Data Evaluation Record on the phototransformation of oryzalin on soil

PMRA Submission Number {.....} EPA MRID Number 41050001

Data Requirement:	PMRA Data Code:	
	EPA DP Barcode:	378627
	OECD Data Point:	
	EPA Guideline:	835.2410

Test material:

Common name:	Oryzalin.
Chemical name:	
IUPAC name:	3,5-Dinitro-4-(dipropylamino)benzenesulfonamide. 3,5-Dinitro-N^4,N^4-dipropylsulfanilamide.
CAS name:	4-(Dipropylamino)-3,5-dinitrobenzenesulfonamide.
CAS No.:	19044-88-3.
Synonyms:	OR-1; EL-119.
Smiles string:	CCCN(CCC)c1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).

Primary Reviewer: Kindra Bozicevich
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Company Code:
Active Code:
Use Site Category:
EPA PC Code: 104201

CITATION: Gohdes, M. 1989. Artificial sunlight photodegradation of ^{14}C-oryzalin on soil. Unpublished study performed by Hazelton Laboratories America, Inc., Madison, Wisconsin; sponsored by W.R. Landis Associates, Inc., Valdosta, Georgia; and submitted by Eli Lilly and Company. Laboratory Project ID: HLA 6237-102. Study initiated March 18, 1988, and terminated March 20, 1988 (pp. 11, 19). Final report issued December 21, 1988, and amended February 13, 1989.

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Smiles string:	C1C(S(=O)(=O)N)=CC(N(O)O)=C(N(CCC)CCC)C=1N(O)O (EpiSuite version 4.0).

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EXECUTIVE SUMMARY

The phototransformation of [^{14}C]-labeled 3,5-dinitro-N^4,N^4-dipropylsulfanilamide (oryzalin; radiochemical purity >95%), at 620 μg/g soil (equivalent to a 6.1 lb/A surface application rate), was studied on air-dried sandy loam soil (pH 5.7, organic matter 1.4%) from Indiana that was continuously irradiated using a filtered xenon arc lamp (*ca.* 290-750 nm) for 61 hours at 24.0-25.5°C. The intensity of the artificial light was equivalent to *ca*. 61.4% of the natural sunlight during equinox at latitude 40°N. The study was conducted in accordance with USEPA Pesticide Assessment Guidelines, Subdivision N §161-3 and in compliance with USEPA FIFRA GLP standards (40 CFR Part 160). The test system consisted of Petri dishes containing a slurry of treated soil that were placed into a water-jacketed cooling tray connected with tubing to a refrigerated circulation water bath contained in a xenon lamp chamber. Samples serving as dark controls were prepared and placed in an enclosed glass chamber that was maintained in a darkened temperature-controlled room. Volatiles were collected by pumping air over the soil plates at a rate of 91-110 mL/min for irradiated samples and 88-117 mL/min for dark controls, then through one ethylene glycol trap and one 2-ethoxyethanol:ethanolamine (1:1, v:v) trap. Duplicate samples were collected at 0, 4, 8, 13, 22, 34, and 61 hours posttreatment for irradiated samples and at 13, 34, and 61 hours for dark controls.

The soils were extracted twice with acetonitrile:water (70:30, v:v) and the extracts were combined. Subsamples of select soil extracts for hours 13 and 61 were extracted by refluxing with acetonitrile:water (90:10, v:v). The soil extracts and trapping solutions were analyzed for total radioactivity using LSC. Initial identification and quantification of orazylin and an unresolved region of radioactivity, identified in the study as Region 1, were conducted using HPLC System 1. To further identify the transformation products in Region 1, samples were removed from the freezer after 4-5 months of storage, were analyzed using HPLC System 2, and transformation products identified by comparison to unlabeled reference. The extracted soils were air-dried, homogenized, and analyzed by LSC following combustion. The trapping solutions were analyzed for total radioactivity using LSC.

The temperature of the irradiated and dark control samples were maintained at 24.0-25.5°C and 24.4-25.0°C, respectively. Soil viability was not addressed.

Overall [^{14}C]residue recoveries averaged 98.0 ± 1.4% of the applied (range 96.2-100.6%) from the irradiated samples and 99.0 ± 1.2% (range 97.6-100.6%) from the dark controls.

In the irradiated samples, oryzalin decreased from an average 93.3% of the nominal application at time 0 to 62.8% at 4 hours posttreatment, 55.4- 60.7% at 8-22 hours, and 48.8% at 61 hours (study termination). Eight minor transformation products were isolated, each at ≤6.8% of the applied. Three of the transformation products were identified as:

- 4-amino-3,5-bis(dihydroxyamino)benzenesulfonamide (OR-3);
- 2-ethyl-7-nitro-1H-benzimidazole-5-sulfonamide (OR-15); and
- 4-(dipropylamino)-3,5-dinitrobenzenesulfonic acid (OR-21).

Total extractable [^{14}C] residues decreased from an average 93.3% of the applied at time 0 to 80.0% at study termination, while nonextractable residues increased to 14.5% at 61 hours. Reflux extraction of the irradiated 61-hour sample removed an additional 4.6-5.8% of the applied, yielding 1.4% of the applied as oryzalin and 1.2% as Unknown 1. At 61 hours posttreatment, volatilized [^{14}C] residues totaled 0.1% of the applied.

In the dark controls, oryzalin decreased from an average 93.3% of the applied at time 0 to 86.1% at 61 hours posttreatment. Transformation products totaled ≤1.4% of the applied at all sampling intervals. Total extractable [^{14}C]residues averaged 86.6% of the applied at study termination, while nonextractable residues increased to 4.2% at 13 hours and were 2.8% at 61 hours. No volatilized [^{14}C]residues radioactivity was detected.

