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TEXT SEARCHABLE DOCUMENT

Data Evaluation Report on the terrestrial field dissipation of pyrasulfotole (AE 0317309)

PMRA Submission Number 2006-2445 EPA MRID Number 46801717

Data Requirement: PMRA Data Code: 8.3.2
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IIIA 9.2.1, IIIA 9.2.2, IIIA 9.2.3
EPA Guideline: §164-1

Test material: AE 0317309

End Use Product name: AE 0317309 02 SE06 A103 **Concentration of a.i.:** 4.32%
Formulation type: Suspo-emulsion

Test material:

Common name: Pyrasulfotole.

Chemical name:

IUPAC name: (5-Hydroxy-1,3-dimethylpyrazol-4-yl)(α,α,α-trifluoro-2-mesyl-*p*-tolyl)methanone.
(5-Hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)(2-mesyl-4-trifluoromethylphenyl)methanone.

CAS name: (5-Hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)[2-methylsulfonyl)-4(trifluoromethyl)phenyl]methanone.
Methanone, (5-hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl].

CAS No: 365400-11-9.

Synonyms: AE 0317309; K-1196; K-1267.

SMILES string: FC(c1cc(c(cc1)C(=O)c1c(n(nc1C)C)O)S(=O)(=O)C)(F)F (ISIS v2.3/Universal SMILES).
No EPI Suite, v3.12 SMILES String found as of 6/7/06.
Cc1nn(C)c(O)c1C(=O)c2ccc(C(F)(F)F)cc2S(C)(=O)=O.
CS(=O)(=O)c1c(ccc(c1)C(F)(F)F)C(=O)c1c(n(nc1C)C)O.

Primary Reviewer: Dan Hunt
Cambridge Environmental
Signature:
Date: 6/14/06

Secondary Reviewer: Joan Harlin
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Final Reviewer: Marietta Echeverria
EPA Reviewer
Signature: Marietta Echeverria
Date: 1/23/07

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Data Evaluation Report on the terrestrial field dissipation of pyrasulfotole (AE 0317309)

PMRA Submission Number 2006-2445 EPA MRID Number 46801717

Final Reviewer: J.D. Whall (Officer #1268)
PMRA Reviewer

Signature: J.D. Whall
Date: 5/16/07

Final Reviewer: Olga Braga
DEH Reviewer

Signature:
Date: 24/01/2007

Company Code : BCZ
Active Code : PSA
Use Site Category: 13,14
EPA PC Code: 000692

CITATION: Lenz, M. 2006. Terrestrial field dissipation of AE 0317309 in North Dakota soil, 2004. Unpublished study performed by Bayer CropScience, Stilwell, KS; AGVISE Laboratories, Northwood, ND; and AGVISE Research, Northwood, ND; and submitted by Bayer CropScience, Research Triangle Park, NC. Study No: MEAIY007. Experiment initiation June 16, 2004 and completion January 20, 2006 (p. 13). Final report issued February 28, 2006.

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EXECUTIVE SUMMARY

Soil dissipation/accumulation of pyrasulfotole [(5-hydroxy-1,3-dimethylpyrazol-4-yl)(α,α,α-trifluoro-2-mesyl-*p*-tolyl)methanone] under US field conditions was conducted in three replicate bare plots and three replicate cropped plots (wheat) of clay loam/loam soil in North Dakota. The experiment was carried out in accordance with the USEPA Pesticide Assessment Guidelines Subdivision N, §164-1 and the Canadian PMRA data code DACO 8.3.2, and in compliance with the USEPA FIFRA (40 CFR, Part 160) GLP standards. Pyrasulfotole was broadcast once with the end-use product AE 0317309 02 SE06 A103 (50 g a.i./L pyrasulfotole), at a target rate of 0.055 kg a.i./ha (0.049 lb a.i./A) to 19.3 x 3 m replicate plots. Application to the crop occurred at the 1 leaf to 4 tiller stage; the height of the wheat at the time of application was 20-25.4 cm. The proposed label rate was reported as 0.050 kg a.i./ha (0.045 lb a.i./A). Total water input during the 498-day study period was 53.74 inches or 168% of the 30-year average precipitation. A control plot was located 15 m from the treated plots.

The application rate was verified for both plots using both solvent saturation pads (6 pads for each treatment) and pans containing control soil (3 pans for each treatment) that were placed in the treated plots prior to the test application. Mean recovery of pyrasulfotole from the pads placed in the bare plot was equivalent to an application rate of 60.82 g a.i./ha or a reviewer-calculated 111% of the 55 g a.i./ha target. Mean recovery of pyrasulfotole from the pads placed in the cropped plot was equivalent to an application rate of 63.04 g a.i./ha or a reviewer-calculated 115% of the target rate. Mean recovery of pyrasulfotole plus the transformation product AE B197555 from the pans was equivalent to an application rate of 39.6 g a.i./ha for the bare plot and 37.8 g a.i./ha for the cropped plot, which corresponds to 72.0% and 68.7% of the target rate, respectively. Field spikes to determine the stability of the parent and transformation products during transport and storage were not prepared.

Soil samples were collected from the bare and cropped plots at 0, 1, 3, 7, 14, 27, 61, 120, 317, 377, and 498 days posttreatment to a depth of 0-122 cm (excluding day-0 samples). Samples were extracted using an Accelerated Solvent Extractor with acetonitrile:water (65:35, v:v) at 100°C and 1500 psi pressure. An aliquot of the extraction solvent was cleaned up using a RP-102 SPE cartridge and analyzed for pyrasulfotole and the transformation product AE B197555 (2-(methylsulfonyl)-4-(trifluoromethyl) benzoic acid) by LC/MS/MS. The LOD and LOQ were 0.1 µg/kg and 0.5 µg/kg, respectively, for both analytes analytes. Soil samples were stored frozen for up to 569 days prior to analysis.

