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Approved by	Richard A. Loranger, Branch Senior Scientist, RAB2	Date: 10/26/06

In the absence of signatures, this document is considered to be a draft with deliberative material for internal use only.

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Suite B; Durham, NC 27713; submitted 2/20/2005). This DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

45322106 Andersen, L, Walter, D. Spillner, C. (1998) Residue Levels on Sunflowers Planted as a Rotational Crop Following Corn From Trials Carried Out in the United States of America During 1996: Lab Project Number: ACET-95-CR-02: RJ2560B. Unpublished study prepared by Zeneca Agrochemicals. 88 p.

EXECUTIVE SUMMARY:

Eight rotational crop field trials were conducted on sunflowers at sites throughout the U.S. during 1996. At each test site, acetochlor (6.4 lb/gal EC) was applied to a primary crop of field corn as a preplant, at-planting, or preemergence broadcast application at 3.0 lb ai/A. The corn was grown and harvested following common agricultural practices. At each site, a rotational crop of sunflower was planted 346-380 days after treatment (DAT). Single control and duplicate treated samples of sunflower seeds were harvested from each test at commercial maturity, 122-146 days after planting (481-519 DAT). Samples were stored frozen for up to 6 months prior to analysis, an interval supported by available storage stability data.

A GC/nitrogen-phosphorus detection (GC/NPD) method (RAM 244/02) was used to determine residues of acetochlor, *per se*. The registrant has not demonstrated that this method can extract field weathered residues. Therefore data on residues of acetochlor *per se* from field samples are not considered supported by adequate validation data and are not appropriate for use in risk assessment or for tolerance setting purposes. Further, since the data generated from analytical method RAM 244/02 are not of utility for regulatory purposes, they are not included in this document.

In addition, a GC/mass selective detector (MSD) method (RAM 280/02) was used to determine residues of acetochlor and its metabolites convertible to ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) type metabolites in sunflower seeds. The LOQ is 0.01 ppm for both EMA and HEMA, or 0.02 ppm when expressed as acetochlor equivalents. The LOD was not reported. The extraction procedure in this method is substantially similar to the extraction scheme employed in the current enforcement method; therefore, HED concludes that this method has been adequately demonstrated to extract weathered residues and has been adequately validated for data collection purposes.

Residues of EMA and HEMA were each <0.02 ppm acetochlor equivalents in all samples of sunflower seeds. Combined residues were <0.04 ppm (EMA plus HEMA, expressed in acetochlor equivalents).

No data were provided on residues of the hydroxymethyl ethyl aniline (HMEA) metabolites.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in this study, the sunflower field rotational crop data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U. S. EPA document entitled *Acetochlor: Petitions for Tolerances on Sweet Corn and Rotational Crops of Nongrass Animal Feeds (Group 18), Sugar Beets, Dried Shelled Beans and Peas (Subgroup 6C), Sunflowers, Potatoes, Cereal Grains (Group 15), and Forage, Fodder, and Straw of Cereal Grains (Group 16). Summary of Analytical Chemistry and Residue Data* (D. Davis, D230310).

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 used for preemergence 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), microencapsulated (Mcap), or granular (G) formulations that can be applied to corn as a preplant, preemergence, or early postemergence application using only ground equipment. Tolerances are established for the combined residues of acetochlor and its metabolites convertible to ethyl methyl aniline (EMA) or hydroxyethyl methyl aniline (HEMA), expressed as acetochlor equivalents [40 CFR ' 180.470]. Tolerances range from 0.05 to 1.5 ppm in/on 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.

The ARP has submitted a petition (PP#1F6263) proposing tolerances for inadvertent residues of acetochlor in rotated dried peas and beans (subgroup 6C), sugar beets, sunflowers, potatoes, cereal grains (group 15, except corn and rice), and the forage, fodder, and straw of cereal grains (group 16, except corn and rice).

TABLE A.1. Acetochlor Nomenclature

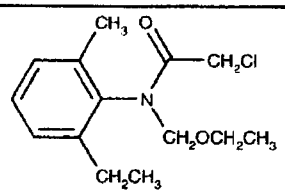
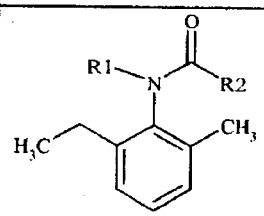
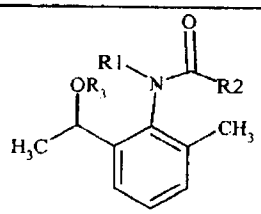
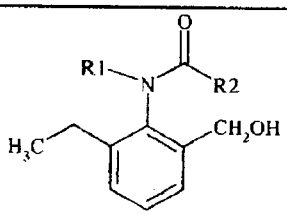
Chemical structure	
Common name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide
CAS name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS #	34256-82-1
PC Code	121601
End-use Product	6.4 lb/gal EC

