2-4-02

Data Evaluation Report on the phototransformation of diflufenzopyr in water

PMRA Submission Number {.....} EPA MRID Number 45444004

Data Requirement: PMRA DATA CODE:
EPA DP Barcode: D276313
OECD Data Point:
EPA Guideline: 161-2

Test material:
Common name: Diflufenzopyr
Chemical name
IUPAC: 2-{1-[4-(3,5-Difluorophenyl)semicarbazono]ethyl}nicotinic acid
CAS name: 2-[1[[[(3,5-Difluorophenyl)amino]carbonyl]hydrazono]ethyl]-3-pyridinecarboxylic acid
CAS No: 109293-97-2
Synonyms: 2-(Methyl-(((3,5-difluorophenylamine)-carbonyl)-hydrazone)-methyl)-3-pyridine carboxylic acid
BAS 654 H
SMILES string:

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Company Code: [for PMRA]
Active Code: [for PMRA]
Use Site Category: [for PMRA]
EPA PC Code: 005108

CITATION: Singh, M. 2001. Photolysis of ^{14}C-BAS 654 H in aqueous media. Unpublished study performed and sponsored by BASF Corporation, Research Triangle Park, NC. BASF Protocol No. 61360 and Registration Document No. 2001/5000872. Study initiated July 24, 2000 and completed June 28, 2001 (p. 8).

EXECUTIVE SUMMARY:

The aqueous phototransformation of [phenyl-U-^{14}C]- and [pyridinyl-4,6-^{14}C]-labeled 2-(methyl-(((3,5-difluorophenylamine)-carbonyl)-hydrazone)-methyl)-3-pyridine carboxylic acid (diflufenzopyr) was studied at 22 ± 1°C in sterile aqueous at pH 5 (0.01 M acetate buffer) and at pHs 7 and 9 (0.01 M tris buffer) at a nominal concentration of 5 mg a.i./L under continuous irradiation using a UV-filtered xenon lamp for 20-29 days. The Trizma pH 7 and 9 buffer solutions reacted with the parent compound, resulting in the formation of an artifact compound (P9); therefore, effect(s) of the buffer component on the degradation rate and/or degradate formation are unknown. The xenon lamp light intensity was comparable to natural sunlight (583 W/m^2) in spring at 40°N latitude. Dark control solutions were maintained at 22 ± 1°C. Irradiated and dark control [phenyl-U-^{14}C]diflufenzopyr pH 5 solutions were harvested at 0, 5, 11, 19 and 24 days, and pH 7 and 9 solutions were collected at 0, 5, 10, 17 and 27 days. Irradiated and dark control [pyridinyl-4,6-^{14}C]diflufenzopyr pH 5 solutions were harvested at 0, 3, 7, 11, 15, 17 and 29 days, and pH 7 and 9 solutions were collected at 0, 5, 9, 13 and 20 days. Test solutions were analyzed directly by reverse-phase HPLC; identifications of diflufenzopyr and transformation products was done by co-chromatography with unlabeled reference standards. Identifications of selected [^{14}C]compounds were confirmed using LC/MS or GC/MS.

Material balances in [phenyl-U-^{14}C]diflufenzopyr solutions were 88.3-100.0%, 91.7-100.0%, and 94.4-101.1% of the applied radioactivity in the irradiated pH 5, 7, and 9 test solutions, respectively. In the dark control solutions, recoveries were 95.7-100.0%, 99.1-102.5% and 96.7-102.3% of the applied for pH 5, 7 and 9, respectively. For [pyridinyl-4,6-^{14}C]diflufenzopyr-treated solutions, recoveries in the irradiated solutions were 96.1-100.6% of the applied at pH 5, 100.0-103.9% at pH 7, and 100.0-105.1% at pH 9. In the dark control solutions, total recoveries were 96.8-100.6%, 99.7-104.1% and 99.4-103.7% of applied at pH 5, 7 and 9, respectively.

In dark control solutions, [phenyl-U-^{14}C]diflufenzopyr accounted for 43.0%, 54.9%, and 57.2% of the applied radioactivity in the pH 5, 7 and 9 test solutions; and [pyridinyl-4,6-^{14}C]diflufenzopyr comprised 44.3%, 72.3%, and 72.5%, respectively, at study termination. Major transformation products detected in the dark control [phenyl-U-^{14}C]diflufenzopyr study were 3,5-difluoroaniline (M2) at maximums of 46.9%, 33.9% and 13.1% of the applied at pH 5, 7 and 9, respectively; and P9 at respective maximums of 1.1%, 11.0% and 30.1%. Minor transformation products, each detected at ≤5.2%, in dark control [phenyl-U-^{14}C]diflufenzopyr solutions were 4-(3,5-diflurophenylphenyl)-semicarbazide (M7), carbamoyl phthalazinone (M5), M23, and P11 (proposed hydrolysis product of M23) plus two unidentified [^{14}C]compounds (P1 and P8). The major transformation product detected in the dark control [pyridinyl-4,6-^{14}C]diflufenzopyr study was 8-methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone (M1) at maximums of 43.1%, 28.2% and 28.4% of the applied at pH 5, 7 and 9, respectively. Minor transformation products in dark control [pyridinyl-4,6-^{14}C]diflufenzopyr solutions were 2-acetyl nicotinic acid (M6; maximum 8.45% at pH 5, ≤1.76% at pH 7 and 9), M5 (≤1.51%), P9 (≤1.37%), P5 (proposed structure p. 29; ≤1.26%), M23 and P11 each (≤0.47%), plus several unidentified [^{14}C]compounds (P6, P7 and P10), each ≤0.57%.

In irradiated solutions at the final sampling intervals, [phenyl-U-^{14}C]diflufenzopyr comprised 36.1%, 45.6%, and 36.8% of the applied radioactivity in the pH 5, 7 and 9 test solutions; and [pyridinyl-4,6-^{14}C]diflufenzopyr accounted for 25.8%, 29.8%, and 55.2%, respectively. Major transformation products detected in the irradiated [phenyl-U-^{14}C]diflufenzopyr study were M2 at maximums of 18.6%, 10.8% and 2.0% of the applied at pH 5, 7 and 9, respectively, and P9 at maximums of 13.4% and 33.9% at pH 7 and 9, respectively. Minor transformation products in irradiated [phenyl-U-^{14}C]diflufenzopyr solutions were M23 (≤8.73%), P11 (≤6.92%), M7 (≤5.52%) and M5 (≤3.38%), plus unidentified [^{14}C]compounds P1 (≤9.72%), P4 (≤5.41%) and P2, P3 and P8 each ≤1.77%. Major transformation products detected in the irradiated [pyridinyl-4,6-^{14}C]diflufenzopyr study were M6 at maximums of 41.0%, 33.1% and 10.4% of the applied, M24 at maximums of 6.8%, 16.7% and 0.58%, and P5 at maximums of 1.8%, 3.0% and 12.6% at pH 5, 7 and 9, respectively. Minor transformation products in irradiated [pyridinyl-4,6-^{14}C]diflufenzopyr solutions were M1 (≤8.67%), M23 (≤8.84%), P11 (≤6.35%), M5 and P9 each ≤0.81%, plus unidentified [^{14}C]compounds P2 (≤7.36%) and P1, P3, P4, P6, P7, P8, P10 and P12 each ≤3.40%. In irradiated [phenyl-U-^{14}C]diflufenzopyr solutions evolved $^{14}CO_2$ increased to 17.18% of the applied after 24 days in the pH 5 solution and 11.43% and 6.70% after 27 days in the pH 7 and 9 solutions, respectively; organic volatiles (pH 5 only) were ≤1.02%. In irradiated [pyridinyl-4,6-^{14}C]diflufenzopyr solutions, evolved $^{14}CO_2$ totaled <1% of the applied at the final sampling interval (29 days for pH 5 and 20 days for pH 7 and 9) and organic volatiles were <0.1% at any sampling interval.

Half-life values of [phenyl-U-^{14}C]diflufenzopyr, based on first-order kinetics and linear regression, were 17 days (r^2 = 0.991), 26 days (r^2 = 0.991) and 20 days (r^2 = 0.981) in irradiated pH 5, 7 and 9 solutions, respectively; and 21 days (r^2 = 0.995), 34 days (r^2 = 0.994) and 35 days (r^2 = 0.990) in respective dark control solutions. Half-life values of [pyridinyl-4,6-^{14}C]diflufenzopyr were 15 days (r^2 = 0.990), 12 days (r^2 = 0.830) and 25 days (r^2 = 0.989) in irradiated pH 5, 7 and 9 solutions, respectively; and 26 days (r^2 = 0.993), 44 days (r^2 = 0.977) and 47 days (r^2 = 0.956) in respective dark control solutions.

Quantum yields (ϕ_{ts}) for diflufenzopyr were 7.98 x 10^{-5}, 4.48 x 10^{-5}, and 14.8 x 10^{-5} in pH 5, 7 and 9 solutions, respectively.

Results Synopsis:

Test medium:	0.01 M acetate buffer at pH 5, 0.01 M tris buffer at pH 7 and 9.
Source of irradiation:	Artificial xenon lamp.
Half-life values:	21 days (r^2 = 0.995) dark pH 5 [phenyl-U-^{14}C]diflufenzopyr.
	34 days (r^2 = 0.994) dark pH 7 [phenyl-U-^{14}C]diflufenzopyr.
	35 days (r^2 = 0.990) dark pH 9 [phenyl-U-^{14}C]diflufenzopyr.
	17 days (r^2 = 0.991) irradiated pH 5 [phenyl-U-^{14}C]diflufenzopyr.
	26 days (r^2 = 0.991) irradiated pH 7 [phenyl-U-^{14}C]diflufenzopyr.
	20 days (r^2 = 0.981) irradiated pH 9 [phenyl-U-^{14}C]diflufenzopyr.
	26 days (r^2 = 0.993) dark pH 5 [pyridinyl-4,6-^{14}C]diflufenzopyr.