In the bare test plot, the measured zero-time recovery of pyrasulfotole in the 0-15 cm soil layer was 24.4 ppb or 71.8% of the theoretical based on the target application rate (reviewer-calculated based on a theoretical day-0 recovery of 34 µg/kg). Pyrasulfotole decreased to 11.9 ppb by 7 days, 4.0 ppb by 27 days, and was last detected above the LOQ at 0.5 ppb at 377 days posttreatment. Pyrasulfotole was not detected above the LOQ in soil below the 0-15 cm soil depth. The major transformation product **AE B197555** was initially detected in the 0-15 cm soil depth at 1.2 ppb at day 0, increased to a maximum of 13.5 ppb by 7 days (which is equivalent to

18.2 ppb parent equivalents or 53.6% of the theoretical applied pyrasulfotole based on the target application rate), then decreased to 5.7 ppb by 27 days, 1.0 ppb by 317 days, and was below the LOQ by 377 days posttreatment. AE B197555 was not detected below the 0-15 cm soil depth.

In the cropped test plot, the measured zero-time recovery of pyrasulfotole in the 0-15 cm soil layer was 25.2 ppb or 68.1% of the theoretical based on the target application rate (reviewer-calculated based on a theoretical day-0 recovery of 37 µg/kg). Pyrasulfotole decreased to 12.1 ppb by 3 days, 4.4 ppb by 27 days, and was last detected above the LOQ at 0.5 ppb at 377 days posttreatment. Pyrasulfotole was not detected above the LOQ in soil below the 0-15 cm depth, but was detected at levels below the LOQ in the 15-30 and 30-45 cm depths. The major transformation product **AE B197555** was initially detected in the 0-15 cm soil depth at 0.9 ppb at day 0, increased to a maximum of 7.9 ppb by 14 days (which is equivalent to 10.7 ppb parent equivalents or 28.8% of the theoretical applied pyrasulfotole based on the target application rate), then decreased to 3.2 ppb by 27 days, 0.6 ppb by 61 days, and was detected below the LOQ from 120-377 days posttreatment. AE B197555 was detected in the 15-30 cm soil depth from 3 to 27 days at ≤0.5 ppb, and was not detected in soil below that depth. The study author-calculated half-life value for AE B197555 was 9 days.

Under field conditions in the bare test plot, pyrasulfotole had a reviewer-calculated half-life value of 84.5 days in the top 15 cm soil layer ($r^2 = 0.8107$; based on all available replicate data, using linear regression and the equation $t_{½} = ln\ 2 / k$, where k is the rate constant); however, dissipation was bi-phasic, and the observed half-life was approximately 7 days. The reviewer calculated DT50 and DT90 values for pyrasulfotole in the whole soil column were 6 and 44 days, respectively (two compartment non-linear regression model; $r^2 = 0.96$). The reviewer calculated DT50 and DT90 values for AE B197555 in the whole soil column were 25 and 227 days, respectively (two-compartment, non-linear regression model; $r^2 = 0.81$).Carryover of pyrasulfotole residues in the soil column was 2.9 and 1.0% of the applied pyrasulfotole at the beginning of the following growing season (i.e. Day 317) and at the end of the study period (i.e. Day 498), respectively, based on observed Day 0 concentrations.

Under field conditions in the cropped test plot, pyrasulfotole had a reviewer-calculated half-life value of 84.5 days in soil ($r^2 = 0.7534$; based on all available replicate data, using linear regression and the equation $t_{½} = ln\ 2 / k$, where k is the rate constant); however, dissipation was bi-phasic and the observed half-life was <3 days. The registrant-calculated DT90 value was 51 days (DFOP model). Carryover of pyrasulfotole residues in the soil column was 4.8 and 1.5% of the applied pyrasulfotole at the beginning of the following growing season (i.e. Day 317) and at the end of the study period (i.e. Day 498), respectively, based on observed Day 0 concentrations.

The major route of dissipation of pyrasulfotole under terrestrial field conditions in both test plots was transformation.

RESULTS SYNOPSIS

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Bare plot
Location/soil type: Grand Forks County, ND/Clay loam (0-15 cm) over loam (15-105 cm).
Half-life: 84.5 days (r^2 = 0.8107; based on all replicate detections in the top 15 cm soil layer; reviewer-calculated).
Approximately 7 days (observed).
DT_{50}: 6 days (reviewer calculated for whole soil column; r^2 = 0.96)
DT_{90}: 44 days (reviewer calculated for whole soil column; r^2 = 0.96).

Major transformation products detected: AE B197555:
DT_{50}: 25 days (reviewer calculated for whole soil column; r^2 = 0.81)
DT_{90}: 227 days (reviewer calculated for whole soil column; r^2 = 0.81)

Dissipation routes: Transformation.
Carryover to following growing season: 2.9%

Cropped plot
Location/soil type: Grand Forks County, ND/ Clay loam (0-15 cm) over loam (15-105 cm).
Half-life: 84.5 days (r^2 = 0.7534; based on all replicate detections; reviewer-calculated).
<3 days (observed).
DT50: 6 days (registrant-calculated).
DT90: 51 days (registrant-calculated).
Major transformation products detected: AE B197555.
Dissipation routes: Transformation.
Carryover to following growing season: 4.8%

Study Acceptability: This study is classified as **acceptable**. No significant deviations from good scientific practices or Subdivision N Guidelines were noted.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The study was conducted according to USEPA Pesticide Assessment Guidelines Subdivision N, §164-1 and Canadian PMRA data code DACO No.8.3.2 (p. 13). There were no deviations from guideline §164-1.

COMPLIANCE: The study was conducted in compliance with USEPA FIFRA (40 CFR Part 160) Good Laboratory Practice standards (p. 13). Signed and dated Data Confidentiality, GLP compliance, Quality Assurance, and Certification of Authenticity statements were provided (pp. 2-5).

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A. MATERIALS:

1. Test Material Pyrasulfotole.

Chemical Structure of the active ingredient(s): See DER Attachment 1.

