

US EPA ARCHIVE DOCUMENT



Clothianidin/264-789/PC Code 044309/Bayer CropScience AG/264
 DACTO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
 Crop Field Trial - Sorghum (Forage, Stover, and Grain)

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 RAB2/HED (7509C)

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This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B: Durham, NC 27713). It has been reviewed by HED and revised to reflect current OPP policies.

STUDY REPORT

MRID #46144901. F. K. Duah (2002) *TI-435 600 FS - Magnitude of the Residue in Sorghum*. Bayer Study #T519SO01, Bayer Report #200233, Gustafson Project #0104001. Unpublished study prepared by Bayer Corporation Agricultural Division, and Gustafson Research and Development Center (GRDC). 182 pages. {OPPTS Residue Chemistry Test Guideline 860.1500}

EXECUTIVE SUMMARY

In a total of 12 sorghum field trials conducted in 2001, clothianidin formulated at 5 pounds active ingredient per gallon as a flowable concentrate (5 lb ai/gal FC) was applied as a single seed treatment to grain sorghum at 0.25 lb ai/100 lb seeds using commercial seed treatment equipment. Based on the seeding rates used at the various field trial sites, roughly 38,000 to 133,000 seeds per acre (seeds/A), which are typical for sorghum production, the actual field use rates were equivalent to 0.006 to 0.026 lb ai/A. Sorghum forage was harvested at 42 to 112 days after planting (DAP), while sorghum stover and grain were harvested at commercial maturity, 97 to 167 DAP. A single control and duplicate treated samples were collected from each trial. Samples were stored frozen from collection to analysis for up to 11 months, a duration supported by available storage stability data.

The LC/MS/MS method used to determine clothianidin residues in/on sorghum forage, stover, and grain (Bayer Method 109240-1) is a current tolerance enforcement method and was adequately validated in conjunction with the field trial analyses. Briefly, residues are extracted with ACN/water, filtered, concentrated, and cleaned up using a ChemElut™ column. Residues are then analyzed by LC/MS/MS and quantified using deuterated clothianidin as an internal standard. The validated limit of quantitation (LOQ) for clothianidin residues is 0.010 ppm for sorghum forage, stover, and grain. The limit of detection (LOD) is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain.

Residues of clothianidin were less than 0.010 ppm (the LOQ) in all samples of sorghum forage, stover, and grain (n = 24 per matrix), with average residues of less than 0.010 ppm (the LOQ) in each matrix.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the sorghum field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming US EPA Residue Chemistry Summary Document (DP Barcode D303164).



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COMPLIANCE

Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.

A. BACKGROUND INFORMATION

Clothianidin (also known by its development code numbers, TM-444, TI-435, or V-10066) is a systemic insecticide, belonging to the chloronicotinyl (and nitroguanidine) class of chemicals, which enters the transpiration stream through the roots and cotyledons of newly germinating seedlings and protects below- and above-ground plant parts from insect damage. It binds (via ingestion and contact routes) with the nicotinic acetylcholine receptor sites, interfering with transmission of stimuli and eventually inhibiting reproduction of the insect. Clothianidin is a major metabolite of thiamethoxam. It is currently registered (40CFR §180.586) for use as a seed treatment for corn and canola.

Bayer CropScience has also requested tolerances for clothianidin residues in/on sorghum commodities in conjunction with a proposed seed treatment use on sorghum (PP#3F6792). The 5 lb ai/gal FC formulation of clothianidin (Poncho™ 600, EPA Registration #264-789) is proposed for use on grain sorghum as a single seed treatment application at up to 0.25 lb ai/100 lb seeds, using commercial seed treatment equipment.

TABLE A.1 Nomenclature of Test Compound.	
Compound	
Empirical Formula	C ₆ H ₈ ClN ₅ O ₂ S
Common Name	Clothianidin
Company Experimental Names	TM-444, TI-435, V-10066
IUPAC Name	(E)-1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine
CAS Name	[C(E)]-N-[(2-Chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitroguanidine
CAS Number	210880-92-5 (formerly 205510-53-8)
Chemical Class	Chloronicotinyl
Known Impurities of Concern	None
End-Use Product (EUP)	Poncho™ 600, EPA Registration #264-789

TABLE A.2 Physicochemical Properties (from MRID #45422301).	
Parameter	Value
Molecular Weight	249.7
Melting Point (°C)	176.8
pH at 23°C	6.24 [1% solution/suspension]
Density (g/cm ³) at 20°C	1.61 [PAI], 1.59 [TGAI]
Water Solubility (g/L) at 20°C	0.327



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 Crop Field Trial - Sorghum (Forage, Stover, and Grain)

TABLE A.2 Physicochemical Properties (from MRID #45422301).