44 days (r^2 = 0.977) dark pH 7 [pyridinyl-4,6-^{14}C]diflufenzopyr.
47 days (r^2 = 0.956) dark pH 9 [pyridinyl-4,6-^{14}C]diflufenzopyr.
15 days (r^2 = 0.990) irradiated pH 5 [pyridinyl-4,6-^{14}C]diflufenzopyr.
12 days (r^2 = 0.830) irradiated pH 7 [pyridinyl-4,6-^{14}C]diflufenzopyr.
25 days (r^2 = 0.989) irradiated pH 9 [pyridinyl-4,6-^{14}C]diflufenzopyr.

Major transformation products: 8-Methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone (M1).
3,5-Difluoroaniline (M2).
2-Acetyl nicotinic acid (M6).
M24 (no chemical name, proposed structure p. 28).
P5 (no chemical name, proposed structure p. 29).
P9 (most probably an artifact; no chemical name, proposed structure p. 28).

Minor transformation products: Carbamoyl phthalazinone (M5).
4-(3,5-Diflurophenylphenyl)-semicarbazide (M7).
M23 (no chemical name, proposed structure p. 30).
P11 (proposed hydrolysis product of M23).
unidentified compounds (P1, P2, P3, P4, P6, P7, P8, P10, P12).

Study Acceptability: This study does not fulfill the guideline requirement for an aqueous photolysis study for diflufenzopyr. Results of the pH 7 and 9 test systems are not scientifically valid and are unacceptable because the compound P9 is reportedly an artifact which formed by a reaction of diflufenzopyr with the Trizma buffer solutions. Results from the pH 5 test system are acceptable, but do not fulfill the guideline requirement for a study on phototransformation in water because pH 5 is not the pH of maximum hydrolytic stability for the test compound.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was conducted in accordance with US EPA Subdivision N Guideline §161-2 and Council Directive 91/414/EEC, 1994 (p. 8). Deviations from US EPA Subdivision N §161-2 are:

A component of the Trizma pH 7 and 9 buffer solutions reacted with the parent compound, diflufenzopyr, resulting in the formation of an artifact compound (P9). Effect(s) of the buffer component on the rate of degradation of diflufenzopyr and/or formation of degradation products of diflufenzopyr could not be determined. This affects the validity of the study results.

The study conducted in pH 5 buffer solution cannot satisfy the requirements for Subdivision N Guideline §161-2 because this is not the pH of maximum hydrolytic stability for diflufenzopyr. Hydrolysis of diflufenzopyr was greatest at pH 5. This does not affect the validity of the aqueous photolysis results.

The study was conducted at a temperature was 22 ± 1°C rather than the recommended 25 ± 1°C. This does not affect the validity of the results.

COMPLIANCE:

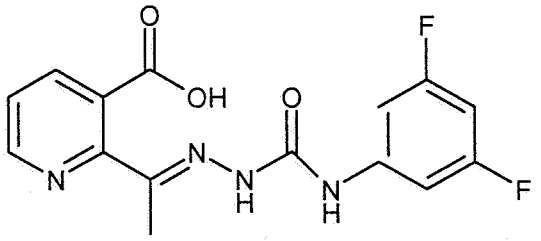
This study was conducted in compliance with US EPA GLP Standards (40 CFR, Part 160; 1989; p. 3). Signed and dated GLP and Data Confidentiality statements were provided (pp. 2, 3). Quality Assurance and Study Authenticity Certification statements were not provided.

A. MATERIALS:

1. Test Materials:

[Phenyl-U-^{14}C]- and [pyridinyl-4,6-^{14}C]-labeled 2-(methyl-(((3,5-difluorophenylamine)-carbonyl)-hydrazone)-methyl)-3-pyridine carboxylic acid.

Chemical Structure:



Description: Technical. Off-white solid (p. 10).

Purity:

[phenyl-U-^{14}C]-labeled: Radiochemical purity: >96% (pp. 10, 11, 51). Inventory/Lot No. 278/980921. Specific activity: 255,137 dpm/µg (115 µCi/mg, 4.25 MBq/mg).

[pyridinyl-4,6-^{14}C]-labeled: Radiochemical purity: >96% (pp. 10, 11, 52). Inventory/Lot No. 279/980921. Specific activity: 243,782 dpm/µg (110 µCi/mg, 4.06 MBq/mg).

Storage conditions of test chemicals: In darkness at a low (unspecified) temperature (p. 10).

Table 1: Physico-chemical properties of diflufenzopyr.

Parameter	Details	Comments
Water solubility:	63 mg/L in unbuffered water pH 6.5. 270 mg/L in pH 5 buffer solution. 5,850 mg/L in pH 7 buffer solution. 10,546 mg/L in pH 9 buffer solution.	
Vapor pressure/volatility:	$<10^{-2}$ mPa.	Obtained from Farm Chemicals Handbook 2001, p. C 144.
UV absorption:	Not reported.	
pK_a:	Not reported.	
K_{ow}/log K_{ow}:	Not reported.	
Stability at room temperature:	Not reported.	

Data obtained from p. 10 in the study report, except where noted.

2. Buffer Solutions: All buffer solutions were prepared using HPLC grade water.

Table 2: Description of buffer solutions.		
pH	**Type of buffer and final molarity**	**Composition**
5	0.01 M sodium acetate.	0.3284 g sodium acetate made up to 400 mL with water; pH adjusted to 5.0 with 50 µL acetic acid.
7	0.01 M Trizma (tromethamine, tris).	0.7741 g Trizma pre-set crystals (Sigma) made up to 500 mL with water.
9	0.01 M Trizma.	0.623 g Trizma pre-set crystals (Sigma) made up to 500 mL with water

Data obtained from p. 13 in the study report.

3. Details of light source:

Table 3: Artificial light source.	
Property	**Details**
Type of lamp used:	Xenon lamp, Atlas Suntest CPS Plus
Emission wavelength spectrum:	300-800 nm
Light intensities: [phenyl-U-^{14}C]diflufenzopyr [pyridinyl-4,6-^{14}C]difulfenzopyr	 Averaged (measured pre- and post-experiment) 578 W/m^2. Averaged 643 W/m^2.
Filters used:	UV filter eliminated wavelengths of <290 nm
Relationship to natural sunlight:	Xenon lamp light intensity determined to be comparable to natural sunlight intensity (583 W/m^2) in spring at 40°N latitude.

Data obtained from pp. 11, 53, 54 in the study report.

B. EXPERIMENTAL CONDITIONS:

1. Preliminary experiments: A preliminary experiment was performed to determine the coolant block temperature setting required to maintain the irradiated test solutions at 22 ± 1°C (pp. 11, 12). A glass vessel containing ca. 18 mL of buffer solution (type not specified) and a thermocouple probe to measure temperature was sealed with a quartz glass disc and placed in a well of the metal coolant block. Air was purged (flow rate not specified) through the vessel headspace and the solution was irradiated for >72 hours. It was determined that the irradiated solution was maintained at 22 ± 1°C when the coolant block temperature was set at 10.9°C.

2. Experimental conditions:

Table 4: Experimental design

Parameter		[Phenyl-U-^{14}C]diflufenzopyr	[Pyridinyl-4,6-^{14}C]diflufenzopyr
Study Duration (hours): pH 5 pHs 7 and 9		 570.43 641.9	 389.65 475.85
Application rates: (mg ai/L) nominal: all pHs measured: pH 5 pH 7 pH 9		 5 4.90 4.85 4.83	 5 5.68 5.36 5.33
Dark controls used (Yes/No):		Yes.	
Replications	Dark controls:	Single.	
	Irradiated:	Single.	
Preparation of the test medium:	Volume used/treatment:	100 mL aliquot of sterile buffer solution treated with 0.8 mL of ca. 500 mg a.i./L [phenyl-U-^{14}C]- or [pyridinyl-4,6-^{14}C]-labeled diflufenzopyr in acetonitrile:DMSO (9.5:0.5, v:v).	
	Method of sterilization:	Prior to use, all glassware was autoclave-sterilized at 120°C for 20 minutes. Prepared buffer solutions were filter-sterilized (0.2 µm) and then autoclave-sterilized at 120°C for 20 minutes.	
	Co-solvent, if any:	Acetonitrile:dimethyl sulfoxide (9.5:0.5, v:v) with a final concentration of 0.8%.	
Test apparatus (Type/material/ volume):	Dark controls:	Capped HPLC vials containing 1.5 mL of test solution were maintained at 22 ± 1°C in darkness in an incubator.	
	Irradiated:	Glass vessels containing ca. 17 mL of test solution were capped with a quartz glass disc and placed into the wells of a metal block. Coolant was circulated through the block to maintain the test solutions at 22 ± 1°C during irradiation. One vessel containing ethylene glycol was incubated alongside the irradiated samples in order to measure solution temperature at each sampling interval.	
Details of traps for CO_2 and organic volatiles, if any:	Dark controls:	None.	
	Irradiated:	Each photolysis vessel was equipped with inlet/outlet ports and the vessels were connected in series with Tygon tubing. Filtered (0.22 µm), humidified, CO_2-free air was purged (flow rate not specified) through the vessels and sequentially into traps containing 1 *N* NaOH (two traps) and ethylene glycol (one trap).	
If no traps were used, is the system closed/open?		Dark control systems were closed. Volatile traps were used with irradiated systems.	

