UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

DATE: 21 November 2006

SUBJECT: **Acetochlor. Tolerance Petition Requesting the Establishment of Permanent Tolerances Associated with Section 3 Registration for Food Use of the Herbicide Acetochlor on Sorghum. Summary of Analytical Chemistry and Residue Data.**

Petition Number:	**5F6918**
PC Code:	**121601**
DP Number:	**D316496**
Decision Number:	**355528**
Regulatory Citation:	**40CFR §180.470**
Chemical Class:	**Chloroacetanilide Herbicide**
Trade Name:	**Degree Xtra™**
MRID Numbers:	**46507101 and 46507102**

FROM: William T. Drew, Chemist
Registration Action Branch 2
Health Effects Division (7509P)

THROUGH: Douglas Dotson, Chemist
Registration Action Branch 2
Health Effects Division (7509P)
and
Richard A. Loranger, Branch Senior Scientist
Registration Action Branch 2
Health Effects Division (7509P)

TO: James Tompkins/Vickie Walters, RM Team 25
Herbicide Branch
Registration Division (7505P)

This Residue Chemistry Summary Document 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 policy.

Executive Summary

Acetochlor, an herbicide with CAS Number 34256-82-1 and CAS Name 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide, is a member of the chloroacetanilide class of compounds.

Monsanto, as a member of the Acetochlor Registration Partnership (ARP), has submitted a petition supporting the direct use of acetochlor, as a 2.7 pounds active ingredient per gallon (lb ai/gal) microencapsulated (Mcap) formulation, on sorghum. The proposed use on sorghum is for a single application of acetochlor (as either a pre-plant incorporated, pre-emergence, or early-season post-emergence broadcast application) at a maximum rate of 2.0 to 2.5 lb ai per acre (lb ai/A), depending on the soil type. The post-emergence application is to be made before the crop exceeds 11 inches in height. In conjunction with this use, Monsanto is proposing permanent tolerances for residues of acetochlor and its metabolites at 1.0 ppm on sorghum forage, 0.05 ppm on sorghum grain, and 1.5 ppm on sorghum stover.

The qualitative nature of acetochlor residues in sorghum is understood, based on adequate corn metabolism studies and the limited sorghum data. The HED Metabolism Committee previously concluded that the regulated residues of concern (ROCs) in corn include parent and any metabolites containing the EMA or HEMA moieties, expressed in acetochlor equivalents (M. Flood, 9/30/1993). EMA and HEMA are hydrolysis products of acetochlor, 2-ethyl-6-methylaniline (EMA) and 2-(1-hydroxyethyl)-6-methylaniline (HEMA). The Metabolism Committee concluded that inclusion of Metabolite 57, a phenolic oxanilic acid metabolite, in the tolerance expression was not necessary, pending further toxicity testing. Because corn and sorghum are closely related crops that are grown under similar conditions, the conclusions for corn will be translated to sorghum.

The qualitative nature of acetochlor residues in animals is adequately understood. Based on adequate studies examining the metabolism of various acetochlor plant metabolites (EMA, HEMA, and Metabolite 57) in both ruminants and poultry, the Agency has concluded that the acetochlor ROCs in ruminants and poultry include EMA- and HEMA-type metabolites and Metabolite 57. Based on the metabolism studies and the available livestock feeding studies, the Agency has also determined that tolerances are not required on livestock commodities to support the current use on corn. As the recommended tolerances for sorghum commodities are equal to or lower than the recommended (re-assessed) tolerances on the equivalent corn commodities (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005), tolerances on animal commodities are not required for the proposed use on sorghum, either.

An adequate HPLC/oxidative coulometric electrochemical detector (OCED) method is available for enforcing tolerances of acetochlor and its metabolites in plant commodities. For this method, residues are solvent-extracted into aqueous acetonitrile (ACN), and then base-hydrolyzed to yield EMA and HEMA. The resulting residues are steam-distilled into dilute acid, adjusted to a basic pH, and then partitioned into dichloromethane (DCM). HEMA is methylated, then residues of EMA and methylated HEMA (MEMA) are separated, and determined via HPLC/OCED. Residues of EMA and HEMA are expressed in acetochlor equivalents; the validated method limits of quantitation (LOQs) are 0.020 ppm for each analyte.

In the current sorghum field trials and processing study, residues of EMA- and HEMA-producing metabolites were determined using an LC/MS/MS method (Method ES-ME-1001-01).

which is similar to the current enforcement method, except that methylation of HEMA is not required, and the residues are determined by LC/MS/MS rather than by HPLC/OCED. For this method, residues are extracted with aqueous ACN, base-hydrolyzed to yield EMA and HEMA, and then steam-distilled into dilute acid. The pH is adjusted to basic, residues are partitioned into DCM, and then concentrated. Residues are re-dissolved in aqueous ACN, then determined via LC/MS/MS using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues are reported in acetochlor equivalents; the LOQs for EMA are 0.015 ppm in stover, and 0.005 ppm in grain, flour, bran, and forage. The LOQs for HEMA are 0.011 ppm in stover, and 0.003 ppm in grain, flour, bran, and forage. The method was adequately validated in conjunction with analyses of the field trial and processing study samples.

Storage stability data are available indicating that acetochlor *per se* is stable in frozen corn, soybean, and peanut forage for intervals of up to approximately 36 months; residues of EMA and HEMA metabolites are stable in frozen corn grain, forage, and fodder for intervals of up to 49 months (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005). These data will support the storage durations and conditions of the sorghum field trials and processing study, in which samples were stored frozen for durations of up to 7.3 months prior to analysis for acetochlor residues.

The available field trial data are adequate, and support the proposed use pattern for acetochlor (2.7 lb ai/gal Mcap; the proposed formulation also includes the safener furilazole) on sorghum. The number and geographic distribution of the field trials are adequate, and samples of forage, grain, and stover were collected at the appropriate stages of maturity. Combined acetochlor residues were 0.018 to 0.515 ppm in forage harvested 82 to 116 days following a pre-emergence application and 0.045 to 0.888 ppm in forage harvested 52 to 77 days following a post-emergence application. In the trial examining residue decline in forage, combined residues were variable, ranging from 0.099 to 0.217 ppm from 48 to 73 days after treatment (DAT). For grain harvested at maturity, combined residues were <0.008 to 0.022 ppm following a pre-emergence application, and <0.008 to 0.033 ppm following a post-emergence application. For stover harvested at maturity, combined residues were <0.026 to 0.744 ppm following a pre-emergence application, and <0.032 to 1.14 ppm following a post-emergence application. Residues were consistently higher in each commodity following the post-emergence application than the pre-emergence application. Of the 13 field trial sites, higher residues were observed from the post-emergence application at 10 sites for forage, and 11 sites for stover. For grain, residues from the post-emergence treatment were equal to or higher than those from the pre-emergence treatment at 12 sites. Average combined residues in forage, grain, and stover were respectively 0.174, 0.009, and 0.251 ppm for the pre-emergence application, and 0.263, 0.015, and 0.342 ppm for the post-emergence application.

Although not currently required, Monsanto provided processing data on grain sorghum from two field trial sites. The processing data are adequate, and indicate that acetochlor residues do not concentrate in flour (processing factor of less than 0.5X), but do concentrate in bran (4.3X).

An adequate confined rotational crop study is available to support the current use on corn at a seasonal rate of up to 3.0 lb ai/A. Based on this study, HED concluded that tolerances for rotational crops should include EMA- and HEMA-producing metabolites. Extensive rotational

field crop trials are available depicting acetochlor residues in sorghum, soybeans, and wheat rotated with corn treated with acetochlor at 3.0 lb ai/A; additional rotational field crop trials on alfalfa, beans, oats, peas, potatoes, sugar beets, and sunflower are currently under review in conjunction with a petition for the use of acetochlor on sweet corn (PP#6F4791). Because the seasonal use rate on corn is higher than the proposed use rate for sorghum (2.5 lb ai/A), issues pertaining to residues in rotational crops, and the need for rotational crop tolerances, are being addressed under the sweet corn petition.

Residue Chemistry Deficiencies

No major deficiencies were noted in the subject petition that would preclude the establishment of permanent tolerances for acetochlor and its regulated metabolites on sorghum commodities. Provided that the proposed label is amended to specify a 60-day pre-harvest interval/pre-grazing interval (PHI/PGI) for sorghum forage following a post-emergence application, HED recommends in favor of establishing permanent tolerances for residues of acetochlor and its metabolites, expressed in acetochlor equivalents, at 1.6 ppm on sorghum forage, 0.05 ppm on sorghum grain, and 1.7 ppm on sorghum stover.

Note to Registration Division (RD): In the regulatory citation for acetochlor (40CFR §180.470), no distinction is made between residues arising from direct application of acetochlor to crops (corn), and indirect or inadvertent residues arising in rotational crops (sorghum, soybeans, and wheat). If and when tolerances are established for acetochlor residues arising from direct application to sorghum, the regulatory citation should be amended to list tolerances for residues on corn and sorghum under 40CFR §180.470[a], while those on soybeans and wheat should be listed under 40CFR §180.470[d].

Background

Acetochlor is a chloroacetanilide herbicide currently used for pre-emergence control of weeds in corn. In the United States, acetochlor is conditionally registered for use on corn to the Acetochlor Registration Partnership (ARP), which is comprised of Monsanto and Dow AgroSciences. Acetochlor is formulated as a variety of emulsifiable concentrate (EC), emulsion in water (EW), granular (G), or Mcap formulations that can be applied to corn as a pre-plant, pre-emergence, or early post-emergence application. Tolerances are established for the combined residues of acetochlor and its metabolites convertible to EMA or HEMA, to be analyzed as acetochlor, and expressed as acetochlor equivalents (40CFR §180.470). Tolerances range from 0.05 to 1.5 ppm on corn commodities resulting from the direct use of acetochlor, and from 0.02 to 1.0 ppm on commodities from the rotational crops, sorghum, soybean, and wheat.

Monsanto has submitted a petition (PP#5F6918) proposing the use of acetochlor, formulated as a 2.7 lb ai/gal Mcap (EPA Registration #524-511), for direct application to sorghum. In conjunction with this use, Monsanto is proposing tolerances for acetochlor residues on the following commodities:

Sorghum, forage	1.0 ppm
Sorghum, grain	0.05 ppm
Sorghum, grain, stover	1.5 ppm

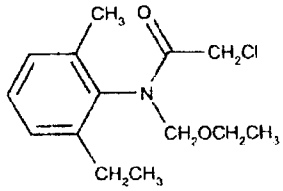
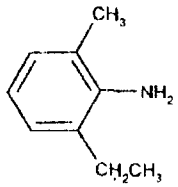
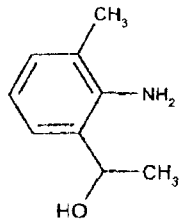
TABLE 1 Acetochlor Nomenclature.	
Chemical Structure	
Common Name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC Name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide
CAS Name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS Number	34256-82-1
PC Code	121601
End-Use Product (EP)	Degree Xtra (2.7 lb/gal Mcap), EPA Registration #524-511
Chemical Structure	
Common Name	EMA
Molecular Weight	337.4
CAS Name	2-ethyl-6-methylaniline
Chemical Structure	
Common Name	HEMA
Molecular Weight	303.3
CAS Name	2-(1-hydroxyethyl)-6-methylaniline

TABLE A.2 Physicochemical Properties of Acetochlor.		
Parameter	**Value**	**Reference**
Boiling Point/Range	163°C at 10 mm Hg. Decomposition occurs before the boiling point at atmospheric pressure (calculated by extrapolation of vapor pressure at lower temperature).	M. Flood, DEB 7474, 2/6/1991
pH	4.41 (1% solution in acetone/water, 1:1 vol/vol)	M. Flood, DEB 7474, 2/6/1991
Density (g/mL, 20°C)	1.123	M. Flood, DEB 7474, 2/6/1991
Water Solubility (mg/L, 25°C)	223	2001 Farm Chem Handbook

TABLE A.2 Physicochemical Properties of Acetochlor.		
Parameter	**Value**	**Reference**
Solvent Solubility (25°C)	Miscible in acetone, benzene, carbon tetrachloride, ethanol, chloroform, and toluene.	M. Flood, HED Memo, 1/21/1994
Vapor Pressure (mm Hg, 25°C)	4.5×10^{-5}	M. Flood, DEB 7474, 2/6/1991
Dissociation Constant (pK_a)	Not applicable (because acetochlor is neither an acid nor a base).	M. Flood, DEB 7474, 2/6/1991
Octanol/Water Partition Coefficient	970 (Dow study) or 1082 (Monsanto study). Differences are likely due to experimental error.	M. Flood, DEB 7474, 2/6/1991
UV/Visible Spectrum	Not available.	

860.1200 Directions for Use

Monsanto is proposing the use of its 2.7 lb ai/gal Mcap formulation, Degree Xtra™ Herbicide (EPA Registration #524-511), for direct application to sorghum as a primary crop. This end-use product (EP) is a multiple active ingredient (MAI) formulation which also contains atrazine at 1.34 lb ai/gal. An example label was provided and the directions for use on sorghum are summarized in Table 3, below. The 2.7 lb ai/gal Mcap product was the formulation that was used in the submitted sorghum field trials.

TABLE 3 Summary of Directions for Use of Acetochlor on Sorghum.					
Application Timing, Type, and Equipment [1]	**Formulation [EPA Registration #]**	**Maximum Single Rate [2] (lb ai/A) [Soil Type]**	**Maximum # Applications per Season**	**Maximum Seasonal Rate (lb ai/A)**	**PHI (Days)**
A pre-plant incorporated, pre-emergence, or post-emergence broadcast application using ground equipment	2.7 lb/gal Mcap [524-511]	2.0 [Coarse] 2.5 [Medium & Fine]	1	2.0-2.5	NS [3]

1. Use limitation: the post-emergence application must be made before the crop exceeds 11 inches in height.
2. The maximum application rate depends on soil type.
3. NS = Not Specified (applications are made early in the season).

Conclusions: The proposed use directions adequately reflect the use patterns utilized at the sorghum field trials. Field data are available reflecting either pre- or post-emergence application at the proposed maximum-use rate (2.5 lb ai/A). Given the long interval between application and harvest of grain and stover, PHIs are not required for these commodities. However, the label should be amended to specify a 60-day PHI/PGI for harvest or grazing of sorghum forage following a post-emergence application. The inclusion of atrazine in the formulation requires no additional data because adequate field trial data and tolerances are available for atrazine in sorghum at a higher use rate than that specified on the proposed label.

