Primary Evaluator	William Cutchin, Chemist SIMB/HED	Date: 7/19/04
Reviewer	Richard Loranger, BSS RAB2/HED	
Contractor	Dynamac Corporation 20440 Century Blvd., Suite 100 Germantown, MD 20874	

STUDY REPORT

45830719 McCormick, R.; Rutherford, L.; Schelle, L. (2002) Magnitude of Residue of XDE-638 in Rice and Rice Processed Products: Lab Project Number: 010063. Unpublished study prepared by Dow AgroSciences LLC. 135 p.

EXECUTIVE SUMMARY

In rice processing studies conducted in MS and CA, mature rice grain was harvested 62 or 92 days following a single broadcast application of the 2 lbs ai/gal suspension concentrate formulation (MS trial) or the 0.11% G formulation (CA trial), respectively, at 0.18 lb ai/A (2x the application rate ~~used in the crop field trials; see 860.1500 DER for MRID 45830719). The suspension concentrate~~ formulation was applied as a broadcast foliar spray to rice at the 32 BBCH growth stage, using water containing a crop oil concentrate. The G formulation was applied directly to flooded rice, ~40 days after seeding, when the permanent flood was established.

Residues of penoxsulam were nondetectable (<0.002 ppm) in/on rice grain treated with the suspension concentrate or G formulation, and residues were nondetectable in hulls, bran, and polished rice processed from treated rice grain. Processing factors could not be determined because the residue levels were nondetectable in both the RAC and processed commodities. The maximum theoretical concentration factor for rice is 8x (OPPTS 860.1520, Table 1), based on concentration factors of 5x for hulls and 7.7x for bran (OPPTS 860.1520, Table 3).

The petitioner did not address the issue of conducting field trials on rice at higher rates, to potentially generate samples containing detectable or quantifiable residues; however, in the rice metabolism study (refer to the DER for MRID 45830712), it was noted that phytotoxic effects were observed in plants treated at 150 g ai/ha, which is equivalent to 0.13 lb ai/A.

Residues of penoxsulam in/on rice grain and its processed commodities were quantitated using the proposed LC/MS/MS enforcement method (GRM 01.25). The reported limit of detection (LOD) and limit of quantitation (LOQ) were 0.002 ppm and 0.01 ppm, respectively, for all rice matrices. This method is adequate for data collection based on acceptable concurrent method recovery and method validation data (refer to the DER for MRID 45830714).

The maximum storage intervals from sample collection to analysis were 58 days (1.9 months) for rice grain and 135 days (4.4 months) for rice processed commodities. The available storage stability data (refer to the DER for MRID 45830717) demonstrate that residues of penoxsulam were stable under frozen conditions for up to 210 days (6.9 months) in rice grain and 197 days (6.5 months) in rice hulls, bran, and polished rice. These data are adequate to support the storage conditions and intervals of samples from the submitted rice processing study.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the rice processing study residue data are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D288152.

COMPLIANCE

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would impact the validity of the study.

A. BACKGROUND INFORMATION

Penoxsulam (company code XDE-638; PC Code 119031) is an herbicide intended for the control of *Echinochloa* grasses, broadleaf weeds, and sedge weeds in both water-injected (transplanted paddy) and postemergence (direct-seeded) rice. A single postemergence application of penoxsulam is to be made to rice from the one-leaf growth stage (7-12 days after seeding) to 60 days prior to rice harvest. The application is to be made by aerial or ground equipment once per growing season at a maximum rate of 0.045 lb ai/A (50 g ai/ha). Penoxsulam is to be formulated as a granular (for water-seeded rice) or suspension concentrate (for direct-seeded rice) formulation.

TABLE A.1. Penoxsulam Nomenclature.

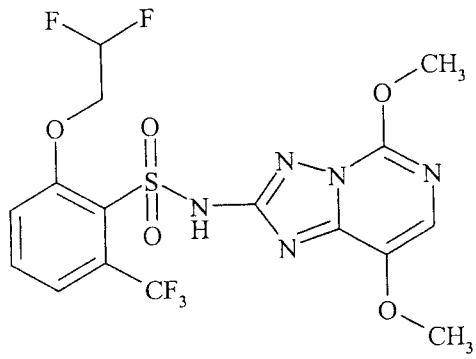
Compound	
Common name (proposed)	Penoxsulam
Company experimental name	XDE-638
IUPAC name	6-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy-s-triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluoro-o-toluenesulfonamide

TABLE A.1. Penoxsulam Nomenclature.	
CAS name	2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c] pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide
CAS #	219714-96-2
End-use product/EP	GF-443 SC SF (File Symbol 62719-LNN); GF-947 Granule SF (File Symbol 62719-LNG); GF-947 Granule CA (File Symbol 62719-LNR).

