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Data Evaluation Report on the phototransformation of prothioconazole (JAU6476) on soil

PMRA Submission Number 2004-0843 EPA MRID Number 46246510

Data Requirement:

PMRA DATA CODE:	8.2.3.3.1
EPA DP Barcode:	DP 303488
OECD Data Point:	IIA 7.1.3
US EPA Guideline:	OPPTS 835.2410; OPP§162-1

Test material:

Common name: Prothioconazole

IUPAC name: 2-[2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione

CAS name: 2-[2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione

CAS No: 178928-70-6

synonyms: JAU 6476 Technical

SMILES string: ClC1(C(Cc2ccccc2Cl)(CN2N=CNC2=S)O)CC1.

Primary Reviewer (officer number): Émilie Larivière (#1269) EAD, PMRA **Date:** June 1, 2005 6/1/05

Secondary Reviewer (officer number): Janine Glaser (#1009) EAD, PMRA **Date:** June 28, 2005

Secondary Reviewer(s) (officer number): Roxolana Kashuba (EPA/OPP/EFED/ERB4) **Date:** Aug. 22, 2005 8/22/05

Company Code BCZ
Active Code PRB
Use Site Category 7, 13, 14 (Industrial Oil Seed Crops and Fibre Crops, Terrestrial Feed Crops, Terrestrial Food Crops)
EPA PC Code 113961

CITATION: Gilges, M. 2001. Photolysis of JAU6476 on Soil Surface. Performing Laboratory: Bayer AG Crop Protection Business Group, Germany. Bayer CropScience, North Carolina. Unpublished. Report No. MR-242-00.

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EXECUTIVE SUMMARY

The phototransformation of [phenyl-UL-^{14}C]2-[2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione (prothioconazole; JAU6476; purity: >99%) was studied on loamy sand (pH 6.8, 0.79% organic carbon) from Byromville, Georgia (USA), at 1.4 mg a.i./kg soil (1 cm depth and bulk density of 1.5 g/cm^3) for 15 days at 20±1 °C and 75% of 1/3 bar moisture. The experiment was conducted in accordance with the US EPA-Guidelines for "Photodegradation Studies on Soil" 161-3 (1982) and SETAC Procedures, and in compliance with the German and OECD Good Laboratory Practice (GLP) standards. An amount of 200 µL of [phenyl-UL-^{14}C]prothioconazole was applied on the soil surface as small droplets using a microlitre syringe. The treated samples were irradiated under continuous simulated sunlight (Heraeus Suntest xenon light NXe 1500B with UV filter (λ > 290 nm)). The average light intensity was 747 W/m^2, comparable to midday midsummer sunlight at 40° N latitude. Test vessels were connected to traps filled with soda lime granules and fitted with a polyurethane foam plug for the collection of $^{14}CO_2$ and organic volatiles, respectively. Irradiated soil samples were collected at 0, 1.5 and 4 hours and 1, 3, 7 and 15 days. Dark control samples were collected at 1, 7 and 15 days. The soil samples were extracted three times with acetonitrile/water (80:20 v/v) to which cysteine hydrochloride was added to prevent oxidative degradation of the active ingredient. Volatile organic compounds were extracted with ethylacetate while $^{14}CO_2$ absorbed to the soda lime was liberated with HCl and purged into Liquid Scintillation cocktails with nitrogen. Extracts were analysed by Liquid Scintillation Counting (LSC) and parent and transformation products were identified with Reverse Phase-Thin Layer Chromatography (RP-TLC) and Normal Phase-TLC (NP-TLC). The non-extracted radioactivity was determined by combusting the post-extraction soil samples in an oxidiser with subsequent quantification by LSC.

The mass balance was 97.0 ± 3.3 % and 99.3 ± 4.3 % of the applied radioactivity in the dark and irradiated samples, respectively. At test termination, 19% of the applied radioactivity remained as parent in the dark samples. The major transformation product identified in the dark samples was JAU6476-desthio (SXX0665; (R,S) 2-(1-chlorocycloproyl)1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol), formed at a maximum of 29.4% of the applied radioactivity observed at study termination (15 days). The minor transformation products in the dark samples were JAU6476-triazolinone (WAK7860; 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-one) and an unidentified transformation product, Unknown 2, formed at a maximum of 3.2% and 1.1% of applied radioactivity, respectively, observed at study termination (15 days) and 7 days. Unknown2 decreased to below the MDL by study termination. The CO_2 and volatile organic compounds in the dark samples were below the limit of detection at all intervals sampled (CO_2 was sampled at 1, 7, and 15 days; VOCs were only sampled at 7 days).

In the irradiated samples, concentration of [phenyl-UL-^{14}C]prothioconazole decreased from 75.1% of the applied radioactivity on day 0 to 18.6% of the applied radioactivity at test termination. The major transformation product was JAU6476-desthio, detected at a maximum of

38.5% of the applied radioactivity on day 7 and decreasing to 38.1% of the applied radioactivity by study termination (day 15). The minor transformation products in the irradiated samples were JAU6476-triazolinone, JAU6476-sulfonic acid (JAU6726; 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-sulfonic acid), and unidentified transformation products Unknown1 and Unknown3, detected at a maximum of 2.5%, 3.0%, 1.4% and 3.1% of the applied radioactivity, respectively. In the irradiated samples, at the end of the study, the evolved CO_2 and volatile organic compounds amounted to 0.7% and 0.1% of the applied radioactivity, respectively. The quantity of JAU6476-desthio and JAU6476-triazolinone transformation products were similar in both dark and irradiated samples. Unknown2 was detected only in a dark sample, and not detected in irradiated sample. JAU6476-sulfonic acid, Unknown1 and Unknown3 were detected only in irradiated samples (albeit in small amounts). It appears that no significant transformation products are specifically generated by phototransformation on a soil surface.