Description: Formulation: Suspo-emulsion (p. 14).

Storage conditions of test chemicals: The test substance was stored in the dark under ambient conditions (9.27-25.20°C; p. 14).

Physico-chemical properties of the active ingredient(s):

Paramater	Value	Comment
Chemical formula	$C_{14}H_{13}F_3N_2O_4S$	
Molecular mass	362.3242	
Water Solubility	Bi-distilled water: 2.3 g/L pH 4: 4.2 g/L pH 7: 69.1 g/L pH 9: 49.0 g/L	At 20°C
Vapor Pressure/Volatility	$2.7x10^{-7}$ Pa $6.8x10^{-7}$ Pa $4.8x10^{-5}$ Pa	At 20°C At 25°C At 50°C
UV Absorption	264 nm: 11127 L/mol*cm 306 nm: 5925 L/mol*cm	In water
Pka	4.2	
K_{ow}/log K_{ow}	pH 4: 1.89/0.276 pH 7: 0.043/-1.362 pH 9: 0.026/-1.580	At 23°C
Stability of compound at room temperature, if provided	Stable in solid state (ambient temperature); stable in aqueous solution at pH 5, 7 and 9 (25°C); no significant degradation in aqueous solution under continuous irradiation.	

Data were obtained from Tables 2 and 11, pp. 27 and 38 of the study report.

2. Test site: The test site was located in Northwood, Grand Forks County, North Dakota on a clay loam (0-15 cm) over loam (15-105 cm) soil (Tables 1 and 5, pp. 26 and 30). The site was located in the market region for the product (p. 15). No hardpan or confining layer was found in the top 6 feet of the test site. A three-year crop and pesticide use history for the test site is reported below in Table 2.

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Table 1: Geographic location, site description and climatic data at the study site.

Details		North Dakota
Geographic coordinates	Latitude	N 47° 49.519'
	Longitude	W 097° 37.037'
	Province/State	North Dakota
	Country	USA
	Ecoregion	9.2
Slope Gradient		0%
Depth to ground water (m)		>1.2 m
Distance from weather station used for climatic measurements		Weather station located on-site station; supplemental weather data were collected from stations located 0.25 miles and 20 miles from the test site.
Indicate whether the meteorological conditions before starting or during the study were within 30 year normal levels (Yes/No). If no, provide details.		Total water input (rainfall plus irrigation) during the 498-day study period was 53.74 inches or 168% of the 30-year average precipitation.

Data were obtained from pp. 15 and 17; Table 3, p. 28; and Appendix 4, Table 1, p. 106 of the study report.

Table 2: Site usage and management history for the previous three years.

Use	Year	North Dakota
Crops grown	Previous year	Fallow
	2 years previous	Fallow
	3 years previous	Wheat
Pesticides used	Previous year	None
	2 years previous	None
	3 years previous	Puma, Curtail M, Lorsban and Folicur
Fertilizers used	Previous year	None
	2 years previous	None
	3 years previous	None
Cultivation methods, if provided (eg., Tillage)	Previous year	Not reported
	2 years previous	Not reported
	3 years previous	Not reported

Data were obtained from Table 4, p. 29 of the study report.

* The test plots were cultivated prior to the test application using a tractor and field cultivator (p. 15).

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3. Soils:

Table 3a: Properties of the soil in the bare test plot.

Property	Depth (cm)							
	0-15	**15-30**	**30-45**	**45-60**	**60-75**	**75-90**	**90-105**	**105-122**
Textural classification	Clay loam	Loam	Loam	Loam	Loam	Loam	Loam	Clay loam
%sand	27	33	39	43	39	33	27	25
%silt	44	40	36	36	37	40	50	46
%clay	29	27	25	21	24	27	23	29
pH (1:1 soil:water)	6.1	6.9	7.8	8.0	8.0	8.2	8.3	8.3
Organic matter (%)	5.2	4.6	2.8	1.9	1.5	1.1	0.8	0.7
Total organic carbon (%)	3.0	2.7	1.6	1.1	0.9	0.6	0.5	0.4
CEC (meq/100 g)	23.9	24.0	22.0	20.8	19.9	18.9	17.3	18.0
Bulk density (g/cm3)	1.07	1.03	1.03	1.04	1.04	1.04	0.99	1.02
Moisture at 1/3 atm (%)	34.6	35.3	32.5	31.7	30.8	32.5	32.1	32.9
Taxonomic classification (e.g., ferro-humic podzol)	Soil Series: Gardena Soil Order: Mollisols, Sub Order: Udolls Great Group: Hapludolls, Subgroup Modifier: Pachic Minerology: Mixed							
Soil mapping unit	Map Unit Symbol 72, Gardena Silt Loam							

Data were obtained from Table 5, p. 30 of the study report. Organic carbon was calculated by the reviewer from percent organic matter (% o.c. = % o.m. x 0.58). The particle distribution of the soil is presented graphically in Appendix 5, p. 124 of the study report.

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Table 3b: Properties of the soil in the cropped test plot.

Property	Depth (cm)							
	0-15	**15-30**	**30-45**	**45-60**	**60-75**	**75-90**	**90-105**	**105-122**
Textural classification	Clay loam	Loam	Loam	Loam	Loam	Loam	Loam	Clay loam
%sand	33	31	31	37	35	35	31	27
%silt	38	42	42	36	38	40	42	45
%clay	29	27	27	27	27	25	27	28
pH (1:1 soil:water)	6.4	6.7	7.2	7.9	8.2	8.3	8.2	8.3
Organic matter (%)	5.0	4.6	2.6	1.6	1.0	0.8	0.7	0.7
Total organic carbon (%)	2.9	2.7	1.5	0.9	0.6	0.5	0.4	0.4
CEC (meq/100 g)	21.7	21.5	20.9	20.9	18.1	17.0	18.1	17.9
Bulk density (g/cm3)	1.00	0.95	1.01	1.07	1.01	1.02	1.03	1.02
Moisture at 1/3 atm (%)	32.5	33.8	31.9	30.3	28.6	29.7	31.6	34.1
Taxonomic classification (e.g., ferro-humic podzol)	Soil Series: Gardena Soil Order: Mollisols, Sub Order: Udolls Great Group: Hapludolls, Subgroup Modifier: Pachic Minerology: Mixed							
Soil mapping unit	Map Unit Symbol 72, Gardena Silt Loam							

Data were obtained from Table 5, p. 30 of the study report. Organic carbon was calculated by the reviewer from percent organic matter (% o.c. = % o.m. x 0.58). The particle distribution of the soil is presented graphically in Appendix 5, p. 124 of the study report.