860.1300 Nature of the Residue - Plants

Acetochlor TRED; D297062; Samuel Ary; 5/31/2005

The qualitative nature of acetochlor residues in sorghum is adequately understood. In conjunction with the current petition, Monsanto submitted the results from a greenhouse metabolism study on sorghum conducted prior to 1984 (MRID #46507102). Given the age of

the study, and the lack of supporting data, a detailed review of the sorghum metabolism study was not conducted because the study is unacceptable under current Agency Guidelines. However, a preliminary review of the data indicates that the metabolites in sorghum were similar to the metabolites observed in the acceptable corn metabolism studies.

In the sorghum study, [^{14}C]-acetochlor was applied to the soil as a post-emergence application at a rate of 1.5 lb ai/A, and mature samples of stalks and grain were harvested 5 months later. Total radioactive residues (TRR) in lyophilized stalks and grain were 10 and 1.7 ppm, respectively. Extraction with 60% aqueous methanol released 81.4% of the TRR from foliage, and 74% of the TRR from grain. Solubilized residues were fractionated by anion exchange chromatography into four primary fractions consisting of a neutral fraction and three acidic fractions, with each fraction consisting of multiple components (each accounting for less than 10% of the TRR). These fractions corresponded to neutral glycosides, weak sulfur conjugate acids, oxanilic acids, and sulfonic acid metabolites. A total of nine metabolites were identified in foliage representing the above classes of metabolites, and four of the same metabolites were identified in grain. Of the nine metabolites, seven contained the EMA moiety, one the HEMA moiety, while the other was a phenolic oxanilic acid metabolite similar to Metabolite 57. The proposed metabolism of acetochlor in sorghum is shown in Appendix 1.

As corn is closely related to sorghum, and acceptable metabolism data are available on corn, the corn metabolism data will support the use on sorghum. Based on the corn data, the HED Metabolism Committee previously concluded that the regulated ROCs include parent and any metabolites containing the EMA or HEMA moiety, expressed in acetochlor equivalents (M. Flood, 9/30/1993). With regard to Metabolite 57, which was identified at slightly higher levels in corn forage and fodder than other metabolites in one metabolism study (ICI study), the Metabolism Committee concluded that this metabolite need not be included in the tolerance expression, pending further toxicity testing.

860.1300 Nature of the Residue - Livestock

Acetochlor TRED; D297062; Samuel Ary; 5/31/2005

The qualitative nature of acetochlor residues in animals is adequately understood, although the available studies in which goats and hens were dosed with [^{14}C]-acetochlor are not fully acceptable. Adequate studies have been submitted examining the metabolism of various plant metabolites (EMA, HEMA, and Metabolite 57) in both ruminants and poultry. Based on these studies, the Agency concluded that acetochlor residues in ruminants and poultry include EMA- and HEMA-type metabolites, along with Metabolite 57. The HED Metabolism Committee (M. Flood, 9/30/1993) concluded that tolerances are not required on livestock commodities to support the use on corn. Because tolerances for sorghum commodities are equal to or lower than the tolerances on the equivalent corn commodities, tolerances on animal commodities are not required for the proposed use on sorghum.

860.1340 Residue Analytical Methods.

A tolerance enforcement method is available for determining residues of acetochlor and its EMA- and HEMA-producing metabolites on corn commodities. The method utilizes HPLC/OCED, and is listed as Method I in PAM Volume II.

For this method, residues are solvent-extracted into aqueous ACN, concentrated, and base hydrolyzed to yield EMA and HEMA. The resulting residues are steam-distilled into dilute acid, adjusted to a basic pH, and partitioned into DCM. HEMA is methylated using acidic methanol, residues of EMA and methylated HEMA (MEMA) are separated, and then determined via HPLC/OCED. Residues of EMA and HEMA are expressed in acetochlor equivalents; the validated method LOQ is 0.020 ppm for each analyte.

The Agency previously noted that metolachlor metabolites can give false positive results for acetochlor EMA and HEMA residues. Instead of developing a separate confirmatory method for acetochlor residues, the registrant has provided adequate data demonstrating that the method available for metolachlor in PAM Volume II (Method I) can be used to determine whether residues in corn commodities are from metolachlor (positive) or acetochlor (negative).

In the current sorghum field trials and processing study, residues of EMA- and HEMA-producing metabolites were determined using an LC/MS/MS method (Method ES-ME-1001-01). This method is similar to the current tolerance enforcement method for acetochlor, except that methylation of HEMA is not required, and residues are determined by LC/MS/MS rather than by HPLC/OCED.

For this method, residues are extracted from homogenized samples with ACN/water (1:4 vol/vol), filtered, and concentrated. Residues are then base-hydrolyzed to yield EMA and HEMA, which are steam-distilled into dilute acid. The acidic distillate is partitioned against DCM, the organic phase is discarded, and the aqueous phase is then adjusted to a basic pH. Residues are partitioned into DCM, concentrated, and re-dissolved in ACN/water (1:9 vol/vol). Residues of EMA and HEMA are then determined via LC/MS/MS. The HPLC system consisted of a C_8 column with a mobile phase gradient of water/methanol (95:5) to methanol/ACN (1:1), each containing 0.2% acetic acid. The retention times were approximately 6.8 and 4.7 minutes for EMA and HEMA, respectively; residues were detected and quantified using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues are reported in acetochlor equivalents.

The statistically derived LOQs for EMA are 0.015 ppm in stover, and 0.005 ppm in grain, flour, bran, and forage, while the LOQs for HEMA are 0.011 ppm in stover, and 0.003 ppm in grain, flour, bran and forage. The LODs for EMA are 0.015 ppm in stover, and 0.004 ppm in grain, flour, bran and forage, while the LODs for HEMA are 0.007 ppm in stover, and 0.002 ppm in grain, flour, bran and forage.

The above method was adequately validated in conjunction with analysis of the field trial and processing study samples. Control samples were fortified with acetochlor *t*-sulfonic acid (EMA metabolite) and hydroxyethyl *t*-oxanilic acid (HEMA metabolite), with each at 0.010 to 0.200 ppm in grain, 0.010 to 2.00 ppm in forage and stover, and 0.010 to 0.050 ppm in flour and bran. Average recoveries from all commodities were 79 to 104% for EMA, and 71 to 88% for HEMA, with standard deviations of 1 to 17%. Apparent residues of EMA and HEMA were less than the LOQ in all control samples of each commodity.

Conclusions: An enforcement method is available for determining acetochlor residues in sorghum commodities. Samples from the sorghum field trials and processing study were analyzed using an adequate LC/MS/MS method for the determination of EMA and HEMA metabolites.

860.1380 Storage Stability

Samples of forage, grain, and stover from the sorghum field trials were stored frozen for durations of up to 7.3 months prior to analysis for acetochlor residues. In the processing study, grain samples were stored frozen for a maximum of 5.6 months, while processed fractions were stored frozen for a maximum of 2.8 months prior to analysis for acetochlor residues.

Adequate storage stability data are available indicating that acetochlor *per se* is stable in frozen corn, soybean, and peanut forage for intervals of up to approximately 36 months, while residues of EMA and HEMA metabolites are stable in frozen corn grain, forage, and fodder for intervals of up to 49 months (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005).

Conclusions: The available storage stability data adequately support the sample storage durations and conditions used in the sorghum field trials and processing study.

860.1400 Water, Fish, and Irrigated Crops

This guideline requirement is not relevant to the current petition, as no aquatic uses are being proposed for acetochlor.

860.1460 Food Handling

This guideline requirement is not relevant to the current petition, as no food handling uses are being proposed for acetochlor.

860.1480 Meat, Milk, Poultry, and Eggs

Because sorghum forage, stover, and grain are all major livestock feedstuffs, the proposed use on sorghum has the potential for exposing livestock to acetochlor residues in their diet. The theoretical dietary burdens (TDBs) for acetochlor residues in livestock were recently calculated in the Acetochlor TRED (D297062; Samuel Ary; 5/31/2005) using re-assessed tolerances for corn and soybean commodities (see Table 4, below). Based on these tolerances, the TDBs are 3.03 and 3.77 ppm for beef and dairy cattle, respectively, while the TDBs for both poultry and swine are 0.044 ppm. The inclusion of sorghum commodities in livestock diets would not increase the exposure of livestock to acetochlor residues, because the recommended tolerances for acetochlor on sorghum commodities are equal to or lower than the re-assessed tolerances on the equivalent corn commodities. Therefore, no changes in animal tolerances are required; the available feeding studies will support the proposed use on sorghum.

Monsanto has submitted three studies reflecting the feeding of EMA-type metabolites to cattle, poultry, and swine, along with one study reflecting the feeding of an HEMA-type metabolite to dairy goats. In considering the available animal metabolism data and the feeding studies, in conjunction with a requested increase in the tolerance on corn forage to 3.0 ppm, the Agency (Memorandum; D214735 and D214738; G. Herndon et al; 6/25/1996) reaffirmed an earlier conclusion by the HED Metabolism Committee finding that there is no reasonable expectation of finite residues occurring in animal commodities (40CFR §180.6[a][3]). Therefore, tolerances for animal commodities are not currently required.

TABLE 4 Calculation of Theoretical Dietary Burdens for Acetochlor Residues in Livestock.				
Feedstuff	**% Dry Matter[1]**	**% Diet[1]**	**Recommended Tolerance (ppm)**	**Dietary Contribution (ppm)[2]**
Beef Cattle				
Corn Forage	40	40	3.0	3.0
Corn Grain	88	45	0.05	0.03
Soybean Meal	92	15	0.02	<0.01
TOTAL BURDEN		100		**3.03**
Dairy Cattle				
Corn Forage	40	50	3.0	3.75
Corn Grain	88	35	0.05	0.02
Soybean Meal	92	15	0.02	<0.01
TOTAL BURDEN		100		**3.77**
Poultry and Swine				
Corn Grain	88	80	0.05	0.04
Soybean Meal	92	20	0.02	0.004
TOTAL BURDEN		100		**0.044**

1. Obtained from Table 1 in OPPTS Residue Chemistry Test Guideline 860.1000.
2. Contribution = ([tolerance / %dry matter] x %diet) for beef and dairy cattle. Contribution = (tolerance x %diet) for poultry and swine.

860.1500 Crop Field Trial

Crop Field Trial DER for MRID #46507101

Monsanto has submitted crop field trials supporting the use of acetochlor (2.7 lb ai/gal Mcap formulation) on sorghum as either a pre-emergence broadcast application or an early-season post-emergence broadcast application at a rate of up to 2.5 lb ai/A. The results from these studies are summarized in Table 5 and discussed below.

TABLE 5 Summary of Residue Data from Sorghum Field Trials.								
Analyte	**Application Method[1]/Timing**	**PHI (Days)**	**Residue Levels (ppm)[2]**					
			n	**Min.**	**Max.**	**HAFT[3]**	**Mean[4]**	**Std. Dev.**
Sorghum Forage								
EMA	Pre-Emergence	82-116	13	0.015	0.458	0.458	0.148	0.111
	Post-Emergence (5-14")	52-77	13	0.032	0.767	0.767	0.226	0.204
HEMA	Pre-Emergence	82-116	13	0.003	0.058	0.058	0.026	0.016
	Post-Emergence (5-14")	52-77	13	0.007	0.121	0.121	0.038	0.033
Combined	Pre-Emergence	82-116	13	0.018	0.515	0.515	0.174	0.124
	Post-Emergence (5-14")	52-77	13	0.045	0.888	0.888	0.263	0.236

TABLE 5 Summary of Residue Data from Sorghum Field Trials.

Analyte	Application Method [1]/Timing	PHI (Days)	Residue Levels (ppm) [2]					
			n	Min.	Max.	HAFT [3]	Mean [4]	Std. Dev.
Sorghum Grain								
EMA	Pre-Emergence	107-171	13	<0.005	0.013	0.013	0.006	0.004
	Post-Emergence (5-14")	90-158	13	<0.005	0.020	0.020	0.009	0.007
HEMA	Pre-Emergence	107-171	13	<0.003	0.009	0.009	0.004	0.002
	Post-Emergence (5-14")	90-158	13	<0.003	0.014	0.014	0.006	0.004
Combined	Pre-Emergence	107-171	13	<0.008	0.022	0.022	0.009	0.006
	Post-Emergence (5-14")	90-158	13	<0.008	0.033	0.033	0.015	0.011
Sorghum Stover								
EMA	Pre-Emergence	116-177	13	<0.015	0.664	0.664	0.217	0.205
	Post-Emergence (5-14")	93-164	13	0.021	1.00	1.00	0.299	0.289
HEMA	Pre-Emergence	116-177	13	<0.011	0.083	0.083	0.033	0.028
	Post-Emergence (5-14")	93-164	13	<0.011	0.142	0.142	0.044	0.041
Combined	Pre-Emergence	116-177	13	<0.026	0.744	0.744	0.251	0.232
	Post-Emergence (5-14")	93-164	13	<0.032	1.14	1.14	0.342	0.329

1. All treatments were made as broadcast applications via ground equipment.
2. All residues are expressed in parent equivalents.
3. HAFT = Highest Average Field Trial.
4. Residues less than LOQ were assumed to be 2 LOQ for calculation of mean and standard deviation.

At 13 sorghum field trials conducted in 2003, acetochlor (2.7 lb ai/gal Mcap formulation) was applied in side-by-side tests at each trial site as either a pre- or post-emergence broadcast application at a rate of 2.44 to 2.58 lb ai/A (1X the proposed maximum seasonal rate). The post-emergence application was made when the sorghum was 5 to 14 inches in height; all applications were made using ground equipment at spray volumes of 10 to 20 GPA. Single control (untreated) and treated samples of forage were collected at 82 to 116 DAT from the pre-emergence application, and 48 to 77 DAT from the post-emergence application. In one of the post-emergence tests, forage samples were also collected at 48, 59, 66, and 73 DAT to investigate residue decline. At crop maturity, single control and treated samples of grain (90 to 171 DAT) and stover (93 to 177 DAT) were collected from each test. Samples were stored frozen for durations of up to 222 days prior to analysis for acetochlor residues. The storage durations for the analysis of acetochlor residues are supported by the available storage stability data on corn commodities.

Residues of acetochlor and its EMA- and HEMA-producing metabolites were determined in sorghum forage, grain and, stover using the adequate LC/MS/MS method (Monsanto Method ES-ME-1001-01). The LOQs for EMA are 0.005 ppm in grain and forage, and 0.015 ppm in stover, while the LOQs for HEMA are 0.003 ppm in grain and forage, and 0.011 ppm in stover. The LODs for EMA are 0.004 ppm in grain and forage, and 0.015 ppm in stover, while the LODs for HEMA are 0.002 ppm in grain and forage, and 0.007 ppm in stover.