TABLE A.2. Physicochemical Properties of Technical Grade Penoxsulam.			
Parameter	Value		Reference
Melting point/range	Not available		
pH	Not available		
Density	Not available		
Water solubility	pH	Solubility (mg/L)	MRID 45830720
	(unbuffered)	4.91	
	5	5.66	
	7	408	
	9	1460	
Solvent solubility	Solvent	Solubility (g/L)	MRID 45830720
	DMSO	78.4	
	NMP	40.3	
	DMF	39.8	
	acetone	20.3	
	acetonitrile	15.3	
	ethyl acetate	3.23	
	methanol	1.48	
	octanol	0.035	
	xylene	0.017	
	heptane	<1 µg/mL	
Vapor pressure	7.16×10^{-16} mm Hg at 25 °C		MRID 45830720
Dissociation constant, pK_a	5.1		MRID 45830720
Octanol/water partition coefficient, $Log(K_{OW})$	pH	$Log(K_{OW})$	MRID 45830720
	(unbuffered)	-0.354	
	5	1.137	
	7	-0.602	
	9	-1.418	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

TABLE B.1.2. Study Use Pattern.								
Location: City, State; Year	EP[1]	Application						Tank Mix Adjuvants
		Timing	Rate (lb ai/A)	RTI[2] (days)	Treat. No.	Method	Total Rate (lb ai/A)	
Greenville, MS; 2001	2 lbs ai/gal suspension concentrate	32 BBCH; 31 inches tall	0.18	N/A	1	Foliar broadcast spray	0.18	Crop oil concentrate (2.5%)
Fresno, CA; 2001	0.11% G	22 BBCH; 16 inches tall	0.18	N/A	1	Broadcast to flooded rice	0.18	None

[1] EP = End-use Product
[2] RTI = Retreatment Interval; N/A = not applicable; only one application was made.

B.2. Processing Procedures

A processing flowchart was not provided.

Rice grain samples were shipped frozen to STAR-Coastal (location not provided) for processing into hull, bran, and polished rice. The grain was dried to 12% moisture and cleaned in a grain cleaner to remove foreign particles. The hulls were then removed from the cleaned grain using a rice huller. The remaining brown rice (hulled grain) was milled to obtain polished rice and bran. Processing of rice grain into hulls, bran and polished rice was completed within 10 days of harvest. No material balance information or any additional details concerning the processing procedures were provided.

B.3. Analytical Methodology

Samples of rice grain and processed hulls, bran, and polished rice were analyzed for residues of penoxsulam using Dow AgroSciences Method GRM 01.25, the proposed enforcement method. A complete description of the method is provided in the DER for MRID 45830714.

Briefly, samples of rice grain and its processed commodities were extracted with ACN:water (8:2; v:v) and centrifuged. An aliquot of the supernatant was diluted with water and purified by solid-phase extraction. Residues were eluted with ACN:formic acid (99.9:0.1, v:v), evaporated to dryness, and redissolved in ACN:methanol:water (15:15:70, v:v:v) mobile phase containing 0.1% acetic acid for analysis by LC/MS/MS. The reported LOD was 0.002 ppm, and the LOQ was 0.01 ppm for all rice matrices.

C. RESULTS AND DISCUSSION

In two trials, mature rice grain was harvested 62 or 92 days following a single broadcast application of the 2 lbs ai/gal suspension concentrate or 0.11% G formulation, respectively, at 0.18 lb ai/A (2x the field trial application rate). The suspension concentrate formulation was applied as a broadcast foliar spray to rice at the 32 BBCH growth stage using ground equipment in 11.4 gal/A water with a crop oil concentrate (2.5%). The G formulation was applied directly to flooded rice, ~40 days after seeding, when the permanent flood was established. The maximum theoretical concentration factor for rice is 8x (OPPTS 860.1520, Table 1).

Residues of penoxsulam in/on rice grain and its processed commodities were quantitated using the proposed LC/MS/MS enforcement method (GRM 01.25). Concurrent method validation data are presented in Table C.1. The reported LOD and LOQ were 0.002 ppm and 0.01 ppm, respectively, for all rice matrices; however, the lowest level of validation in the concurrent method recovery analyses was 0.015 ppm for each commodity. Adequate method validation data on rice matrices (including processed commodities) at the LOQ level were provided for the enforcement method (see the DER for MRID 45830714). This method is adequate for data collection based on acceptable concurrent and method validation recovery data.