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B. EXPERIMENTAL DESIGN:

1. Experimental design:

Table 4: Experimental design.

Details		Bare plot	Cropped plot
Duration of study		498 days	498 days
Uncropped (bare) or cropped		Bare	Cropped
Control used (Yes/No)		Yes	No
No. of replications	Controls	One	N/A
	Treatments	Three	Three
Plot size (L x W m)	Controls	1.9 x 3 m	N/A
	Treatments	19.3 x 3 m	19.3 x 3 m
Distance between control plot and treated plot		15.24 m	N/A
Distance between treated plots		1.5 m	1.5 m
Application rate(s) used (g a.i/ha)		55 g a.i./ha	55 g a.i./ha
Was the maximum label rate per ha used in study? (Yes/No)		110% of the proposed label rate	110% of the proposed label rate
Number of applications		One	One
Application Date(s) (dd mm yyyy)		16/06/2004	16/06/2004
For multiple applications, application rate at Day 0 and at each application time (mg a.i./kg soil)		0.034 mg a.i./kg soil[1]	0.037 mg a.i./kg soil[1]
Application method (eg., spraying, broadcast etc.)		Liquid broadcast spray	Liquid broadcast spray
Type of spray equipment, if used		Boom sprayer equipped with #1100067 flat fan nozzles spaced 20 inches apart and set at 18 inches above the ground	Boom sprayer equipped with #1100067 flat fan nozzles spaced 20 inches apart and set at 18 inches above the ground
Total volume of spray solution applied/plot **OR** total amount broadcasted/plot		186.9 L/ha	186.9 L/ha
Identification and volume of carrier (e.g., water), if used		Water	Water
Name and concentration of co-solvents, adjuvants and/or surfactants, if used		None	None
Indicate whether the following monthly reports were submitted:			
Precipitation:		Yes	Yes
Average minimum and maximum air temperature:		Yes	Yes
Average minimum and maximum soil temperature:		No (mean only, depth not reported)	No (mean only, depth not reported)
Average annual frost-free periods:		No	No

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Details		Bare plot	Cropped plot
Indicate whether the Pan evaporation data were submitted		Yes (Penman evapotranspiration)	Yes (Penman evapotranspiration)
Meteorological conditions during application	Cloud cover	60%	60%
	Temperature (EC)	22.2	22.2
	Humidity	60%	60%
	Sunlight (hr)	15	15
Pesticides used during study: Name of product/a.i concentration: Amount applied: Application method: Name of product/a.i concentration: Amount applied: Application method:		 Puma 0.6 L/ha Broadcast MCPA 1.2 L/ha Broadcast	 Puma 0.6 L/ha Broadcast MCPA 1.2 L/ha Broadcast
Supplemental irrigation used (Yes/No) If yes, provide the following details: No. of irrigation: Interval between irrigation: Amount of water added each time: Method of irrigation:		Yes 7 1 day-11 months 1-7 mm Overhead sprinkler	Yes 7 1 day-11 months 1-7 mm Overhead sprinkler
Indicate whether water received through rainfall + irrigation equals the 30 year average rainfall (Yes/No)		Yes	Yes
Were the application concentrations verified?		Yes	Yes
Were field spikes used?		No	No
Good agricultural practices followed (Yes or No)		Yes	Yes
Indicate if any abnormal climatic events occurred during the study (eg., drought, heavy rainfall, flooding, storm etc.)		None	None
If cropped plots are used, provide the following details: Plant - Common name/variety: Details of planting: Crop maintenance:		N/A	 Briggs wheat Drilled to 1 inch with JD 9350 drill Weeds controlled with Puma and MCPA
Volatilization included in the study (Yes/No)		No	No
Leaching included in the study (Yes/No)		Yes	Yes
Run off included in the study (Yes/No)		No	No

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Data were obtained from pp. 15-17; Table 6, pp. 32-33; Appendix 4, Tables 1-2, pp. 106-107; and Appendix 5, Table 2, pp. 111-123 of the study report.
1 Reviewer-calculated for the 0-15 cm soil depth based on one application at 0.049 lb a.i./A and a site-specific bulk density of 1.07 g/cm^3 for the bare plot, and one application at 0.049 lb a.i./A and a site-specific bulk density of 1.00 g/cm^3 for the cropped plot.
2 It was not specified which plot received the maintenance pesticides or if both plots received all applications.

2. Application Verification: To verify the application rate, one pair of solvent saturation pads (13.7 cm x 22 cm) was placed in individual aluminum pans (17.5 cm x 23.5 cm) that were then placed in each of the three replicate bare plots and three replicate cropped test plots (p. 16). Following application, the saturation pans and pads were collected, grouped by pairs, and stored frozen prior to analysis. The pads were extracted with acetonitrile:water (65:35, v:v) by shaking for two hours (p. 17). The extract was diluted to volume with acetonitrile:0.1% acetic acid in water (10:90, v:v), filtered using an Acrodisc 0.45-mm syringe filter, and analyzed for pyrasulfotole by LC/MS/MS.