Based on first order linear regression analysis, oryzalin dissipated from the irradiated samples with a reviewer-calculated half-life of 95.0 hours, based on the continuous irradiation used in the study. The calculated half-life in the dark control was 630 hours (26.25 days), which is of uncertain value because it is extrapolated well beyond the termination of the experiment. The **phototransformation half-life** of oryzalin in soil, determined using the equation

(Ln 2) ÷ [(Ln 2/dark control half-life) - (Ln 2/irradiated half-life)]

is 112 hours based on the continuous irradiation used in the study, or 224 hours (9.3 days) based on a 12-hour light/12-hour dark cycle. Since light intensity of the artificial light was equivalent to *ca*. 61.4% of the natural sunlight during equinox at latitude 40°N (Table C-1, p. 86), the **environmental phototransformation half-life** of oryzalin is *ca*. 7.6 days (112 hrs/24 hrs/day/0.614).

A transformation pathway was not provided by the study author. Based on the study results, oryzalin photodegrades to numerous minor compounds.

Results Synopsis

	Half-life (hours)	**Transformation products**	
		Major	**Minor**
Corrected*	182	None	4-Amino-3,5-bis(dihydroxyamino)benzenesulfonamide (OR-3; maximum 2.6% of the applied) 2-Ethyl-7-nitro-1H-benzimidazole-5-sulfonamide (OR-15; maximum 3.6% of the applied) 4-(Dipropylamino)-3,5-dinitrobenzenesulfonic acid (OR-21; maximum 4.6% of the applied)

* Corrected for dark control and phototransformation.

Study Acceptability: This study is classified as **supplemental**. Samples were irradiated for only 61 hours, at which time 45.6-51.9% of the nominal application of oryzalin (*ca*. 52% of time 0 or the actual application) remained undegraded. No storage stability data were provided, although samples were stored for up to 5 months prior to analysis for transformation products (the samples used to determine the half-life were not stored for this duration.) Limits of Detection and Quantification were not reported.

The page numbers referenced in the DER are those that appear in the bottom right corner of the MRID pages.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The study was conducted in accordance with USEPA Pesticide Assessment Guidelines, Subdivision N §161-3 (p. 17). Deviations from the objectives of Subdivision N guidelines included:

Samples were irradiated for only 61 hours (*ca*. 2.5 days; continuous irradiation), at which time 45.6-51.9% of the applied oryzalin (*ca*. 52% of time 0) remained undegraded.

Samples analyzed to quantify the transformation products of oryzalin were stored frozen for 4-5 months prior to analysis. No storage stability data were provided.

Limits of Detection and Quantification were not reported.

COMPLIANCE: This study was conducted in compliance with USEPA FIFRA GLP standards (40 CFR Part 160; pp. 4, 8). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements and Signatures pages were provided (pp. 2, 4-6, 8, 10, 66). A certification of the authenticity of the study methods is included as part of the Quality Assurance Statement (pp. 5, 10).

A. MATERIALS:

1. Test Material		[Phenyl-U-^{14}C]oryzalin (p. 19; Figure 1, p. 47).
Chemical Structure:		See DER Attachment 1.
Description:		Technical grade (p. 19).
Purity:	Radiochemical purity:	>95% (p. 19; Appendix B, pp. 86-88).
	Lot No.:	553-KBO-211 (p. 19).
	Analytical purity:	Not reported.
	Specific activity:	25,800 dpm/µg.
	Location of the radiolabel:	Uniformly on the phenyl ring (Figure 1, p. 47).
Storage conditions of test chemical:		The test chemical was stored in a freezer (p. 19). Storage conditions for the reference standards were not reported.

Physico-chemical properties of oryzalin:

Parameter	Value	Comment
Molecular weight (g/mole)	Not reported.	
Chemical formula	$C_{12}H_{18}N_4O_6S$	
Water Solubility	2.6 ± 0.1 ppm	
UV Absorption	Maximum at *ca*. 290 nm with a second peak at *ca*. 390 nm.	In acetonitrile.
Vapor Pressure/Volatility (nPa)	Not reported.	
pKa	Not reported.	
K_{ow}/log K_{ow}	Not reported.	
Stability of compound at room temperature, if provided	Not reported.	

UV adsorption from p. 29 and Appendix C, Figure C-3, p. 95 of the study report. Water solubility obtained from MRID 41378401.

2. Characteristics

Table 1: Field information and handling procedures.

Information	Details
Geographic location	Johnson County, Indiana
Pesticide use history at the collection site	Not reported.
Collection procedures	Not reported.
Sampling depth (cm)	Not reported.
Storage conditions	Not reported.
Storage length	Not reported.
Soil preparation	Sieved (2.0 mm).

Data obtained from pp. 20, 22 of the study report.

Table 2: Properties of the soil.

Property	Details
Soil texture	Sandy loam
% Sand	66
% Silt	22
% Clay	12
pH	5.7
Organic carbon (%)[1]	0.8
Organic matter (%)	1.4
CEC (meq/100 g)	4.9
Water holding capacity at 0.33 bar (%)	11.86
Bulk density (gm/mL)	1.28
Microbial biomass (units)	Not reported.
Soil taxonomic classification	Not reported.
Soil mapping unit (for EPA)	Not reported.

Data obtained from p. 20 of the study report. Assuming that the particle size distribution was according the USDA soil classification system, the soil texture is correct (http://soils.usda.gov/technical/aids/investigations/texture/).
1 Calculated by the reviewer using the equation: % organic carbon = % organic matter/ 1.72.