Parameter	Value
Solvent Solubility (g/L) at 25°C	n-Heptane <0.00104
	Xylene 0.0128
	1-Octanol 0.938
	Dichloromethane 1.32
	Ethyl Acetate 2.03
	Methanol 6.26
	Acetone 15.2
Vapor Pressure (Pa) at 25°C	1.3 x 10 ⁻¹⁰
Dissociation Constant (pK _a) at 20°C	11.09
Octanol/Water Partition Coefficient (Log K _{ow}) at 25°C	0.7
UV/Visible Absorption Spectrum, Maximum (nm)	265.5 [acidic, neutral sol'n]. 246.0 [basic sol'n].

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

The sorghum seeds used in all trials were treated at the GRDC in McKinney, Texas, using a Hege 11 commercial seed treater. For application, clothianidin (5 lb ai/gal FC) was diluted with water to form a slurry. The treated seeds were then shipped to the appropriate field trial sites for planting (see Table B.1.1).

TABLE B.1.1 Trial Site Conditions.

Trial Identification (City, State/Year)	Soil Characteristics				Meteorological Data	
	Type	%OM	pH	CEC	Total Rainfall (Inches) ¹	Overall Temperature Range (°C)
Chula, GA/2001	NR ²		NA ³		13.5	NR
Benoit, MS/2001	NR		NA		21.2	NR
Stilwell, KS/2001	NR		NA		23.4	NR
Oxford, IN/2001	NR		NA		19.9	NR
Louisville, NE/2001	NR		NA		15.1	NR
New Holland, OH/2001	NR		NA		17.8	NR
Comanche, OK/2001	NR		NA		5.4	NR
Brookshire, TX/2001	NR		NA		7.3	NR
Jamestown, ND/2001	NR		NA		13.5	NR
Claude, TX/2001	NR		NA		5.9	NR
Plainview, TX/2001	NR		NA		3.6	NR
Levelland, TX/2001	NR		NA		5.3	NR

1. Total rainfall from first application to last sampling.
 2. NR = Not Reported.
 3. NA = Not Applicable.



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A general summary of weather conditions was not provided for each field trial site; the only weather data provided was total rainfall for the study period. Average historical values for the residue study period were not reported. Rainfall was supplemented with irrigation as needed.

TABLE B.1.2 Study Use Pattern on Sorghum.

Trial Identification (City, State/Year)	EUP	Method ¹ /Timing	Application				
			Seeding Rate (Seeds/A) ²	Single Rate (lb ai/A) ³	Number	RTI ⁴ (Days)	Total Rate (lb ai/A)
Chula, GA/2001	Poncho™ 600	Seed treatment/prior to planting.	115,082	0.019	1	NA ⁵	0.019
Benoit, MS/2001	Poncho™ 600	Seed treatment/prior to planting.	72,906	0.012	1	NA	0.012
Stilwell, KS/2001	Poncho™ 600	Seed treatment/prior to planting.	74,574	0.012	1	NA	0.012
Oxford, IN/2001	Poncho™ 600	Seed treatment/prior to planting.	82,605	0.013	1	NA	0.013
Louisville, NE/2001	Poncho™ 600	Seed treatment/prior to planting.	111,513	0.017	1	NA	0.017
New Holland, OH/2001	Poncho™ 600	Seed treatment/prior to planting.	42,312	0.008	1	NA	0.008
Comanche, OK/2001	Poncho™ 600	Seed treatment/prior to planting.	38,188	0.006	1	NA	0.006
Brookshire, TX/2001	Poncho™ 600	Seed treatment/prior to planting.	112,549	0.018	1	NA	0.018
Jamestown, ND/2001	Poncho™ 600	Seed treatment/prior to planting.	133,242	0.026	1	NA	0.026
Claude, TX/2001	Poncho™ 600	Seed treatment/prior to planting.	43,379	0.008	1	NA	0.008
Plainview, TX/2001	Poncho™ 600	Seed treatment/prior to planting.	107,491	0.019	1	NA	0.019
Levelland, TX/2001	Poncho™ 600	Seed treatment/prior to planting.	43,125	0.008	1	NA	0.008

1. Applications were made using a commercial seed-treater (Hege 11 treater) at GRDC in McKinney TX; no tank mix adjuvants were used.

2. Typical seeding rates for grain sorghum range from 50,000 to 150,000 seeds/A.

3. All seeds were treated at a rate of 0.25 lb ai/100 lb seeds; the equivalent field use rates were 0.006 to 0.026 lb ai/A based on the actual seeding rates.