Table 4: Experimental design			
Parameter		**[Phenyl-U-^{14}C]diflufenzopyr**	**[Pyridinyl-4,6-^{14}C]diflufenzopyr**
Any indication of the test material adsorbing to the walls of the test apparatus?		No	
Experimental conditions.	Temperature (°C):	22 ± 1°C	
	Duration of light/darkness:	Continuous irradiation.	
Other details, if any:		None.	

Data obtained from pp. 11-15, 55 in the study report.

3. Supplementary experiments: The following supplemental experiments were conducted:

Determination of quantum yield: A chemical actinometer system was utilized to determine the quantum yield for diflufenzopyr under the test conditions (pp. 12-15, 17). An aliquot (ca. 20 mL) of a sterile aqueous solution containing 2.57 x 10^{-5} M *p*-nitroacetophenone (PNAP) and 0.02 M pyridine (PYR) was transferred to a photolysis vessel and incubated alongside the [pyridinyl-4,6-^{14}C]difulfenzopyr-treated test solutions and sampled at the same intervals (described in Table 5 below). Sterile, CO_2-free air was purged through the vessel headspace during incubation. At each sampling interval after time 0, an aliquot (0.5 mL) of solution was removed from the irradiated actinometer vessel and analyzed by reverse-phase HPLC as described below for the [^{14}C]diflufenzopyr test solutions.

Generation of degradates: To identify degradates, additional experiments were conducted at an exaggerated rate (pp. 12, 15). Additional aliquots of pH 5 (20 mL) and 9 (60 mL) buffer solutions were each treated separately with [phenyl-U-^{14}C]diflufenzopyr at 20 ppm or [pyridinyl-4,6-^{14}C]diflufenzopyr at 28 ppm and irradiated as described for the test samples.

Sterility determination: To determine sterility at the initiation and termination of the study, selected aliquots of test solutions and actinometer were placed on agar plates (media not described) and incubated (interval not specified) at ambient temperature (pp. 13, 14). Results indicated that sterility was maintained; tabular plate count data were not reported.

4. Sampling:

Table 5: Sampling details		
Parameters	**[Phenyl-U-^{14}C]diflufenzopyr**	**[Pyridinyl-4,6-^{14}C]diflufenzopyr**
Sampling intervals: pH 5 (hours) pHs 7 and 9	0, 116.7, 256.5, 449.0 and 570.4 0, 116.7, 235.0, 399.4 and 641.9	0, 69.9, 164.8, 259.4, 355.2, 399.5 and 689.7 0, 116.5, 210.2, 304.6 and 475.9
Sampling method:	Entire sample collected.	
Method of collection of volatile compounds, if any:	Trapping solutions removed/replaced at each sampling interval after time 0.	
Sampling intervals/times for: sterility check: pH measurement:	 Initial and final sampling intervals. Measured at each sampling interval	
Sample storage before analysis:	5 ppm [^{14}C]diflufenzopyr-treated solutions and actinometer solutions were analyzed immediately upon collection.	
Other observations, if any:	None	

Data obtained from pp. 12, 15-17, 20 of the study report.

C. ANALYTICAL METHODS:

Extraction/clean up/concentration methods: Test solutions were analyzed directly to determine quantitative distributions of parent diflufenzopyr and its degradates (p. 16).

Total ^{14}C measurement: Triplicate aliquots (25 or 50 µL) of the irradiated and dark control test solutions were analyzed for total radioactivity by LSC (p. 16).

Triplicate aliquots (1 mL) of each trapping solution were analyzed for total radioactivity by LSC (p. 16). To quantify $^{14}CO_2$, an aliquot (2 mL) of the sodium hydroxide trapping solution was reacted with 5 N sulphuric acid, then released $^{14}CO_2$ was trapped in Harvey cocktail solution contained in a vigreux column and aliquots were analyzed by LSC; the remaining neutralized $NaOH:H_2SO_4$ solution was also analyzed by LSC (pp. 16, 56).

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

Identification and quantification of parent compound and transformation products: Aliquots of the test solutions were analyzed by reverse-phase HPLC under the following conditions: YMC ODS AQ column (4.6 x 250 mm, 5 µm particle size), mobile phase gradient of (A) 0.1% aqueous trifluoroacetic acid to (B) acetonitrile (A:B, v:v, 98:2, 60:40, 20:80), injection volume 100 µL, flow rate 1 mL/minute, UV (280 nm) and radioactive flow detection (pp. 16, 17). To isolate photodegradates, test solutions were fractionated using a semi-prep reverse-phase HPLC column

(YMC ODS AQ, 10 x 250 mm, 5 µm particle size) with the same gradient mobile phase gradient as previously described, and a flow rate of 1.7 mL/minute (p. 17). To isolate degradates in the [pyridinyl-4,6-^{14}C]diflufenzopyr study, selected irradiated samples were combined and concentrated by rotary evaporation prior to HPLC fractionation (pp. 17, 18). To isolate degradates in the [phenyl-U-^{14}C]diflufenzopyr study, selected samples were applied to a SPE cartridge and eluted with acetone; the resulting eluant was diluted with ethyl acetate, washed with water, concentrated by rotary evaporation following the addition of DMSO, and fractionated by HPLC (p. 19). Eluent fractions containing isolated [^{14}C]compounds were collected. Respective fractions were combined and processed if necessary (ethyl acetate phase partitioning, pH adjustment prior to partitioning), concentrated, and co-chromatographed with corresponding non-radiolabeled reference standards (p. 35) of diflufenzopyr (p. 59), M1 (pp. 57, 65), M2 (p. 69), M4 (p. 71), M6 (pp. 57, 65), M7 (p. 68), M9 (p. 65), and M10 (p. 65). The identity of M1, M6, diflufenzopyr and M7 were confirmed by LC/MS (pp. 76-77, 78-79, 81-82, 92, respectively) and M2 was confirmed by GC/MSD (pp. 93-94).

Detection limits (LOD, LOQ) for the parent compound and transformation products: For HPLC analyses, the detection limit was reported as <1000 dpm or <0.005% of total applied radioactivity (p. 21).

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: Only test solutions sampled at time 0 and the final sampling interval were analyzed for sterility; it was reported that no microbial growth resulted from those samples (p. 13). Dark control test solutions were maintained at 22 ± 1°C (pp. 183-186); however, temperature records were not provided to confirm that the irradiated test solutions were also maintained at the reported 22 ± 1°C throughout the study. It could not be determined if the pH of each test solution was maintained throughout the course of the study; it was reported that the pH of each test solution was measured at the time of analysis, but those pH values were not reported (p. 13).

B. MATERIAL BALANCE: For [phenyl-U-^{14}C]diflufenzopyr-treated solutions, total recoveries of radiolabeled material were 88.3-100.0%, 91.7-100.0%, and 94.4-101.1% of the applied radioactivity in the irradiated pH 5, 7, and 9 test solutions, respectively (p. 37). In dark control solutions, total recoveries were 95.7-100.0%, 99.1-102.5% and 96.7-102.3% of applied at pH 5, 7 and 9, respectively (p. 45). **For [pyridinyl-4,6-^{14}C]diflufenzopyr-treated solutions,** total recoveries in the irradiated solutions were 96.1-100.6% of applied at pH 5, 100.0-103.9% at pH 7, and 100.0-105.1% at pH 9. In the dark control solutions, total recoveries were 96.8-100.6%, 99.7-104.1% and 99.4-103.7% of applied at pH 5, 7 and 9, respectively (p. 44).

Table 6: Phototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 5**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	11	19	24
Diflufenzopyr (BAS 654 H)	irradiated	95.05	80.53	58.56	46.71	36.07
	dark		80.75	63.6	51.81	42.97
3,5-Difluoroaniline (M2)	irradiated	1.57	11.63	18.59	17.82	8.97
	dark		13.55	30.54	40.28	46.94
Carbamoyl phthalazinone (M5)	irradiated	3.38	1.03	0.97	<LOD[1]	<LOD
	dark		0.58	0.62	<LOD	0.57
4-(3,5-Diflurophenylphenyl)-semicarbazide (M7)	irradiated	<LOD	1.23	1.09	1.32	0.8
	dark		1.62	3.44	4.01	5.21
M23	irradiated	<LOD	1.93	3.73	5.49	8.73
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P1	irradiated	<LOD	<LOD	<LOD	0.52	3.41
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P2	irradiated	<LOD	<LOD	<LOD	<LOD	0.49
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P3	irradiated	<LOD	<LOD	<LOD	<LOD	0.28
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P4	irradiated	<LOD	<LOD	1.45	4.29	5.41
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P9	irradiated	<LOD	<LOD	<LOD	<LOD	<LOD
	dark		1.14	<LOD	<LOD	<LOD
Unidentified P11	irradiated	<LOD	0.65	1.9	4.54	6.92
	dark		<LOD	0.75	0.7	<LOD
CO_2 (n = 3):	irradiated	NA[2]	1.09	5.49	11.82	16.16
	dark		NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	1.02

Table 6: Phototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 5**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	11	19	24
	dark		NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	98.1	91.76	92.53	88.27
	dark		97.65	98.97	96.79	95.69

[1]LOD = Limit of detection, <0.005% of applied radioactivity (p. 21).
[2]NA = Not analyzed.
Data obtained from pp. 37, 41, 45, 47, 126-129 of the study report.