Extracted [^{14}C]residues decreased from 85.2% of applied radioactivity at day 0 in both treatments to 62.6% and 70.4% of applied radioactivity at test termination, in the dark and irradiated samples, respectively. In the irradiated samples, non-extracted [^{14}C]residues increased from 8.4% of the applied radioactivity at day 0 to 25.5% of the applied radioactivity by study termination. Non-extracted [^{14}C]residues in the dark samples increased from 8.4% of the applied radioactivity at day 0 to a maximum of 36.5% of the applied radioactivity on day 7 and decreased to 26.4% of the applied radioactivity at study termination. No phototransformation pathway was proposed.

The half-lives of [phenyl-UL-^{14}C]prothioconazole in the dark and irradiated samples were 7.8 and 8.6 days, respectively, calculated using linear regression on ln-transformed data. The half-life for phototransformation (the difference between irradiated and dark samples, calculated by EPA by subtracting rate constants calculated from linear regression on ln-transformed data) could not be calculated because the transformation rate constant was greater for the dark samples than for the irradiated samples (ie., mathematically, [phenyl-UL-^{14}C]prothioconazole transformed faster in the dark samples than in the irradiated samples). Essentially, the half-lives are very similar between treatments, confirming that phototransformation is not an important route of dissipation for prothioconazole in soil. It is likely that the dissipation in the irradiated samples was microbially mediated, as opposed to being driven by phototransformation.

The predicted environmental phototransformation half-life of [phenyl-UL-^{14}C]prothioconazole could not be calculated as the rate constant for phototransformation corrected for natural sunlight in New York and Edmonton was also less than that for the dark samples.

Results Synopsis

Soil type:	loamy sand
Source of irradiation:	Xenon lamp with UV filter ($\lambda > 290$ nm)
Half-life in dark controls:	7.8 days

Half-life in irradiated samples: 8.6 days
Half-life for phototranformation: Not applicable
(Similar rates of transformation for dark and irradiated samples;
photransformation rate does not appear to affect overall transformation rate on soil).

In dark controls:
Major transformation products: JAU6476-desthio
Minor transformation products: JAU6476-triazolinone, Unknown2

In irradiated samples:
Major transformation products: JAU6476-desthio
Minor transformation products: JAU6476-triazolinone, JAU6476-sulfonic acid, Unknown1, Unknown3

Study Acceptability: This study is classified acceptable for a study on phototransformation on soil.

I. MATERIALS AND METHODS

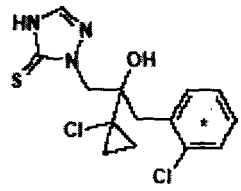
GUIDELINE FOLLOWED: EPA-Guidelines for "Photodegradation Studies on Soil" 161-3 (1982) and SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995). No deviations were reported.

COMPLIANCE: This study was conducted in compliance with German (Chemikaliengesetz, attachment 1, dated 1994/1997) and OECD (1997) GLP. Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided.

A. MATERIALS:

1. Test Material [phenyl-UL-^{14}C]prothioconazole (p. 9)

Chemical Structure:



* indicates the position of the radiolabel.

Description: Technical, solid, dried *in vacuo* (p. 9)

Purity: Analytical purity: >99%
Lot No. 13094/1
Purity Protocol (Batch ID) THS4986
Radiochemical purity: >99%
Specific activity: 2.77 MBq/mg
Locations of the radio label: phenyl ring

Storage conditions of test chemicals: As cool as possible until application (Appendix 2, p. 24)

Table 1: Physico-chemical properties of prothioconazole.

Parameter	Values	Comments
Water solubility (20°C)	pH / Solubility (mg/L) 4 / 5 8 / 300 9 / 2000	low solubility at acidic pH, very soluble at alkaline pHs.
Vapour pressure/volatility	Temperature (°C) / Vapour pressure(Pa) 20 / $<<4 \times 10^{-7}$ 25 / $<<4 \times 10^{-7}$	relatively non-volatile under field conditions.
UV absorption	peak maxima at 275 nm. No absorption at > 300 nm.	Phototransformation is not expected to be an important route of transformation
pK_a	$pK_a = 6.9$	Weak acid, anion at neutral and alkaline pHs
log K_{ow}	pH / log K_{ow} 4 / 4.16 7 / 3.82 9 / 2.0 unbuffered / 4.05	Potential for bioaccumulation at neutral and acidic pH.
Stability of compound at room temperature, if provided	Thermally stable at room temperature under air. Stable to most metals. Colour changes observed in the presence of copper materials.	Thermally stable at room temperature under air.

Data were obtained from Chemistry Review.

2. Soil Characteristics:

Table 2: Field information and handling procedures.

Information	Details
Geographic location	Byromville, Georgia, USA
Pesticide use history at the collection site	None
Collection procedures	Not reported.
Sampling depth (cm)	0-15.2 cm (0-6 inches)
Storage conditions	The soil was stored in a climatic board at about 5°C (p.9), and/or at ambient temperatures, not closed air-tight (Appendix 4, p. 26).
Storage length	January 26, 1998 - June 21, 1999 (pp. 8-9)
Soil preparation (eg: 2 mm sieved; air dried etc.)	Stones and plants were removed and soil was air-dried and screened to ≤2 mm.

Data obtained from p. 9, Appendix 4, p. 26.

Table 3: Properties of the soil.

Property	Details	
Soil texture (USDA)	loamy sand	
% sand	86.8	
% silt	7.6	
% clay	5.6	
pH (in water)	6.8	
pH (in $CaCl_2$)	6.1	
Organic carbon (%)	0.79	
Organic matter (%)	1.36	
CEC (meq/100 g CM)	4.3	
Moisture at 1/3 atm / Water holding capacity (g/100 g dry matter)	4.8	
Bulk density (g/cm^3)	1.59	
Microbial biomass (mg microbial carbon/kg soil)	Initial	Final
	51	Not reported
Soil Taxonomic classification	Loamy, siliceous, thermic Arenic Kandiudults	
Soil mapping unit (for EPA)	Not reported	

Data obtained from p. 16, Appendix 4, p. 26.

3) **Details of light source:** Details of the artificial light source are provided in Table 4.

Table 4: Artificial light source.