For forage, combined residues were 0.018 to 0.515 ppm at 82 to 116 days following a pre-emergence application, and 0.045 to 0.888 ppm at 52 to 77 days following a post-emergence application. In the test examining residue decline in forage, the combined residues were variable, ranging from 0.099 to 0.217 ppm from 48 to 73 DAT. For grain harvested at maturity,

combined residues were <0.008 to 0.022 ppm following a pre-emergence application, and <0.008 to 0.033 ppm following a post-emergence application. For stover harvested at maturity, combined residues were <0.026 to 0.744 ppm following a pre-emergence application, and <0.032 to 1.143 ppm following a post-emergence application.

For each commodity, residues were generally higher following the post-emergence application than the pre-emergence application. Of the 13 trial sites, higher residues were observed from the post-emergence application at 10 sites for forage, and 11 sites for stover. For grain, residues from the post-emergence treatment were equal to or higher than those from the pre-emergence treatment at 12 sites. Average combined residues in forage, grain and stover were (respectively) 0.174, 0.009, and 0.251 ppm for the pre-emergence application, and 0.263, 0.015, and 0.342 ppm for the post-emergence application.

Conclusions: The field trial data are adequate, and support the use of a single broadcast application of acetochlor (2.7 lb ai/gal Mcap) to sorghum at approximately 2.5 lb ai/A, as either a pre-emergence application or a post-emergence application, made when plants are no taller than 11 inches. The data support a PHI of 60 days for sorghum forage following a post-emergence application. PHIs are not required for either grain or stover, nor for forage following a pre-emergence application.

860.1520 Processed Food and Feed

Processed Food/Feed DER for MRID #46507101

Although the Agency does not currently require a processing study to support uses on sorghum, Monsanto has provided data from a sorghum processing study in anticipation of the possible future use of sorghum flour as human food. At two field trials conducted during 2003 in NE and OK, acetochlor (2.7 lb ai/gal Mcap) was applied to grain sorghum as a single, early-season, post-emergence application at a rate of 2.5 lb ai/A (1X rate). Single bulk control and treated samples of grain were harvested from each test at maturity, 97 to 112 DAT; these were subsequently processed into sorghum flour and bran using simulated commercial procedures. Sorghum grain and processed fractions were stored frozen for durations of up to 5.4 and 1.4 months, respectively, prior to analysis for acetochlor residues. The storage durations for the analysis of acetochlor residues are supported by the available storage stability data on corn grain.

Acetochlor residues were determined in sorghum grain and processed fractions using the adequate LC/MS/MS method (Monsanto Method ES-ME-1001-01). The LOQs for EMA and HEMA are 0.005 and 0.003 ppm, respectively, in grain and processed fractions, while the LODs are 0.004 and 0.002 ppm.

At maturity, combined acetochlor residues were 0.033 and 0.017 ppm in grain, the raw agricultural commodity (RAC), from the NE and OK trials, respectively. Combined residues in cleaned grain were 0.030 and 0.021 ppm from the two trials. After processing, combined acetochlor residues were <0.013 and <0.008 ppm in flour from the respective trial sites, with residues of 0.101 and 0.092 ppm in bran. The processing factors for combined acetochlor residues were similar for the two trials and averaged 1.1X for cleaned grain, less than 0.5X for flour, and 4.3X for bran.

Conclusions: The sorghum processing data on acetochlor residues are adequate, and indicate that acetochlor residues do not concentrate in flour (processing factor of less than 0.5X),

but can concentrate in bran (4.3X). Because the Agency does not currently regulate any processed commodities from sorghum, no further action is required.

860.1650 Submittal of Analytical Reference Standards

As of December 2003, analytical reference standards for acetochlor were available at the EPA National Pesticide Standards Repository.

860.1850 Confined Accumulation in Rotational Crops

The requirement for confined accumulation in rotational crops is satisfied. Based on data from the confined accumulation study, and data from extensive rotational crop field trials, the HED Metabolism Committee concluded that tolerances for rotational crops should be expressed as acetochlor and its EMA- and HEMA-producing metabolites (M. Flood, 9/30/1993).

860.1900 Field Accumulation in Rotational Crops

Extensive rotational field crop trials are available depicting acetochlor residues in sorghum, soybeans, and wheat planted as rotational crops following corn treated with acetochlor at a rate of 3.0 lb ai/A (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005). In addition, rotational field crop trials on alfalfa, beans, oats, peas, potatoes, sugar beets, and sunflower have been submitted, and are under review in conjunction with a petition for use of acetochlor on sweet corn at a rate of up to 3.0 lb ai/A (PP#6F4791; D2303130 and D275019). Since the maximum seasonal use rate on corn is higher than the proposed maximum use rate on sorghum (2.5 lb ai/A), issues pertaining to residues in rotational crops, and the need for rotational crop tolerances are being addressed under the sweet corn petition.

860.1550 Proposed Tolerances

HED has determined that the tolerance expression for primary and rotational crops should include acetochlor and its metabolites, HEMA and EMA. Tolerances for these residues are currently established on plant commodities at levels ranging from 0.05 to 1.5 ppm in corn commodities resulting from the direct use of acetochlor, and from 0.02 to 1.0 ppm in commodities from rotational crops of sorghum, soybean, or wheat (40CFR § 180.470). The tolerances proposed by Monsanto in the sorghum petition are listed below (in Table 6), along with the Agency's recommended tolerance levels.

The recommended tolerance levels for sorghum forage, grain, and stover were determined using recent Agency Guidance (*Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP). Because the post-emergence treatment consistently resulted in higher residues in forage, grain, and stover, only residue data from the post-emergence application were used to calculate tolerance levels. Although inclusion of the residue data from the pre-emergence treatment resulted in the larger dataset (26 versus 13), these lower residue values increased the variability of the dataset, and thereby resulted in inflated tolerance values. There are no international harmonization issues associated with this petition, because there are neither established nor proposed Canadian, Mexican, or Codex MRLs for residues of acetochlor in plant commodities.

TABLE 6 Tolerance Summary for Acetochlor on Sorghum.			
Crop Commodity	**Proposed Tolerance (ppm)**	**Recommended Tolerance (ppm)**	**Comments**
Sorghum, Forage	1.0	1.6	Tolerance levels were determined using residue data from the post-emergence applications only.
Sorghum, Grain	0.05	0.05	
Sorghum, Grain, Stover	1.5	1.7	

References

PP#5F4505. Section 3 Registration and Permanent Tolerance Petition to Expand Use of Acetochlor End-Use Products to Include Post-Emergence Application to Corn.; D214735 and D214738; G. Herndon, W. Dykstra and C. Lewis; 6/25/1996.

Acetochlor. Summary of Analytical Chemistry and Residue Data for the Tolerance Reassessment Eligibility Decision (TRED) Document.; DP #D297062; Samuel Ary; 5/31/2005.

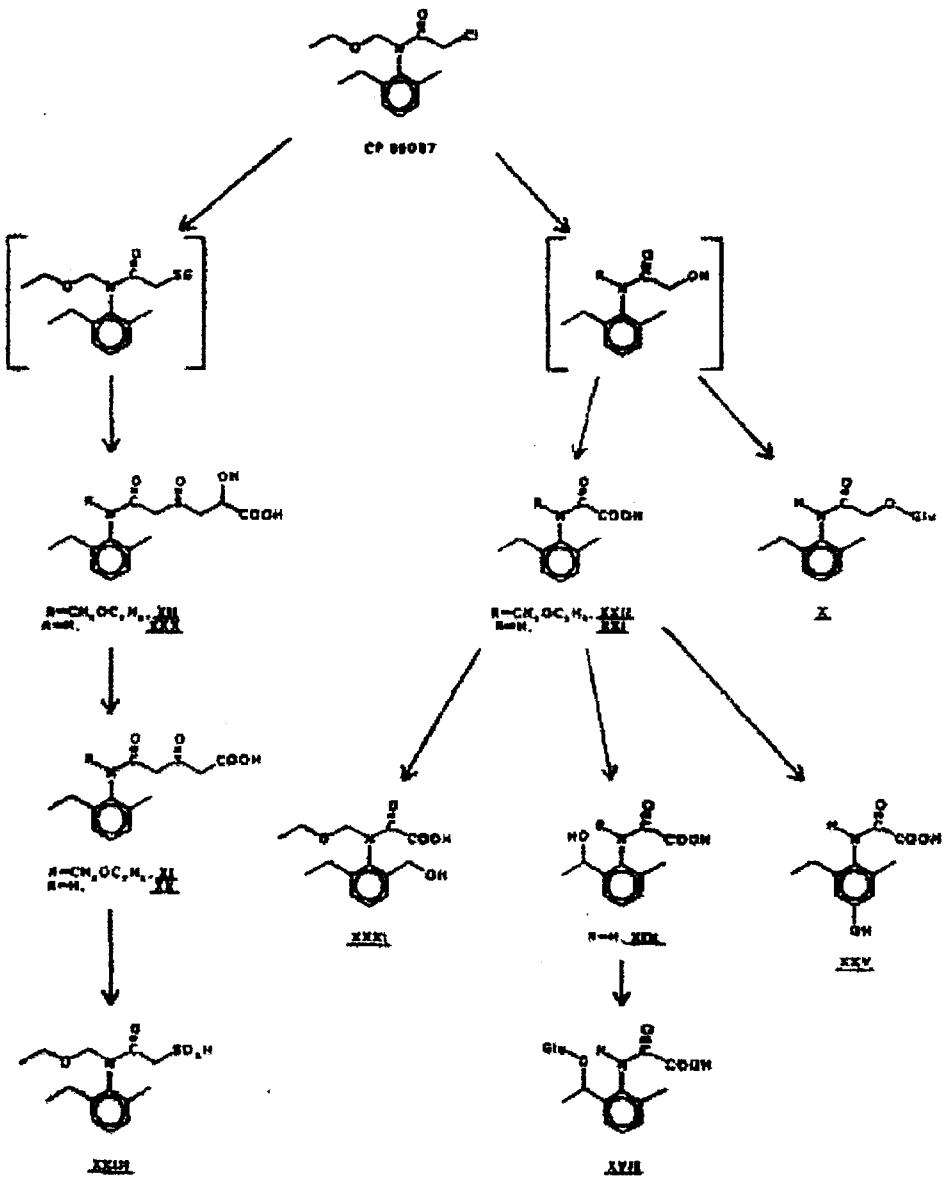
Attachments

Appendix 1 – International Residue Limit Status Sheet.
Appendix 2 - Metabolic Pathway in Sorghum.
Appendix 3 - Tolerance Assessment Calculations.

APPENDIX 1: International Residue Limit Status Sheet.

INTERNATIONAL RESIDUE LIMIT STATUS			
Chemical Name: 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide	**Common Name:** Acetochlor	**X Recommended Tolerances** [ ] Reevaluated tolerance [ ] Other	**Date:** 3/20/2006
Codex Status (Maximum Residue Limits)		**US Tolerances (Recommended)**	
X No Codex proposal step 6 or above [ ] No Codex proposal step 6 or above for the crops requested		**Petition Number:** 5F6918 **DP Number:** D316496 **Other Identifier:** PC Code 121601	
Residue definition (step 8/CXL): Acetochlor		**Reviewer (Branch):** William T. Drew (RAB2)	
		Residue Definition: Acetochlor	
Crop(s)	MRL (mg/kg)	**Crops**	**Tolerance (ppm)**
		Sorghum Forage	1.6
		Sorghum Grain	0.05
		Sorghum Grain Stover	1.7
Limits for Canada		Limits for Mexico	
X No Limits [ ] No Limits for the crops requested		[ ] No Limits [ ] No Limits for the crops requested	
Residue definition: NA		Residue definition: Acetochlor	
Crop(s)	MRL (mg/kg)	Crop	MRL (mg/kg)
		Corn	0.04
NOTES: per Stephen Funk, 3/20/2006. NA = Not Applicable.			

APPENDIX 2. Proposed Metabolic Pathway of Acetochlor in Sorghum.



APPENDIX 3. Tolerance Assessment Calculations.

The dataset used to establish tolerances for acetochlor on sorghum forage, grain, and stover consisted of field trial data representing a single post-emergence application at a rate of 2.5 lb ai/A, made before the crop exceeded 14 inches in height. PHIs were 52 to 77 days for forage, 90 to 158 days for grain, and 93 to 164 days for stover. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates are within 25% of the proposed maximum label application rate, and the PHIs are consistent with the appropriate stage of maturity for each commodity. No PHIs were proposed, and none are required, for grain and stover; however, a label PHI of 60 days should be specified for forage following a post-emergence application. The residues values used to calculate the tolerance are provided in Table A-3.

The datasets for acetochlor residues in forage, grain, and stover were entered into the tolerance spreadsheet. Visual inspection of the lognormal probability plots (Figures A-3a and A-3c) indicates that the datasets are reasonably lognormal for forage and stover. The result from the approximate Shapiro-Francia test statistic (Figures A-3b and A-3d) confirmed that the assumption of lognormality should not be rejected. Although the result from the approximate Shapiro-Francia test statistic (Figure A-3f) indicated that the assumption of lognormality should not be rejected for grain, visual inspection of the lognormal probability plot (Figure A-3e) indicates that the dataset is not lognormal.

Because the field trial data for acetochlor on forage and stover represent a small dataset (n less than 15) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% upper confidence limit (UCL) on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, the 95% UCL on the 95th percentile rounds to the values of 1.6 and 1.7 ppm for forage and stover, respectively (Figures A-3b and A-3d). Because this value was the minimum value, 1.6 and 1.7 ppm are the recommended tolerance levels for acetochlor residues on sorghum forage and stover, respectively.

Because the field trial data for acetochlor on grain are not lognormal, the upper bound on the 89th percentile should be selected as the tolerance value (distribution-free method). Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the upper bound on the 89th percentile rounds to the value 0.05 ppm. Therefore, 0.05 ppm is the recommended tolerance level for acetochlor residues on sorghum grain.

