling. Organic extracts analyzed by HPLC, initially, within one week of sampling. Actinometers, concentrated soil extracts, and ascarite trap extracts were stored refrigerated. Organic soil extracts were stored in freezer.
Other observations, if any	N/A

C. ANALYTICAL METHODS

Extraction/clean up/concentration methods:
The trapping of volatiles was limited to carbon dioxide (CO_2). At each sampling point, the samples were removed from the water bath and the silica gel and ascarite in the traps were poured into separate glass vials. The silica gel vial was capped and stored at room temperature. As no activity was expected to be trapped in the silica gel layer, no analysis of the gel was performed. The ascarite was dissolved and extracted with water. The dissolved ascarite solutions were weighed, the density determined, and triplicate 0.5-mL aliquots were analyzed by LSC to determine the amount of evolved $^{14}CO_2$.

The dark control soil samples were extracted in their sample vials by adding approximately 5 mL of 90:10 acetonitrile:0.1 N HCl and shaking on a mechanical shaker for one hour. The samples

were then centrifuged at 2000 rpm for 15 minutes. The supernatant was decanted into a 24-mL Pyrex vial. This process was repeated twice using 5 mL of extraction solution, shaking for 30 minutes, and centrifuging at 2000 rpm for 15 minutes. The extracts were combined and weighed. Three 0.1-mL aliquots of the extract were assayed for ^{14}C by LSC. Aliquots of sample extracts were then prepared for HPLC analysis.

For the irradiated samples, 5 mL of the 90:10 acetonitrile:0.1 N HCl extraction solution was added to the quartz flask. The samples were swirled and poured into 24-mL Pyrex vials. The samples were then extracted using the same process as for the dark control samples.

The extracted soil pellet was allowed to air dry in a hood for at least one week prior to combustion analysis to determine the amount of non-extractable residues present. Approximately 0.30-g sub-samples of each extracted soil pellet were weighed in triplicate into glass boats and combusted using a Harvey biological oxidizer. The generated $^{14}CO_2$ was then collected in Harvey scintillation cocktail and assayed by LSC.

Non-extractable residue determination:
Non-extractable residues were characterized by partitioning into fulvic acid, humic acid, and humin pools. Sub-samples (ca. 0.5 g) of previously extracted, air-dried irradiated and dark control soils from the 15 DAT sampling point were transferred to a centrifuge tube and extracted with 2.5 mL of 0.5 M NaOH on a mechanical shaker at room temperature for approximately 16 hr. The sample was centrifuged at 3000 rpm for 15 min and the supernatant transferred to a centrifuge tube. The sample was briefly mixed with another 2.5-mL aliquot of 0.5 M NaOH and centrifuged as above, and the supernatant was combined with the original extract. The soil pellet was then rinsed with 2.5 mL of deionized water, centrifuged as above, and the supernatant was combined with the original extract. The soil pellet was air-dried and combusted to determine the amount of radioactivity associated with the humin.

The supernatant was acidified to pH 1- pH 3 and allowed to stand at room temperature for approximately 24 hr. After this period, the sample was centrifuged at 2500 rpm for 15 minutes. The supernatant was decanted, transferred to a 10-mL volumetric flask and diluted to volume using deionized water. Triplicate 0.10-mL aliquots of the supernatant (fulvic acid) were assayed for ^{14}C by LSC using ScintiSafe Plus scintillation cocktail. The precipitate (humic acid) was redissolved in 2 mL of 0.5 M NaOH. Triplicate 0.10-mL aliquots of the humic acid fraction were assayed by LSC using Hionic Fluor as the scintillation fluid.