3. Details of light source:

Table 3: Artificial light source

Property	Details
Nature of light source	Xenon arc lamp (Hanau Suntest unit).
Emission wavelength spectrum	290-750 nm.
Light intensity	399 photons x 10^{19}/cm^2·day
Filters used	Present but not described.
Relationship to natural sunlight	The wavelength distribution of the artificial light was comparable to that of natural sunlight. A graphical comparison of the artificial light to sunlight is presented in Appendix C, Figure C-1, p. 93. The intensity of the artificial light was equivalent to *ca*. 61.4% of the natural sunlight during equinox at latitude 40°N (650 photons x 10^{19}/cm^2·day). An illustration of the irradiation apparatus is presented in Figure 2, p. 48

Data obtained from pp. 21, 25, 29; Figure 2, p. 48; and Appendix C, pp. 90-93 of the study report.

B. EXPERIMENTAL DESIGN

1. Preliminary Study: In a preliminary experiment, portions (*ca*. 2 g) of the test soil were added to petri dishes, mixed with water to form a uniform slurry, and air-dried at room temperature prior to fortification with [^{14}C]oryzalin in acetonitrile at a concentration of *ca.* 4.3 µg/g (equivalent to 0.04 lb/A surface application rate; p. 22). Four replicates were placed under the irradiation apparatus and were connected to ethylene glycol and 2-ethoxyethanol:ethanolamine (1:1, v:v) traps for collection of volatiles. Air was pumped through the samples at 92-102 mL/minute. The samples were maintained at soil temperatures of 25-33°C. An additional four replicates served as dark controls and were placed into an enclosed glass chamber maintained in a dark, temperature controlled room

at 24.4-25°C. The dark controls were also connected to traps as previously described. Air was pumped through the samples at 29-92 mL/minute. Duplicate samples were analyzed as time 0 samples. Single sample were removed for analysis following 2.9, 6.7, and 24.0 hours of irradiation and 3.0, 6.5, and 24.0 hours in the dark. The samples were extracted with acetonitrile:water (70:30, v:v). The radioactivity in the acetonitrile:water (10:30) extracts, extracted soil (oxidized by combustion), and trapping media was analyzed by LSC. Aliquots of the acetonitrile:water (10:30) extracts were analyzed by HPLC for distribution of radioactivity.

Based on the results of the preliminary experiment, it was determined that the analytical method and procedures were adequate to study the photodegradation of oryzalin and the potential degradation of oryzalin under dark control conditions (p. 27). The total applied radioactivity recovered for the irradiated samples ranged from an average of 98.7% at 24 hours to 108.7% at time 0. For dark controls, total applied radioactivity recovered ranged from an average of 102.9% at 6.5 hours to 108.7% at time 0.

2. Experimental Design

Table 4: Experimental design.

Parameter			Details
Duration of the test			61 hours.
Condition of soil:		Air dried/fresh:	The soil was slurried with water, transferred to the test vessels, and allowed to air-dry prior to treatment.
		Sterile/Non-sterile:	Non-sterile.
Test concentration		Nominal:	620 µg/g soil (3,071,825 dpm/sample; equivalent to 6.1 lb/A surface application rate).
		Measured:	Not reported.
Dark controls used (Yes/No):			Yes.
Identity and concentration of co-solvent			Acetonitrile, concentration not reported.
Pesticide application		Volume of test solution used/treatment:	Not reported.
		Method of application:	Not reported.
		Is the co-solvent evaporated:	Not reported. However, based on the design of the test system, evaporation is likely.
Test apparatus: Type/Material/Volume			The test system consisted of Petri dishes (not described) containing air-dried treated sieved soil (*ca.* 2 g dry weight). Irradiated: Thirteen samples were placed on a water-jacketed cooling tray within a glass chamber in the Suntest apparatus. The chamber was sealed with a Pyrex glass plate and Teflon tape, and connected to a continuous flow-through volatile trapping system. The test apparatus is illustrated in Figure 2, p. 48. Dark controls: Ten samples were placed in a glass chamber that was sealed and connected to a continuous flow-through volatile trapping system. The chamber was maintained in a darkened temperature-controlled room. The test apparatus is illustrated in Figure 3, p. 49.
Details of traps for volatile, if any			Air was pumped (88-117 mL/minute) through the chambers containing the dishes of soil, then through one ethylene glycol trap and one 2-ethoxyethanol:ethanolamine (1:1, v:v) trap. The volatile trapping systems are illustrated in Figures 2-3, pp. 48-49.
If no traps were used, is the system closed/open			Volatile traps were used.
Any indication of the test material adsorbing to the walls of the test apparatus?			Not reported.
Experimental Conditions		Temperature:	24.0-25.5°C.
		Temperature maintenance method:	Irradiated: Samples were placed on a temperature-controlled water-jacketed platform. Dark controls: The samples were maintained in a temperature-controlled room.
		Moisture content:	The soil was air-dry throughout the study.
		Moisture maintenance method	The soil was dry.
		Duration of light/darkness:	Continuous.
Other details, if any			None.

Data were obtained from pp. 22-23 and Figures 2-3, pp. 48-49 of the study report.

3. Supplementary experiments: No supplementary studies were described.

4. Sampling:

Table 5: Sampling details.