TABLE A-3 Acetochlor Residues in Sorghum Forage, Grain, and Stover.			
Regulator	**EPA**		
Chemical	**Acetochlor**		
Application Rate	**2.5 lb ai/A (Post-Emergence)**		
Submitter	**Monsanto**		
MRID Number	**46507101**		
Crop	**Sorghum Forage**	**Sorghum Grain**	**Sorghum Stover**
PHIs (Days)	**52-77**	**90-158**	**93-164**
	Residues (EMA + HEMA)		
	0.221	0.017	0.493
	0.083	**0.004**	0.109
	0.056	**0.004**	0.021
	0.113	0.008	0.176
	0.217	0.033	0.230
	0.074	**0.004**	0.065
	0.274	0.019	0.363
	0.888	0.031	1.14
	0.480	0.019	0.302
	0.184	0.027	0.212
	0.454	0.017	0.900
	0.338	**0.004**	0.211
	0.045	0.005	0.228
NOTE: Values at ½LOQ are in **bold** typeface.			

Figure A-3a Lognormal probability plot of acetochlor field trial data for sorghum forage.

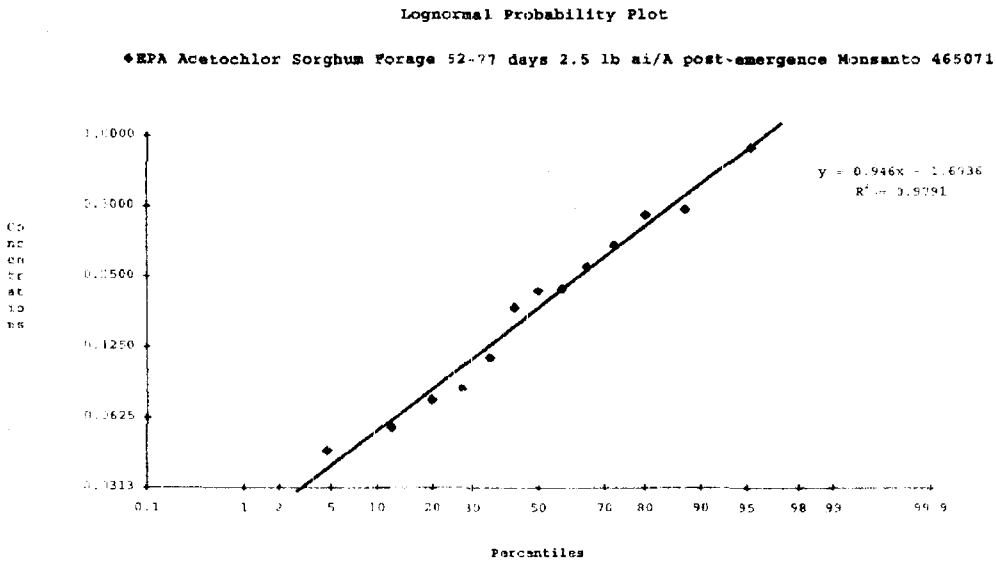


Figure A-3b Tolerance summary of acetochlor field trial data for sorghum forage.

Regulator:	EPA
Chemical:	Acetochlor
Crop:	Sorghum Forage
PHI:	52-77 days
App. Rate:	lb ai/A post-emergence
Submitter:	Monsanto
MRID Citation:	46507101
n:	13
min:	0.04
max:	0.89
median:	0.22
average:	0.26

	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	0.70 (0.90)	0.90 (1.2)	1.0 (--)
EU Method I Log Normal	0.90 (2.5)	**1.6** (6.0)	3.5 (--)
EU Method II Distribution-Free		0.80	
California Method $\mu + 3\sigma$		1.0	
UPLMedian95th		**1.6**	
Approximate Shapiro-Francia Normality Test		0.9791 p-value > 0.05 : Do not reject lognormality assumption	

Would you like the above values rounded? (Y or N)==> Y

Figure A-3c Lognormal probability plot of acetochlor field trial data for sorghum stover.

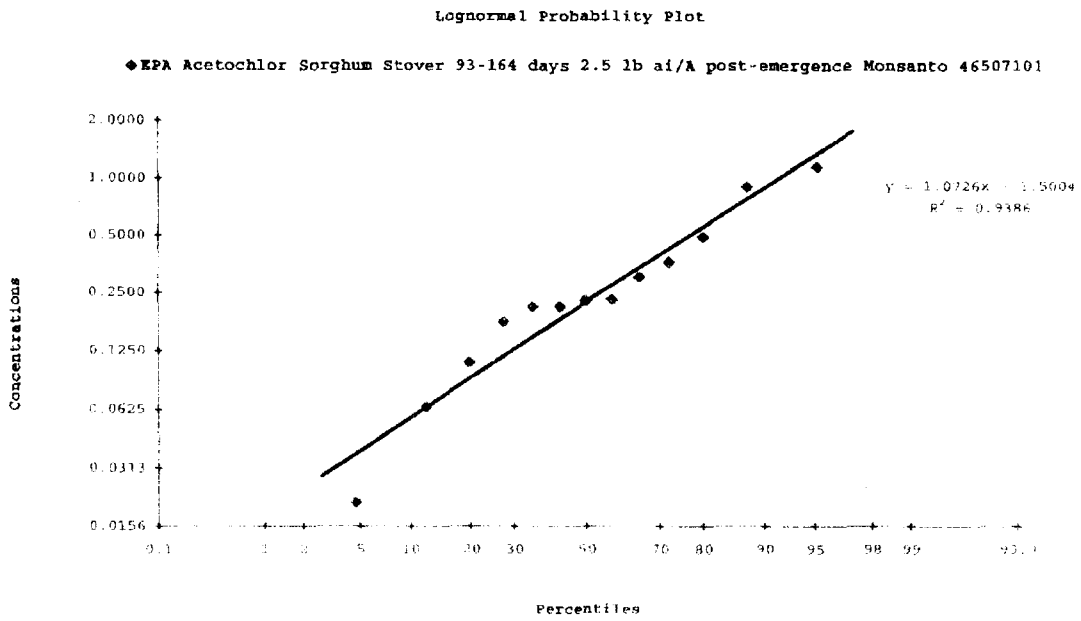


Figure A-3d Tolerance summary of acetochlor field trial data for sorghum stover.

Regulator:	EPA
Chemical:	Acetochlor
Crop:	Sorghum Stover
PHI:	93-164 days
App. Rate:	lb ai/A post-emergence
Submitter:	Monsanto
MRID Citation:	46507101
n:	13
min:	0.02
max:	1.14
median:	0.23
average:	0.34

	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	0.90 (1.3)	1.2 (1.6)	1.4 (--)
EU Method I Log Normal	1.3 (4.0)	3.0 (11)	6.0 (--)
EU Method II Distribution-Free		0.90	
California Method $\mu + 3\sigma$		1.4	
UPLMedian95th		1.7	
Approximate Shapiro-Francia Normality Test		0.9386 p-value > 0.05 : Do not reject lognormality assumption	

Would you like the above values rounded? (Y or N)==>

Figure A-3e Lognormal probability plot of acetochlor field trial data for sorghum grain.

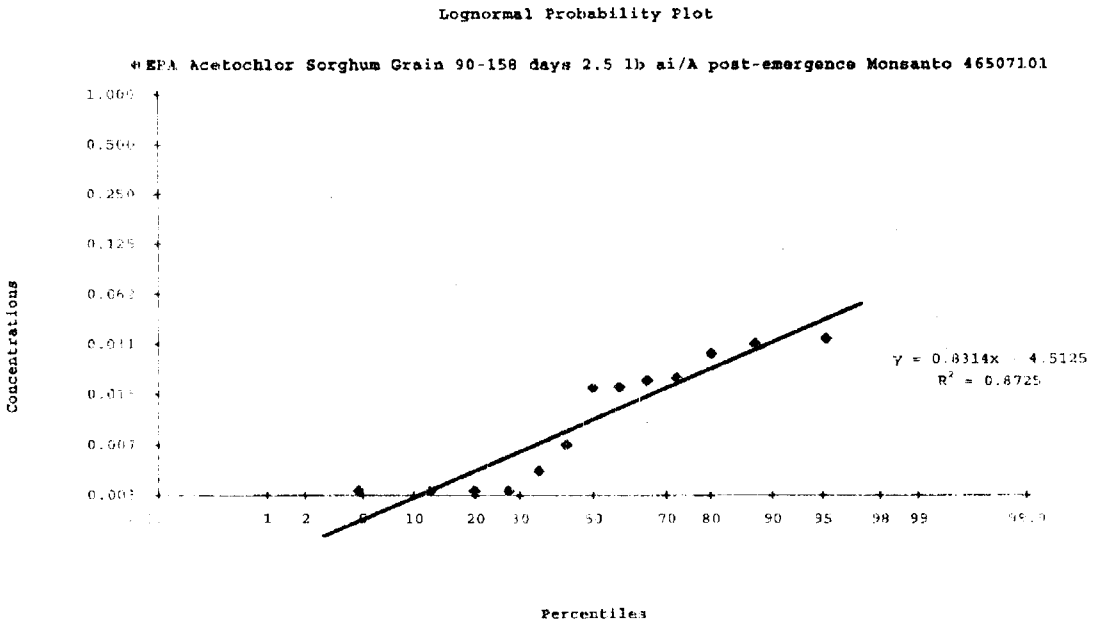


Figure A-3f Tolerance summary of acetochlor field trial data for sorghum grain.

Regulator:	EPA
Chemical:	Acetochlor
Crop:	Sorghum Grain
PHI:	90-158 days
App. Rate:	1b ai/A post-emergence
Submitter:	Monsanto
MRID Citation:	46507101
n:	13
min:	0.00
max:	0.03
median:	0.02
average:	0.01

	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	0.04 (0.05)	0.04 (0.06)	0.05 (--)
EU Method I Log Normal	0.05 (0.15)	**0.08** (0.25)	0.15 (--)
EU Method II Distribution-Free	0.05		
California Method $\mu + 3\sigma$	**0.05**		
UPLMedian95th	0.15		
Approximate Shapiro-Francia Normality Test	0.8725 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Acetochlor/524-511/PC Code 121601/Monsanto Company/524
Furilazole/524-511/PC Code 911596/Monsanto Company/524
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, Grain, and Stover)

Primary Evaluator:	William T. Drew, Chemist, HED/RAB2	Date: 2/23/2006
Peer Reviewer:	Douglas Dotson, Chemist, HED/RAB2	Date: 3/20/2006
Approved by:	Richard A. Loranger, Branch Senior Scientist, HED/RAB2	Date: 10/26/06

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 policy.

STUDY REPORT

MRID #46507101. Sharon J. Moran (2004) *Magnitude of Acetochlor and MON 13900 Residues in Sorghum Raw Agricultural Commodities and Processed Commodities Following Applications of Degree Xtra™.* Protocol #03-27-R-2. Report #MSL-18670, RD 1638. Unpublished study prepared by Monsanto Company. 303 pages. {OPPTS Residue Chemistry Test Guideline 860.1500}

EXECUTIVE SUMMARY

At 13 sorghum trials conducted in 2003, acetochlor, as a 2.7 pounds active ingredient per gallon (lb ai/gal) microencapsulated (Mcap) formulation, was applied in side-by-side tests at each trial site as either a pre- or post-emergence broadcast application at a rate of 2.44 to 2.58 lb ai per acre (lb ai/A). The pre-emergence application timing was from immediately following planting to 8 days after planting, while the post-emergence application was made when the sorghum was 5 to 14 inches in height. All applications were made using ground equipment in spray volumes of 10 to 20 gallons per acre (GPA). Because sorghum is sensitive to acetochlor, the formulation included [redacted] of the safener furilazole; however, the actual concentration (lb/gal) and field use rates (lb/A) for furilazole were not reported. Single control (untreated) and treated samples of forage were collected at 82 to 116 days after treatment (DAT) from the pre-emergence application plot, and 48 to 77 DAT from the post-emergence application plot. At one of the post-emergence tests, forage samples were also collected at 48, 59, 66, and 73 DAT to examine residue decline. At crop maturity, single control and treated samples of grain (90 to 171 DAT) and stover (93 to 177 DAT) were collected from each test. Samples were stored frozen for durations of up to 222 days prior to analysis of acetochlor residues, and up to 282 days prior to analysis of furilazole residues. The storage durations for the analysis of acetochlor residues are supported by the available storage stability data on corn commodities, but no data were provided

supporting the stability of furilazole residues.

The LC/MS/MS method (Monsanto Method ES-ME-1001-01) used to determine acetochlor residues in sorghum forage, grain, and stover was adequately validated in conjunction with the field trials. For this method, residues are extracted with acetonitrile (ACN)/water, then base-hydrolyzed to yield two separate hydrolysis products, 2-ethyl-6-methylaniline (EMA) and 2-(1-hydroxyethyl)-6-methylaniline (HEMA), which are steam-distilled into dilute acid. Residues are partitioned into dichloromethane (DCM), concentrated, and then re-dissolved in ACN/water. EMA and HEMA are determined via LC/MS/MS using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues are reported in acetochlor equivalents. The validated limits of quantitation (LOQ) for EMA are 0.005 ppm in grain and forage, and 0.015 ppm in stover, while the LOQs for HEMA are 0.003 ppm in grain and forage, and 0.011 ppm in stover. The limits of detection (LOD) for EMA are 0.004 ppm in grain and forage, and 0.015 ppm in stover, while the LODs for HEMA are 0.002 ppm in grain and forage, and 0.007 ppm in stover.

The GC/MS method (Monsanto Method ES-1008-01) used to determine furilazole residues in sorghum commodities was also adequately validated in conjunction with the field trials. For this method, residues are extracted with ACN/water, diluted with saturated NaCl, and partitioned into ethyl acetate/isooctane. Residues are then cleaned up using an alumina solid-phase extraction (SPE) column. Residues are determined via GC/MS using the m/z 262 ion for quantitation, and the m/z 220 ion for confirmation. The validated LOQ for furilazole in sorghum commodities is 0.010 ppm; the LOD was not reported.

For each commodity, residues were generally higher following the post-emergence application than the pre-emergence application. For forage, combined residues were 0.018 to 0.515 ppm at 82 to 116 days following a pre-emergence application, and 0.045 to 0.888 ppm at 52 to 77 days following a post-emergence application. At the trial examining residue decline in forage, the combined residues were variable, ranging from 0.099 to 0.217 ppm from 48 to 73 DAT. For grain harvested at maturity, combined residues were <0.008 to 0.022 ppm following a pre-emergence application, and <0.008 to 0.033 ppm following a post-emergence application. For stover harvested at maturity, combined residues were <0.026 to 0.744 ppm following a pre-emergence application, and <0.032 to 1.143 ppm following a post-emergence application. Average combined residues in forage, grain, and stover were (respectively) 0.174, 0.009, and 0.251 ppm following the pre-emergence application, and 0.263, 0.015, and 0.342 ppm following the post-emergence application. Regardless of whether a pre- or post-emergence application was used, residues of the safener furilazole were non-quantifiable (less than the LOQ of 0.010 ppm) in all samples of forage, grain, and stover.