Total ^{14}C measurement:
Material balance was determined by taking the sum of the radioactivity measured in each compartment (organic extract, ascarite trap, and combustion) and dividing by the amount of radioactivity initially applied to the test system.

$$\text{Mass balance} = \frac{\text{ascarite trap}_{(dpm)} + \text{organic extract}_{(dpm)} + \text{soil pellet}_{(dpm)}}{\text{Amount } ^{14}\text{C Applied}_{(dpm)}} \times 100$$

Identification and quantification of parent compound:
The reverse phase HPLC methods used for soil extract analysis are presented below. Reverse phase method 2 was used for the 15 DAT TP-labeled soil extract sample; method 1 was used for all other soil extract samples. Fractions (0.1 minute) were collected for all radiolabeled samples. The collected fractions were counted by LSC and used to generate reconstructed radiochromatograms. A direct spike of each sample analyzed by HPLC was compared to the sum of the radioactivity eluted from the column and used to determine chromatographic recovery. A UV detector at 254 nm wavelength was used to determine the retention times of the non-radiolabeled XDE-742 and transformation product reference standards. A RAM flow-through detector was used in conjunction with the fraction collector to characterize the radioactivity in solution.

Reverse phase method 1 (used to analyze soil extracts)
Zorbax 300SB-C18, 5 µm, 4.6x250 mm
Solvent A: Water + 1% Acetic acid
Solvent B: Acetonitrile + 1% Acetic acid
1.0 mL/min flow rate
UV: 254 nm

Time (minutes)	% Solvent A	% Solvent B
0	95	5
5	95	5
20	5	95
24.2	5	95
30	95	5

Reverse phase method 2 (used to analyze 15 DAT TP-labeled soil extract)
Zorbax 300SB-C18, 5 µm, 4.6x250 mm
Solvent A: Water + 1% Acetic acid
Solvent B: Acetonitrile + 1% Acetic acid
1.0 mL/min flow rate
UV: 254 nm

Time (minutes)	% Solvent A	% Solvent B
0	95	5
5	95	5
40	5	95
43.2	5	95
48	95	5
50	95	5

A separate chromatographic method was used to analyze the actinometer samples:
Actinometer method
Spherisorb ODS-2, 5 µm
50:50 Water:Acetonitrile ,Isocratic conditions for 10 minutes
1.5 mL/min flow rate, UV: 288 nm

Identification and quantification of transformation products:
Initial identification of transformation products was conducted by comparing retention times of reference standards with unknown peaks in the samples. The initial identifications were confirmed by LC-MS/MS.

Five milliliters of the organic extract for the XDE-742-PY radiolabel of the 15 DAT dark control sample were concentrated under nitrogen separately to near dryness in a Turbo Evaporator set at 30 °C. The samples were reconstituted in 0.5 mL of a methanol:acetonitrile:water:acetic acid solution (5:5:90:0.1).

Five milliliters of the organic extract for the XDE-742-TP radiolabel of the 15 DAT dark control sample were concentrated under nitrogen separately to dryness in a Rota-evaporator set at 40 °C. The samples were reconstituted in 1.0 mL of a methanol:acetonitrile:water:acetic acid solution (5:5:90:0.1). The concentrated organic extracts and the reference standards were submitted for LC-MS/MS analysis.

Transformation products in the dark control samples were identified using LC-MS/MS analysis. Reference standards were also analyzed. Transformation products were identified by comparing retention time, molecular adductions and MS/MS fragments with the reference standards.

Detection limits (LOD, LOQ) for the parent compound:
Using the method of Currie (4), the quantitation limit of ^{14}C for the sub-samples (e.g., ascarite traps, organic extracts, combustions) and HPLC analyses were <1.2% of applied radiocarbon for each process. Limits of quantitation and detection for each sub-sample as a percentage of the applied radiocarbon are given in Table 6.

Table 6: Limits of Detection and Quantitation

Sub-sample Identification	Radiolabel	% of Applied ^{14}C	
		LOD	LOQ
Ascarite Trap	TP	0.030	0.121
Ascarite Trap	PY	0.025	0.100
Organic Extracts	TP	0.112	0.455
Organic Extracts	PY	0.092	0.375
Soil Combustions	TP	0.006	0.025
Soil Combustions	PY	0.005	0.021
HPLC Analyses - Organic	TP	0.261	1.106
HPLC Analyses - Organic	PY	0.215	0.912

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: Daily average temperatures were recorded for the lamp room and incubator chamber for the study. The soil temperatures were also manually recorded.