Residues data from the study are presented in Table C.3. Residues of penoxsulam were nondetectable (<0.002 ppm) in/on rice grain (RAC) and hulls, bran, and polished rice processed from rice treated with either the suspension concentrate or G formulation. Processing factors could not be determined because the residue levels were nondetectable in both the RAC and processed commodities. Apparent residues of penoxsulam were reported as nondetectable in/on two samples each of untreated rice grain, hulls, bran, and polished rice.

The petitioner did not address the issue of conducting field trials on rice at higher rates, to potentially generate samples containing detectable or quantifiable residues; however, in the rice metabolism study (refer to the DER for MRID 45830712), it was noted that phytotoxic effects were observed in plants treated at 150 g ai/ha, which is equivalent to 0.13 lb ai/A.

Sample storage conditions and intervals are summarized in Table C.2. Bulk samples of rice grain were frozen at the field sites within 4 hours of sampling and were shipped frozen to STAR-Coastal for processing. Rice grain samples were processed within 10 days of harvest, and the frozen processed hull, bran, and polished rice samples were shipped overnight to Dow AgroSciences for analysis. The maximum storage intervals from sample collection to analysis were 58 days (1.9 months) for rice grain and 135 days (4.4 months) for rice processed commodities. The available storage stability data (refer to the DER for MRID 45830717) demonstrate that residues of penoxsulam are stable under frozen conditions for up to 210 days (6.9 months) in rice grain and 197 days (6.5 months) in rice hulls, bran, and polished rice. These data are adequate to support the storage conditions and intervals of samples from the submitted rice processing studies.

TABLE C.1. Summary of Concurrent Recoveries of Penoxsulam from Rice.

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev
Rice, grain	Penoxsulam	0.015	2	93, 96	96 ± 3
		0.15	1	99	
Rice, hulls	Penoxsulam	0.015	2	109, 110	112 ± 3
		0.075	2	111, 116	
Rice, bran	Penoxsulam	0.015	2	107, 108	109 ± 3
		0.15	1	112	
Polished rice	Penoxsulam	0.015	2	105, 116	110 ± 6
		0.15	1	109	

TABLE C.2. Summary of Storage Conditions.

Matrix	Storage Temp. (°C)	Actual Storage Duration from Collection (Processing) to Analysis [1]	Limit of Demonstrated Storage Stability
Rice, grain	-20	28-58 days (0.9-1.9 months)	210 days[2]
Rice, hulls		95-135 days (3.1-4.4 months)	197 days in rice hulls, bran, and polished rice[2]
Rice, bran		95-135 days (3.1-4.4 months)	
Polished rice		95-135 days (3.1-4.4 months)	

[1] Rice grain was processed within 10 days of harvest.
[2] Refer to the DER for MRID 45830717.

TABLE C.3. Residue Data from Rice Processing Study with Penoxsulam.					
RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Penoxsulam Residues (ppm) [1]	Processing Factor
Rice Treated with the 2 lbs ai/gal Suspension Concentrate					
Rice	Grain (RAC)	0.18	62	ND	--
	Hulls			ND	No processing factor could be calculated because residues in the RAC and processed commodities were nondetectable.
	Bran			ND	
	Polished Rice			ND	
Rice Treated with the 0.11% G					
Rice	Grain (RAC)	0.18	92	ND	--
	Hulls			ND	No processing factor could be calculated because residues in the RAC and processed commodities were nondetectable.
	Bran			ND	
	Polished Rice			ND	

[1] Residues in the RAC and processed commodities were reported as nondetectable (ND); the reported LOD and LOQ were 0.002 and 0.01 ppm, respectively, in all rice matrices.

D. CONCLUSIONS

The submitted rice processing data reflect the use of penoxsulam as a suspension concentrate or G formulation to rice at 0.18 lb ai/A. Application of the suspension concentrate formulation was made to rice at the 32 BBCH growth stage, and application of the G formulation was made ~40 days after seeding, when the permanent flood was established. Residues of penoxsulam were nondetectable (<0.002 ppm) in/on rice grain (RAC) and hulls, bran, and polished rice processed from rice treated with either the suspension concentrate or G formulation. An acceptable method was used for quantitation of residues in/on rice grain and its processed commodities.

The petitioner did not address the issue of conducting field trials on rice at higher rates, to potentially generate samples containing detectable or quantifiable residues; however, in the rice metabolism study (refer to the DER for MRID 45830712), it was noted that phytotoxic effects were observed in plants treated at 150 g ai/ha, which is equivalent to 0.13 lb ai/A.

E. REFERENCES

None.

F. DOCUMENT TRACKING

RDI: R. Loranger (7/9/04)
Petition Number(s): 3F06542
DP Barcode(s): D288152
PC Code: 119031