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 regarding the acetochlor residue data. However, to

INERT INGREDIENT INFORMATION IS NOT INCLUDED

upgrade the residue data on furilazole to adequate, information on the concentration (lb/gal) of furilazole in the test formulation is required, along with supporting storage stability data for furilazole in sorghum commodities. The acceptability of this study for regulatory purposes is addressed in the US EPA Residue Chemistry Summary Document (DP Barcode D316496).

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

Acetochlor is a chloroacetanilide herbicide currently used for pre-emergence control of weeds in corn. In the United States, acetochlor is conditionally registered for use on corn to the Acetochlor Registration Partnership (ARP), which is comprised of Monsanto and Dow AgroSciences. Acetochlor is formulated as a variety of emulsifiable concentrate (EC), emulsion in water (EW), granular (G), or Mcap formulations that can be applied to corn as a pre-plant, pre-emergence, or early post-emergence application. Tolerances are established for the combined residues of acetochlor and its metabolites convertible to EMA or HEMA, to be analyzed as acetochlor, and expressed as acetochlor equivalents (40CFR §180.470). Tolerances range from 0.05 to 1.5 ppm in corn commodities resulting from the direct use of acetochlor, and from 0.02 to 1.0 ppm in commodities from the rotational crops, sorghum, soybeans, and wheat.

Monsanto has submitted a petition (PP#5F6918) proposing the use of acetochlor, formulated as a 2.7 lb ai/gal Mcap, on sorghum. Because sorghum is sensitive to phytotoxicity from acetochlor, the petitioner is proposing the inclusion of the safener furilazole with the herbicide at a concentration of [redacted] Tolerances are established for residues of furilazole in field and pop corn commodities at 0.01 ppm (40CFR §180.471).

TABLE A.1 Acetochlor and Furilazole Nomenclature.

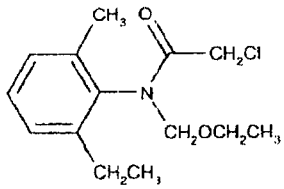
Chemical Structure	
Common Name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC Name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide

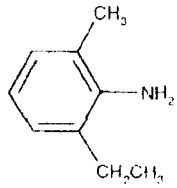
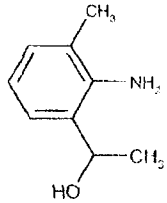
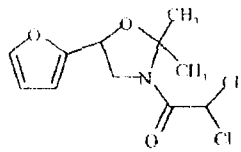
TABLE A.1 Acetochlor and Furilazole Nomenclature.	
CAS Name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS Number	34256-82-1
PC Code	121601
End-Use Product (EP)	Degree Xtra (2.7 lb/gal Mcap), EPA Registration #524-511
Chemical Structure	
Common Name	EMA
Molecular Weight	337.4
CAS Name	2-ethyl-6-methylaniline
Chemical Structure	
Common Name	HEMA
Molecular Weight	303.3
CAS Name	2-(1-hydroxyethyl)-6-methylaniline
Chemical Structure	
Common Name	Furilazole (MON 13900)
Molecular Formula	$C_{11}H_{13}Cl_2NO_3$
Molecular Weight	278.1
IUPAC Name	(*RS*)-3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyloxazolidine
CAS Name	3-(dichloroacetyl)-5-(2-furanyl)-2,2-dimethyloxazolidine
CAS Number	121776-33-8
PC Code	911596

TABLE A.2 Physicochemical Properties of Acetochlor.

Parameter	Value	Reference
Boiling Point/Range	163°C at 10 mm Hg. Decomposition occurs before the boiling point at atmospheric pressure (calculated by extrapolation of vapor pressure at lower temperature).	M. Flood, DEB 7474, 2/6/1991
pH	4.41 (1% solution in acetone/water, 1:1 vol/vol)	M. Flood, DEB 7474, 2/6/1991
Density (g/mL, 20°C)	1.123	M. Flood, DEB 7474, 2/6/1991
Water Solubility (mg/L, 25°C)	223	2001 Farm Chem Handbook
Solvent Solubility (25°C)	Miscible in acetone, benzene, carbon tetrachloride, ethanol, chloroform, and toluene.	M. Flood, HED Memo, 1/21/1994
Vapor Pressure (mm Hg, 25°C)	4.5×10^{-5}	M. Flood, DEB 7474, 2/6/1991
Dissociation Constant (pK_a)	Not applicable (because acetochlor is neither an acid nor a base).	M. Flood, DEB 7474, 2/6/1991
Octanol/Water Partition Coefficient	970 (Dow study) or 1082 (Monsanto study). Differences are likely due to experimental error.	M. Flood, DEB 7474, 2/6/1991
UV/Visible Spectrum	Not available.	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Thirteen sorghum field trials were conducted with acetochlor in the US during 2003 (see Table B.1.1, below). Precipitation and mean monthly minimum and maximum temperatures were reported for each trial site for the entire growing season, along with historical precipitation and temperature data. Although the growing season was reported to be drier than normal, the field trials were supplemented with irrigation as needed in order to maintain normal sorghum growth. Each trial site consisted of three test plots: a control (untreated), a pre-emergence application, and a post-emergence application made when the crop was between 5 and 14 inches in height (see Table B.1.2, below).

Acetochlor/524-511/PC Code 121601/Monsanto Company/524
Furilazole/524-511/PC Code 911596/Monsanto Company/524
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, Grain, and Stover)

TABLE B.1.1 Trial Site Conditions for Sorghum.

Trial Identification (City, State/Year)	Soil Characteristics			
	Type	%OM	pH	CEC
Plains, GA/2003	Sandy Loam	Low	5.1-5.5	NR*
Cord, AR/2003	Silty Clay	0.6	6.0	NR
Carlyle, IL/2003	Silt loam	1.2	6.5	NR
New Holland, OH/2003	Silt Loam	NR	NR	NR
York, NE/2003	Silt Loam	2.1	7.1	NR
Richland, IA/2003	Silty Clay Loam	3.6	6.5	NR
Osceola, NE/2003	Sandy Loam	1.5	7.8	NR
Colony, OK/2003	Sandy Loam	<1.0	6.5	NR
East Benard, TX/2003	Fine Sandy Loam	~1	~6	NR
Grand Island, NE/2003	Silt Loam	2.1	7.5	NR
Dill City, OK/2003	Sand	0.7	6.5	NR
Claude, TX/2003	Clay Loam	2.2	6.8	NR
Levelland, TX/2003	Sandy Loam	0.9	7.9	NR

* NR = Not Reported.

TABLE B.1.2 Study Use Pattern on Sorghum.

Location (City, State/Year) [Trial ID]	Application Information [1]				
	End-Use Product [2]	Method [3], Timing	Volume (GPA) [4]	Number of Applications	Rate (lb ai/A)
Plains, GA/2003 [GA]	Degree Xtra™	Pre-emergence broadcast	14-15	1	2.47
		Post-emergence broadcast, crop at 6-8"		1	2.49
Cord, AR/2003 [AR]	Degree Xtra™	Pre-emergence broadcast	19	1	2.48
		Post-emergence broadcast, crop at 9"		1	2.50
Carlyle, IL/2003 [IL]	Degree Xtra™	Pre-emergence broadcast	14-16	1	2.56
		Post-emergence broadcast, crop at 10"		1	2.58
New Holland, OH/2003 [OH-1]	Degree Xtra™	Pre-emergence broadcast	15-16	1	2.44
		Post-emergence broadcast, crop at 10"		1	2.48
York, NE/2003 [NE-1]	Degree Xtra™	Pre-emergence broadcast	20	1	2.49
		Post-emergence broadcast, crop at 5-6"		1	2.50
Richland, IA/2003 [IA]	Degree Xtra™	Pre-emergence broadcast	15	1	2.55
		Post-emergence broadcast, crop at 11"		1	2.50
Osceola, NE/2003 [NE-2]	Degree Xtra™	Pre-emergence broadcast	20	1	2.50
		Post-emergence broadcast, crop at 6-8"		1	2.51
Colony, OK/2003 [OK-1]	Degree Xtra™	Pre-emergence broadcast	10-13	1	2.47
		Post-emergence broadcast, crop at 12-14"		1	2.52
East Benard, TX/2003 [TX-1]	Degree Xtra™	Pre-emergence broadcast	12-14	1	2.49
		Post-emergence broadcast, crop at 10-11"		1	2.55
Grand Island, NE/2003 [NE-3]	Degree Xtra™	Pre-emergence broadcast	20	1	2.49
		Post-emergence broadcast, crop at 5-6"		1	2.50

INERT INGREDIENT INFORMATION IS NOT INCLUDED

TABLE B.1.2 Study Use Pattern on Sorghum.

Location (City, State/Year) [Trial ID]	Application Information [1]				
	End-Use Product [2]	Method [3], Timing	Volume (GPA) [4]	Number of Applications	Rate (lb ai/A)
Dill City, OK/2003 [OK-2]	Degree Xtra™	Pre-emergence broadcast	11	1	2.58
		Post-emergence broadcast, crop at 11-14"		1	2.50
Claude, TX/2003 [TX-2]	Degree Xtra™	Pre-emergence broadcast	19	1	2.51
		Post-emergence broadcast, crop at 6"		1	2.53
Levelland, TX/2003 [TX-3]	Degree Xtra™	Pre-emergence broadcast	20	1	2.55
		Post-emergence broadcast, crop at 6-11"		1	2.53

1. No spray adjuvants were used in any of the tank mixes at any of the field trials.
2. Because sorghum is sensitive to acetochlor, the test substance included furilazole [redacted] as a safener; however, the use rate was not reported in terms of lb/A: the formulation also included atrazine at 1.34 lb ai/gal.
3. All applications were made using ground equipment.
4. GPA = Gallons Per Acre.

TABLE B.1.3 Trial Numbers and Geographical Locations.

NAFTA Growing Region [1]	Submitted Sorghum Trials	Requested Sorghum Trials	
		Canada	US
1	--	NA [2]	--
2	1	NA	1
3	--	NA	--
4	1	NA	1
5	5	NA	4
6	2	NA	2
7	1	NA	1
8	3	NA	3
9	--	NA	--
10	--	NA	--
11	--	NA	--
12	--	NA	--
Total	**13**	**NA**	**12**

1. Regions 13 to 21, and 1A, 5A, 5B, and 7A were not included because the proposed use is for the US only.
2. NA = Not Applicable.

B.2. Sample Handling and Preparation

Samples of forage were collected from each test at the soft to hard dough stage, which was 82 to 116 days after the pre-emergence treatment, or 48 to 77 days after the post-emergence treatment. To examine residue decline, additional samples of forage were collected from one trial at 48, 59, 66, and 73 days following the post-emergence treatment. Samples of grain were collected at maturity (90 to 171 DAT), when moisture content of the grain was no more than 20%. Samples of stover were collected from mature dried stalks following grain harvest at a

moisture content of roughly 15% (93 to 177 DAT). Single control and treated samples of forage (at least 1.5 kg), grain (at least 1.0 kg), and stover (at least 0.2 kg) were collected from each test, with the exception of the residue decline trial, in which duplicate treated samples of forage were collected. All samples were frozen within 4 hours of collection, and stored frozen at the field facilities for 1 to 59 days prior to shipment. Samples were shipped by ACDS freezer truck (–20°C) to the analytical laboratory, Monsanto Company (in St. Louis, MO). The maximum frozen storage durations for sorghum forage, grain, and stover were 211 to 222 days prior to analysis for EMA and HEMA, and 225 to 282 days prior to analysis for furilazole.

B.3. Analytical Methodology

Samples of each sorghum commodity were analyzed for EMA- and HEMA-producing metabolites using an LC/MS/MS method (Method ES-ME-1001-01). This method is similar to the current tolerance enforcement method for acetochlor, except that methylation of HEMA is not required, and residues are determined by LC/MS/MS rather than by HPLC with an oxidative coulometric electrochemical detector.

For this method, residues are extracted from homogenized samples with ACN/water (1:4 vol/vol), then filtered and concentrated. Residues are then base-hydrolyzed to yield EMA and HEMA, which are steam-distilled into dilute acid. The acidic distillate is partitioned against DCM, the organic phase is discarded, and the aqueous phase is then adjusted to a basic pH. Residues are partitioned into DCM, concentrated, and re-dissolved in ACN/water (1:9 vol/vol). Residues of EMA and HEMA are then determined by LC/MS/MS. The HPLC system consisted of a C_8 column with a mobile phase gradient of water/methanol (95:5) to methanol/ACN (1:1), each containing 0.2% acetic acid. The retention times were approximately 6.8 and 4.7 minutes for EMA and HEMA, respectively; residues were detected and quantified using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues were reported in acetochlor equivalents.

The statistically derived LOQs for EMA are 0.005 ppm in grain and forage, and 0.015 ppm in stover, while the LOQs for HEMA are 0.003 ppm in grain and forage, and 0.011 ppm in stover. The LODs for EMA are 0.004 ppm in grain and forage, and 0.015 ppm in stover, while the LODs for HEMA are 0.002 ppm in grain and forage, and 0.007 ppm in stover.

The above method was validated in conjunction with analysis of the field trial samples. Control samples were fortified with acetochlor *t*-sulfonic acid (EMA metabolite) and hydroxyethyl *t*-oxanilic acid (HEMA metabolite), with each at 0.010 to 0.200 ppm in grain, and at 0.010 to 2.00 ppm in forage and stover. Fortification levels and recovered residues were expressed in parent equivalents.

Samples were also analyzed for residues of furilazole using a GC/MS method (Method ES-ME-1008-01). For this method, residues are extracted with 20% ACN/water, then centrifuged, and filtered. The extract is diluted with saturated NaCl, 40% ethyl acetate/isooctane is added, and residues are partitioned into the organic phase. Residues are then concentrated, re-

dissolved in 3% ethyl acetate/isooctane, and cleaned up using an alumina SPE column eluted with 10% ethyl acetate/isooctane. Residues are determined by GC/MS using the m/z 262 ion for quantitation, and the m/z 220 ion for confirmation. The validated LOQ for furilazole in sorghum commodities is 0.010 ppm; the LOD was not reported.

This GC/MS method was validated in conjunction with analysis of the field trial samples, using control samples of forage, grain, and stover fortified with furilazole at 0.010 and 0.200 ppm.