Table 7: ~~Ph~~ototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 7**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	10	17	27
Diflufenzopyr (BAS 654 H)	irradiated	94.87	85.07	74.37	64.34	45.59
	dark		87.6	80.71	69.3	54.85
3,5-Difluoroaniline (M2)	irradiated	<LOD[1]	7.79	10.84	10.13	8.11
	dark		8.85	14.27	21.88	33.91
Carbamoyl phthalazinone (M5)	irradiated	0.81	0.91	0.74	<LOD	<LOD
	dark		0.47	0.52	<LOD	<LOD
4-(3,5-Diflurophenylphenyl)-semicarbazide (M7)	irradiated	<LOD	<LOD	<LOD	<LOD	2.09
	dark		<LOD	<LOD	<LOD	<LOD
M23	irradiated	0.54	<LOD	<LOD	<LOD	1.68
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P1	irradiated	<LOD	<LOD	<LOD	<LOD	4.77
	dark		0.53	<LOD	<LOD	<LOD
Unidentified P4	irradiated	<LOD	0.76	1.17	1.49	3.43
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P9	irradiated	1.14	3.37	6.36	8.88	13.36

Table 7: Phototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 7**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	10	17	27
	dark		4.01	4.84	7.95	11
Unidentified P11	irradiated	2.64	0.44	1.26	2.43	5.16
	dark		1.05	<LOD	<LOD	0.77
CO_2 (n = 3):	irradiated	NA[2]	0.6	1.24	4.4	11.43
	dark		NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	<0.01
	dark		NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	99.54	95.98	91.66	95.62
	dark		102.5	100.34	99.13	100.53

[1]LOD = Limit of detection, <0.005% of applied radioactivity (p. 21).
[2]NA = Not analyzed.
Data obtained from pp. 37, 42, 45, 47, 132-135 of the study report.

Table 8: Phototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 9**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	10	17	27
Diflufenzopyr (BAS 654 H)	irradiated	95.05	82.43	73.93	56.92	36.8
	dark		89.02	81.57	68.53	57.24
3,5-Difluoroaniline (M2)	irradiated	<LOD[1]	2.03	1.68	0.94	<LOD
	dark		3.43	5.23	8.31	13.1
Carbamoyl phthalazinone (M5)	irradiated	<LOD	0.62	<LOD	<LOD	<LOD
	dark		0.64	0.78	0.85	<LOD
4-(3,5-Diflurophenylphenyl)-semicarbazide (M7)	irradiated	<LOD	<LOD	1.54	3.24	5.52
	dark		<LOD	<LOD	<LOD	<LOD

Table 8: Phototransformation of **[phenyl-U-^{14}C]diflufenzopyr at pH 9**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	10	17	27
Unidentified P1	irradiated	<LOD	0.38	0.9	2.08	9.72
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P3	irradiated	<LOD	<LOD	0.92	0.42	1.77
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P8	irradiated	<LOD	<LOD	<LOD	<LOD	0.65
	dark		<LOD	<LOD	<LOD	0.59
Unidentified P9	irradiated	2.93	13.28	18.94	26.98	33.87
	dark		8.84	14.34	19.04	30.08
Unidentified P11	irradiated	2.02	0.94	0.77	1.1	1.28
	dark		0.39	<LOD	<LOD	<LOD
CO_2 (n = 3):	irradiated	NA[2]	0.29	1.06	2.67	6.7
	dark		NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	<0.01
	dark		NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	101.07	99.72	94.35	96.3
	dark		102.32	101.93	96.74	100.31

[1]LOD = Limit of detection, <0.005% of applied radioactivity (p. 21).
[2]NA = Not analyzed.
Data obtained from pp. 37, 43, 45, 47, 138-141 of the study report.

Table 9: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 5**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)						
		0	3	7	11	15	17	29
Diflufenzopyr (BAS 654 H)	irradiated	97.42	88.13	78.08	60.09	53.49	50.05	25.8
	dark		88.92	79.93	71.53	65.39	64.73	44.26

Table 9: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 5**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)						
		0	3	7	11	15	17	29
2-Acetyl nicotinic acid (M6)	irradiated	<LOD[1]	5.21	12.35	18.92	25.32	30.11	41
	dark		2.39	3.89	4.51	5.72	5.92	8.45
8-Methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone (M1)	irradiated	1.18	3.61	3.35	2.11	1.49	1.83	0.79
	dark		5.98	13.21	20.01	25.09	29.61	43.05
Carbamoyl phthalazinone (M5)	irradiated	0.67	0.5	0.37	0.51	0.81	0.35	0.33
	dark		0.64	0.44	1.02	0.46	<LOD	<LOD
M23	irradiated	0.34	0.47	2.08	2.93	3.9	5.1	5.15
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
M24	irradiated	<LOD	1.21	2.74	3.69	4.3	5.08	6.82
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P1	irradiated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.4
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P2	irradiated	<LOD	<LOD	<LOD	<LOD	2.62	<LOD	1.71
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P3	irradiated	<LOD	<LOD	<LOD	1.23	<LOD	<LOD	1.52
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P4	irradiated	<LOD	<LOD	<LOD	1.37	<LOD	0.37	2.19
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P5	irradiated	<LOD	<LOD	<LOD	1.84	1.79	0.57	1.62
	dark		<LOD	<LOD	<LOD	1.26	0.31	0.99
Unidentified P6	irradiated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.58
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P7	irradiated	<LOD	<LOD	0.81	2.02	1.87	2.72	3.4
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P8	irradiated	<LOD	<LOD	0.72	<LOD	<LOD	<LOD	<LOD

Table 9: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 5**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)						
		0	3	7	11	15	17	29
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P9	irradiated	0.39	<LOD	<LOD	<LOD	<LOD	<LOD	0.5
	dark		0.87	0.69	0.63	0.56	<LOD	<LOD
Unidentified P10	irradiated	<LOD	<LOD	<LOD	0.62	1.91	2.14	0.34
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P11	irradiated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.54
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Unidentified P12	irradiated	<LOD	<LOD	<LOD	0.6	<LOD	<LOD	<LOD
	dark		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
CO_2 (n = 3):	irradiated	NA[2]	0.04	0.08	0.12	0.16	0.18	0.47
	dark		NA	NA	NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	dark		NA	NA	NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	98.19	100.6	96.07	97.68	98.53	96.17
	dark		98.8	98.16	97.69	98.49	100.6	96.75

[1]LOD = Limit of detection, <0.005% of applied radioactivity (p. 21).
[2]NA = Not analyzed.
Data obtained from pp. 36, 38, 44, 46, 104-109 of the study report.

Table 10: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 7**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	9	13	20
Diflufenzopyr (BAS 654 H)	irradiated	96.86	90.82	75.76	72.41	29.83
	dark		91.76	84.32	77.59	72.31
2-Acetyl nicotinic acid (M6)	irradiated	0.85	5.28	17.01	20	33.05

Table 10: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 7**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	9	13	20
	dark		1.26	1.56	1.39	1.76
8-Methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone (M1)	irradiated	<LOD[1]	4.03	1.28	2.55	0.88
	dark		8.18	13.87	18.11	28.2
Carbamoyl phthalazinone (M5)	irradiated	0.54	<LOD	<LOD	<LOD	0.63
	dark		1.51	0.42	0.64	0.38
M23	irradiated	0.28	<LOD	1.2	<LOD	8.84
	dark		<LOD	<LOD	<LOD	<LOD
M24	irradiated	<LOD	2.26	5.38	5.74	16.65
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P1	irradiated	<LOD	≤LOD	<LOD	<LOD	1.39
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P2	irradiated	<LOD	<LOD	<LOD	<LOD	0.27
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P4	irradiated	<LOD	0.71	<LOD	<LOD	<LOD
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P5	irradiated	<LOD	<LOD	0.26	<LOD	3.04
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P6	irradiated	<LOD	0.25	0.4	<LOD	<LOD
	dark		<LOD	0.64	0.57	<LOD
Unidentified P7	irradiated	0.18	0.23	0.58	<LOD	<LOD
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P9	irradiated	0.8	<LOD	<LOD	<LOD	0.44
	dark		1	0.77	0.81	<LOD
Unidentified P10	irradiated	0.27	<LOD	<LOD	<LOD	<LOD
	dark		<LOD	<LOD	0.27	<LOD

Table 10: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 7**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	9	13	20
Unidentified P11	irradiated	0.22	0.28	1.26	<LOD	6.35
	dark		0.37	0.47	0.29	<LOD
Unidentified P12	irradiated	<LOD	<LOD	<LOD	<LOD	0.23
	dark		<LOD	<LOD	<LOD	<LOD
CO_2 (n = 3):	irradiated	NA[2]	0.05	0.1	0.21	0.92
	dark		NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	<0.01
	dark		NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	103.91	103.23	100.91	102.51
	dark		104.08	102.05	99.66	102.64

[1]LOD = Limit of detection reported as <0.005% of applied radioactivity (p. 21).
[2]NA = Not analyzed.
Data obtained from pp. 36, 39, 44, 46, 112-115 of the study report.