Property	Details
Type of lamp used	irradiation cabinet Suntest (Heraeus Original Hanau) with Xenon lamp NXe 1500B
Emission wavelength spectrum	280-830 nm
Light intensity	average of 747 W/m^2
Filters used	UV glass filter system cutting off wavelengths below 290 nm.
Relationship to natural sunlight	Comparable to global daylight radiation. Fifteen days of continuous irradiation is equal to 53.9 days of natural sunlight (solar summer days in June) in Phoenix, USA, 77.3 days of natural sunlight (solar summer days in June) in New York, USA, 83.6 days of sunlight (solar summer days in June) in Athens, Greece and 76.3 days of natural sunlight (solar summer days in June) in Edmonton, Canada

Data obtained from pp. 12, 16, Appendix 6, p. 28, Appendix 9, p. 31.

B. EXPERIMENTAL DESIGN

1) Preliminary Study: No preliminary studies were described.

2) Experimental Design

Table 5: Experimental design.

Parameter		Details
Duration of the test		15 days
Condition of soil:	Air dried/fresh:	air-dried, moisture adjusted to 75% of the 1/3 bar water holding capacity
	Sterile/Non-sterile:	Non-sterile
Test concentrations (mg a.i/kg soil) dark irradiated		Nominal: 4 µg ai./3 g dry soil (200 g ai/ha, at 1 cm depth and bulk density of 1.5 g/cm^3) Measured: 4.2 µg ai./3 g dry soil; equivalent to 1.4 mg ai/kg dry soil
Dark controls used (Yes/No) Is it foil wrapped and kept in darkness?		Yes; control samples were kept in a dark room, but not foil wrapped.
Replications	Dark control:	1 vessel per sampling interval

	Irradiated:	2 vessels per sampling interval
Identity and concentration of co-solvent:		acetonitrile/water (50:50, v:v)
Pesticide application	Volume of test solution used/treatment:	200 µL
	Method of application (eg., spraying):	Small droplets of application solution were applied to the soil in the test vessels using microlitre syringe.
	Is the co-solvent evaporated:	Yes
Test apparatus: Type/Material/Volume		Glass vessels with quartz glass lid and trap attachments for volatile organic products and CO_2.
Details of traps for volatile, if any		Trap attachments were filled with soda lime for absorption of CO_2 and fitted with a polyurethane foam plug for absorption of volatile organic transformation products. Trap attachments are permeable to oxygen.
If no traps were used, is the system closed/open		No traps were used for day 0 samples, but the production of volatiles on day 0 was not expected or measured.
Any indication of the test material adsorbing to the walls of the test apparatus		No
Experimental Conditions	Temperature: Temperature maintenance method:	20±1 °C; Suntest cooling platform connected to cryostat. Temperatures were continuously monitored by a temperature probe connected to a data logger.
	Moisture content: Moisture maintenance method	75 % of 1/3 bar water holding capacity. Soil moisture was measured by weighing at each sampling date, but no data reported.
	Duration of light/darkness:	Continuous irradiation for irradiated samples; darkness for controls.
Other details, if any		

Data obtained from pp. 10-11.

3) Supplementary experiments: No supplementary experiments were described.

4) Sampling:

Table 6: Sampling details.

Criteria	Details
Sampling intervals of soil samples	Irradiated samples: 0, 1.5 and 4 hours and 1, 3, 7 and 15 days Dark Controls: 1, 7 and 15 days

Sampling method	Entire vessel was processed at each sampling interval.
Method of sampling CO_2 and volatile organic compounds, if any	Prior to opening the incubation vessels, volatile compounds possibly still present in the vessel were transferred into the trap attachment by purging with humid air for 5 minutes.
Sampling intervals/times for: Sterility check, if any Moisture content:	 n/a (not sterile; microbial biomass was determined prior to study initiation) moisture was checked at every sampling interval
Sample storage before analysis	Extracts were analyzed no later than on the day after preparation. Traps were stored in the freezer until processing. Analyzed extracts were stored in the freezer for further investigations if necessary.
Other observations, if any	

Data obtained from pp. 12-13.

C. ANALYTICAL METHODS

Extraction/clean up/concentration methods: The soil was extracted immediately after sampling. The total soil portion of each test vessel was transferred into a centrifuging beaker and extracted three times at room temperature on a shaker with 3 mL of acetonitrile/water (80:20, v/v), and 1 g/L cysteine hydrochloride to prevent oxidative degradation of the active ingredient. After shaking an unreported number of minutes, the solution was centrifuged for 15 min and the clear supernatant decanted. The extraction efficiency on Day 0 was 85.2% of the applied radioactivity (p.17).

Non-extractable residue determination: The non-extracted radioactivity was determined by combusting the extracted soil samples in an oxidizer with subsequent quantification by LSC.

Total ^{14}C measurement: The radioactivity in solution was measured by LSC.

Derivatization method, if used: Not applicable.

Identification and quantification of parent compound and transformation products: Soil chromatographic analyses of soil extracts by RP-TLC were performed no later than on the day after preparation. The solutions were Analyzed directly without enrichment or conditioning. Aliquots of 100 µL of extracts were spotted as bands of 10 mm width on reversed phase RP-18 plates of 200 mm height, F-254 coated (Merck) using an automatic plate spotter (Linomat IV, Camag) at 20 mm from the edge. The plates were developed in a glass tank using the following solvent system: MeCN/water/MeOH (70:25:5, v/v/v) containing 1 mL/L glacial acetic acid and 1 g/L cysteine · HCl (to prevent degradation of the active ingredient). In addition, 10 µL of a

solution containing 1 mg/mL non-radiolabelled prothioconazole and 1 g/L cysteine · HCl were spotted on the plate prior to spotting the sample.

The radioactive zones were visualized and quantified by digital autoradiography of the thin-layer plates by Bio-Imaging Analyser Fujix BAS 2000 (Fuji Co.) and evaluated by TINA software (Version 2.09G, Raytest). The co-chromatographed spots of the non-radioactively labelled reference compounds were detected by means of a UV chamber (Camag) at 254 nm.