The actinometry data indicate that 1 DAT of exposure to the xenon lamp was equivalent to 2.09 days in the spring sun at 50° N latitude. Therefore, the sample exposure time of 1, 3, 7, 10, and 15 DAT were converted to 2, 6, 14, 20, and 30 days in the spring sun at 50° N latitude. These converted sampling times were used in the kinetics calculations for the irradiated samples.

B. MASS BALANCE: The mass balance was 97.1 ± 5.7% and 96.2 ± 4.8% in the dark and irradiated samples, respectively. The material balance of the dark control and irradiated samples remained between 90 and 110% of applied radiocarbon throughout the study, except for two samples which were 87.8 and 82.8% of applied. The results from these samples were included in all study calculations.

Table 7: Phototransformation and Biotransformation of XDE-742 Expressed as Percent of Applied Radioactivity in Charentilly Silt Loam Soil (mean values from both radiolabels).

Compound		Sampling Times (DAT)					
		0	1	3	7	10	15
XDE-742	Irradiated	98.5	92.4	82.7	83.7	69.7	60.7
	Dark	98.5	91.8	70.7	61.8	45.5	31.1
5-OH-XDE-742	Irradiated	NA	NA	NA	NA	NA	NA
	Dark	NA	2.1	4.1	9.0	9.4	9.2
7-OH-XDE-742	Irradiated	NA	NA	NA	NA	NA	NA
	Dark	NA	2.7	5.7	10.9	11.5	11.4
7-OH-6-Cl-XDE-742	Irradiated	NA	NA	NA	NA	NA	NA
	Dark	NA	NA	NA	2.0	1.7	3.7
Unidentified radioactivity	Irradiated	0.3	2.4	4.7	9.2	11.7	14.8
	Dark	0.3	0.5	0.1	0.0	1.3	0.0
Total extractable residues	Irradiated	98.9	94.8	87.3	92.9	81.4	75.6
	Dark	98.9	97.1	80.7	83.7	69.4	55.4
Non-extractable residue	Irradiated	0.3	2.8	5.1	7.9	12.1	16.2
	Dark	0.3	2.9	7.8	19.3	26.7	39.0
CO_2	Irradiated	NA	0.1	0.6	0.5	0.3	0.3
	Dark	NA	NA	NA	NA	NA	NA
Total % recovery	Irradiated	99.2	97.7	93.0	101.3	93.8	92.1
	Dark	99.2	99.9	88.5	103.0	96.1	95.8

C. TRANSFORMATION OF PARENT COMPOUND: For the dark control samples, extractable XDE-742 decreased from 98.5% at Day 0 to 31.1% of the applied radioactivity at study termination. At the end of the study, HPLC analysis showed approximately 55% of the

radioactivity present in the extract was still XDE-742. Two major transformation products were identified as the 5-OH-XDE-742 transformation product and the 7-OH-XDE-742 transformation product. The transformation products first appeared at the 1 DAT sampling point at 2.1 and 2.7% of applied for the 5-OH and the 7-OH, respectively. By study termination, the 5-OH and the 7-OH accounted for 9.2 and 11.4% of applied radiocarbon, respectively. A minor transformation product, 7-OH-6-Cl-XDE742, accounted for 3.7% of applied radiocarbon at study termination.

The amount of XDE-742 extractable from irradiated soil samples decreased from 98.5% at Day 0 to 60.7% of the applied radioactivity at study termination. At the end of the study, HPLC analysis showed approximately 80% of the radioactivity present in the extract was still XDE-742. The 15 DAT TP-labeled soil extract sample was analyzed using an HPLC method with a longer gradient to better separate the numerous transformation products. Even though 14.8% of the applied radioactivity was unidentified at the end of the study, no single phototransformation product of greater than 6% of applied was observed in any single sample.