C. RESULTS AND DISCUSSION

The number and geographic distribution of the sorghum field trials are adequate. At 13 sorghum field trials conducted in 2003, acetochlor (2.7 lb ai/gal Mcap) was applied in side-by-side tests at each trial site as either a pre- or post-emergence broadcast application at a rate of 2.44 to 2.58 lb ai/A. The pre-emergence application timing was from immediately following planting to 8 days after planting, while the post-emergence application was made when the sorghum was 5 to 14 inches in height. All applications were made using ground equipment in spray volumes of 10 to 20 GPA. Because sorghum is sensitive to acetochlor, the test substance included the safener furilazole at [redacted] however, field use rates (lb/A) were not reported for furilazole.

Single control and treated samples of forage were collected at 82 to 116 DAT following the pre-emergence application, and 48 to 77 DAT following the post-emergence application. In one of the post-emergence tests, forage samples were also collected at 48, 59, 66, and 73 DAT to examine residue decline. At crop maturity, single control and treated samples of grain (90 to 171 DAT) and stover (93 to 177 DAT) were collected from each test.

The LC/MS/MS Method ES-ME-1001-01 used to determine EMA and HEMA metabolite residues in sorghum forage, grain, and stover is adequate for data collection. Average concurrent recoveries from grain samples fortified with each type of metabolite at 0.010 to 0.200 ppm were 92 to 99% for EMA, and 76 to 83% for HEMA (see Table C.1, below). Average concurrent recoveries from forage samples fortified with each type of metabolite at 0.010 to 2.00 ppm were 82 to 104% for EMA, and 73 to 86% for HEMA. Average concurrent recoveries from stover samples fortified with each type of metabolite at 0.010 to 2.00 ppm were 79 to 94% for EMA, and 71 to 83% for HEMA. Apparent residues of EMA and HEMA were less than the LOQ in all control samples of each commodity. Adequate sample calculations and example chromatograms were provided.

The GC/MS Method ES-ME-1008-01 used to determine furilazole residues in sorghum forage, grain, and stover is also adequate for data collection. Average concurrent recoveries (and standard deviations) were 86% (4%) from forage, 78% (6%) from stover, and 84% (4%) from grain (see Table C.2, below). Apparent residues of furilazole were less than the LOQ in all

control samples of each commodity. Adequate sample calculations and example chromatograms were provided.

Prior to analysis of acetochlor residues, samples were stored frozen for durations of up to 211 days for grain, 222 days for forage, and 221 days for stover (see Table C.3, below). Storage stability data are available indicating that acetochlor *per se* is stable in frozen corn for intervals of up to approximately 36 months, while residues of EMA and HEMA metabolites are stable in frozen corn grain, forage, and stover for intervals of up to 49 months (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005). Prior to analysis of furilazole residues, samples were stored frozen for durations of up to 282 days for forage, 240 days for grain, and 225 days for stover. No supporting storage stability data were available for furilazole.

TABLE C.1 Summary of Method Recoveries for EMA and HEMA from Sorghum Commodities.

Matrix	Analyte[1]	Spike Level (mg/kg)[2]	Sample Size (n)	Recoveries (%)[3]	Mean Recovery [Std. Dev.] (%)
Grain	EMA	0.010	4	109, 95, 97, 94	99 [7]
		0.050	2	91, 93	92 [1]
		0.100	3	88, 103, 95	95 [7]
		0.200	3	88, 96, 92	92 [4]
	HEMA	0.010	4	84, 84, 76, 83	82 [4]
		0.050	2	76, 76	76 [0]
		0.100	3	72, 84, 75	77 [6]
		0.200	3	79, 88, 80	83 [5]
Forage	EMA	0.010	3	93, 119, 101	104 [13]
		0.050	3	81, 70, 78	82 [12]
		0.100	3	89, 106, 101	99 [9]
		0.200	3	92, 99, 96	95 [3]
		0.500	3	102, 97, 93	97 [4]
		1.00-2.00	2	88, 95	91 [5]
	HEMA	0.010	3	65, 92, 76	78 [14]
		0.050	3	74, 68, 78	73 [5]
		0.100	3	80, 93, 86	86 [6]
		0.200	3	77, 80, 82	80 [2]
		0.500	3	79, 81, 75	78 [3]
		1.00-2.00	2	80, 77	78 [2]

TABLE C.1 Summary of Method Recoveries for EMA and HEMA from Sorghum Commodities.					
Matrix	**Analyte [1]**	**Spike Level (mg/kg) [2]**	**Sample Size (n)**	**Recoveries (%) [3]**	**Mean Recovery [Std. Dev.] (%)**
Stover	EMA	0.010	3	69, 98, 69	79 [17]
		0.050	2	92, 96	94 [3]
		0.100	2	94, 86	90 [6]
		0.200	2	96, 97	96 [1]
		0.500	4	94, 98, 89, 95	94 [4]
		1.00-2.00	2	96, 87	92 [7]
	HEMA	0.010	4	96, 65, 74, 96	83 [16]
		0.050	2	72, 71	71 [1]
		0.100	2	79, 72	76 [5]
		0.200	2	74, 82	78 [6]
		0.500	4	75, 88, 71, 76	78 [7]
		1.00-2.00	2	80, 67	74 [9]

1. Samples were fortified with either acetochlor *t*-sulfonic acid (which yields EMA), or hydroxyethyl *t*-oxanilic acid (which yields HEMA).
2. Spiking levels were reported in total parent equivalents.
3. Residues were corrected for any control interference prior to calculation of recoveries.

TABLE C.2 Summary of Method Recoveries for Furilazole from Sorghum Commodities.					
Matrix	**Analyte**	**Spike Level (mg/kg)**	**Sample Size (n)**	**Recoveries (%)**	**Mean Recovery [Std. Dev.] (%)**
Forage	Furilazole	0.010	7	85, 87, 81, 80, 85, 83, 91	86 [4%]
		0.200	9	81, 91, 89, 88, 82, 89, 91, 83, 85	
Stover	Furilazole	0.010	7	77, 82, 76, 81, 82, 69, 66	78 [6%]
		0.200	6	86, 85, 84, 76, 81, 74	
Grain	Furilazole	0.010	7	82, 85, 83, 89, 85, 78, 90	84 [4%]
		0.050	6	85, 83, 89, 83, 81, 84	

Residues in forage were generally higher following the post-emergence application than the pre-emergence application, with 10 out of the 13 field trials having higher residues in forage from the post-emergence treatment. Following a pre-emergence application of acetochlor, residues in forage at 82 to 116 DAT were 0.015 to 0.458 ppm for EMA, and 0.003 to 0.058 ppm for HEMA, with combined residues of 0.018 to 0.515 ppm (see Table C.4, below). Following a post-emergence application of acetochlor, residues in forage at 52 to 77 DAT were 0.032 to 0.767 ppm for EMA, and 0.007 to 0.121 ppm for HEMA, with combined residues of 0.045 to 0.888 ppm. Average combined residues (and standard deviations) in forage were 0.174 ppm (0.124 ppm) following the pre-emergence application, and 0.263 ppm (0.236 ppm) following the post-emergence application. In the post-emergence test examining acetochlor residue decline in forage over time, the combined residues were variable, at 0.099 to 0.217 ppm from 48 to 73 DAT.

Residue levels of EMA and HEMA were both low (no more than 0.020 ppm) in all grain samples, but were slightly higher following the post-emergence application. For 12 of the field trials, the post-emergence treatment had residues equal to or higher than the pre-emergence treatment. Following the pre-emergence application, residues in grain harvested at maturity were <0.005 to 0.013 ppm for EMA, and <0.003 to 0.009 ppm for HEMA, with combined residues of <0.008 to 0.022 ppm (see Table C.5, below). Following a post-emergence application, residues in grain at maturity were <0.005 to 0.020 ppm for EMA, and <0.003 to 0.014 ppm for HEMA, with combined residues of <0.008 to 0.033 ppm. Average combined residues (and standard deviations) in grain were 0.009 ppm (0.006 ppm) following the pre-emergence application, and 0.015 ppm (0.011 ppm) following the post-emergence application.

As with forage and grain, residue levels of EMA and HEMA in stover were higher following the post-emergence application than the pre-emergence application, with 11 field trials having higher residues in the post-emergence treatment. Following the pre-emergence application, residues in stover harvested at maturity were <0.015 to 0.664 ppm for EMA, and <0.011 to 0.083 ppm for HEMA, with combined residues of <0.026 to 0.744 ppm (see Table C.6, below). Following a post-emergence application, residues in stover at maturity were 0.021 to 1.001 ppm for EMA, and <0.011 to 0.142 ppm for HEMA, with combined residues of <0.032 to 1.143 ppm. Average combined residues (and standard deviations) in stover were 0.251 ppm (0.232 ppm) following the pre-emergence application, and 0.342 ppm (0.329) ppm following the post-emergence application.

Regardless of whether a pre- or post-emergence application was used, residues of furilazole were non-quantifiable (less than the LOQ of 0.010 ppm) in all samples of forage, grain, and stover (n = 26 per commodity).

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

TABLE C.3 Summary of Freezer Storage Conditions.

Matrix	Storage Temperature (°C)	Analytes	Actual Storage Duration (Days) [Months]	Limit of Demonstrated Storage Stability (Months)*
Forage	< –18	EMA & HEMA	149-222 [4.9-7.3]	49
Grain			110-211 [3.6-6.9]	
Stover			99-221 [3.3-7.3]	
Forage		Furilazole	213-282 [7.0-9.3]	Not available.
Grain			130-240 [4.3-7.9]	
Stover			122-225 [4.0-7.4]	

* Acetochlor TRED; D297062; Samuel Ary; 5/31/2005.

TABLE C.4 Residue Data on Forage from Sorghum Field Trials with Acetochlor.

Location (City, State, Year) [Trial ID]	EPA Region	Sorghum Variety	Application Timing [1]	Rate (lb ai/A)	PHI [2] (Days)	Residues (ppm) [3]		
						EMA	HEMA	Combined
Plains, GA 2003 [GA]	2	A571	Pre	2.47	85	0.157	0.031	0.187
			Post	2.49	71	0.182	0.039	0.221
Cord, AR 2003 [AR]	4	Garst 5515	Pre	2.48.	87	0.147	0.033	0.180
			Post	2.50	68	0.064	0.019	0.083
Carlyle, IL 2003 [IL]	5	KS 585	Pre	2.56	84	0.015	0.003	0.018
			Post	2.58	55	0.049	0.007	0.056
New Holland, OH 2003 [OH-1]	5	A571	Pre	2.44	116	0.052	0.008	0.060
			Post	2.48	77	0.095	0.018	0.113
York, NE 2003 [NE-1]	5	Eclipse	Pre	2.49	92	0.148	0.019	0.167
			Post	2.50	48	0.091	0.080	0.099
					59	0.154	0.009	0.163
					66	0.199, 0.084	0.018, 0.016	0.217, 0.100
					73	0.124	0.024	0.149
Richland, IA 2003 [IA]	5	Dekalb AS71	Pre	2.55	82	0.065	0.012	0.077
			Post	2.50	52	0.065	0.010	0.074
Osceola, NE 2003 [NE-2]	5	NC+ 6B50	Pre	2.50	96	0.141	0.029	0.170
			Post	2.51	64	0.233	0.041	0.274
Colony, OK 2003 [OK-1]	6	Cherokee	Pre	2.47	106	0.458	0.058	0.515
			Post	2.52	69	0.767	0.121	0.888
East Benard, TX 2003 [TX-1]	6	DKS36-00	Pre	2.49	88	0.223	0.040	0.263
			Post	2.55	65	0.408	0.071	0.480
Grand Island, NE 2003 [NE-3]	7	NC+ 6B50	Pre	2.49	100	0.120	0.017	0.137
			Post	2.50	72	0.161	0.023	0.184
Dill City, OK 2003 [OK-2]	8	Eclipse	Pre	2.58	103	0.093	0.046	0.139
			Post	2.50	67	0.384	0.071	0.454
Claude, TX 2003 [TX-2]	8	Y363	Pre	2.51	99	0.220	0.027	0.247
			Post	2.53	86	0.295	0.043	0.338
Levelland, TX 2003 [TX-3]	8	F-270E	Pre	2.55	90	0.089	0.015	0.104
			Post	2.53	69	0.032	0.013	0.045

1. Relative to crop emergence; post-emergence applications were made when sorghum was 5 to 14 inches in height.
2. PHI = Pre-Harvest Interval.
3. All residues are expressed in parent equivalents. In forage, the LOQs are 0.005 and 0.003 ppm for EMA and HEMA, respectively; the LODs are 0.004 and 0.002 ppm.

Acetochlor/524-511/PC Code 121601/Monsanto Company/524
Furilazole/524-511/PC Code 911596/Monsanto Company/524
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, Grain, and Stover)

TABLE C.5 Residue Data on Grain from Sorghum Field Trials with Acetochlor.

Location (City, State, Year) [Trial ID]	EPA Region	Sorghum Variety	Application Timing [1]	Rate (lb ai/A)	PHI (Days)	Residues (ppm) [2]		
						EMA	HEMA	Combined
Plains, GA 2003 [GA]	2	A571	Pre	2.47	107	0.006	0.006	0.012
			Post	2.49	93	0.008	0.009	0.017
Cord, AR 2003 [AR]	4	Garst 5515	Pre	2.48.	123	(0.004) [3]	0.003	0.008
			Post	2.50	104	(0.004)	(0.003)	0.008
Carlyle, IL 2003 [IL]	5	KS585	Pre	2.56	133	ND [4]	ND	ND
			Post	2.58	104	ND	ND	ND
New Holland, OH 2003 [OH-1]	5	A571	Pre	2.44	160	ND	ND	ND
			Post	2.48	121	(0.004)	0.004	0.008
York, NE 2003 [NE-1]	5	Eclipse	Pre	2.49	138	0.013	0.009	0.022
			Post	2.50	112	0.019	0.014	0.033
Richland, IA 2003 [IA]	5	Dekalb AS71	Pre	2.55	134	ND	ND	ND
			Post	2.50	104	ND	ND	ND
Osceola, NE 2003 [NE-2]	5	NC+ 6B50	Pre	2.50	147	0.006	0.004	0.010
			Post	2.51	115	0.011	0.008	0.019
Colony, OK 2003 [OK-1]	6	Cherokee	Pre	2.47	133	ND	(0.002)	ND
			Post	2.52	96	0.020	0.011	0.031
East Benard, TX 2003 [TX-1]	6	DKS36-00	Pre	2.49	113	0.010	0.005	0.015
			Post	2.55	90	0.012	0.007	0.019
Grand Island, NE 2003 [NE-2]	7	NC+ 6B50	Pre	2.49	148	0.012	0.005	0.017
			Post	2.50	120	0.020	0.007	0.027
Dill City, OK 2003 [OK-2]	8	Eclipse	Pre	2.58	133	0.005	0.006	0.011
			Post	2.50	97	0.010	0.007	0.017
Claude, TX 2003 [TX-2]	8	Y363	Pre	2.51	171	(0.005)	ND	ND
			Post	2.53	158	ND	ND	ND
Levelland, TX 2003 [TX-3]	8	F-270E	Pre	2.55	119	0.009	(0.002)	0.011
			Post	2.53	98	0.005	ND	0.005

1. Relative to crop emergence; post-emergence applications were made when sorghum was 5 to 14 inches in height.
2. All residues are expressed in parent equivalents. In grain the LOQs are 0.005 and 0.003 ppm for EMA, and HEMA, respectively; the LODs are 0.004 and 0.002 ppm.
3. Values in parentheses are less than the LOQ, but greater than or equal to the LOD.
4. ND = Not Detected (less than the LOD).