The agreement of the R_f value of the radioactive zone in the soil extracts with that of the co-chromatographed reference was considered to be indicative of the identity of a substance in a radioactive zone.

NP-TLC analysis was used to confirm results obtained by the primary RP method. Aliquots of 100 µL of extracts were spotted as bands of 10 mm width on silica gel 60 plates of 200 mm height, F-254 coated (Merck) using an automatic plate spotter (Linomat IV, Camag) at 20 mm from the edge. The plates were developed in a saturated glass tank using dichloromethane/methanol/ aqueous ammonia (25%) (90:10:1, v/v/v. Again, 10 µL of a solution containing 1 mg/mL non-radiolabelled prothioconazole and 1 g/L cysteine · HCl were spotted on the plate prior to spotting the sample.

High Performance Liquid Chromatography (HPLC) was employed for purity control of the active ingredient in the stock solution and application solution.

Detection limits (LOD, LOQ) for the parent compound and the transformation products: The limit of detection (LOD) for RP-TLC analyses was 1.0% of the applied radioactivity, equivalent to14 µg/kg.

Volatile compounds: Any volatile organic compounds in the polyurethane plugs were extracted with ethylacetate and radioassayed by LSC. The $^{14}CO_2$ absorbed by the soda lime was quantified by LSC.

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS:

Moisture data were not provided, but the study author claims that the soil moisture was measured by weighing at each sampling date (p. 11). Losses of weight due to evaporation of soil moisture were reported to be negligible (p. 16).

Soil temperature averaged 19.9 °C (range: 18.9-22.5 °C) in the irradiated samples and 20.5 °C (range: 20.1-21.0 °C) in the dark controls (p. 27).

B. MASS BALANCE: The mass balance was 97.0 ± 3.3 % (range of 92.9-101.0% in single replicates) and 99.3 ± 4.3 % (range of 92.9-109.2% in single replicates) of the applied

radioactivity in the dark and irradiated samples, respectively. At test termination, 19% of the applied radioactivity remained as parent in the dark samples.

Table 7: Phototransformation of [phenyl-UL-^{14}C]prothioconazole, expressed as percentage of applied radioactivity (mean ± s.d.; n=2 for irradiated samples, n = 1 for dark controls), on soil.

Compound		Sampling times (days)						
		0	0.06	0.17	1	3	7	15
Parent compound	irradiated	75.1 ± 0.8	56.2 ± 6.8	50.1 ± 4.7	35.8 ± 1.6	28.9 ± 2.8	20.0 ± 2.2	18.6 ± 4.2
	dark		n.m.	n.m.	39.0	n.m.	21.4	19.0
JAU6476-desthio	irradiated	3.9 ± 0.6	20.6 ± 1.8	25.0 ± 1.8	31.3 ± 0.1	34.2 ± 2.5	38.5 ± 0.3	38.1 ± 1.3
	dark		n.m.	n.m.	21.6	n.m.	25.4	29.4
JAU6476-triazolinone	irradiated	n.d.	<1	1.2 ± 0.1	1.7 ± 0.3	2.0 ± 0.2	2.5 ± 0.3	2.5 ± 0.2
	dark		n.m.	n.m.	1.6	n.m.	2.1	3.2
JAU6476-sulfonic acid	irradiated	<1	<1	1.2 ± 0.1	1.3 ± 0.1	2.4 ± 0.4	2.6 ± 0.0	3.0 ± 0.9
	dark		n.m.	n.m.	<1	n.m.	<1	<1
Unknown Transformation product 1	irradiated	n.d.	n.d.	n.d.	n.d.	n.d.	<1	1.4 ± 0.4
	dark		n.m.	n.m.	n.d.	n.m.	n.d.	n.d.
Unknown Transformation product 2	irradiated	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	dark		n.m.	n.m.	n.d.	n.m.	1.1	n.d.
Unknown Transformation product 3	irradiated	n.d.	n.d.	n.d.	<1	1.5 ± 0.3	3.1 ± 0.0	2.0 ± 0.8
	dark		n.m.	n.m.	n.d.	n.m.	n.d.	n.d.
Unidentified (origin and diffuse radioactivity)	irradiated	6.2 ± 0.1	8.3 ± 0.3	8.3 ± 1.0	6.6 ± 0.2	7.4 ± 0.1	6.1 ± 0.3	5.0 ± 0.4
	dark		n.m.	n.m.	3.6	n.m.	5.2	3.9
Total extracted residues	irradiated	85.2 ± 1.4	86.7 ± 4.5	85.6 ± 7.4	77.4 ± 1.2	76.2 ± 0.0	73.4 ± 1.4	70.4 ± 1.7
	dark		n.m.	n.m.	74.5	n.m.	61.7	74.5
Non-extracted residues	irradiated	8.4 ± 0.3	16.9 ± 0.2	19.1 ± 1.2	22.0 ± 1.8	22.6 ± 0.1	23.9 ± 0.9	25.5 ± 0.4

	dark		n.m.	n.m.	26.4	n.m.	36.5	26.4
CO_2	irradiated	n.m.	<0.1	0.1	<0.1	0.1 ± 0.0	0.5 ± 0.1	0.7 ± 0.2
	dark		n.m.	n.m.	<0.1	n.m.	0.1	<0.1
Volatile organic compounds	irradiated	n.m.	<0.1	<0.1	<0.1	<0.1	0.1 ± 0.0	0.1 ± 0.0
	dark		n.m.	n.m.	n.m.	n.m.	<0.1	n.m.
Total % recovery	irradiated	93.7 ± 1.1	103.7 ± 4.3	104.7 ± 6.3	99.6 ± 0.6	99.0 ± 0.1	97.9 ± 0.5	96.7 ± 1.9
	dark		n.m.	n.m.	100.9	n.m.	98.3	98.3

n.d. = not detected (LOD = 1 % of the AR; p. 15); n.m. = not measured

Data obtained from p.11, Appendices 13 and 14, pp.35 and 36 of the study report.