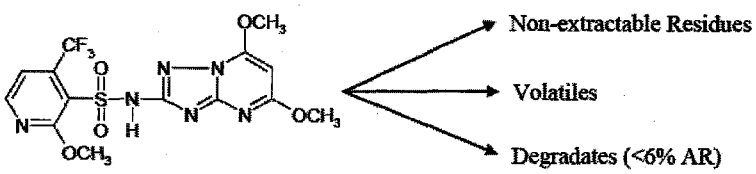
Non-Extractable and Extractable Residues: Extractable ^{14}C residues in the soil decreased from 98.9% at Day 0 to 75.6% of the applied radioactivity at the end of the irradiation period. Non-extractable ^{14}C residues in the soil increased from 0.3% at Day 0 to 16.2% of the applied radioactivity at study termination.

For the dark control soil system, extractable ^{14}C residues in the soil decreased from 98.9% at Day 0 to 56.9% of the applied radioactivity at the end of the incubation period. Non-extractable ^{14}C residues in the soil increased from 0.3% at Day 0 to 39.0% of the applied radioactivity at study termination.

XDE-742 transformed into non-extractable residues in both the irradiated and dark control samples. Characterization of these residues from irradiated samples shows that approximately 68% of the ^{14}C-non-extractable residues were associated with the fulvic acid fraction (acid and base soluble). Approximately 6% and 18% of the ^{14}C-non-extractable residues were associated with the humic acid and humin fractions, respectively.

Characterization of the non-extractable residues from the dark control samples shows that approximately 45% of the ^{14}C-non-extractable residues were associated with the fulvic acid fraction (acid and base soluble). Approximately 14% and 41% of the ^{14}C-non-extractable residues were associated with the humic acid and humin fractions, respectively.

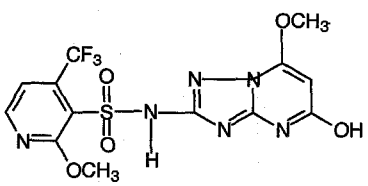
Pathway:
XDE-742 transformed into numerous transformation products (all <6% of applied radiocarbon), nonextractable residue and CO_2 in the Charentilly silt loam soil. No phototransformation products were identified.



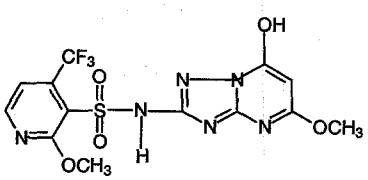
XDE-742

Table 7: Chemical names for the transformation products of XDE-742 (pyroxsulam).

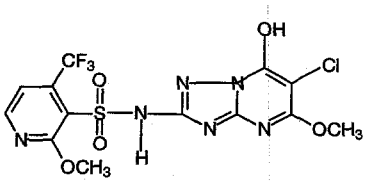
Common Name	5-OH-XDE-742
Synonyms	X11250642, TSN104232
IUPAC Nomenclature	*N*-(5-hydroxy-7-methoxy[1,2,4]triazolo[1,5-α]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide
SMILES Code	c1(c(ccnc1OC)C(F)(F)F)S(Nc2nn3c(n2)nc(cc3OC)O)(=O)=O
Molecular Formula	$C_{13}H_{11}F_3N_6O_5S$
Molecular Weight	420.3 g/mole
GLP	Yes
Expiration Date	28 Jul 2005
Purity	100.0 %



Common Name	7-OH-XDE-742
Synonyms	X11250641, TSN104231
IUPAC Nomenclature	N-(7-hydroxy-5-methoxy[1,2,4]triazolo[1,5-α]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide
SMILES Code	c1(c(ccnc1OC)C(F)(F)F)S(Nc2nn3c(n2)nc(cc3O)OC)(=O)=O
Molecular Formula	$C_{13}H_{11}F_3N_6O_5S$
Molecular Weight	420.3 g/mole
GLP	Yes
Expiration Date	28 Jul 2005
Purity	99.0%



Common Name	6Cl-7-OH-XDE-742
Synonyms	TSN104660, X11301338
IUPAC Nomenclature	N-(6-chloro-7-hydroxy-5-methoxy[1,2,4]triazolo[1,5-α]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide
SMILES Code	c1(c(ccnc1OC)C(F)(F)F)S(Nc2nn3c(n2)nc(c(c3