Criteria	Details
Sampling intervals of soil samples	Irradiated: 0, 4, 8, 13, 22, 34, and 61 hours posttreatment. Dark: 13, 34, and 61 hours posttreatment.
Sampling method	Duplicate irradiated and dark control samples were collected at each sampling interval.
Method of sampling CO_2 and volatile organic compounds, if any	Irradiated: 4, 13, 34, and 61 hours posttreatment. Dark: 13, 34, and 61 hours posttreatment. At each sampling interval, aliquots (2 x 1-2 mL) were removed from the traps and replaced with sufficient fresh solution to maintain a volume of *ca.* 100 mL.
Sampling intervals/times for: Sterility check, if any: Moisture content:	 Sterile controls were not used. The soil was air-dry.
Sample storage before analysis	Not reported.
Other observations, if any	None.

Data were obtained from p. 23 of the study report.

C. ANALYTICAL METHODS

Extraction/clean up/concentration methods: The soils were transferred from the Petri dishes into tared vials (p. 23). The dishes were rinsed with acetonitrile:water (70:30, v:v; 5 mL), which was added to the tared vials, and the mixture stirred on a magnetic stir plate for 15 minutes, then centrifuged (15 minutes at >2,000 rpm). The supernatant was removed and the extraction was repeated. The two extracts were combined and mixed on a vortex mixer and weighed. Prior to HPLC analysis, the combined extracts were centrifuged for 10 minutes and aliquots (1-2 mL) were transferred to aluminum foil-wrapped vials (p. 24).

Portions (ca. 1 g) of the extracted irradiated samples collected at 13 and 61 hours posttreatment were further extracted by refluxing for *ca*. 3 hours with acetonitrile:water (90:10, v:v; 15 mL; p. 26). The extracts were allowed to cool to room temperature, transferred to tared vials, and the test vessels were rinsed with acetonitrile:water (90:10, v:v; 2 x *ca*. 2 mL). The rinsates were added to the extracts and centrifuged for 15 minutes (2,000 rpm). The supernatants were removed for analysis using LSC and HPLC.

Volatile residue determination: Aliquots (2 x 1.0 or 2.0 mL) of the trapping solutions were analyzed in 9 mL of water and 10 mL of a scintillation cocktail for total radioactivity using LSC (p. 25).

Nonextractable residue determination: The extracted soils (2 x *ca*. 0.1-0.2 g) were air-dried at room temperature, homogenized by stirring, and combusted. The resulting $^{14}CO_2$ was trapped and analyzed by LSC. Combustion efficiency was 93%.

Total ^{14}C measurement: Total [^{14}C]residues were determined by summing the concentration of [^{14}C]residues measured in the soil extracts, extracted soil, and volatile trapping solutions (Tables 3-4, pp. 34-35).

Derivatization method, if used: A derivatization method was not employed.

Identification and quantification of parent compound: Aliquots of the soil extracts were analyzed for oryzalin using HPLC (System 1) under the following conditions (pp. 21, 24): ODS-2 Spherisorb column (150 x 4.6 mm, 5 μm), isocratic mobile phase of methanol:0.01M ammonium acetate (66:34, v:v), flow rate 1.0 mL/minute, with UV (254 or 260 nm) detection. Forty fractions (one fraction/0.5 minutes) were collected and analyzed using LSC. [^{14}C]Oryzalin was identified by comparison to the retention time of an unlabeled reference standard (purity not reported; Lot No. L1252A; HLA Sample No. 80100820; p. 19; Rt 80.2 minutes; Table 10, p. 41).

Identification and quantification of transformation products: Since HPLC System 1 resulted in a peak corresponding to oryzalin and a cluster of peaks designated Region 1 (Figure 4, p. 50), transformation products were separated and quantified using a second HPLC system (System 2; p. 25). Soil extracts were removed after *ca*. 4-5 months of frozen storage and aliquots were analyzed under the following conditions (p. 25): ODS-2 Spherisorb column (250 x 4.6 mm, 5 μm), step gradient mobile phase of methanol:0.01M ammonium acetate [percent A:B (v:v) at 0.1-5 min., 0:100; 5-15 min., 20:80; 15-25 min., 40:60; 25-45 min., 45:55; 45-55 min., 50:50; 55-65 min., 60:40; 65-75 min., 70:30; 75-85 min., 100:0], flow rate 1.0 mL/minute, with UV (unspecified) detection. One hundred eighty fractions (one fraction/0.5 minutes) were collected and analyzed using LSC. Samples were identified by comparison of retention times with unlabeled reference standards (p. 26).

Samples were identified by comparison of retention times with the following unlabeled reference standards:

Common Name	Chemical Name	HLA Sample No.	Purity (%)	HPLC System 2 Rt (minutes)
OR-2	3,5-Dinitro-4-(propylamino)benzenesulfonamide.	80100007	--	48.0
OR-3	4-Amino-3,5-bis(dihydroxyamino)benzenesulfonamide	80100002	--	22.3
OR-4	3-Amino-4-(dipropylamino)-5-nitrobenzenesulfonamide	80100005	--	72.9
OR-5	3-Amino-5-(dihydroxyamino)-4-(propylamino)-benzenesulfonamide	80100006	--	32.8
OR-6	3,4-Diamino-5-(dihydroxyamino)benzenesulfonamide	80100003	--	15.6
OR-7	3,5-Diamino-4-(dipropylamino)benzenesulfonamide.	80100004	--	38.6
OR-13	2-Ethyl-7-nitro-1-propyl-1H-benzimidazole-5-sulfonamide.	80100009	--	43.2
OR-15	2-Ethyl-7-nitro-1H-benzimidazole-5-sulfonamide	80100010	--	24.3
OR-20	4-Hydroxy-3,5-dinitro-benzenesulfonamide.	80100008	--	9.5
OR-21	4-(Dipropylamino)-3,5-dinitrobenzenesulfonic acid	80100001	--	45.6

Data obtained from p. 20; Table 10, p. 41; Figure 1, p. 47; Figure 4, p. 50; and Figure 14, p. 60 of the study report.
Chemical names from DER Attachment 1.
-- = Not reported.