Table 11: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 9**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	9	13	20
Diflufenzopyr (BAS 654 H)	irradiated	96.38	85.6	75.66	71.04	55.21
	dark		93.56	82.52	80.6	72.53
2-Acetyl nicotinic acid (M6)	irradiated	1.13	3.24	4.64	7.74	10.38
	dark		0.72	0.95	0.8	1.07
8-Methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone (M1)	irradiated	0.5	5.61	6.27	6.31	8.67
	dark		7.97	13.58	19.68	28.42
Carbamoyl phthalazinone (M5)	irradiated	0.77	0.68	0.46	<LOD[1]	<LOD
	dark		0.47	0.37	0.24	<LOD

Table 11: Phototransformation of **[pyridinyl-4,6-^{14}C]diflufenzopyr at pH 9**, expressed as percentage of applied radioactivity (n = 1, except where noted)

Compound (code)	Test System	Sampling times (days)				
		0	5	9	13	20
M24	irradiated	<LOD	0.38	<LOD	<LOD	0.58
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P1	irradiated	<LOD	<LOD	<LOD	<LOD	2.15
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P2	irradiated	<LOD	1.77	2.3	4.48	7.36
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P3	irradiated	<LOD	0.51	<LOD	<LOD	<LOD
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P5	irradiated	<LOD	5.84	9.43	11.73	12.55
	dark		<LOD	0.56	0.94	0.36
Unidentified P7	irradiated	<LOD	0.57	0.55	<LOD	0.81
	dark		<LOD	0.2	<LOD	<LOD
Unidentified P9	irradiated	0.56	<LOD	<LOD	<LOD	<LOD
	dark		1.02	1.02	1.37	0.57
Unidentified P10	irradiated	0.19	<LOD	<LOD	<LOD	0.49
	dark		<LOD	<LOD	<LOD	<LOD
Unidentified P11	irradiated	0.47	<LOD	<LOD	<LOD	<LOD
	dark		<LOD	0.21	<LOD	<LOD
CO_2 (n = 3):	irradiated	NA[2]	<0.01	0.01	0.01	0.04
	dark		NA	NA	NA	NA
Other volatiles (n = 3):	irradiated	NA	<0.01	<0.01	<0.01	<0.01
	dark		NA	NA	NA	NA
Total % recovery (n = 3):	irradiated	100	105.06	102	103.47	102.09
	dark		103.72	99.41	103.63	102.94

[1]LOD = Limit of detection, <0.005% of applied radioactivity (p. 21).

[2]NA = Not analyzed.
Data obtained from pp. 36, 40, 44, 46, 118-121 of the study report.

C. TRANSFORMATION OF PARENT COMPOUND: At the final sampling interval, in dark control [phenyl-U-^{14}C]diflufenzopyr solutions, diflufenzopyr comprised 43.0%, 54.9%, and 57.2% of the applied radioactivity at pH 5, 7, and 9, respectively (p. 47). In dark control [pyridinyl-4,6-^{14}C]diflufenzopyr solutions, diflufenzopyr comprised 44.3%, 72.3% and 72.5% of the applied at pH 5, 7 and 9, respectively (p. 46).

In continuously irradiated [phenyl-U-^{14}C]diflufenzopyr solutions, diflufenzopyr decreased from 94.9-95.1% of the applied radioactivity at time 0 in each of the pH 5, 7 and 9 solutions to 36.1% in the pH 5 solution (24 days), 45.6% in the pH 7 solution (27 days), and 36.8% in the pH 9 solution (27 days) (pp. 41-43). In continuously irradiated [pyridinyl-4,6-^{14}C]diflufenzopyr solutions, diflufenzopyr decreased from 96.4-97.4% of the applied at time 0 in each of the pH 5, 7 and 9 solutions to 25.8% in the pH 5 solution (29 days), 29.8% in the pH 7 solution (20 days), and 55.2% in the pH 9 solution (20 days; pp. 38-40).

HALF-LIFE: Half-life values of [phenyl-U-^{14}C]- and [pyridinyl-4,6-^{14}C]-labeled diflufenzopyr in irradiated and dark control solutions were determined by the registrant using least squares linear regression analysis assuming degradation followed first order kinetics (pp. 21, 22, 49, 146-158). Half-life calculations were confirmed by the Dynamac reviewer (see attached spreadsheets).

Table 12: Half-lives of diflufenzopyr in irradiated and dark control solutions at pH 5, 7 and 9

Test system	First order half-life		
	Half-life (days)	r^2	Regression equation
Dark:			Linear form y = mx + b as $\ln C = -kt + \ln C_0$; $\ln C_0$ is initial concentration (b = y intercept), lnC is concentration at time t (y), k is the slope (m), t is time (x) or $kt = \ln C_0 - \ln C$. Half-life (t ½) = -(ln/k).
[phenyl-U-^{14}C]diflufenzopyr, pH 5	21.0	0.995	
[phenyl-U-^{14}C]diflufenzopyr, pH 7	33.6	0.994	
[phenyl-U-^{14}C]diflufenzopyr, pH 9	35.3	0.993	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 5	25.9	0.994	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 7	44.5	0.977	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 9	46.6	0.956	

Table 12: Half-lives of diflufenzopyr in irradiated and dark control solutions at pH 5, 7 and 9			
Test system	**First order half-life**		
	Half-life (days)	**r^2**	**Regression equation**
Irradiated:			
[phenyl-U-^{14}C]diflufenzopyr, pH 5	17.2	0.991	
[phenyl-U-^{14}C]diflufenzopyr, pH 7	25.6	0.991	
[phenyl-U-^{14}C]diflufenzopyr, pH 9	19.7	0.986	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 5	15.0	0.990	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 7	12.1 (0-20 days)	0.830	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 7	27.8 (0-13 days)	0.934	
[pyridinyl-4,6-^{14}C]difulfenzopyr, pH 9	25.1	0.989	

Data obtained from pp. 49, 146-158 of the study report.

TRANSFORMATION PRODUCTS: Unless indicated otherwise, the following results indicate detections in all test solutions (pH 5, 7 and 9).

Table 13: Chemical names for identified transformation products of diflufenzopyr in irradiated and dark control buffer solutions			
BASF Code	**Chemical Name(s)**	**HPLC retention time (minutes)**	**Molecular weight (g/mol)**
M6	2-Acetyl nicotinic acid	12:00-13:50	165
M1	8-Methyl-5-hydroxy-pyrido-(2,3-d)-pyridazinone	13:20-14:80	161
M7	4-(3,5-Diflurophenylphenyl)-semicarbazide	15:10-16:80	187
M2	3,5-Difluoroaniline	18:30-20:90	129
M5	Carbamoyl phthalazinone	26:10-27:50	316

Data obtained from pp. 35, 38-43 of the study report.

In [phenyl-U-^{14}C]diflufenzopyr dark control solutions, M2 was the major degradate detected at maximums of 46.9%, 33.9%, and 13.1% in the pH 5 (24 days), pH 7 (27 days), and pH 9 (27 days) test solutions, respectively (47). P9 (proposed structure p. 28), reportedly an artifact resulting from the reaction of diflufenzopyr and trihydroxyaminomethane (Trizma buffer solution component), was detected at maximums of 1.1% at time 0 in the pH 5 solution and 11.0% and 30.1% in the pH 7 and 9 solutions, respectively, at 27 days. M7 was detected at a maximum 5.2% at 24 days (pH 5). M5, M23 (pH 7; chemical name not provided, proposed structure p. 30) and P11 (proposed hydrolysis

product of M23, p. 30) were each detected at ≤3.38% of the applied. Two unidentified [^{14}C]compounds, P1 (pH 7) and P8 (pH 9), were each detected at ≤0.59% of the applied.

In [pyridinyl-4,6-^{14}C]diflufenzopyr dark control solutions, M1 was the major degradate detected at maximums of 43.05% of the applied at 29 days (689.7 hours) in the pH 5 solution and 28.20% and 28.42% in the pH 7 and 9 solutions, respectively, at 20 days (475.9 hours, p. 46). M6 was detected at a maximum 8.45% at 29 days in the pH 5 solution and was ≤1.76% in the pH 7 and 9 solutions. M5, M23 (pH 5, 7), P5 (pH 5, 9; proposed structure p. 29), P9 and P11 (pH 7, 9) were each ≤1.51%. Three unidentified [^{14}C]compounds, P6 (pH 7), P7 (pH 7, 9) and P10 (pH 7, 9), were each ≤0.64% of the applied.

In irradiated [phenyl-U-^{14}C]diflufenzopyr solutions, P9 was detected at maximums of 13.36% and 33.87% of the applied in the pH 7 and 9 solutions, respectively, at 27 days and was not detected (<0.01%) in the pH 5 solution (pp. 41-43). M2 was detected at maximums of 18.59% at 11 days (256.5 hours) in the pH 5 solution, 10.84% at 10 days (235.1 hours) in the pH 7 solution and was ≤2.03% in the pH 9 solution. M23 (pH 5, 7) was detected at 0.54-8.73% of the applied, P11 at 0.44-6.92%, M5 at 0.62-3.38% of the applied and M7 at 0.80-5.52%. Unidentified [^{14}C]compound P1 was detected at 0.38-9.72%, P4 (pH 5, 7) at 0.76-5.41% and P2 (pH 5), P3 (pH 5, 9) and P8 (pH 9) were each ≤1.77%.

In irradiated [pyridinyl-4,6-^{14}C]diflufenzopyr solutions, M6 was detected at maximums of 41.0% of the applied at 29 days in the pH 5 solution and 33.05% and 10.38% in the pH 7 and 9 solutions, respectively, at 20 days (pp. 38-40). M24 (proposed structure p. 28) was detected at maximums of 6.82% at 29 days in the pH 5 solution, 16.65% at 20 days in pH 7 solution, but was ≤0.58% in pH 9 solution. M1 was detected at 0.50-8.37% of the applied, M23 (pH 5, 7) at 0.28-8.84%, P5 at 0.26-12.55%, P11 at 0.22-6.35%, and M5 and P9 were each ≤0.80%. Unidentified [^{14}C]compound P2 was detected at 0.27-7.36%, with P1, P3 (pH 5, 9), P4 (pH 5, 7), P6 (pH 5, 7), P7, P8 (pH 5, 9), P10 and P12(pH 5, 7) each ≤3.40%.

VOLATILIZATION: Volatilization of $^{14}CO_2$ was only significant in irradiated [phenyl-U-^{14}C]diflufenzopyr solutions increasing to 17.18% of the applied after 24 days in the pH 5 solution and 11.43% and 6.70% after 27 days in the pH 7 and 9 solutions, respectively; organic volatiles (pH 5 only) were ≤1.02% at the final sampling interval (pp. 37, 126-129, 132-135, 138-141). In irradiated [pyridinyl-4,6- ^{14}C]diflufenzopyr solutions, volatilized $^{14}CO_2$ totaled <1% of the applied at the final sampling interval (29 days for pH 5 and 20 days for pH 7 and 9) and organic volatiles were <0.1% at any sampling interval (p. 36).