In addition, an aluminum pan containing a layer of sieved, air-dried control soil was placed into each of the three replicate plots of the bare and cropped test plots prior to application (p. 16). Following application, the soil from the pans was transferred to a plastic bag and stored frozen until analysis. The soil was extracted using an Accelerated Solvent Extractor with acetonitrile:water (65:35, v:v) at 100°C and 1500 psi pressure (p. 17). Following dilution with acetonitrile, the extract was concentrated by evaporation, cleaned up using a RP-102 SPE cartridge, diluted to 5 mL with 0.1% acetic acid in water:acetonitrile (90:10, v:v), and analyzed for pyrasulfotole and AE B197555 by LC/MS/MS.

3. Field Spiking: Field spikes were not prepared to determine the stability of the parent and transformation products during transport and storage.

4. Volatilization: Volatilization was not measured.

5. Leaching: Fifteen cores were taken from the bare and cropped plots at -7, 0, 1, 3, 7, 14, 27, 61, 120, 317, 377, and 498 days posttreatment to a depth of 122 cm (excluding day-0 samples which were collected to a depth of 15 cm) to determine the mobility of the test substance in the soil profile (p. 16 and Table 7, p. 34).

6. Run off: Run off was not studied.

7. Supplementary Study: An on-going storage stability study is currently being conducted using soil collected from the test site and fortified with pyrasulfotole and the transformation product AE B197555 (p. 16; Appendix 10, p. 186). Soil samples were fortified with pyrasulfotole and AE B197555 at 0.010 ppm; results through 10 months of storage were reported.

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8. Sampling:

Table 5: Soil sampling.

Details	Bare plot	Cropped plot
Method of sampling (random or systematic)	Random	Random
Sampling intervals	-7, 0, 1, 3, 7, 14, 27, 61, 120, 317, 377, and 498 days	-7, 0, 1, 3, 7, 14, 27, 61, 120, 317, 377, and 498 days
Method of soil collection (eg., cores)	Cores	Cores
Sampling depth	122 cm, except for day-0 samples which were collected to a depth of 15 cm.	122 cm, except for day-0 samples which were collected to a depth of 15 cm.
Number of cores collected per plot	5 per replicate plot (15 total)	5 per replicate plot (15 total)
Number of segments per core	Eight	Eight
Length of soil segments (after sectioning)	15 cm	15 cm
Core diameter	5.7 cm	5.7 cm
Method of sample processing, if any	Samples were composited by replicate plot and depth. Composited samples were milled with dry ice by a hammer mill and mixed using a bucket mixer with fixed inner paddles.	Samples were composited by replicate plot and depth. Composited samples were milled with dry ice by a hammer mill and mixed using a bucket mixer with fixed inner paddles.
Storage conditions	Frozen	Frozen
Storage length (days)	569 days	569 days

Data were obtained from p. 16 and Table 7, p. 34 of the study report.

9. Analytical Procedures:

Number of soil samples analysed per treatment or composite sample: Not reported.

Extraction, clean up and concentration of soil samples: Samples (maximum 25 g) were extracted using an Accelerated Solvent Extractor with acetonitrile:water (65:35, v:v) at 100°C and 1500 psi pressure (p. 18; Appendix 3, pp. 63-66 and 103). An aliquot of the extract was concentrated, cleaned up using a RP-102 SPE cartridge, and diluted to 5 mL with 0.1% acetic acid in water:acetonitrile (90:10, v:v).

Identification and quantification of parent compound: Extracts were fortified with an isotopic internal standard containing pyrasulfotole-d_3, and analyzed for pyrasulfotole by LC/MS/MS (Phenomenex Prodigy 5µ C8 50 x 2.00 mm column; p. 18; Appendix 3, p. 66 and Table 1, p. 70). The mobile phase for the separation was A: 0.1% acetic acid in water; B: acetonitrile:water + 0.2% formic acid (85:15, v:v); A:B, 97:3 to 7:93 to 97:3 (Appendix 3, p. 75). The retention time of pyrasulfotole was approximately 3.4 minutes.

Identification and quantification of transformation products: Extracts were fortified with an isotopic internal standard containing AE B197555-$^{13}C_6$, and analyzed for AE B197555 by

LC/MS/MS (Phenomenex Prodigy 5µ C8 50 x 2.00 mm column; p. 18; Appendix 3, p. 66 and Table 1, p. 70). The retention time of AE B197555 was approximately 3.8 minutes.

Detection limits (LOD, LOQ) for the parent compound in soil: The LOD and LOQ were 0.1 µg/kg and 0.5 µg/kg, respectively (p. 18).

Detection limits (LOD, LOQ) for the transformation products in soil: The LOD and LOQ were 0.1 µg/kg and 0.5 µg/kg, respectively (p. 18).

II. RESULTS AND DISCUSSION

APPLICATION MONITORS: Mean recovery of pyrasulfotole from the solvent saturation pads placed in the bare plot was equivalent to an application rate of 60.82 g a.i./ha or a reviewer-calculated 111% of the 55 g a.i./ha target (Appendix 7, Table 1, p. 157). Mean recovery from the pads placed in the cropped plot was equivalent to an application rate of 63.04 g a.i./ha or a reviewer-calculated 115% of the target rate. Mean recovery of pyrasulfotole plus the transformation product AE B197555 from the pans was equivalent to an application rate of 39.6 g a.i./ha for the bare plot and 37.8 g a.i./ha for the cropped plot, which corresponds to 72.0% and 68.7% of the target rate, respectively (Appendix 7, Table 2, p. 157).

2. RECOVERY FROM FIELD SPIKES: Field spikes were not prepared.

3. MASS ACCOUNTING: A mass balance was not determined.

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Table 6a. Concentration of pyrasulfotole residues expressed as ppb in soil from the bare plot.