HPLC System 2 was also used to characterize residues in the reflux extracts from the 13- and 61-hour irradiated samples (p. 26).

Detection limits (LOD, LOQ) for the parent compound: Limits of Detection (LOD) and Limits of Quantification (LOQ) were not reported.

Detection limits (LOD, LOQ) for the transformation: Limits of Detection (LOD) and Limits of Quantification (LOQ) were not reported.

II. RESULTS AND DISCUSSION

A. TEST CONDITIONS: During the study, temperatures of irradiated and dark control samples were 24.0-25.5°C and 24.4-25.0°C, respectively (p. 23; Table 1, p. 32). Soil viability was not addressed.

B. MASS BALANCE: Overall [^{14}C]residue recoveries averaged 98.0 ± 1.4% of the applied (range 96.2-100.6%) from the irradiated samples and 99.0 ± 1.2% (range 97.6-100.6%) from the dark controls (DER Attachment 2).

Table 6: Phototransformation of oryzalin, expressed as a percentage of nominally applied radioactivity (mean ± s.d; n = 2), on sandy loam soil (HPLC System 1).

Compound		Sampling intervals (hours)						
		0	4	8	13	22	34	61
Oryzalin	Irradiated	93.3 ± 1.6	62.8 ± 0.8	57.4 ± 2.4	60.7 ± 6.4	55.4 ± 1.3	51.2 ± 1.8	48.8 ± 4.5
	Dark		--	--	88.5 ± 2.6	--	87.9 ± 2.5	86.1 ± 2.9
Region 1	Irradiated	ND	22.2 ± 2.8	24.5 ± 0.6	24.7 ± 1.5	28.4 ± 0.8	29.8 ± 1.1	31.3 ± 1.2
	Dark		--	--	1.2 ± 0.2	--	1.2 ± 0.4	0.6 ± 0.1
Total extractable residues	Irradiated	93.3 ± 1.6	85.0 ± 3.6	81.9 ± 1.8	85.3 ± 4.9	83.8 ± 2.1	81.0 ± 2.9	80.0 ± 3.3
	Dark		-	--	89.6 ± 2.8	--	89.1 ± 2.9	86.6 ± 3.0
Nonextractable residues	Irradiated	2.3 ± 0.0	6.9 ± 0.3	12.0 ± 4.0	10.8 ± 0.5	9.5 ± 1.4	10.7 ± 0.1	14.5 ± 0.6
	Dark		--	--	4.2 ± 3.3	--	2.3 ± 0.1	2.8 ± 0.6
Volatile organics	Irradiated	--	ND	--	<0.1 ± 0.0	--	0.1 ± 0.0	0.1 ± 0.0
	Dark		--	--	ND	--	ND	ND
Total % recovery	Irradiated	95.6 ± 1.6	91.9 ± 3.9	93.9 ± 2.2	96.1 ± 4.5	93.3 ± 3.5	91.7 ± 2.8	94.5 ± 2.7
	Dark		--	--	89.6 ± 2.8	--	89.1 ± 2.9	86.6 ± 3.0

Means and standard deviations calculated by the reviewer using data obtained from Table 3, p. 34 and Table 7, p. 38 in the study report (DER Attachment 2).
-- = Not analyzed.
ND = Not detected.

C. TRANSFORMATION OF PARENT COMPOUND: In the irradiated samples, oryzalin decreased from an average 93.3% of the nominal application at time 0 to 62.8% at 4 hours posttreatment, 55.4- 60.7% at 8-22 hours, and 48.8% at 61 hours (study termination; Table 7, p. 38; DER Attachment 2). The 61-hr parent data are equivalent to approximately 52% of the actual application at time 0. In the dark controls, oryzalin decreased from an average 93.3% of the nominal application at time 0 to 86.1% at 61 hours posttreatment.

HALF-LIFE: Based on first-order linear regression analysis (Excel 2003) and using all data points from HPLC System 1, oryzalin dissipated from the irradiated samples with a reviewer-calculated half-life of 95.0 hours (4.0 days), based on the continuous irradiation used in the study (DER Attachment 2). The observed DT50 was >61 hours (study termination). The calculated half-life in the dark control was 630 hours (26.25 days), which is of uncertain value because it is extrapolated well beyond the termination of the experiment.

The study author stated that linear regression resulted in a correlation coefficient of -0.717 and the y-intercept of the regression line corresponded to only 69% of oryzalin at time 0 (p. 29). Therefore, biphasic kinetics were used to describe the degradation of oryzalin (Figure 13, p. 59). The study author did not calculate a half-life, but concluded that approximately 30% of oryzalin degraded in the first 4 hours of irradiation and no appreciable degradation occurred from 34-61 hours posttreatment.

Half-lives/DT50/DT90

Test system	First order linear			Observed DT50 (hours)	Observed DT90 (hours)
	Half-life (hours)	Regression equation	r^2		
Irradiated	95.0	y = -0.0073x + 4.2437	0.5147	*ca*. 61	>61
Dark	630	y = -0.0011x + 4.5179	0.5387	>61	>61

Half-lives were calculated by the reviewer using Excel 2003 and data obtained from Table 7, p. 38 of the study report (DER Attachment 2).

The **phototransformation half-life** of oryzalin in soil, determined using the equation

(Ln 2) ÷ [(Ln 2/dark control half-life) - (Ln 2/irradiated half-life)]

is 112 hours based on the continuous irradiation used in the study, or 224 hours (9.3 days) based on a 12-hour light/12-hour dark cycle. Since light intensity of the artificial light was equivalent to *ca*. 61.4% of the natural sunlight during equinox at latitude 40°N (Table C-1, p. 86), the **environmental phototransformation half-life** of oryzalin is *ca*. 7.6 days (112 hrs/24 hrs/day/0.614).