TABLE C.6 Residue Data on Stover from Sorghum Field Trials with Acetochlor.

Location (City, State, Year) [Trial ID]	EPA Region	Sorghum Variety	Application Timing [1]	Rate (lb ai/A)	PHI (Days)	Residues (ppm) [2]		
						EMA	HEMA	Combined
Plains, GA 2003 [GA]	2	A571	Pre	2.47	142	0.546	0.083	0.629
			Post	2.49	128	0.414	0.079	0.493
Cord, AR 2003 [AR]	4	Garst 5515	Pre	2.48.	123	0.126	0.023	0.149
			Post	2.50	104	0.093	0.017	0.109
Carlyle, IL 2003 [IL]	5	KS585	Pre	2.56	133	ND [3]	ND	ND
			Post	2.58	104	0.021	ND	0.021
New Holland, OH 2003[OH-1]	5	A571	Pre	2.44	160	0.091	(0.010) [4]	0.100
			Post	2.48	121	0.156	0.020	0.176
York, NE 2003 [NE-1]	5	Eclipse	Pre	2.49	144	0.140	0.026	0.165
			Post	2.50	118	0.201	0.029	0.230
Richland, IA 2003 [IA]	5	Dekalb AS71	Pre	2.55	140	0.052	0.011	0.063
			Post	2.50	110	0.054	(0.011)	0.065
Osceola, NE 2003 [NE-2]	5	NC+ 6B50	Pre	2.50	141	0.221	0.028	0.249
			Post	2.51	109	0.320	0.043	0.363
Colony, OK 2003 [OK-1]	6	Cherokee	Pre	2.47	140	0.664	0.080	0.744
			Post	2.52	103	1.00	0.142	1.143
East Benard. TX 2003[TX-1]	6	DKS36-00	Pre	2.49	116	0.172	0.037	0.209
			Post	2.55	93	0.237	0.065	0.302
Grand Island, NE 2003[NE-2]	7	NC+ 6B50	Pre	2.49	152	0.129	0.018	0.147
			Post	2.50	124	0.189	0.023	0.212
Dill City, OK 2003 [OK-2]	8	Eclipse	Pre	2.58	142	0.463	0.072	0.535
			Post	2.50	106	0.800	0.100	0.900
Claude, TX 2003 [TX-2]	8	Y363	Pre	2.51	177	0.132	0.014	0.146
			Post	2.53	164	0.192	0.019	0.211
Levelland, TX 2003 [TX-3]	8	F-270E	Pre	2.55	126	0.0830	0.024	0.107
			Post	2.53	105	0.2060	0.022	0.228

1. Relative to crop emergence; post-emergence applications were made when sorghum was 5 to 14 inches in height.
2. All residues are expressed in parent equivalents. In stover the LOQs are 0.015 and 0.011 ppm for EMA and HEMA, respectively; the LODs are 0.004 and 0.002 ppm.
3. ND = Not Detected (less than the LOD).
4. Values in parentheses are less than the LOQ, but greater than or equal to the LOD.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

TABLE C.7 Summary of Residue Data for Sorghum Field Trials with Acetochlor.

Analyte	Application Timing	PHI (Days)	Residue Levels (ppm) [1]						
			n	Min.	Max.	HAFT [2]	Median [3]	Mean	Std. Dev.
Sorghum Forage									
EMA	Pre	82-116	13	0.015	0.458	0.458	0.141	0.148	0.111
	Post	52-77	13	0.032	0.767	0.767	0.182	0.226	0.204
HEMA	Pre	82-116	13	0.003	0.058	0.058	0.027	0.026	0.016
	Post	52-77	13	0.007	0.121	0.121	0.023	0.038	0.033
Combined	Pre	82-116	13	0.018	0.515	0.515	0.167	0.174	0.124
	Post	52-77	13	0.045	0.888	0.888	0.217	0.263	0.236
Sorghum Grain									
EMA	Pre	107-171	13	<0.005	0.013	0.013	0.005	0.006	0.004
	Post	90-158	13	<0.005	0.020	0.020	0.008	0.009	0.007
HEMA	Pre	107-171	13	<0.003	0.009	0.009	0.003	0.004	0.002
	Post	90-158	13	<0.003	0.014	0.014	0.007	0.006	0.004
Combined	Pre	107-171	13	<0.008	0.022	0.022	0.010	0.009	0.006
	Post	90-158	13	<0.008	0.033	0.033	0.017	0.015	0.011
Sorghum Stover									
EMA	Pre	116-177	13	<0.015	0.664	0.664	0.132	0.217	0.205
	Post	93-164	13	0.021	1.001	1.00	0.201	0.299	0.289
HEMA	Pre	116-177	13	<0.011	0.083	0.083	0.024	0.033	0.028
	Post	93-164	13	<0.011	0.142	0.142	0.023	0.044	0.041
Combined	Pre	116-177	13	<0.026	0.744	0.744	0.149	0.251	0.232
	Post	93-164	13	<0.032	1.143	1.143	0.228	0.342	0.329

1. All residues are expressed in parent equivalents. The method LOQs for EMA are 0.005 ppm in forage and grain, and 0.015 ppm in stover; the LOQs for HEMA are 0.003 ppm in forage and grain, and 0.011 ppm in stover.
2. HAFT = Highest Average Field Trial.
3. Residues less than the LOQ were estimated as 2 LOQ for calculation of the median, mean and standard deviation.

D. CONCLUSION

The field trial data are adequate, and reflect the use of a single broadcast application of acetochlor (2.7 lb ai/gal Mcap) to sorghum, made at roughly 2.5 lb ai/A as either a pre-emergence application or a post-emergence application (when plants were 5 to 14 inches in height). The data support a pre-harvest interval (PHI) of 60 days for sorghum forage following a post-emergence application. PHIs are not required for grain and stover, nor for forage following a pre-emergence application. The data also support the inclusion of the safener furilazole in the formulation at a level of [redacted] However, information is needed on the actual concentration (lb/gal) of furilazole in the formulation, along with data supporting the stability of furilazole in sorghum forage, grain, and stover for intervals of up to 9.3 months.

E. REFERENCES

Acetochlor. Summary of Analytical Chemistry and Residue Data for the Tolerance Reassessment Eligibility Decision (TRED) Document.; DP #D297062; Samuel Ary; 5/31/2005.

F. DOCUMENT TRACKING

RDI: W.T. Drew (2/23/2006); D. Dotson (3/20/2006); R.A. Loranger (10/26/2006)
Petition Number: 5F6918
DP Number: 316496
PC Codes: 121601 and 911596

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Acetochlor/524-511/PC Code 121601/Monsanto Company/524
Furilazole/524-511/PC Code 911596/Monsanto Company/524
DACO 7.4.4/OPPTS 860.1520/OECD IIA 6.6.3, 6.8.7 and IIIA 8.6
Processed Food and Feed – Sorghum (Grain, Bran, and Flour)

Primary Evaluator:	William T. Drew, Chemist, HED/RAB2	Date: 2/28/2006
Peer Reviewer:	Douglas Dotson, Chemist, HED/RAB2	Date: 3/22/2006
Approved by:	Richard A. Loranger, Branch Senior Scientist, HED/RAB2	Date: 10/26/2006

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 policy.

STUDY REPORT

MRID #46507101. Sharon J. Moran (2004) *Magnitude of Acetochlor and MON 13900 Residues in Sorghum Raw Agricultural Commodities and Processed Commodities Following Applications of Degree Xtra™.* Protocol #03-27-R-2. Report #MSL-18670, RD 1638. Unpublished study prepared by Monsanto Company. 303 pages. {OPPTS Residue Chemistry Test Guideline 860.1520}

EXECUTIVE SUMMARY

At two field trials conducted during 2003 in Nebraska and Oklahoma, acetochlor, as a 2.7 pounds active ingredient per gallon (lb ai/gal) microencapsulated (Mcap) formulation, was applied to grain sorghum as a single, early-season, post-emergence application. The application rate was 2.5 lb ai per acre (lb ai/A), which is 1X the proposed maximum use rate. Because sorghum is sensitive to acetochlor, the formulation included [redacted] of the safener furilazole; however, the actual concentration (lb/gal) and field use rates (lb/A) for furilazole were not reported. Single bulk control (untreated) and treated samples of grain were harvested from each trial at maturity, 97 to 112 days after treatment (DAT), and were then processed into sorghum flour and bran using simulated commercial procedures. Sorghum grain and processed fractions were stored frozen for durations of up to 5.3 and 1.4 months, respectively, prior to analysis for acetochlor residues, and up to 5.5 and 2.8 months, respectively, prior to analysis for furilazole residues. The storage durations for the analysis of acetochlor residues are supported by the available storage stability data on corn grain, but no data were provided supporting the stability of furilazole residues.

The LC/MS/MS method (Monsanto Method ES-ME-1001-01) used to determine acetochlor residues in sorghum grain, flour, and bran was adequately validated in conjunction with the processing study. For this method, residues are extracted with acetonitrile (ACN)/water,

then base-hydrolyzed to yield two separate hydrolysis products, 2-ethyl-6-methylaniline (EMA) and 2-(1-hydroxyethyl)-6-methylaniline (HEMA), which are steam-distilled into dilute acid. Residues are partitioned into dichloromethane (DCM), concentrated, and then re-dissolved in ACN/water. EMA and HEMA are determined via LC/MS/MS using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues are reported in acetochlor equivalents. The validated limits of quantitation (LOQ) are 0.005 and 0.003 ppm for EMA and HEMA, respectively, in grain and all processed fractions, while the limits of detection (LOD) are 0.004 and 0.002 ppm.

The GC/MS method (Monsanto Method ES-1008-01) used to determine furilazole residues in sorghum commodities was also adequately validated. For this method, residues are extracted with ACN/water, diluted with saturated NaCl, and partitioned into ethyl acetate/isooctane. Residues are then cleaned up using an alumina solid-phase extraction (SPE) column. Residues are determined by GC/MS using the m/z 262 ion for quantitation, and the m/z 220 ion for confirmation. The validated LOQ is 0.010 ppm for furilazole in sorghum grain and processed fractions; the LOD was not reported.

At maturity, combined acetochlor residues were 0.033 ppm and 0.017 ppm in grain from the Nebraska and Oklahoma trials, respectively. Sorghum grain is the raw agricultural commodity (RAC). Combined residues in cleaned grain were 0.030 ppm and 0.021 ppm from the two trials, and after processing, combined acetochlor residues were <0.013 ppm and <0.008 ppm in flour, with 0.101 ppm and 0.092 ppm in bran. The processing factors for combined acetochlor residues were similar for the two trials, averaging 1.1X for cleaned grain, less than 0.5X for flour, and 4.3X for bran.

Processing factors for furilazole residues could not be determined because residues of furilazole were non-quantifiable (less than 0.010 ppm) in all samples of grain (RAC) and processed fractions from both trials. Although furilazole residues were less than the LOQ in the RAC at 1X, the use of an exaggerated rate is not required because sorghum is sensitive to acetochlor, and higher use rates of the Mcap formulation (including the furilazole) would result in phytotoxicity.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in this study, the sorghum processing data are classified as scientifically acceptable regarding the acetochlor residue data. However, to upgrade the residue data on furilazole to adequate, data supporting the stability of furilazole in sorghum grain is required. The acceptability of this study for regulatory purposes is addressed in the US EPA Residue Chemistry Summary Document (DP Barcode D316496).

INERT INGREDIENT INFORMATION IS NOT INCLUDED

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

Acetochlor is a chloroacetanilide herbicide currently used for pre-emergence control of weeds in corn. In the United States, acetochlor is conditionally registered for use on corn to the Acetochlor Registration Partnership (ARP), which is comprised of Monsanto and Dow AgroSciences. Acetochlor is formulated as a variety of emulsifiable concentrate (EC), emulsion in water (EW), granular (G), or Mcap formulations that can be applied to corn as a pre-plant, pre-emergence, or early post-emergence application. Tolerances are established for the combined residues of acetochlor and its metabolites convertible to EMA or HEMA, to be analyzed as acetochlor, and expressed as acetochlor equivalents (40CFR ' 180.470). Tolerances range from 0.05 to 1.5 ppm in corn commodities resulting from the direct use of acetochlor, and from 0.02 to 1.0 ppm in commodities from the rotational crops, sorghum, soybeans, and wheat.

Monsanto has submitted a petition (PP#5F6918) proposing the use of acetochlor, formulated as a 2.7 lb ai/gal Mcap, on sorghum. Because sorghum is sensitive to phytotoxicity from acetochlor, the petitioner is proposing the inclusion of the safener furilazole with the herbicide at a concentration of [redacted]. Tolerances are established for residues of furilazole in field and pop corn commodities at 0.01 ppm (40CFR ' 180.471).

TABLE A.1 Acetochlor and Furilazole Nomenclature.