Compound	Soil depth (cm)	Sampling times (days)										
		0	**1**	**3**	**7**	**14**	**27**	**61**	**120**	**317**	**377**	**498**
Pyrasulfotole (AE 0317309)	0-15	**24.4**	**19.7**	**13.9**	**11.9**	**9.0**	**4.0**	**2.0**	**1.0**	**0.7**	**0.5**	0.2
	15-30	NS	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	45-60	NS					ND	ND	ND	ND	ND	ND
	60-75	NS							ND			
	75-90	NS										
	90-105	NS										
	105-120	NS										
	Total	24.4	19.9	13.9	11.9	9.0	4.0	2.0	1.0	0.7	0.5	0.2
AE B197555	0-15	**1.2**	**1.8**	**5.7**	**13.5**	**10.7**	**5.7**	**3.5**	**2.8**	**1.0**	0.3	0.2
	15-30	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	45-60	NS					ND	ND	ND	ND	ND	ND
	60-75	NS							ND			
	75-90	NS										
	90-105	NS										
	105-120	NS										
	Total	1.2	1.8	5.7	13.5	10.7	5.7	3.5	2.8	1.0	0.3	0.2

Residue data were obtained from Table 9, p. 36 of the study report; values are registrant-calculated means of three replicates. Total extractable and non-extractable residues were not determined. NS = No sample. ND = Not detected. Blank cell indicates sample not analyzed. Values in bold are above the LOQ.

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Table 6b. Concentration of pyrasulfotole residues expressed as ppb in soil from the cropped plot.

Compound	Soil depth (cm)	Sampling times (days)										
		0	1	3	7	14	27	61	120	317	377	498
Pyrasulfotole (AE 0317309)	0-15	**25.2**	**17.5**	**12.1**	**8.7**	**8.8**	**4.4**	**1.6**	**1.0**	**0.8**	**0.5**	ND
	15-30	NS	0.2	0.2	0.1	0.3	0.4	0.1	0.2	0.2	0.2	0.2
	30-45	NS	ND	ND	ND	ND	ND	ND	0.1	0.1	0.1	0.1
	45-60	NS				ND	ND	ND	ND	ND	ND	ND
	60-75	NS										
	75-90	NS										
	90-105	NS										
	105-120	NS										
	Total	25.2	17.7	12.3	8.8	9.1	4.8	1.7	1.3	1.1	0.8	0.3
AE B197555	0-15	**0.9**	**2.0**	**3.9**	**5.1**	**7.9**	**3.2**	**0.6**	0.3	0.3	0.2	ND
	15-30	NS	ND	0.1	0.1	**0.5**	0.4	ND	ND	ND	ND	ND
	30-45	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	45-60	NS				ND	ND	ND	ND	ND	ND	ND
	60-75	NS										
	75-90	NS										
	90-105	NS										
	105-120	NS										
	Total	0.9	2.0	4.0	5.2	8.4	3.6	0.6	0.3	0.3	0.2	ND

Residue data were obtained from Table 10, p. 37 of the study report; values are registrant-calculated means of three replicates. Total extractable and non-extractable residues were not determined. NS = No sample. ND = Not detected. Blank cell indicates sample not analyzed. Values in bold are above the LOQ.

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4. PARENT COMPOUND: In the bare test plot, the measured zero-time recovery of pyrasulfotole in the 0-15 cm soil layer was 24.4 ppb or 71.8% of the theoretical based on the target application rate (reviewer-calculated based on a theoretical day-0 recovery of 34 µg/kg; Table 9, p. 36; see footnote to DER Table 4). Pyrasulfotole decreased to 11.9 ppb by 7 days, 4.0 ppb by 27 days, and was last detected above the LOQ at 0.5 ppb at 377 days posttreatment. Pyrasulfotole was not detected in soil below the 0-15 cm depth except was detected in the 15-30 cm depth below the LOQ at 1 day posttreatment.

In the cropped test plot, the measured zero-time recovery of pyrasulfotole in the 0-15 cm soil layer was 25.2 ppb or 68.1% of the theoretical based on the target application rate (reviewer-calculated based on a theoretical day-0 recovery of 37 µg/kg; Table 10, p. 37; see footnote to DER Table 4). Pyrasulfotole decreased to 12.1 ppb by 3 days, 4.4 ppb by 27 days, and was last detected above the LOQ at 0.5 ppb at 377 days posttreatment. Pyrasulfotole was not detected above the LOQ in soil below the 0-15 cm depth, but was detected at levels below the LOQ in the 15-30 and 30-45 cm depths.

HALF-LIFE: Under field conditions in the bare test plot, pyrasulfotole had a reviewer-calculated half-life value of 84.5 days in soil ($r^2 = 0.8107$; based on all available replicate data, using linear regression and the equation $t_{½} = ln\ 2 / k$, where k is the rate constant; DER Attachment 2). However, dissipation was bi-phasic, with a rapid decline phase occurring through the first month of the study. The observed half-life of pyrasulfotole was approximately 7 days. The registrant-calculated DT90 value was 71 days for pyrasulfotole (DFOP model, p. 21). The PMRA reviewer-calculated DT50 and DT90 estimates were 5.7 and 44 days, respectively using a 2-compartment, 4-parameter non-linear regression model ($r^2 = 0.96$; estimates calculated using Sigma Plot equation solver for 0.5x and 0.1x average initial soil concentration).

Under field conditions in the cropped test plot, pyrasulfotole had a reviewer-calculated half-life value of 84.5 days in soil ($r^2 = 0.7534$; based on all available replicate data, using linear regression and the equation $t_{½} = ln\ 2 / k$, where k is the rate constant, DER Attachment 2). However, dissipation was bi-phasic, with a rapid decline phase occurring through the first month of the study. The observed half-life of pyrasulfotole was <3 days. The registrant-calculated DT90 value was 51 days for pyrasulfotole (DFOP model, p. 21).