TRANSFORMATION PRODUCTS: HPLC System 1 did not adequately separate the oryzalin transformation products (Figure 4, p. 50). In the irradiated samples, Region 1 (Rt <6 minutes) averaged a maximum of 31.3% of the applied at 61 hours (Table 7, p. 38; DER Attachment 2). In the corresponding dark controls, Region 1 was ≤1.4% of the applied at all sampling intervals.

HPLC System 2 was used to quantify the individual transformation products in select extracts (one irradiated sample/sampling interval) following frozen storage of the extracts for *ca*. 4-5 months (pp. 25-26). Using System 2, eight minor transformation products were isolated, each at ≤6.8% of the applied (Table 12, p. 43). Three of the transformation products were identified as:

4-amino-3,5-bis(dihydroxyamino)benzenesulfonamide (OR-3);
2-ethyl-7-nitro-1H-benzimidazole-5-sulfonamide (OR-15); and
4-(dipropylamino)-3,5-dinitrobenzenesulfonic acid (OR-21).

Table 7: Phototransformation of oryzalin, expressed as percentage of applied radioactivity (n = 1), on irradiated sandy loam soil (HPLC System 2).

Compound	Sampling intervals (hours)					
	4	8	13	22	34	61
Oryzalin	63.3	61.1	61.4	--	54.3	43.9
Unknown 1	0.9	2.4	2.2	2.6	2.7	2.3
Unknown 2	2.1	1.8	1.2	2.4	2.7	2.0
OR-3	1.4	1.2	1.5	2.5	2.3	2.6
OR-15	3.1	3.6	2.0	3.1	2.8	3.2
Unknown 3	2.3	3.0	4.6	4.7	6.8	5.8
Unknown 4	0.4	ND	ND	ND	ND	0.7
OR-21	3.7	4.1	3.0	4.6	3.6	4.6
Unknown 5	1.2	ND	ND	ND	ND	ND

Data obtained from Table 12, p. 43 in the study report. Only a single irradiated sample from each sampling interval was analyzed.
ND = Not detected.

Table 8: Chemical names and CAS numbers for the transformation products of oryzalin.

Applicants Code Name	Chemical Name	Chemical Formula	MW (g/mol)	Smiles String
OR-3	4-Amino-3,5-bis(dihydroxyamino)benzenesulfonamide	$C_6H_6N_4O_6S$	262.2	a
OR-15	2-Ethyl-7-nitro-1H-benzimidazole-5-sulfonamide	$C_9H_{10}N_4O_4S$	270.6	a
OR-21	4-(Dipropylamino)-3,5-dinitrobenzenesulfonic acid	$C_{12}H_{17}N_3O_7S$	347.35	a

Data were obtained from Figure 1, p. 47 of the study report. Chemical names from DER Attachment 1.
a. See Attachment 1.

NONEXTRACTABLE AND EXTRACTABLE RESIDUES: Total extractable [^{14}C]residues decreased from an average 93.3% of the applied at time 0 to 80.0% at study termination, while nonextractable residues increased to 14.5% at 61 hours (DER Attachment 2). In the dark controls, total extractable [^{14}C]residues averaged 86.6% of the applied at study termination, while nonextractable residues increased to 4.2% at 13 hours and were 2.8% at 61 hours.

Reflux extraction of the irradiated 13-hour and 61-hour samples removed an additional 6.5-7.0% and 4.6-5.8% of the applied, respectively, from the extracted soils (Table 13, p. 44). Analysis of the 13-hour reflux extract identified 3.5% of the applied as oryzalin, 0.2% of the applied as OR-21, and 0.7% as Unknown 1 (Table 15, p. 46). Analysis of the 61-hour extract identified 1.4% of the applied as oryzalin and 1.2% as Unknown 1.

VOLATILIZATION: In irradiated samples at 61 hours posttreatment, no [^{14}C]residues were detected in the ethylene glycol and an average ≤0.1% of the applied was recovered from the 2-ethoxyethanol:ethanolamine (1:1, v:v; Table 3, p. 34). No radioactivity was detected in the dark controls at any sampling intervals.

TRANSFORMATION PATHWAY: A transformation pathway was not provided by the study author. Based on the study results, oryzalin photodegrades to numerous minor compounds, with residues ultimately bound to the soil.

D. SUPPLEMENTARY EXPERIMENT-RESULTS: No supplementary studies were described.

III. STUDY DEFICIENCIES

1. Samples were irradiated for only 61 hours (*ca*. 2.5 days; continuous irradiation), at which time 45.6-51.9% of the nominal application of oryzalin (*ca*. 52% of the actual application at time 0) remained undegraded (Table 7, p. 38). According to OPPTS 835.2410, "Soil samples should be taken for analysis at four or more sampling time intervals, with at least one observation made after one-half of the test substance has degraded or 30 days, whichever comes first." Given that approximately 48% of the nominal application of oryzalin degraded by the study termination, the study should have been continued beyond 61 hours.

2. Sample extracts that were used to quantify transformation products were stored frozen for 4-5 months prior to analysis (p. 25). No data were provided to confirm the stability of the residues during frozen storage.