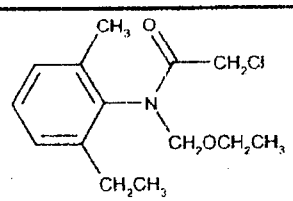
Chemical Structure	
Common Name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC Name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide
CAS Name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS Number	34256-82-1
PC Code	121601
End-Use Product (EP)	Degree Xtra (2.7 lb/gal Mcap), EPA Registration #524-511

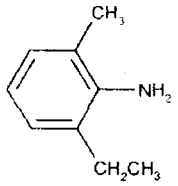
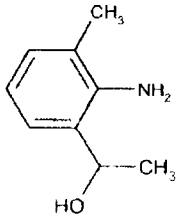
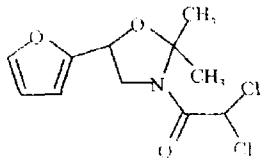
TABLE A.1 Acetochlor and Furilazole Nomenclature.	
Chemical Structure	
Common Name	EMA
Molecular Weight	337.4
CAS Name	2-ethyl-6-methylaniline
Chemical Structure	
Common Name	HEMA
Molecular Weight	303.3
CAS Name	2-(1-hydroxyethyl)-6-methylaniline
Chemical Structure	
Common Name	Furilazole (MON 13900)
Molecular Formula	$C_{11}H_{13}Cl_2NO_3$
Molecular Weight	278.1
IUPAC Name	(*RS*)-3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyloxazolidine
CAS Name	3-(dichloroacetyl)-5-(2-furanyl)-2,2-dimethyloxazolidine
CAS Number	121776-33-8
PC Code	911596

TABLE A.2 Physicochemical Properties of Acetochlor.		
Parameter	**Value**	**Reference**
Boiling Point/Range	163°C at 10 mm Hg. Decomposition occurs before the boiling point at atmospheric pressure (calculated by extrapolation of vapor pressure at lower temperature).	M. Flood, DEB 7474, 2/6/1991
pH	4.41 (1% solution in acetone/water, 1:1 vol/vol)	M. Flood, DEB 7474, 2/6/1991
Density (g/mL, 20°C)	1.123	M. Flood, DEB 7474, 2/6/1991
Water Solubility (mg/L, 25°C)	223	2001 Farm Chem Handbook
Solvent Solubility (25°C)	Miscible in acetone, benzene, carbon tetrachloride, ethanol, chloroform, and toluene.	M. Flood, HED Memo, 1/21/1994
Vapor Pressure (mm Hg, 25°C)	4.5×10^{-5}	M. Flood, DEB 7474, 2/6/1991
Dissociation Constant (pK_a)	Not applicable (because acetochlor is neither an acid nor a base).	M. Flood, DEB 7474, 2/6/1991
Octanol/Water Partition Coefficient	970 (Dow study) or 1082 (Monsanto study). Differences are likely due to experimental error.	M. Flood, DEB 7474, 2/6/1991
UV/Visible Spectrum	Not available.	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Two field trials were conducted in Oklahoma and Nebraska during 2003 using acetochlor as a post-emergence application in order to generate grain for processing studies (see Tables B.1.1 and B.1.2, below). Precipitation and mean monthly minimum and maximum temperatures were reported for both trial sites for the entire growing season, along with historical precipitation and temperature data. Although the growing season was reported to be drier than normal, the field trials were supplemented with irrigation as needed in order to maintain normal crop growth.

TABLE B.1.1 Trial Site Conditions.				
Trial Identification (City, State/Year)	**Soil Characteristics**			
	Type	**%OM**	**pH**	**CEC (meq/g)**
Dill City, OK/2003	Sand	0.7	6.5	NR*
York, NE/2003	Silt Loam	2.1	7.1	NR

* NR = Not Reported.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Acetochlor/524-511/PC Code 121601/Monsanto Company/524
Furilazole/524-511/PC Code 911596/Monsanto Company/524
DACO 7.4.4/OPPTS 860.1520/OECD IIA 6.6.3, 6.8.7 and IIIA 8.6
Processed Food and Feed – Sorghum (Grain, Bran, and Flour)

TABLE B.1.2 Study Use Pattern.

Location (County, State/Year) [Trial ID]	Application Information [1]				
	End-Use Product [2]	Method [3]; Timing	Volume (GPA) [4]	Number of Applications	Rate (lb ai/A)
Dill City, OK/2003 [OK-2]	Degree Xtra™	Post-emergence broadcast application; crop 11" to 14" high.	11	1	2.50
York, NE/2003 [NE-1]	Degree Xtra™	Post-emergence broadcast application; crop 5" to 6" high.	20	1	2.50

1. Neither application included the use of any surfactants or spray adjuvants.
2. Because sorghum is sensitive to acetochlor, the test substance included furilazole [redacted] as a safener; however, the use rate was not reported in terms of lb/A; the formulation also included atrazine at 1.34 lb ai/gal.
3. All applications were made using ground equipment.
4. GPA = Gallons Per Acre.

B.2. Sample Handling and Preparation

Single bulk samples of control (untreated) and treated sorghum grain (75 or 90 lbs) were harvested from each trial at commercial maturity, 97 or 112 days after treatment. Samples were frozen within 2.5 hours of harvest. Samples from the Oklahoma trials were shipped by ACDS freezer truck directly to the processing facility, Food Protein Research and Development Center, Texas A&M University (in Bryan, TX). Samples from the Nebraska trial were first shipped frozen to Monsanto (in St. Louis, MO), and then on to the processing facility. The grain samples were stored frozen for 118 days prior to processing.

Sorghum grain was processed into flour and bran using simulated commercial procedures. The grain was dried to a moisture content of 10 to 13%, cleaned using a Kice aspirator, and then screened. The resulting "cleaned seed" was milled in a Satake abrasion mill to remove most of the bran, which was screened out. The remaining sample was then separated into decorticated grain, large grits, and small grits by screening. The decorticated grain was ground into flour. Samples of cleaned seed, bran, and flour were collected during processing. The whole grain (RAC) and processed fractions were placed in frozen storage, then shipped by ACDS freezer truck within 12 days of processing to the analytical laboratory (Monsanto), where samples were stored at -18EC until analysis.

B.3. Analytical Methodology

Samples of sorghum grain, flour, and bran were analyzed for EMA- and HEMA-producing metabolites using an LC/MS/MS method (Method ES-ME-1001-01). This method is similar to the current tolerance enforcement method for acetochlor except that methylation of HEMA is not required, and residues are determined by LC/MS/MS rather than by HPLC with an oxidative coulometric electrochemical detector.

For this method, residues are extracted from homogenized samples with ACN/water (1:4 vol/vol), then filtered and concentrated. Residues are then base-hydrolyzed to yield EMA and

HEMA, which are steam-distilled into dilute acid. The acidic distillate is partitioned against DCM, the organic phase is discarded, and the aqueous phase is then adjusted to a basic pH. Residues are partitioned into DCM, concentrated, and re-dissolved in ACN/water (1:9 vol/vol). Residues of EMA and HEMA are then determined by LC/MS/MS. The HPLC system consisted of a C_8 column with a mobile phase gradient of water/methanol (95:5) to methanol/ACN (1:1), each containing 0.2% acetic acid. The retention times were approximately 6.8 and 4.7 minutes for EMA and HEMA, respectively; residues were detected and quantified using the 136 to 91 m/z transition for EMA, and the 152 to 134 m/z transition for HEMA. Residues were reported in acetochlor equivalents. The LOQs for grain, flour and bran are 0.005 and 0.003 ppm for EMA and HEMA, respectively, while the LODs are 0.004 and 0.002 ppm.

The above method was validated in conjunction with analysis of the processing study samples. Control samples were fortified with acetochlor *t*-sulfonic acid (EMA metabolite) and hydroxyethyl *t*-oxanilic acid (HEMA metabolite), with each at 0.010 to 0.200 ppm in grain, and at 0.010 to 0.050 ppm in flour and bran. Fortification levels and recovered residues were expressed in parent equivalents.

Samples were also analyzed for residues of furilazole using a GC/MS method (Method ES-ME-1008-01). For this method, residues are extracted with 20% ACN/water, then centrifuged, and filtered. The extract is diluted with saturated NaCl, 40% ethyl acetate/isooctane is added, and residues are partitioned into the organic phase. Residues are then concentrated, re-dissolved in 3% ethyl acetate/isooctane, and cleaned up using an alumina SPE column eluted with 10% ethyl acetate/isooctane. Residues are determined by GC/MS using the m/z 262 ion for quantitation, and the m/z 220 ion for confirmation. The validated LOQ for furilazole in sorghum grain, flour, and bran is 0.010 ppm; the LOD was not reported.

This GC/MS method was also validated in conjunction with the processing study, using control samples of grain, flour, and bran fortified with furilazole at 0.010 and 0.20 ppm.

C. RESULTS AND DISCUSSION

Samples of whole grain (RAC) were stored frozen for durations of up to 163 days (5.3 months) prior to analysis for acetochlor residues, and up to 169 days (5.5 months) prior to analysis for furilazole residues (see Table C.1, below). Processed fractions were stored frozen for durations of up to 42 days prior to analysis of acetochlor residues, and up to 86 days prior to analysis of furilazole residues. Storage stability data are available indicating that acetochlor *per se* is stable in frozen corn for intervals of up to approximately 36 months, while residues of EMA and HEMA metabolites are stable in frozen corn grain for intervals of up to 49 months (Acetochlor TRED; D297062; Samuel Ary; 5/31/2005). These data will support the storage durations and conditions for the sorghum processing study samples. However, no supporting storage stability data were available for furilazole.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

The LC/MS/MS Method ES-ME-1001-01 used to determine EMA and HEMA metabolite residues in sorghum grain and processed fractions is adequate for data collection. Average concurrent recoveries from grain and processed fractions fortified with each type of metabolite at 0.010 to 0.050 ppm were 96 to 100% for EMA, and 85 to 88% for HEMA (see Table C.2, below). Apparent residues of EMA and HEMA were less than the LOQ in all control samples of each commodity. Adequate sample calculations and example chromatograms were provided.

The GC/MS Method ES-ME-1008-01 used to determine furilazole residues in sorghum grain and processed fractions is also adequate for data collection. Average concurrent recoveries were 78 to 93% from grain and processed fractions fortified with furilazole at 0.010 to 0.200 ppm. Apparent residues of furilazole were less than the LOQ in all control samples; adequate sample calculations and example chromatograms were provided.

At both field trials, sorghum was treated with acetochlor (2.7 lb ai/gal Mcap), also containing [redacted] furilazole, as a single early-season, post-emergence broadcast application at a rate of 2.5 lb ai/A (1X rate). An exaggerated rate was not used for the processing studies because sorghum is sensitive to acetochlor, and higher use rates would reportedly result in phytotoxicity.

At maturity (97 to 112 DAT), combined acetochlor residues (EMA + HEMA) were 0.033 ppm in grain from the Nebraska trial, and 0.017 ppm in grain from the Oklahoma trial (see Table C.3, below). After cleaning, combined residues in grain were 0.030 ppm and 0.021 ppm from the two trials. After processing, combined acetochlor residues were <0.008 ppm and <0.0134 ppm in flour, with 0.0916 ppm and 0.1011 ppm in bran. The processing factors for combined acetochlor residues were similar for the two trials, averaging 1.1X for cleaned grain, less than 0.5X for flour, and 4.3X for bran.

Processing factors for furilazole residues could not be determined as residues of furilazole were non-quantifiable (less than 0.010 ppm) in all samples of grain (RAC) and processed fractions from both trials.

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

TABLE C.1 Summary of Freezer Storage Conditions.

Matrix	Storage Temperature (°C)	Analytes	Actual Storage Duration (Days) [Months] [1]	Limit of Demonstrated Storage Stability (Months) [2]
Grain (RAC)	< –18	EMA & HEMA	153-163 [5.0-5.4]	49
Cleaned Seed, Bran, Flour			33-42 [1.1-1.4]	
Grain (RAC)		Furilazole	162-169 [5.3-5.6]	Not available.
Cleaned Seed, Bran, Flour			81-86 [2.7-2.8]	

1. The storage durations for processed fractions are from processing to analysis.
2. Acetochlor TRED; D297062; Samuel Ary; 5/31/2005.

TABLE C.2 Summary of Method Recoveries for Acetochlor and Furilazole Residues from Sorghum Grain and Processed Fractions.

Matrix	Analyte	Spike Level (mg/kg)	Sample Size (n)	Recoveries (%)	Mean [Std. Dev.] (%)
Acetochlor Residues					
Grain	EMA	0.010, 0.050	4	93, 93, 105, 100	98 [6]
	HEMA		4	76, 83, 96, 84	85 [8]
Bran	EMA	0.010, 0.050	2	109, 90	100 [13]
	HEMA		2	98, 77	88 [15]
Flour	EMA	0.010, 0.050	2	97, 95	96 [1]
	HEMA		2	88, 83	86 [4]
Furilazole Residues					
Grain	Furilazole	0.010, 0.200	2	86, 93	89 [5]
Bran		0.010, 0.200	2	77, 79	78 [1]
Flour		0.010, 0.200	2	92, 93	93 [1]

TABLE C.3 Residue Data from Sorghum Processing Studies.

RAC	Processed Commodity	Total Rate (lb ai/A)	Trial Location	PHI [1] (Days)	Residues (ppm) [2]			Processing Factor
					EMA	HEMA	Combined [3]	
Sorghum	Grain (RAC)	2.50	NE	112	0.019	0.014	0.033	NA [4]
			OK	97	0.010	0.007	0.017	NA
	Cleaned Grain		NE	112	0.018	0.012	0.030	0.9X
			OK	97	0.012	0.009	0.021	1.2X
	Flour		NE	112	0.010	ND	<0.013	<0.4X
			OK	97	ND	ND	<0.008	<0.5X
	Bran		NE	112	0.049	0.052	0.101	3.0X
			OK	97	0.052	0.040	0.092	5.5X

1. PHI = Pre-Harvest Interval.
2. The LOQs are 0.005 and 0.003 ppm for EMA and HEMA, respectively; the LODs are 0.004 and 0.002 ppm.
3. For calculating the combined residues, the LOQ was used for residues less than the LOQ.
4. NA = Not Applicable.

D. CONCLUSION

The sorghum processing study is adequate, and indicates that combined acetochlor residues (EMA + HEMA) do not concentrate in sorghum flour (processing factor of less than 0.5X), but can concentrate by 4.3X in bran. Processing factors could not be determined for furilazole because residues of furilazole were non-quantifiable (less than 0.010 ppm) in samples of grain (RAC) and all processed fractions. Although the field trials were conducted at only a 1X rate, the furilazole processing data are adequate as furilazole is a safener included in the acetochlor formulation, and higher use rates of the acetochlor formulation would result in crop damage.

E. REFERENCES

Acetochlor. Summary of Analytical Chemistry and Residue Data for the Tolerance Reassessment Eligibility Decision (TRED) Document.; DP #D297062; Samuel Ary; 5/31/2005.

F. DOCUMENT TRACKING

RDI: W.T. Drew (2/28/2006); D. Dotson (3/22/2006); R.A. Loranger (10/26/2006)
Petition Number: 5F6918
DP Number: 316496
PC Codes: 121601 and 911596