5. TRANSFORMATION PRODUCTS: In the bare test plot, the major transformation product AE B197555 (2-(methylsulfonyl)-4-(trifluoromethyl) benzoic acid) was initially detected in the 0-15 cm soil depth at 1.2 ppb at day 0, increased to a maximum of 13.5 ppb by 7 days (which is equivalent to 18.2 ppb parent equivalents or 53.6% of the theoretical applied pyrasulfotole based on the target application rate), then decreased to 5.7 ppb by 27 days, 1.0 ppb by 317 days, and was below the LOQ by 377 days posttreatment. AE B197555 was not detected below the 0-15 cm soil depth. The study author-calculated half-life value for AE B197555 was 22 days (p. 22). The PMRA reviewer calculated DT50 and DT90 estimates for AE B197555 were 25 and 227 days, respectively (2-compartment, 4-parameter non-linear regression model; $r^2 = 0.81$; estimates calculated using Sigma Plot equation solver for 0.5x and 0.1x average Day 7 soil concentration).

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In the cropped test plot, the major transformation product AE B197555 was initially detected in the 0-15 cm soil depth at 0.9 ppb at day 0, increased to a maximum of 7.9 ppb by 14 days (which is equivalent to 10.7 ppb parent equivalents or 28.8% of the theoretical applied pyrasulfotole based on the target application rate), then decreased to 3.2 ppb by 27 days, 0.6 ppb by 61 days, and was detected below the LOQ from 120-377 days posttreatment. AE B197555 was detected in the 15-30 cm soil depth from 3 to 27 days at ≤0.5 ppb, and was not detected below that depth. The study author-calculated half-life value for AE B197555 was 9 days (p. 22).

Table 7: Chemical names and CAS numbers for the transformation products of pyrasulfotole.

Applicants Code Name	CAS Number	Chemical Name	Chemical Formula	Molecular Weight (g/mol)	Smiles String
AE B197555	142994-06-7	2-(Methylsulfonyl)-4-(trifluoromethyl) benzoic acid	$C_9H_7F_3O_4S$	268.2097	CS(=O)(=O)c1cc(ccc1C(=O)O)C(F)(F)F

Data were obtained from Table 11, p. 38 and Figure 1, p. 40 of the study report.

6. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES: Non-extractable residues were not measured.

Table 8: Dissipation routes of pyrasulfotole under field conditions.

Route of dissipation		% of applied amount	
		Bare plot	Cropped plot
Soil residues of pyrasulfotole at beginning of following growing season (i.e., 317 days post treatment).		2.9%	4.8%
Accumulation (residues) in soil at study termination (i.e., 498 days post treatment)		1.0%	1.5%
Transformation (% of transformation products)[1]		53.6% (day 7)	30.7% (day 14)
Leaching, if measured (maximum depth detected)	Pyrasulfotole	15-30 cm	30-45 cm
	AE B197555	0-15 cm	15-30 cm
Volatilization, if measured		Not measured	Not measured
Plant uptake, if measured		N/A	Not measured
Run off, if measured		Not measured	Not measured
Total			

Data obtained from Tables 9-10, pp. 36-37 of the study report. Determined by peer-reviewer as proportion of total amount of parent equivalents present at beginning of following growing season (i.e, Day 317 posttreatment), to the amount present in the soil at Day 0 (sum of concentrations in whole soil column).
1 Maximum concentration of AE B197555 in the soil after converting to parent equivalents (sum of all soil depths).
N/A = Not applicable.

7. VOLATILIZATION: The concentration of applied pyrasulfotole lost through volatilization was not determined.

8. PLANT UPTAKE: N/A.

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9. LEACHING: In the bare test plot, pyrasulfotole and AE B197555 were confined to the upper 0-15 cm soil layer for the duration of the study period with one exception; parent was detected in the 15-30 cm layer below the LOQ at 1 day posttreatment (Table 9, p. 36). In the cropped test plot, pyrasulfotole was not detected above the LOQ in soil below the 0-15 cm depth, but was detected at levels below the LOQ in the 15-30 and 30-45 cm depths (Table 10, p. 37). Residues of AE B197555 were confined to the upper 0-30 cm depth.

Total water input was much greater than historic rainfall for the study site for the duration of the study (168% of the 30-year average). The first water input event was a rainfall of approximately 3.5 mm at 8 days posttreatment (Appendix 5, Table 2, p. 111). The test plots received 7.31 cm or 2.88 inches of water over the first 30 days of the study. Accumulated water input throughout the study period is presented graphically in Appendix 5, Figure 3, p. 126; daily changes in soil moisture are shown in Appendix 5, Figures 4-5, pp. 127-128.

10. RUN OFF: Run off was not studied.

11. RESIDUE CARRYOVER: Residues as a percentage of applied amount were calculated by the peer-reviewer as the total amount of parent material present in the whole soil column relative to observed concentrations at Day 0. At the start of the following growing season (i.e., at 317 days post treatment), carryover of residues was 2.9% of the applied pyrasulfotole for the bare plot and 4.8% for the cropped plot. By the end of the study period (i.e., 498 days post treatment), 1.0 and 1.5% of the applied pyrasulfotole was present in the bare and cropped plots, respectively.

12. SUPPLEMENTARY STUDY RESULTS: Results from the on-going storage stability study indicated that pyrasulfotole and the transformation product AE B197555 were stable through 10 months of storage (Appendix 10, p. 186). Corrected recoveries of pyrasulfotole ranged from 96-121% from 0 to 10 months. Corrected recoveries of AE B197555 ranged from 110-128% from 0 to 10 months. The study author did not state how long the stability study would be conducted.

III. STUDY DEFICIENCIES

No deficiencies were noted.

IV. REVIEWER'S COMMENTS

1. The storage stability study was on-going, and preliminary data could not confirm the stability of the parent and AE B197555 for the maximum duration that the test samples were stored. Test samples were stored frozen for up to 569 days prior to analysis, while preliminary storage stability data were available only for 10 months of storage (Appendix

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10, p. 186). The study author stated that the results would be reported in a separate study report when finished.