3. The HPLC analytical method that was initially used to analyze the soil extracts was not adequate to clearly separate the transformation products of oryzalin (Figure 4, p. 50). After several months of storage, select samples were reanalyzed using an alternate HPLC system (Figure 14, p. 60). Since the second HPLC system appears to have adequately separated oryzalin from its transformation products (Table 7, p. 38; Table 12, p. 43), it appears that it could have been used as the only HPLC system. The reviewer believes that the initial HPLC analytical method was not adequately evaluated prior to use.

4. Limits of Detection (LOD) and Limits of Quantification (LOQ) were not reported.

IV. REVIEWER'S COMMENTS

1. The rate of dissipation of oryzalin was calculated using data from the HPLC System 1 because these samples were not stored for 4-5 months prior to analysis. It was noted that the measured concentrations of oryzalin using HPLC System 2 (45.6-65.2% of the applied at 4-61 hours posttreatment) were in close agreement with the radioactivity recovered for oryzalin using HPLC system 1 (43.9-63.3% at 4-61 hours; p. 30; Table 7, p. 38; Table 12, p. 43).

2. The diagram of the volatile trapping system for the irradiated samples does not show a source for the air that was pulled through the sample chamber (Figure 2, p. 48).

3. Mean column recoveries for the soil extracts using HPLC system 1 ranged from 97.4-101.3% of the applied throughout the study period for the irradiated samples and 90.8-101.0% for dark

control samples (p. 28; Tables 5-6, pp. 36-37; DER Attachment 2). Column recoveries for the soil extracts using HPLC system 2 ranged from 93.9-104.6% at 4-61 hours posttreatment (Table 11, p. 42). Column recoveries for the refluxed soil extracts using HPLC system 2 were 117.1% at 13 hours and 125.8% at 61 hours (Table 14, p. 45).

V. REFERENCES

1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 161-3. Phototransformation studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.

2. U.S. Environmental Protection Agency. 2008. Fate, Transport and Transformation Test Guidelines, OPPTS 835.2410, photodegradation in soil. Office of Prevention, Pesticides and Toxic Substances, Washington, DC. EPA 712-C-08-019.

Attachment 1: Structures of Parent Compound and Transformation Products

Oryzalin [OR-1; EL-119]

IUPAC Name: 3,5-Dinitro-4-(dipropylamino)benzenesulfonamide.
3,5-Dinitro-N^4,N^4-dipropylsulfanilamide.
CAS Name: 4-(Dipropylamino)-3,5-dinitrobenzenesulfonamide.
CAS Number: 19044-88-3.
SMILES String: CCCN(CCC)c1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{18}N_4O_6S$ **Molecular formula:** $C_{12}H_{18}N_4O_6S$

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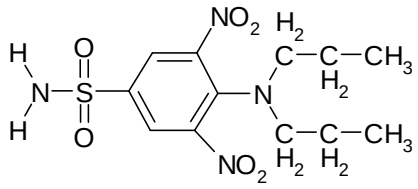
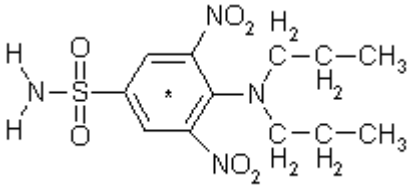


*** structure complexity/form was sacrificed to obtain SMILES string**
[ring-UL-^{14}C]Oryzalin
[benzene-U-^{14}C]Oryzalin
[^{14}C]Oryzalin

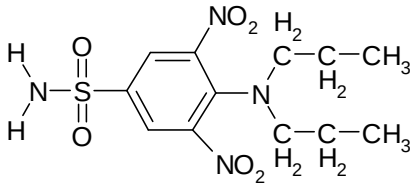


* = Location of the radiolabel.

Identified Compounds

Oryzalin [OR-1; EL-119]

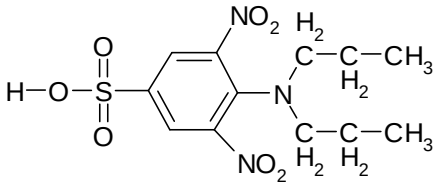
IUPAC Name: 3,5-Dinitro-4-(dipropylamino)benzenesulfonamide.
3,5-Dinitro-N^4,N^4-dipropylsulfanilamide.
CAS Name: 4-(Dipropylamino)-3,5-dinitrobenzenesulfonamide.
CAS Number: 19044-88-3.
SMILES String: CCCN(CCC)c1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{18}N_4O_6S$ **Molecular formula:** $C_{12}H_{18}N_4O_6S$



*** structure complexity/form was sacrificed to obtain SMILES string**

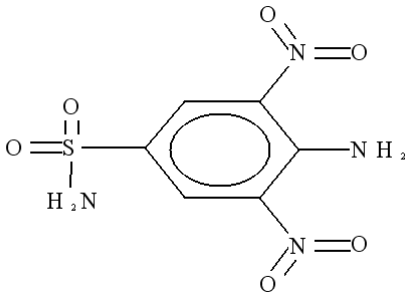
OR-21

IUPAC Name: 4-(Dipropylamino)-3,5-dinitrobenzenesulfonic acid (ACD Name Add-In for ISIS/Draw 2.3).
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: CCCN(CCC)c1c(cc(cc1N(=O)=O)S(O)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{17}N_3O_7S$ **Molecular formula:** $C_{12}H_{17}N_3O_7S$



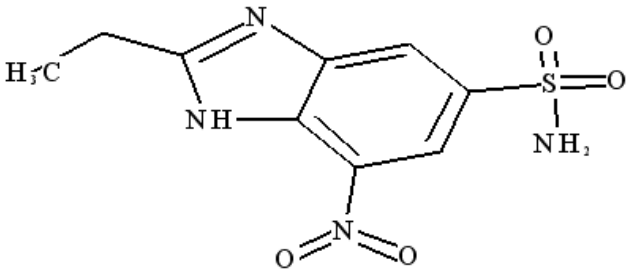
OR-3

IUPAC Name: 4-Amino-3,5-bis(dihydroxyamino)benzenesulfonamide (ACD Name Add-In for ISIS/Draw 2.3).
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: Nc1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_6H_6N_4O_6S$ **Molecular formula:** $C_6H_6N_4O_6S$