TRANSFORMATION PATHWAY: A phototransformation pathway for the degradation of diflufenzopyr in aqueous solution was proposed by the registrant (p. 74). The proposed phototransformation pathway is not supported by the results because the portions of this study conducted at pH 7 and 9 and were considered unacceptable and the portions of this study conducted

at pH 5 do not satisfy the requirement that photolysis be conducted at a pH which minimizes hydrolytic degradation.

D. SUPPLEMENTARY EXPERIMENT-RESULTS: Using molar absorptivities (ε_λ) at 290-400 nm (pp. 163-178), quantum yields (ϕ_{ts}) for diflufenzopyr were determined to be 7.98 x 10^{-5}, 4.48 x 10^{-5}, and 14.8 x 10^{-5} in pH 5, 7 and 9 solutions, respectively (pp. 31, 50).

III. STUDY DEFICIENCIES: The objective of this study was to investigate the degradation of diflufenzopyr in pH 5, 7 and 9 buffer solutions under artificial light conditions (p. 8). The experiments conducted using pH 7 and 9 buffer solutions cannot be used to fulfill Subdivision N Guideline §161-2 because formation of the compound P9 (proposed structure p. 28) was reportedly (p. 29) an artifact resulting from a reaction of diflufenzopyr with a component of the Trizma buffer solutions. The effect(s) of the buffer component on the rate of degradation of diflufenzopyr and/or formation of degradation products could not be determined. The experiment conducted in pH 5 buffer solution is scientifically valid, but can not fulfill Subdivision N Guideline §161-2 because hydrolytic degradation of diflufenzopyr is greatest at pH 5.

IV. REVIEWER'S COMMENTS:

1. This study does not fulfill Subdivision N Guidelines for aqueous photolysis. The formation of the compound P9 (proposed structure p. 28) in the pH 7 and 9 experiments was reportedly (p. 29) an artifact from a reaction of diflufenzopyr with a component of the Trizma buffer solutions. Therefore, the effect of the buffer on the formation of degradates and decline of the parent could not be determined. P9 was 11.0-13.36% of the applied radioactivity at pH 7 and 30.08-33.87% at pH 9 in both the irradiated and dark control [phenyl-U-^{14}C]diflufenzopyr solutions, and was <1.5% in all other test solutions.

2. The incubation temperature was 22 ± 1°C rather than the recommended 25 ± 1°C.

3. The study author reported the average light intensities of the xenon lamp were measured at 643 W/m^2 and 578 W/m^2 for the phenyl ring- and pyridine ring-labeled studies, respectively (p. 11). Although graphic representations of the measured light intensities were provided (pp. 53-54), the quantified results should be reported in tabular form.

4. Distance between the light source and the irradiated solutions was not reported. Also not reported was the distance from the light source where the light source intensity measurements were taken.

5. The current recommended seasonal application rate for diflufenzopyr was reported as 0.14-0.18 lb a.i./A (0.16-0.20 kg a.i./ha; p. 8).

V. REFERENCES: The following references were cited in the study:

1. Dulin, D. and T. Mill. 1982. Development and evaluation of sunlight actinometers. Environ. Sci. Technol. 16: 815-820.

2. Guirguis, A. and C. Yu. 1990. Hydrolysis of SAN-835 H. Sandoz Agro Inc. Project No. 414055. BASF Reg. Doc. No. 1990/5172.

3. Guirguis, A. and C. Yu. 1989. Determination of the water solubility for SAN-835 H. Sandoz Agro Inc. Project No. 414055-4. BASF Reg. Doc. No. 1989/5244.

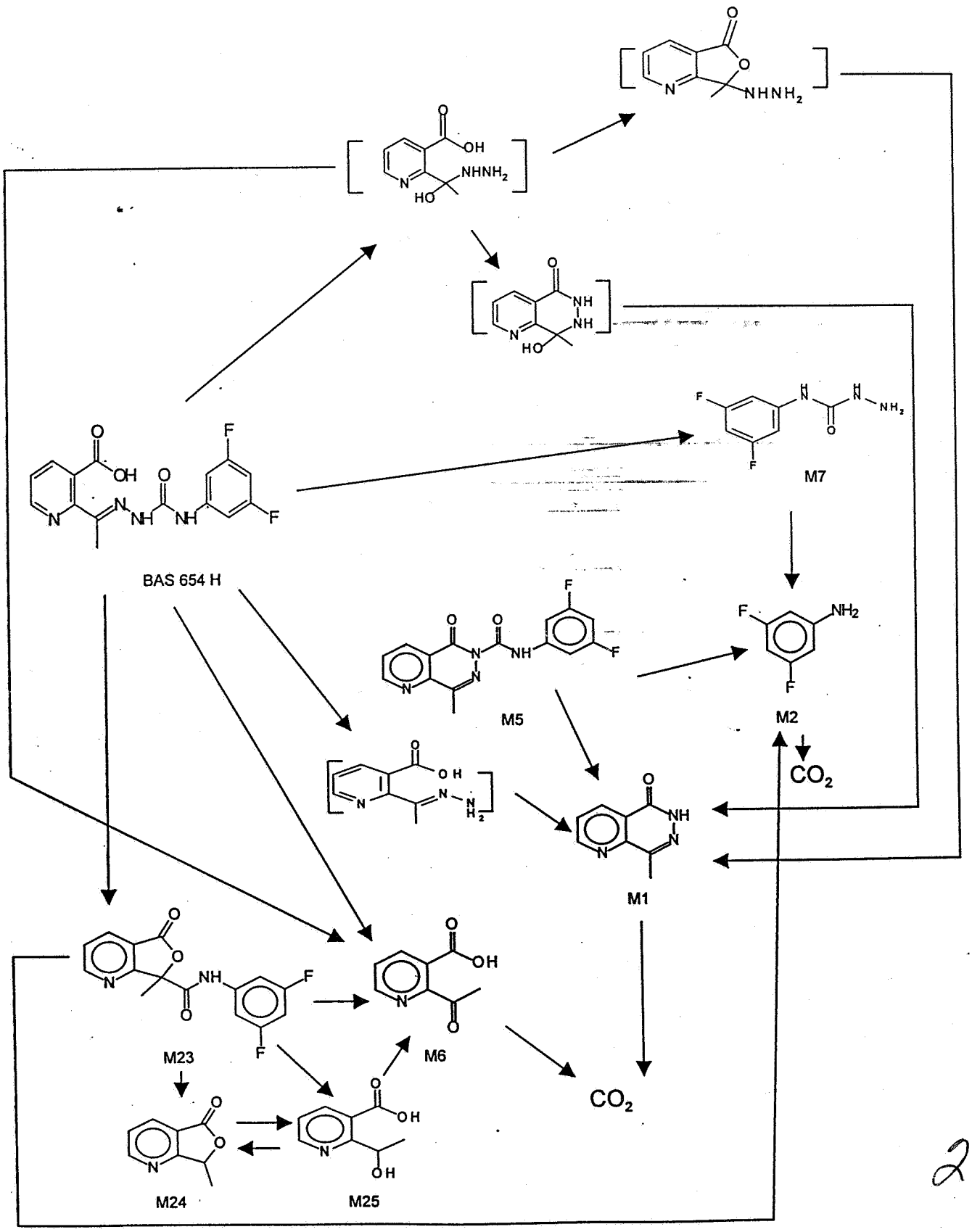
4. Singh, M. 2001. Aerobic soil metabolism of ^{14}C-BAS 654 H. Study No. 61198. BAS Reg. Doc. No. 2001/5000085.

5. Singh, M. 2000. Photolysis of ^{14}C-BAS 654 H on soil. Study No. 61359. BAS Reg. Doc. No. 2000/5267.

6. Yu, C. and S. Sherman. 1997. SAN 835 H: photodegradation study in aqueous solutions at pH 5, pH 7 and pH 9. Sandoz Agro Inc. Project No. 414205, Report No. 3. BASF Reg. Doc. No. 97/5096.

7. Zepp, R. and D. Cline. 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11: 359-366.

Figure 24. Proposed Photolysis Degradation Pathway for BAS 654 H.