4. RTI = Re-Treatment Interval.

5. NA = Not Applicable.



TABLE B.1.3 Sorghum Field Trial Numbers and Geographical Locations.			
NAFTA Growing Region ¹	Submitted	Requested	
		Canada	US
1	--	NA ²	--
2	1	NA	1
3	--	NA	--
4	1	NA	1
5	4	NA	4
6	2	NA	2
7	1	NA	1
8	3	NA	3
9	--	NA	--
10	--	NA	--
11	--	NA	--
12	--	NA	--
Total	12	NA	12

1. Regions 13 to 21 and 1A, 5A, 5B, and 7A were not included as the proposed use is for the US only.

2. NA = Not Applicable.

B.2. Sample Handling and Preparation

Sorghum forage was harvested at 42 to 112 DAP, while sorghum stover and grain were harvested at commercial maturity, 97 to 167 DAP. A single control and duplicate treated samples (each weighing more than 2½ lb) of each commodity were collected from each trial and placed in frozen storage at the test facility within 4 hours, and stored frozen for 1 to 117 days. Percent dry matter at harvest was 13 to 58% for forage, 23 to 72% for stover, and 82 to 90% for grain. Samples were then shipped by freezer truck to the analytical laboratory, Residue Analysis Laboratory, at the Bayer Research Park (BRP) in Stilwell, Kansas. At BRP, all sorghum samples were homogenized, then stored frozen (at less than -15°C) prior to analysis. Samples were stored frozen from collection to analysis for durations of up to 11 months.

B.3. Analytical Methodology

Samples were analyzed using an LC/MS/MS method entitled *Modification M001 of the Method 00552 for the Determination of Residues of TI-435 in/on Plant Materials*, Bayer Ag Div Report #109240-1 (MRID #45422537), which is essentially Method 00552 with the use of an internal standard for quantitation. Both methods have been validated by the Agency and accepted for tolerance enforcement. A brief description of the method follows.

Residues are extracted with ACN/water and filtered. The deuterated internal standard is added to the filtrate, which is then concentrated for cleanup using a ChemElut™ column eluted with cyclohexane/ethyl acetate. Residues are then analyzed by HPLC using a C₁₈ column, a gradient mobile phase of acidic water and ACN, and MS/MS quantitation (m/z 248 and 251 ions). The sorghum forage, stover, and grain residues were quantified using the deuterated clothianidin internal standard. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum forage, stover, and grain. The LOD is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain.



C. RESULTS AND DISCUSSION

The number and geographic representation of the sorghum field trials are adequate. In a total of 12 sorghum field trials conducted in 2001, clothianidin (5 lb ai/gal FC) was applied to grain sorghum as a single seed treatment at 0.25 lb ai/100 lb seeds. Based on the seeding rates used at the various field sites, the actual field application rates were equivalent to 0.006 to 0.026 lb ai/A per season. Sorghum forage was harvested at commercial maturity 42 to 112 DAP, while sorghum stover and grain were harvested at commercial maturity 97 to 167 DAP. Single control and duplicate treated samples were collected from each trial.

The LC/MS/MS method (Bayer Method 109240-1) used to determine clothianidin residues in/on sorghum forage, stover, and grain is adequate for data collection. Average concurrent method recoveries were $85 \pm 10\%$ from forage samples, $87 \pm 3\%$ from stover samples, and $91 \pm 8\%$ from grain samples fortified with clothianidin at 0.010 ppm (see Table C.1). Apparent residues of clothianidin were less than the LOD in all control samples. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum forage, stover, and grain. The LOD is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for durations of up to 11 months (see Table C.2). Storage stability data are available on corn, sugar beet, and canola matrices indicating that clothianidin is stable in frozen storage for intervals of up to 24 months (MRID #45422611). These data will support the current sorghum field trials.

Residues of clothianidin were less than 0.010 ppm (the LOQ) in all sorghum forage, stover and grain samples, and were detectable (0.006 ppm) in only one forage sample (see Table C.3). Average residues in forage, grain and stover were less than 0.010 ppm, the LOQ (see Table C.4).

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

Analyte	Crop [Matrix]	Spiking Level (mg/kg)	Sample Size	Recoveries (%)	Mean Recovery \pm Std Dev (%)
Clothianidin	Sorghum [Forage]	0.010	4	77-94	85 ± 10
	Sorghum [Stover]	0.010	4	83-90	87 ± 3
	Sorghum [Grain]	0.010	7	80-106	91 ± 8

Sorghum Matrix	Storage Temperature (°C)	Actual Storage Duration (Months) ¹	Limit of Demonstrated Storage Stability (Months) ²
Forage	<-15	~9-11	24
Stover		~7-10	
Grain		~7-10	

1. Extracts were stored frozen for 0 to 3 days prior to analysis.

2. Storage stability data are available indicating that clothianidin is stable under frozen conditions in corn, sugar beet, and canola for intervals of up to 24 months (MRID #45422611).