C. TRANSFORMATION OF PARENT COMPOUND: At test termination, 19% of the applied radioactivity remained as parent in the dark samples. The major transformation product identified in the dark samples was JAU6476-desthio (SXX0665; (R,S) 2-(1-chlorocycloproyl)1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol), formed at a maximum of 29.4% of the applied radioactivity observed at study termination (15 days). The minor transformation products in the dark samples were JAU6476-triazolinone (WAK7860; 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-one) and an unidentified transformation product, Unknown 2, formed at a maximum of 3.2% and 1.1% of applied radioactivity, respectively, observed at study termination (15 days) and 7 days. Unknown2 decreased to below the MDL by study termination. The CO_2 and volatile organic compounds in the dark samples were below the limit of detection at all intervals sampled (CO_2 was sampled at 1, 7, and 15 days; VOCs were only sampled at 7 days).

In the irradiated samples, concentration of [phenyl-UL-^{14}C]prothioconazole decreased from 75.1% of the applied radioactivity on day 0 to 18.6% of the applied radioactivity at test termination.

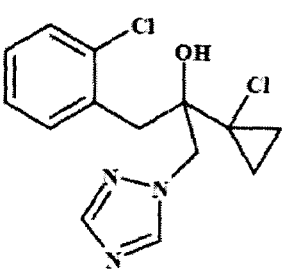
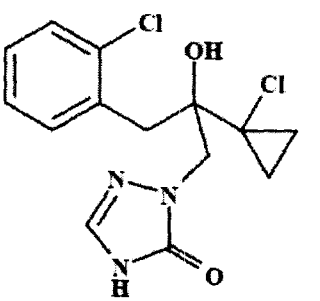
The major transformation product formed in the irradiated samples was JAU6476-desthio, detected at a maximum of 38.5% of the applied radioactivity on day 7 and decreasing to 38.1% of the applied radioactivity by study termination (day 15). The minor transformation products in the irradiated samples were JAU6476-triazolinone, JAU6476-sulfonic acid (JAU6726; 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-sulfonic acid), and unidentified transformation products Unknown1 and Unknown3, detected at a maximum of 2.5%, 3.0%, 1.4% and 3.1% of the applied radioactivity, respectively. In the irradiated samples, at the end of the study, the evolved CO_2 and volatile organic compounds amounted to 0.7% and 0.1% of the applied radioactivity, respectively. Total unidentified radioactivity (sum of diffuse radioactivity and that attributed to the origin) was a maximum of

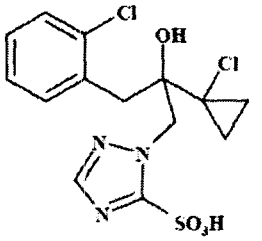
12.0% and 8.4% of the applied radioactivity in the dark and irradiated samples, at 1.5 hours and 1 day, respectively. The quantity of JAU6476-desthio and JAU6476-triazolinone transformation products were similar in both dark and irradiated samples. Uknown2 was detected only in a dark sample, and not detected in irradiated sample. JAU6476-sulfonic acid, Unknown1 and Unknown3 were detected only in irradiated samples (albeit in small amounts). It appears that no significant transformation products are specifically generated by phototransformation on a soil surface.

NON-EXTRACTABLE AND EXTRACTABLE RESIDUES: Extracted [^{14}C]residues decreased from 85.2% of applied radioactivity at day 0 in both treatments to 62.6% and 70.4% of applied radioactivity at test termination, in the dark and irradiated samples, respectively. In the irradiated samples, non-extracted [^{14}C]residues increased from 8.4% of the applied radioactivity at day 0 to 25.5% of the applied radioactivity by study termination. Non-extracted [^{14}C]residues in the dark samples increased from 8.4% of the applied radioactivity at day 0 to a maximum of 36.5% of the applied radioactivity on day 7 and decreased to 26.4% of the applied radioactivity at study termination.

PATHWAY: Phototransformation is not an important route of transformation for prothioconazole on soil. No phototransformation pathway was proposed.

Table 8: Chemical names and CAS numbers and chemical structures for the transformation products of prothioconazole.

Applicant's Code Name	CAS Number	CAS and/or IUPAC Chemical Name(s)	Chemical Structure
JAU6476-desthio (SXX0665)	120983-64-4	(R,S) 2-(1-chlorocycloproyl)1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol	
JAU6476-triazolinone (WAK7860)	Not reported	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-one	

JAU6476-sulfonic acid (JAU6726)	Not reported	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-sulfonic acid	

HALF-LIFE: The dissipation observed in the dark controls was as fast as with light exposed samples. This result, as well as similarities in the identity and quantity of transformation products in the dark and irradiated samples indicate that phototransformation is not an important route of transformation for prothioconazole on soil. The dissipation appears to be biphasic, indicating that it may likely microbially mediated, as opposed to being driven by phototransformation. An increase in bound residues over time was also noted in both treatments.

The half-lives of [phenyl-UL-^{14}C]prothioconazole in the dark and irradiated samples were 7.8 and 8.6 days, respectively, calculated using linear regression on ln-transformed data. The estimated first-order half-lives half-lives of [phenyl-UL-^{14}C]prothioconazole in the dark and irradiated samples were 8.9 and 8.7 days, respectively, calculated by PMRA using using linear regression on ln-transformed data. The half-life for phototransformation (the difference between irradiated and dark samples, calculated by EPA by subtracting rate constants calculated from linear regression on ln-transformed data) could not be calculated because the transformation rate constant was greater for the dark samples than for the irradiated samples (ie., mathematically, [phenyl-UL-^{14}C]prothioconazole transformed faster in the dark samples than in the irradiated samples). Essentially, the half-lives are very similar between treatments, confirming that phototransformation is not an important route of dissipation for prothioconazole in soil. It is likely that the dissipation in the irradiated samples was microbially mediated, as opposed to being driven by phototransformation.

The predicted environmental phototransformation half-life of [phenyl-UL-^{14}C]prothioconazole could not be calculated as the rate constant for phototransformation corrected for natural sunlight in New York and Edmonton was also less than that for the dark samples.