26

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

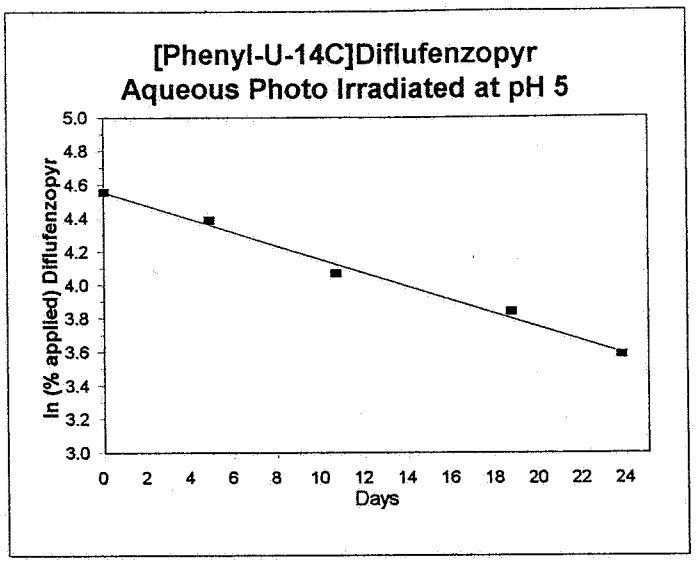
Irradiated
Phenyl-U-^{14}C in pH 5 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	95.05	4.554403
4.9	80.53	4.38863
10.7	58.56	4.070052
18.7	46.71	3.843958
23.8	36.07	3.585461

Regression Output:

Constant	4.556
Std Err of Y Est	0.044
R Squared	0.991
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.04024
Std Err of Coef.	0.002256

half-life 17.2 days



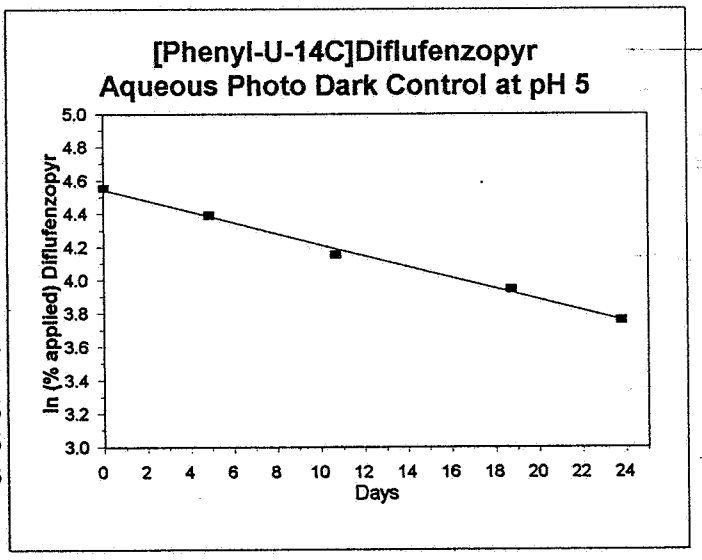
Dark Control
Phenyl-U-^{14}C in pH 5 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	95.05	4.554403
4.9	80.75	4.391358
10.7	63.60	4.152613
18.7	51.81	3.947583
23.8	42.97	3.760502

Regression Output:

Constant	4.544
Std Err of Y Est	0.027
R Squared	0.995
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.03294
Std Err of Coef.	0.001361

half-life 21.0 days



AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 7 and 13, pp. 41 and 47, respectively, of study report.

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

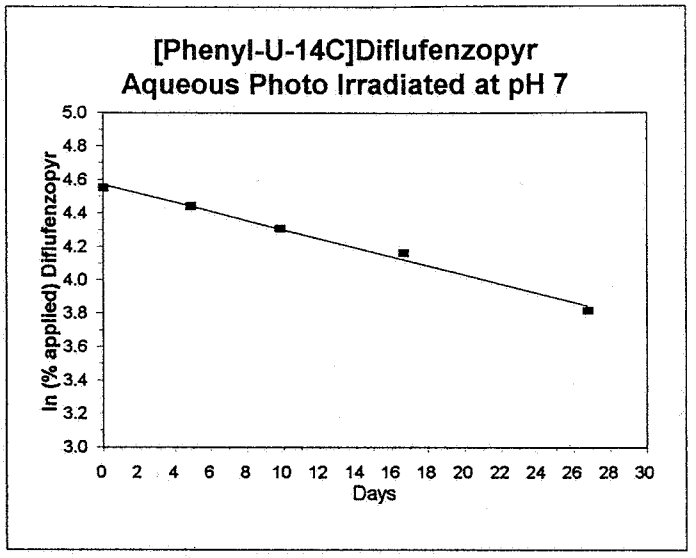
Irradiated
Phenyl-U-^{14}C in pH 7 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	94.87	4.552508
4.9	85.07	4.443474
9.8	74.37	4.309053
16.6	64.34	4.164182
26.7	45.59	3.819688

Regression Output:

Constant	4.572
Std Err of Y Est	0.032
R Squared	0.991
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.0271
Std Err of Coef.	0.001516

half-life 25.6 days



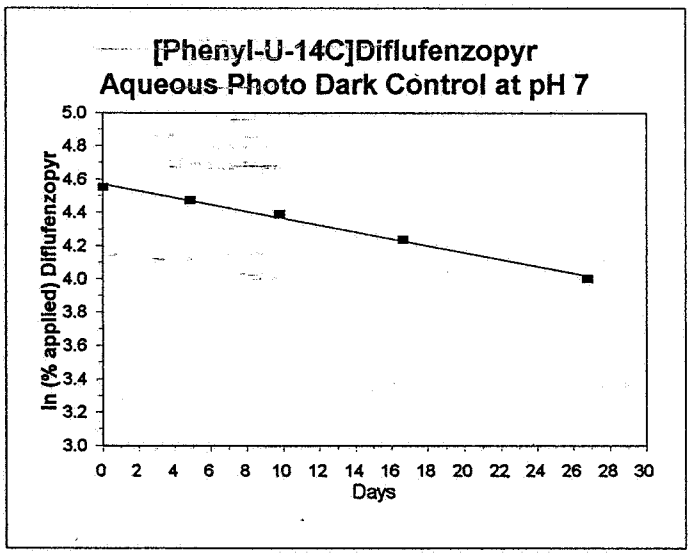
Dark Control
Phenyl-U-^{14}C in pH 7 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	94.87	4.552508
4.9	87.60	4.472781
9.8	80.71	4.390862
16.6	69.30	4.238445
26.7	54.85	4.004602

Regression Output:

Constant	4.572
Std Err of Y Est	0.02
R Squared	0.994
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.02064
Std Err of Coef.	0.000939

half-life 33.6 days



AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 8 and 13, pp. 42 and 47, respectively, of study report.

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

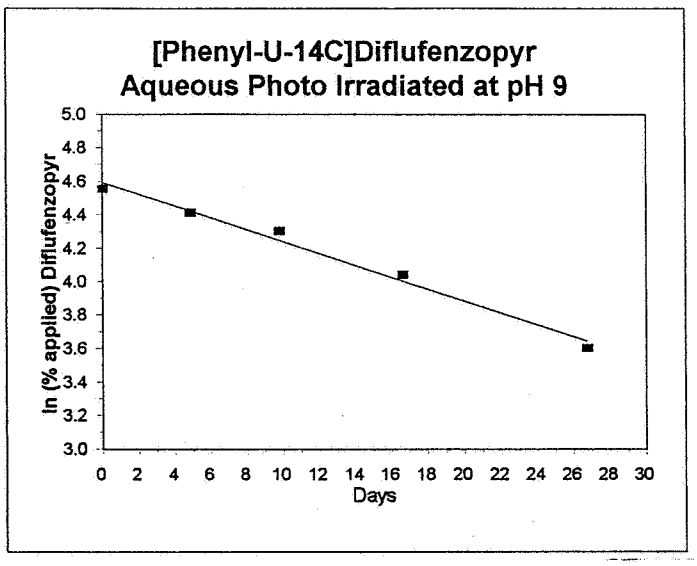
Irradiated
Phenyl-U-^{14}C in pH 9 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	95.05	4.554403
4.9	82.43	4.411949
9.8	73.93	4.303119
16.6	56.92	4.041647
26.7	36.80	3.605498

Regression Output:

Constant	4.595
Std Err of Y Est	0.051
R Squared	0.986
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.03545
Std Err of Coef.	0.00245

half-life 19.6 days



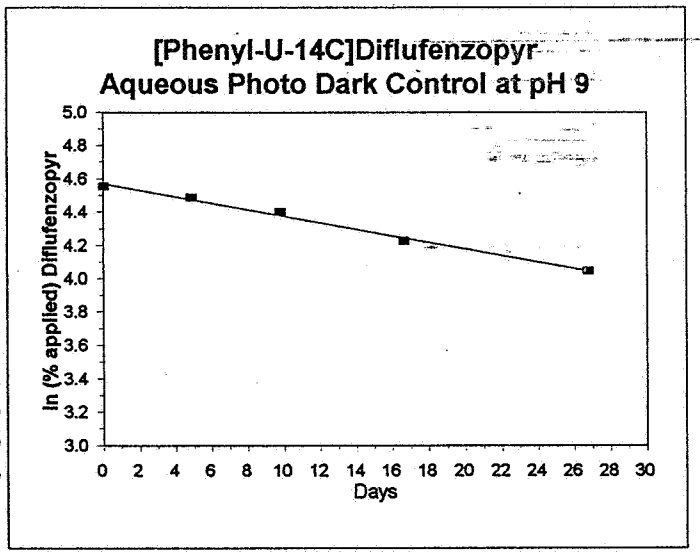
Dark Control
Phenyl-U-^{14}C in pH 9 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	95.05	4.554403
4.9	89.02	4.488861
9.8	81.57	4.401462
16.6	68.53	4.227272
26.7	57.24	4.047253

Regression Output:

Constant	4.572
Std Err of Y Est	0.02
R Squared	0.993
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.01964
Std Err of Coef.	0.000979

half-life 35.3 days

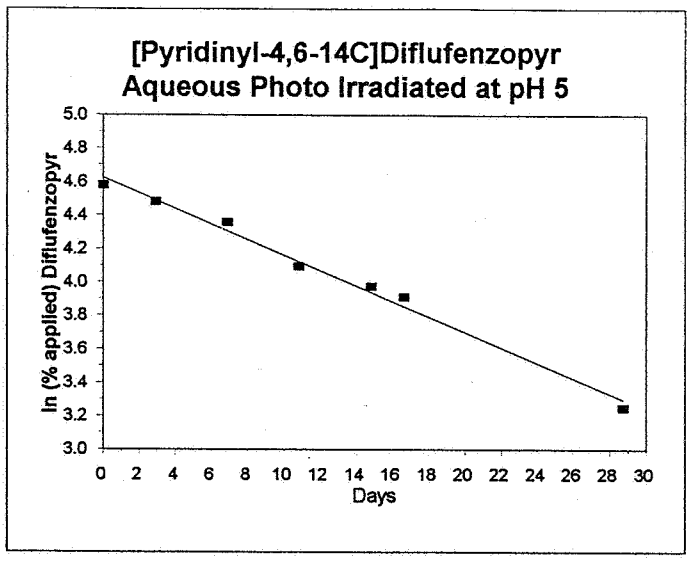


AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 9 and 13, pp. 43 and 47, respectively, of study report.