	O)Cl)OC)(=O)=O
Molecular Formula	$C_{13}H_{10}ClF_3N_6O_5S$
Molecular Weight	454.77 g/mol
GLP	Yes
Expiration Date	7 Jun 2006
Purity	96%

Half-life: First-order, non-linear rate constants of XDE-742 were calculated to be 0.017 and 0.079 $days^{-1}$ for the irradiated and dark control soils. Because the transformation rate is faster in the dark than the phototransformation rate, a $k_{photolysis}$ could not be calculated. Therefore, XDE-742 is considered stable to photolysis in soil. These results are summarized in the following table.

Half-lives/DT50

Charentilly Soil	K ($days^{-1}$)	Regression Equation	R^2	DT_{50}	DT_{90}
Irradiated	0.017[a]	$[XDE\text{-}742]_t = [XDE\text{-}742]_0 e^{(-0.017)(t)}$	0.765	44	135
Dark Control	0.079[b]	$[XDE\text{-}742]_t = [XDE\text{-}742]_0 e^{(-0.079)(t)}$	0.956	9	29
$k_{photolysis}$	NA[c]	NA			NA

[a] k_{total}

[b] $k_{metabolism}$

c Since $k_{metabolism} > k_{total}$, a $k_{photolysis}$ cannot be calculated.

D. SUPPLEMENTARY EXPERIMENT-RESULTS: None.

III. STUDY DEFICIENCIES: No deficiencies were noted.

IV. REVIEWER COMMENTS:

1. The transformation rate constants of XDE-742 in the dark and irradiated samples were 0.079 and 0.017 $days^{-1}$, respectively. The transformation rate in the dark was greater than the total (phototransformation + non-phototransformation) rate; therefore, a $k_{photolysis}$ could not be calculated. Reviewer calculated first order kinetic half-life values were 23 (r^2=>0.92) and 9 (r^2=>0.92) days for the light and dark samples, respectively. Since the soil samples were not sterilized, other possible routes of transformation such as biotransformation might contribute to the transformation rates in this study.

2. USEPA: The light intensity of the Xenon lamp was compared to natural sunlight in the spring sun at 50° N latitude. To be consistent with the submitted aqueous photolysis study (Dow AgroSciences Study ID: 040002) and the Rejection Rate Analysis (USEPA, 1993), the light intensity should have been compared to summer sunlight at 40° N latitude as well. However, because XDE-742 is stable to photolysis on soil, this is not a study deficiency.

3. Australian Reviewer's Comments. The Australian reviewer has confirmed the Canadian

half lives for the light and dark exposed samples. The r^2 are calculated as 0.985 and 0.938 for dark and light samples respectively.

V. REFERENCES:

1. Byrne, S. L., Meitl, T. J., , Crabtree, A. B., Linder, S. L., and Balcer, J. L., 2006, Aqueous Photolysis of XDE-742 in pH 7 Buffer Using a Xenon Lamp, Regulatory Laboratories—Indianapolis Lab (Indianapolis, Indiana), Study number 040002, Dow AgroSciences LLC, February 10, 2006.

2. Currie, L. A. "Limits for Qualitative Deatection and Quantitative Determination - Application to Radiochemistry", Anal. Chem. 1968, 40, 586-593.

3. Madsen, S., "Determination of the Surface Tension, Density, and Vapour Pressure of the Pure Active Ingredient XDE-742," NAFST814, 2003, unpublished report of Dow AgroSciences LLC.

4. Turner, B. J., "Determination of Octanol/Water Partition Coefficient for XDE742," NAFST807, 2004, unpublished report of Dow AgroSciences LLC.

5. Turner, B. J., "Determination of Water Solubility for XDE-742," NAFST806, 2004, unpublished report of Dow AgroSciences LLC.

6. USEPA, 1993, Pesticide Registration Rejection Rate Analysis - Environmental Fate, Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC, EPA 738-R-93-010.