OR-15

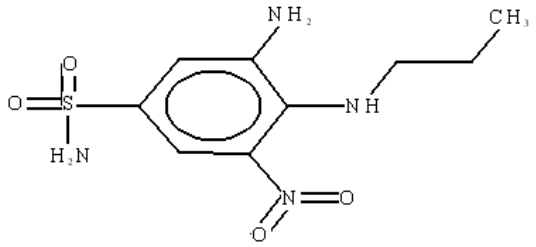
IUPAC Name: 2-Ethyl-7-nitro-1H-benzimidazole-5-sulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: C1(S(=O)(=O)N)=CC(N(=O)(=O))=C2NC(CC)=NC2=C1 (EpiSuite version 4.0).
Empirical formula: $C_9H_{10}N_4O_4S$ **Molecular formula:** $C_9H_{10}N_4O_4S$



Unidentified Reference Compounds

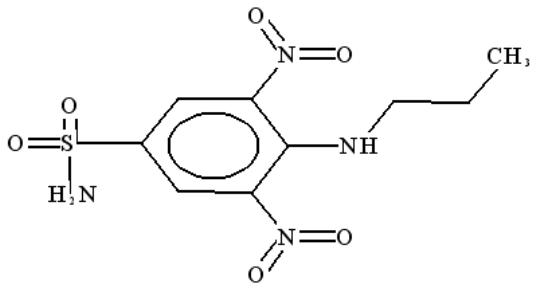
OR-5

IUPAC Name: 3-Amino-5-(dihydroxyamino)-4-(propylamino)benzenesulfonamide (ACD Name Add-In for ISIS/Draw 2.3).
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: N(CCC)c1c(cc(cc1N)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_9H_{14}N_4O_4S$ **Molecular formula:** $C_9H_{14}N_4O_4S$



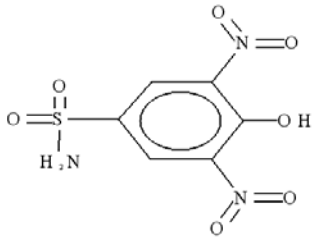
OR-2

IUPAC Name: 3,5-Dinitro-4-(propylamino)benzenesulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: N(CCC)c1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_9H_{12}N_4O_6S$ **Molecular formula:** $C_9H_{12}N_4O_6S$



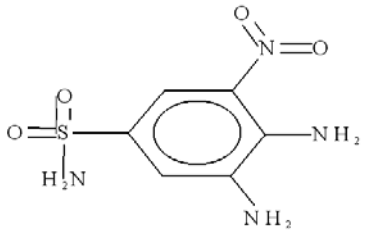
OR-20

IUPAC Name: 4-Hydroxy-3,5-dinitro-benzenesulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: Oc1c(cc(cc1N(=O)=O)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_6H_5N_3O_7S$ **Molecular formula:** $C_6H_5N_3O_7S$



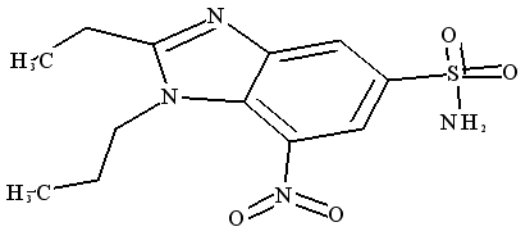
OR-6

IUPAC Name: 3,4-Diamino-5-(dihydroxyamino)benzenesulfonamide (ACD Name Add-In for ISIS/Draw 2.3).
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: Nc1c(cc(cc1N(=O)=O)S(N)(=O)=O)N (EpiSuite version 4.0).
Empirical formula: $C_6H_8N_4O_4S$ **Molecular formula:** $C_6H_8N_4O_4S$



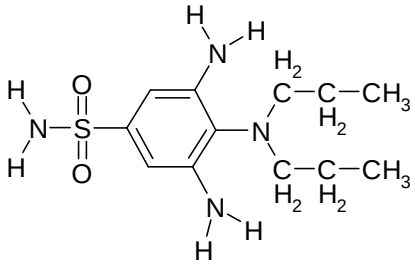
OR-13

IUPAC Name: 2-Ethyl-7-nitro-1-propyl-1H-benzimidazole-5-sulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: C1(S(=O)(=O)N)=CC(N(=O)(=O))=C2N(CCC)C(CC)=NC2=C1 (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{16}N_4O_4S$ **Molecular formula:** $C_{12}H_{16}N_4O_4S$



OR-7

IUPAC Name: 3,5-Diamino-4-(dipropylamino)benzenesulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: CCCN(CCC)c1c(cc(cc1N)S(N)(=O)=O)N (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{22}N_4O_2S$ **Molecular formula:** $C_{12}H_{22}N_4O_2S$



OR-4

IUPAC Name: 3-Amino-4-(dipropylamino)-5-nitrobenzenesulfonamide.
CAS Name: Not reported.
CAS Number: Not reported.
SMILES String: CCCN(CCC)c1c(cc(cc1N)S(N)(=O)=O)N(=O)=O (EpiSuite version 4.0).
Empirical formula: $C_{12}H_{20}N_4O_4S$ **Molecular formula:** $C_{12}H_{20}N_4O_4S$