2. The study author calculated half-lives using ModelMaker Version 4.0 using both a single first order model and a bi-exponential kinetic model or double first order in parallel (DFOP) model (pp. 18-19). Simple first-order half-lives were 6 days for the bare plot and 8 days for the cropped plot (pp. 20-21). Using the DFOP model, the study author reported a DT50 value for pyrasulfotole of 5 days and a DT90 of 71 days for the bare plot; corresponding DT50 and DT90 values for the cropped plot were 6 days and 51 days. The study author-calculated half-life values for AE B197555 were 22 days for the bare plot and 9 days for the cropped plot (p. 22).

3. The reviewer converted the concentration of AE B197555 in soil to parent equivalents by dividing by the molecular weight conversion factor 0.74. The molecular weight conversion factor was calculated by dividing the molecular weight of AE B197555 (268.2 g/mol) by the molecular weight of the parent (362.3 g/mol). AE B197555 concentrations were converted to parent equivalents by dividing the AE B197555 concentration by the molecular weight conversion factor.

4. The percent of AE B197555 in terms of percent of the applied pyrasulfotole was calculated by dividing the concentration of AE B197555 in parent equivalents (see above comment on how to convert to parent equivalents) by the theoretical day-0 concentration of pyrasulfotole in the 0-15 cm soil depth, based on the target application rate (see footnote to DER Table 4).

5. The study author stated that based on aerobic soil metabolism studies, biodegradation to AE B197555 and subsequent biodegradation to non-extractable residues and mineralization to CO_2 are the major dissipation pathways for pyrasulfotole (pp. 19-20). The author further stated that aerobic soil metabolism studies have shown that non-extractable residue can account for up to 50% of the total applied radioactivity after 100 days, and that mineralization to CO_2 can account for up to 40.5% of the applied after 358 days.

6. Mean method validation recoveries from soil samples fortified with pyrasulfotole at 0.5 ng/g (LOQ) and 2.5 ng/g (5x LOQ) were 87 ± 7% and 98 ± 4%, respectively; corresponding recoveries for AE B197555 were 93 ± 6% and 96 ± 3%, respectively (Appendix 3, p. 78).

7. Mean recoveries of pyrasulfotole and AE B197555 from fortified control soil samples prepared with each sample set were 79 ± 12% for pyrasulfotole and 89 ± 10% for AE B197555 (Table 8, p. 35). The fortification level was not reported for parent or transformation product.

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8. The PMRA secondary reviewer re-calculated % carryover at Day 317 posttreatment (i.e., start of following growing season) as a function of the observed amount of parent + metabolite found in the soil column on Day 0 rather than on the theoretical applied amount. This was done to determine the total amount of residue present in the soil prior to application in the following growing season.

9. The PMRA re-calculated expected DT50 and DT90 values for bare soil plots using a 2 compartment, 4 parameter model from Sigma Plot. This model appears to provide the optimal fit to the observed dissipation data. The PMRA assumed non-detects were equal to ½ LOD, rather than 0 ug/kg as done by the study authors. Given the similar field dissipation characteristics of pyrasulfotole under bare and cropped plots, the PMRA will model field dissipation based on data from bare plots only to avoid potential confounding factors with vegetation on interpreting chemical dissipation.

V. REFERENCES

1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 164-1, Terrestrial Field Dissipation Studies. Office of Pesticide and Toxic Substances, North Dakota, DC. EPA 540/9-82-021.
2. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, North Dakota, DC. EPA 738-R-93-010.

3. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, North Dakota, DC. EPA 540/09-90-078.

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Attachment 1: Structures of Parent Compound and Transformation Products

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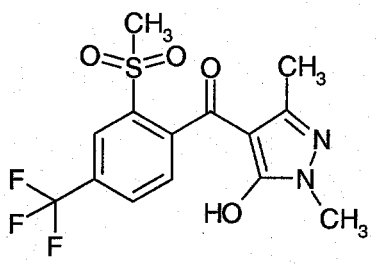
Pyrasulfotole [AE 0317309; K-1196; K-1267]

IUPAC Name: (5-Hydroxy-1,3-dimethylpyrazol-4-yl)(α,α,α-trifluoro-2-mesyl-*p*-tolyl)methanone.
(5-Hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)(2-mesyl-4-trifluoromethylphenyl)methanone.

CAS Name: (5-Hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)[2-methylsulfonyl)-4(trifluoromethyl)phenyl]methanone.
Methanone, (5-hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl].

CAS Number: 365400-11-9.

SMILES String: FC(c1cc(c(cc1)C(=O)c1c(n(nc1C)C)O)S(=O)(=O)C)(F)F (ISIS v2.3/Universal SMILES).
No EPI Suite, v3.12 SMILES String found as of 6/7/06.
Cc1nn(C)c(O)c1C(=O)c2ccc(C(F)(F)F)cc2S(C)(=O)=O.
CS(=O)(=O)c1c(ccc(c1)C(F)(F)F)C(=O)c1c(n(nc1C)C)O.



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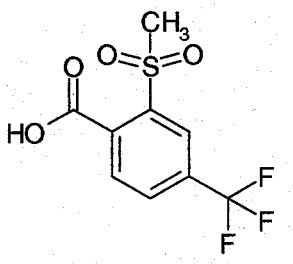
RPA 203328 [AE B197555-benzoic acid; AE B197555; K-1198; K-1367]

IUPAC Name: 2-Mesyl-4-trifluoromethylbenzoic acid.
CAS Name: Benzoic acid, 2-(methylsulfonyl)-4-(trifluoromethyl)-.
CAS Number: 142994-06-7.
SMILES String: O=C(c1ccc(cc1S(=O)(=O)C)C(F)(F)F)O (ISIS v2.3/Universal SMILES).
No EPI Suite, v3.12 SMILES String found as of 6/7/06.
CS(=O)(=O)c1cc(C(F)(F)F)ccc1C(=O)O.
CS(=O)(=O)c1cc(ccc1C(=O)O)C(F)(F)F.



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