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

Irradiated
Pyridinyl-4,6-^{14}C in pH 5 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	97.42	4.579032
2.9	88.13	4.478813
6.9	78.08	4.357734
10.8	60.09	4.095843
14.8	53.49	3.979495
16.6	50.05	3.913023
28.7	25.80	3.250374



Regression Output:

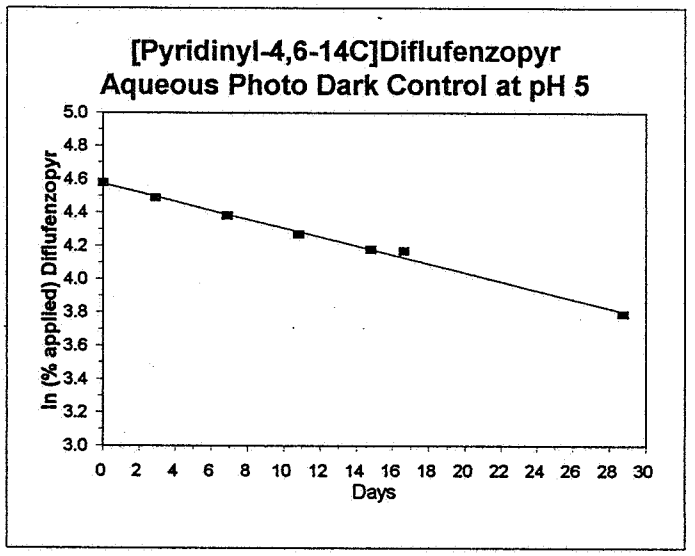
Constant	4.626
Std Err of Y Est	0.050
R Squared	0.990
No. of Observations	7
Degrees of Freedom	5

X Coefficient(s)	-0.04615
Std Err of Coef.	0.002112

half-life 15.0 days

Dark Control
Pyridinyl-4,6-^{14}C in pH 5 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	97.42	4.579032
2.9	88.92	4.487737
6.9	79.93	4.381151
10.8	71.53	4.270117
14.8	65.39	4.180369
16.6	64.73	4.170225
28.7	44.26	3.790081



Regression Output:

Constant	4.574
Std Err of Y Est	0.022
R Squared	0.994
No. of Observations	7
Degrees of Freedom	5

X Coefficient(s)	-0.02671
Std Err of Coef.	0.000915

half-life 25.9 days

AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 4 and 12, pp. 38 and 46, respectively, of study report.

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

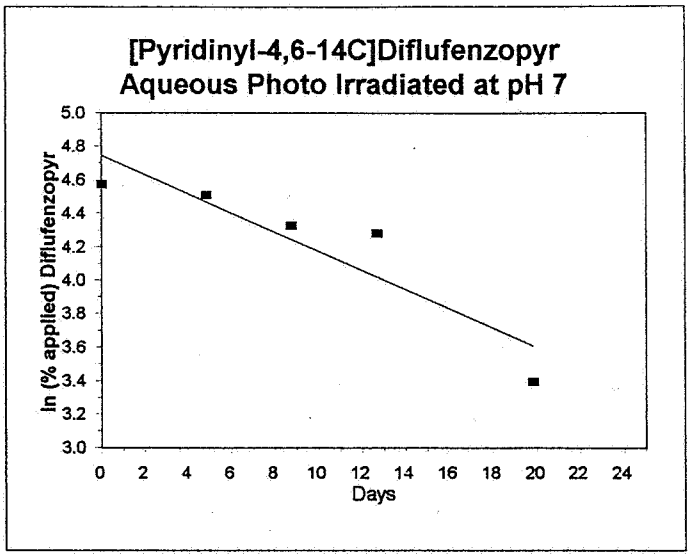
Irradiated
Pyridinyl-4,6-^{14}C in pH 7 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	96.86	4.573267
4.9	90.82	4.50888
8.8	75.76	4.32757
12.7	72.41	4.282344
19.8	29.83	3.395515

Regression Output:

Constant	4.746
Std Err of Y Est	0.226
R Squared	0.830
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.05723
Std Err of Coef.	0.014969

half-life 12.1 days



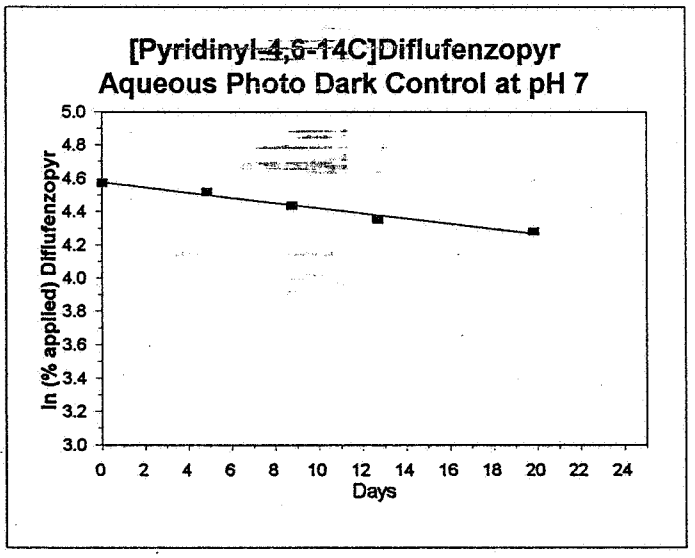
Dark Control
Pyridinyl-4,6-^{14}C in pH 7 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	96.86	4.573267
4.9	91.76	4.519176
8.8	84.32	4.434619
12.7	77.59	4.351439
19.8	72.31	4.280962

Regression Output:

Constant	4.576
Std Err of Y Est	0.021
R Squared	0.977
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.01558
Std Err of Coef.	0.001375

half-life 44.5 days



AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 5 and 12, pp. 39 and 46, respectively, of study report.

Diflufenzopyr (BAS 654 H) Photodegradation in Water
MRID 45444004

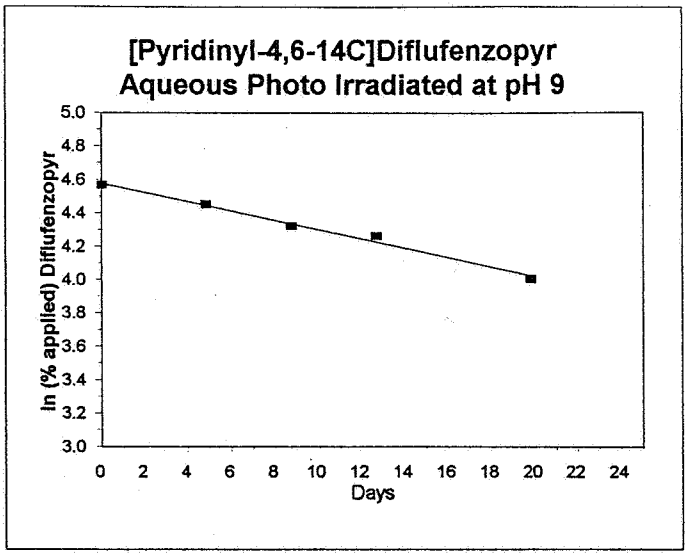
Irradiated
Pyridinyl-4,6-^{14}C in pH 9 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	96.38	4.568299
4.9	85.60	4.449685
8.8	75.33	4.321878
12.7	71.04	4.263243
19.8	55.21	4.011144

Regression Output:

Constant	4.578
Std Err of Y Est	0.026
R Squared	0.989
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.02766
Std Err of Coef.	0.001697

half-life 25.1 days



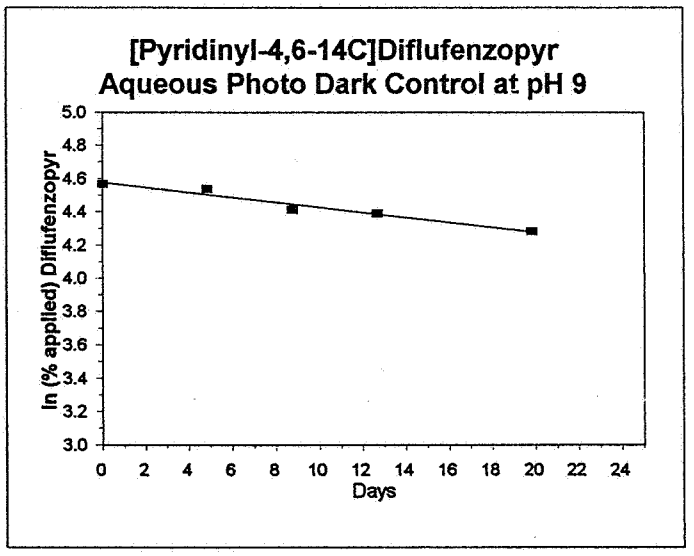
Dark Control
Pyridinyl-4,6-^{14}C in pH 9 buffer

Half-life		
Diflufenzopyr		
Day	% AR	Ln(% AR)
0.0	96.38	4.568299
4.9	93.56	4.538603
8.8	82.52	4.413041
12.7	80.60	4.389499
19.8	72.53	4.284

Regression Output:

Constant	4.577
Std Err of Y Est	0.028
R Squared	0.956
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	-0.01499
Std Err of Coef.	0.00185

half-life 46.2 days



AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8
Results from Tables 6 and 12, pp. 40 and 46, respectively, of study report.