Table 9a: Half-lives calculated by reviewers

Test system	First-order half-life		
	half-life (days)	Regression equation	r^2
Dark	7.8	y = -0.0883x + 4.0677	0.7607
Irradiated	8.6	y = -0.0803x + 3.8853	0.6839

Table 9b: DT_{50} values calculated by PMRA

Test system	DT_{50} (days) observed by linear interpolation	DT_{90} (days) observed by linear interpolation
Dark	1.25	>15
Irradiated	0.8	>15

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

III. STUDY DEFICIENCIES: Only the phenyl label was used in this study. The triazole label was not used in this study, which does not allow for the tracking of the 1,2,4-triazole degradate, a potentially toxic degradate. Although no significant difference between the phenyl and the triazole label was found in the soil biotransformation study (p. 7; [2]), 1,2,4-triazole is a transformation product detected in samples treated with the triazole label in soil and aquatic biotransformation studies. A study with the triazole label may be required at a later time. However, this study is classified acceptable for a study on phototransformation on soil.

IV. REVIEWER'S COMMENTS:

(1) Prothioconazole dissipated rapidly in both the irradiated samples and the dark controls. The similarity between the half-lives, as well as the identity and quantity of transformation products in the dark and irradiated samples indicate that phototransformation is not an important route of transformation for prothioconazole on soil. It is likely that differences observed between the dark and irradiated samples can be explained by natural variability due to metabolism.

(2) Only four sampling points were available to calculate the half-life in the dark controls, compared to the 14 data points available of the irradiated samples. In addition, there was only one replicate per sampling interval in the dark controls. It is preferred that two or more samples be collected from each treatment interval, so that within sample variation can be quantified.

(3) The soils were extracted only with 80:20 acetonitrile/water and 1 g/L cysteine hydrochloride (unreported number of minutes shaking, 15 minutes centrifugation, 3 times), resulting in extraction efficiency of 82.5%. It is difficult to know whether the radioactive material unextracted from the soil has become a bound, organic part of the soil or whether it has not been extracted harshly enough or for a long enough time.

(4) Metabolite Unknown2 was present in dark samples and not irradiated samples– this calls into question the assumption that irradiated samples are soil metabolism plus photolysis and dark samples are just soil metabolism. Irradiated samples should contain everything in the dark samples in addition to anything else produced by photolysis. A potential explanation is that the

Unknown2 metabolite is produced by soil metabolism and gets so quickly photolyzed that it is not captured in measures of the irradiated samples.

(5) It is not clear whether irradiated samples or dark controls were moistened at any time other than the beginning of the experiment. All conditions except irradiation status should have been similar in both dark and irradiated soils so that differences between dark and irradiated samples can be attributed only to photodegradation. Moisture content optimal for microbial degradation should have been maintained in both dark and irradiated samples. Lack of moisture control and, hence, lack of consistency in microbial degradation processes may be a reason why there were small amounts of different minor degradates detected in dark and irradiated samples. Moisture data were not provided to confirm or deny this potential explanation.

(6) Dark controls were not wrapped in foil in order to ensure no uv light penetration.

(7) Microbial mass at end of test not provided (only at beginning: 51 mg microbial carbon/kg soil; p. 16).

(8) Data on pH were not reported for intervals other than prior to starting the test (6.3; p. 16).

V. REFERENCES:

1 Federal Register, Part II EPA 40 CFR Parts 796, 797, and 798 Toxic Substances Control Act Test Guidelines; Final Rules, Friday September 27, 1985, p. 39318.

2 Hellpointner, E. 2001. Proazolthion (proposed) [JAU6476]: Degradation and Metabolism of JAU6476 in Aerobic Soils. Performing Laboratory: Bayer AG Crop Protection Business Group, Germany. Bayer CropScience, North Carolina. Unpublished. Report No. MR-104/01. July 25, 2001.

Chemical: Prothioconazole
PC Code: 113961
MRID: 46246510
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Table 7 Phototransformation of [phenyl-UL-C^{14}]prothioconazole on Byromville silt loam (irradiated samples), expressed as percentage of the applied radioactivity.