TABLE C.3 Residue Data from Sorghum Field Trials using Clothianidin as a Seed Treatment.

Trial ID (City, State/Year)	EPA Region	Variety	Sorghum Matrix	% Dry Matter	Use Rate (lb ai/A) ¹	PHI ² (Days)	Residues (ppm) ³	
Chula, GA/2001	2	DK 52	Forage	26	0.019	82	ND ⁴ , ND	
			Stover	69			113	ND, ND
			Grain	86			113	ND, ND
Benoit, MS/2001	4	DK 52	Forage	13	0.012	42	ND, [0.006] ⁵	
			Stover	31			134	ND, ND
			Grain	84			134	ND, ND
Stilwell, KS/2001	5	KS 711Y	Forage	58	0.012	112	ND, ND	
			Stover	72			133	ND, ND
			Grain	90			133	ND, ND
Oxford, IN/2001	5	KS 711Y	Forage	34	0.013	102	ND, ND	
			Stover	39			142	ND, ND
			Grain	82			142	ND, ND
Louisville, NE/2001	5	NK 711Y KS	Forage	35	0.017	112	ND, ND	
			Stover	40			148	ND, ND
			Grain	87			148	ND, ND
New Holland, OH/2001	5	G 444	Forage	34	0.008	103	ND, ND	
			Stover	23			147	ND, ND
			Grain	83			147	ND, ND
Comanche, OK/2001	6	DK 52	Forage	35	0.006	82	ND, ND	
			Stover	57			167	ND, ND
			Grain	86			167	ND, ND
Brookshire, TX/2001	6	DK 52	Forage	30	0.018	75	ND, ND	
			Stover	48			97	ND, ND
			Grain	89			97	ND, ND
Jamestown, ND/2001	7	G 444	Forage	26	0.026	107	ND, ND	
			Stover	27			151	ND, ND
			Grain	85			151	ND, ND
Claude, TX/2001	8	Y363	Forage	32	0.008	91	ND, ND	
			Stover	53			161	ND, ND
			Grain	89			161	ND, ND
Plainview, TX/2001	8	NCY 363	Forage	33	0.019	77	ND, ND	
			Stover	54			109	ND, ND
			Grain	84			109	ND, ND
Levelland, TX/2001	8	Y 363	Forage	39	0.008	82	ND, ND	
			Stover	51			114	ND, ND
			Grain	87			114	ND, ND

1. Seeds treated at 0.25 lb ai/100 lb seeds; field use rate depended on seeding rate (~38,000 to 133,000 seeds/A).
2. PHI = Pre-Harvest Interval (= DAP in this case, because use was as a seed treatment).
3. The LOQ is 0.010 ppm; the LOD is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain.
4. ND = Not Detected.
5. Value in brackets is between the LOD and the LOQ.



Clothianidin/264-789/PC Code 044309/Bayer CropScience AG/264.
 DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
 Crop Field Trial - Sorghum (Forage, Stover, and Grain)

TABLE C.4 Summary of Residue Data for Sorghum Field Trials with Clothianidin.

Commodity	Rate (lb ai/100 lb Seeds)	PHI (Days)	Residue Levels (ppm)					
			n	Min.	Max.	HAFT*	Mean	Std. Dev.
Sorghum Forage	0.25	42-112	24	<0.010	<0.010	<0.010	<0.010	0
Sorghum Stover		97-167	24	<0.010	<0.010	<0.010	<0.010	0
Sorghum Grain		97-167	24	<0.010	<0.010	<0.010	<0.010	0

* HAFT = Highest Average Field Trial.

D. CONCLUSION

The sorghum field trial data are adequate and reflect the use of a single seed treatment of clothianidin (5 lb ai/gal FC) on grain sorghum at 0.25 lb ai/100 lb seeds. Based on the actual seeding rates of roughly 38,000 to 133,000 seeds/A, the field use rates were equivalent to 0.006 to 0.026 lb ai/A.

E. REFERENCES

Subject: *Modification M001 of the Method 00552 for the Determination of Residues of TI-435 in/on Plant Materials*, Bayer Ag Div Report #109240-1

Author: F. Nuesslein

Dated: 2000

MRID: 45422537

Subject: *Determination of the Storage Stability of TI-435 Residues in Fortified Analytical Samples of Plant Materials*, Bayer Ag Div Report #109734

Author: F. Nuesslein

Dated: 2001

MRID: 45422611

F. DOCUMENT TRACKING

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