Time			-triazo-	-sulfonic	un-	un-	un-	Unidentified		Uniden.	Total	Non-			
(days)	JAU6476	-desthio	linone	acid	known1	known2	known3	Origin	Diffuse	Total	extracted	extracted	CO2	VOCs	**Total**
0	74.5	3.4	<MDL	<MDL	<MDL	<MDL	<MDL	2.8	3.4	6.2	84.2	8.6	N/A	N/A	92.9
0	75.6	4.3	<MDL	<MDL	<MDL	<MDL	<MDL	2.6	3.5	6.1	86.3	8.2	N/A	N/A	94.4
AVG	75.1	3.9	<MDL	<MDL	<MDL	<MDL	<MDL	2.7	3.5	6.2	85.2	8.4	N/A	N/A	93.7
STDEV	0.8	0.6	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1	0.1	1.4	0.3	N/A	N/A	1.1
0.06	61.0	19.3	<MDL	<MDL	<MDL	<MDL	<MDL	3.7	4.5	8.2	89.9	16.7	<MDL	<MDL	106.7
0.06	51.4	21.9	<MDL	<MDL	<MDL	<MDL	<MDL	3.9	4.7	8.6	83.6	17.0	<MDL	<MDL	100.7
AVG	56.2	20.6	<MDL	<MDL	<MDL	<MDL	<MDL	3.8	4.6	8.4	86.7	16.9	<MDL	<MDL	103.7
STDEV	6.8	1.8	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1	0.3	4.5	0.2	<MDL	<MDL	4.3
0.17	53.4	26.3	1.1	1.2	<MDL	<MDL	<MDL	3.7	5.3	9.0	90.8	18.2	0.1	0.1	109.2
0.17	46.8	23.7	1.2	1.1	<MDL	<MDL	<MDL	3.4	4.2	7.6	80.3	19.9	<MDL	<MDL	100.3
AVG	50.1	25.0	1.2	1.2	<MDL	<MDL	<MDL	3.6	4.8	8.3	85.6	19.1	<MDL	<MDL	104.7
STDEV	4.7	1.8	0.1	0.1	<MDL	<MDL	<MDL	0.2	0.8	1.0	7.4	1.2	<MDL	<MDL	6.3
1	36.9	31.4	1.5	1.2	<MDL	<MDL	<MDL	2.3	4.1	6.4	78.3	20.7	<MDL	<MDL	99.1
1	34.6	31.2	1.9	1.4	<MDL	<MDL	<MDL	2.0	4.7	6.7	76.6	23.3	0.1	<MDL	100.0
AVG	35.8	31.3	1.7	1.3	<MDL	<MDL	<MDL	2.2	4.4	6.6	77.4	22.0	<MDL	<MDL	99.5
STDEV	1.6	0.1	0.3	0.1	<MDL	<MDL	<MDL	0.2	0.4	0.2	1.2	1.8	<MDL	<MDL	0.6
3	30.9	32.4	1.8	2.1	<MDL	<MDL	1.7	2.0	5.5	7.5	76.3	22.5	0.2	<MDL	99.0
3	27.0	35.9	2.1	2.6	<MDL	<MDL	1.3	1.7	5.6	7.3	76.2	22.7	0.1	<MDL	99.1
AVG	29.0	34.2	2.0	2.4	<MDL	<MDL	1.5	1.9	5.6	7.4	76.2	22.6	0.1	<MDL	99.0
STDEV	2.8	2.5	0.2	0.4	<MDL	<MDL	0.3	0.2	0.1	0.1	0.0	0.1	0.0	<MDL	0.1
7	18.4	38.7	2.7	2.6	<MDL	<MDL	3.1	1.7	4.6	6.3	72.4	24.5	0.6	0.1	97.6
7	21.5	38.3	2.3	2.6	<MDL	<MDL	3.1	1.6	4.3	5.9	74.4	23.3	0.5	0.1	98.3
AVG	20.0	38.5	2.5	2.6	<MDL	<MDL	3.1	1.7	4.5	6.1	73.4	23.9	0.5	0.1	97.9
STDEV	2.2	0.3	0.3	0.0	<MDL	<MDL	0.0	0.1	0.2	0.3	1.4	0.9	0.1	0.0	0.5
15	21.5	37.1	2.3	2.3	1.7	<MDL	1.4	1.9	3.4	5.3	71.6	25.8	0.6	0.0	98.1
15	15.6	39.0	2.6	3.6	1.1	<MDL	2.5	1.4	3.3	4.7	69.2	25.2	0.9	0.1	95.4
AVG	18.6	38.1	2.5	3.0	1.4	<MDL	2.0	1.7	3.4	5.0	70.4	25.5	0.7	0.1	96.7
STDEV	4.2	1.3	0.2	0.9	0.4	<MDL	0.8	0.4	0.1	0.4	1.7	0.4	0.2	0.0	1.9
														AVR	99.3
														STDEV	4.3

Applied radioactivity= 11522 Bq/100g (p. 11 of the study report).
Data were obtained from p. 11, Appendix 13 and 14, pp. 35 and 36 of the study report.
The limit of detection (LOD) for RP-TLC analyses was 1.0% of the applied radioactivity.
N/A= Not Applicable because not sampled

Chemical: Prothioconazole
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Table 7 Phototransformation of [phenyl-UL-C^{14}]prothioconazole on Byromville silt loam (dark samples), expressed as percentage of the applied radioactivity.

Time (days)	JAU6476	-desthio	-triazo-linone	-sulfonic acid	un-known1	un-known2	un-known3	Unidentified Origin	Unidentified Diffuse	Uniden. Total	Total extracted	Non-extracted	CO2	VOCs	**Total**
0	74.5	3.4	<MDL	<MDL	<MDL	<MDL	<MDL	2.8	3.4	6.2	84.2	8.6	N/A	N/A	92.9
0	75.6	4.3	<MDL	<MDL	<MDL	<MDL	<MDL	2.6	3.5	6.1	86.3	8.2	N/A	N/A	94.4
AVG	75.1	3.9	<MDL	<MDL	<MDL	<MDL	<MDL	2.7	3.5	6.2	85.2	8.4	N/A	N/A	93.7
STDEV	0.8	0.6	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1	0.1	1.4	0.3	N/A	N/A	1.1
1	39.0	21.6	1.6	<MDL	<MDL	<MDL	<MDL	3.6	8.4	12.0	74.5	26.4	<MDL	N/A	101.0
7	21.4	25.4	2.1	<MDL	<MDL	1.1	<MDL	5.2	6.2	11.4	61.7	36.5	0.1	<MDL	98.3
15	19.0	29.4	3.2	<MDL	<MDL	<MDL	<MDL	3.9	6.7	10.6	62.6	35.7	<MDL	N/A	98.3
														AVR	**97.0**
														STDEV	**3.3**

Applied radioactivity= 11522 Bq/100g (p. 11 of the study report).
Data were obtained from p. 11, Appendix 13 and 14, pp. 35 and 36 of the study report.
The limit of detection (LOD) for RP-TLC analyses was 1.0% of the applied radioactivity.
N/A= Not Applicable because not sampled

Chemical: Prothioconazole
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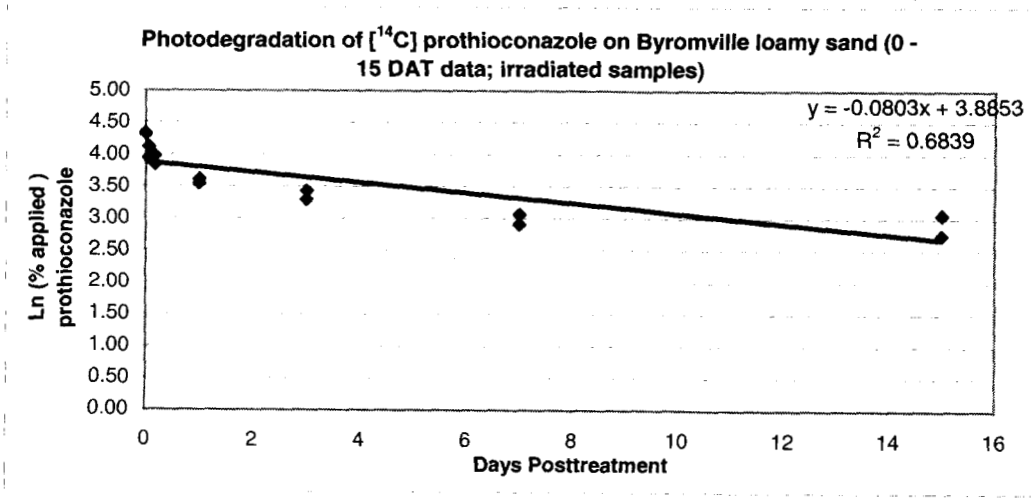
Days posttreatment	New York equivalent days in summer sun	Edmonton equivalent days in summer sun	% applied	Ln (% applied)
0.00	0.00	0.00	74.5	4.31
0.00	0.00	0.00	75.6	4.33
0.06	0.31	0.31	61.0	4.11
0.06	0.31	0.31	51.4	3.94
0.17	0.88	0.86	53.4	3.98
0.17	0.88	0.86	46.8	3.85
1.00	5.15	5.08	36.9	3.61
1.00	5.15	5.08	34.6	3.54
3.00	15.46	15.25	30.9	3.43
3.00	15.46	15.25	27.0	3.30
7.00	36.08	35.59	18.4	2.91
7.00	36.08	35.59	21.5	3.07
15.00	77.31	76.25	21.5	3.07
15.00	77.31	76.25	15.6	2.75

Data were obtained from Appendix 9, 10 and 14, pp. 31, 32 and 36 of the study report.

First order linear half-life = 8.6 days



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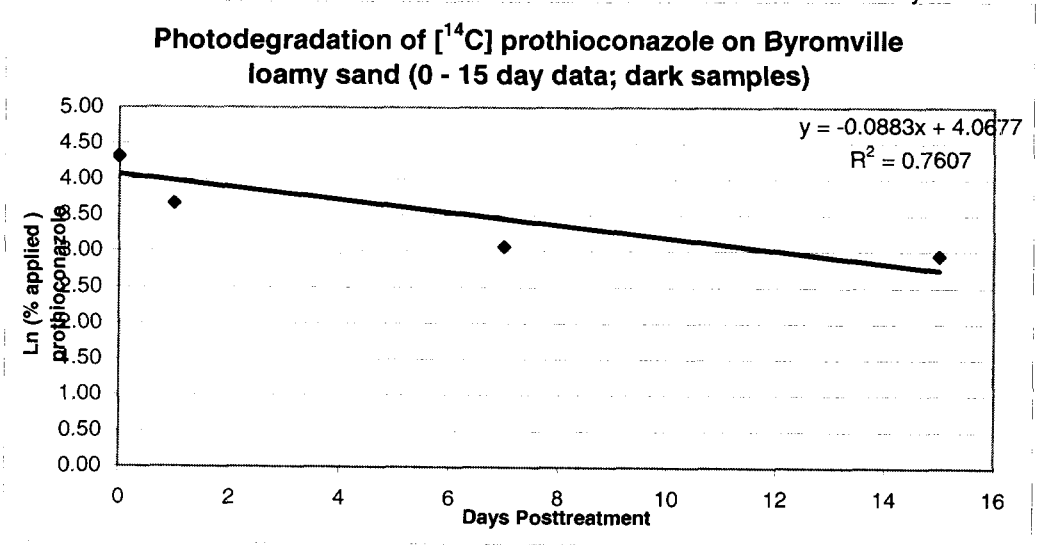
Days	% applied	Ln (% applied)
0	74.5	4.31
0	75.6	4.33
1	39.0	3.66
7	21.4	3.06
15	19.0	2.94

Data were obtained from Appendix D, pp. 78 of the study report.

First order linear half-life = 7.8 days



k (irradiated)=	0.0803 DAT^{-1}
k (dark)=	0.0883 DAT^{-1}
Difference between dark and irradiated k values=	-0.008 DAT^{-1}
k (irradiated, NY-corrected)=	0.0156 $days^{-1}$
Difference between dark and irradiated, corrected k values=	-0.0727 $days^{-1}$
k (irradiated, Ed-corrected)=	0.0158 $days^{-1}$
Difference between dark and irradiated, corrected k values=	-0.0725 $days^{-1}$

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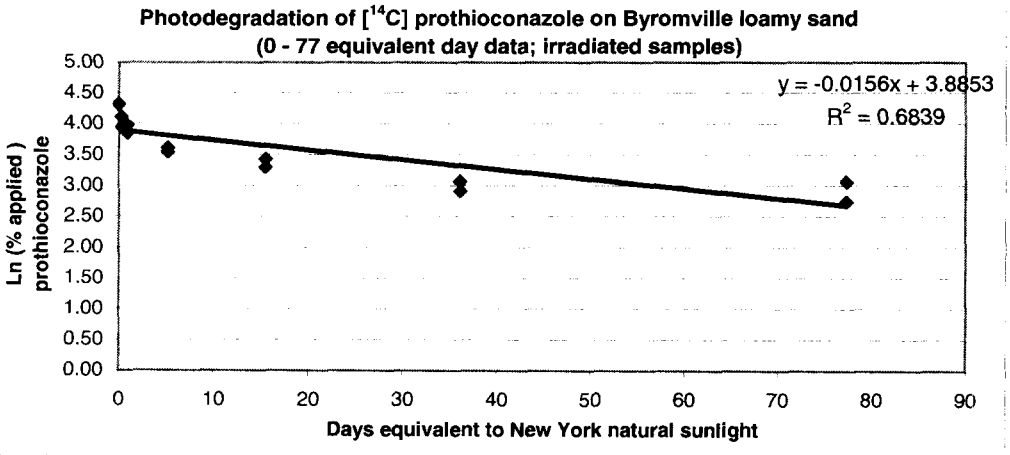
(Predicted New York) First order linear half-life = 44.4 days



(Predicted Edmonton) First order linear half-life = 43.9 days