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)	HED Chapter of TRED, 3/1/06
pH	4.41, 1% solution in acetone:water (1:1, v:v)	
Density at 20 °C	1.123 g/mL	
Water solubility at 25 °C	223 mg/L	
Solvent solubility at 25 °C	Infinitely soluble in acetone, benzene, carbon tetrachloride, ethanol, chloroform, and toluene	
Vapor pressure at 25 °C	0.045 μ Hg (4.5×10^{-5} mm Hg)	
Dissociation constant, pK_a	Not applicable because acetochlor is neither an acid nor a base.	
Octanol/water partition coefficient	970 or 1082	
UV/visible absorption spectrum	Not available	

Table A.3. Acetochlor Metabolite Structures

Metabolite Type	Structure
EMA-type metabolites	
HEMA-type metabolites	
HMEA-type metabolites	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Eight field rotational crop trials were conducted using sunflowers at field sites throughout the U.S. during 1996. At each test site, field corn was planted and treated once with acetochlor (6.4 lb/gal EC) at a target rate of 3 lb ai/A using ground equipment (Table B.1.1). At each site, a rotational crop of sunflowers was planted 346-380 DAT (~12 months).

Detailed soil characteristics and meteorological data were not provided, but maintenance pesticides and detailed plot history were provided. A general summary of the overall weather conditions was provided noting that usual weather conditions occurred at two of the sites. However, the weather conditions had no adverse impact to the residue data. Rainfall was supplemented with irrigation as needed.

TABLE B.1.1. Study Use Pattern to Primary Corn Crop.

Location (County, State) Year, Trial ID	End-use Product	Application Information				Rotational Crop
		Method [1]; Timing	Vol. (GPA)	Application Rate (lb ai/A) [2]	PBI [3] (days)	
Brownton, MN 1996 36-MN-96-431	6.4 lb/gal EC	Broadcast Soil: preemergence	15	3	346	Sunflower
Grove City, MN 1996 36-MN-96-432	6.4 lb/gal EC	Broadcast Soil: preemergence	15	3	350	Sunflower
Doran, MN 1996 36-MN-96-433	6.4 lb/gal EC	Broadcast Soil: preemergence	15	3	357	Sunflower
Washburn, ND 1996 34-ND-96-434	6.4 lb/gal EC	Broadcast Soil: at-planting	11	3	379	Sunflower
Kulon, ND 1996 34-ND-96-435	6.4 lb/gal EC	Broadcast Soil: at-planting	14	3	371	Sunflower
Mansfield, SD 1996 34-SD-96-436	6.4 lb/gal EC	Broadcast Soil: at-planting	14	3	371	Sunflower
Madrid, NE 1996 48-NE-96-437	6.4 lb/gal EC	Broadcast Soil: preplant incorporated	20	3	373	Sunflower
Eaton, CO 1996 48-CO-96-438	6.4 lb/gal EC	Broadcast Soil: preemergence	20	3	380	Sunflower

1 All applications were made using ground equipment.
2 Actual application rates were not reported, but application rates were reported to be ± 3% of target.
3 Plant-back interval.

TABLE B.1.2. Trial Numbers and Geographical Locations.

NAFTA Growing Zones[1]	Sunflower		
	Submitted	Requested	
		Canada	US
1	--	NA	--
2	--	NA	--
3	--	NA	--
4	--	NA	--
5	3	NA	3
6	--	NA	--
7	4	NA	4
8	1	NA	1
9	--	NA	--
10	--	NA	--
11	--	NA	--
12	--	NA	--
Total	8	NA	8

[1] Regions 13-21 and 1A, 5A, 5B, and 7A were not included as the use is restricted to the US.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples of sunflower seeds (>3 lbs) were harvested at commercial maturity, 122-146 days after planting (481-519 DAT). After collection, samples were placed in frozen storage at the test facility within 18 hours of collection, and then shipped frozen to the analytical laboratory, Jealott's Hill Research Station, Berkshire, UK and stored frozen (~ -18 °C) prior to analysis. Samples were stored frozen from collection to analysis for up to 5-6 months prior to the analysis of EMA and HEMA.

B.3. Analytical Methodology

Samples of sunflower seeds were analyzed for residues of acetochlor *per* se using a GC/NPD Method RAM 244 (D. Davis, 44107102.der). The registrant has not demonstrated that this method can extract field weathered residues. Therefore data on residues of acetochlor *per se* from field samples are not considered supported by adequate validation data and are not appropriate for use in risk assessment or for tolerance setting purposes. Further, since the data generated from analytical method RAM 244/02 are not of utility for regulatory purposes, they are not included in this document.

In addition, samples of sunflower seed were analyzed for residues of acetochlor (converted to EMA) and its metabolites convertible to ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) using GC/MSD Method RAM 280 (D. Davis, 44107103.der).

For Method RAM 280, residues are extracted with acetonitrile:water (80:20, v/v), concentrated, and base hydrolyzed by refluxing with saturated potassium hydroxide and methanol to yield

EMA and HEMA. The resulting hydrolysate is diluted with water and saturated sodium chloride, and residues of EMA and HEMA are partitioned into toluene. Residues are acylated with heptafluorobutryic acid anhydride, and partitioned against a sodium bicarbonate solution to remove the derivatizing agent. Residues are then analyzed by GC/MSD operating in the selective ion monitoring (SIM) mode, and using the 162 and 314 ions for quantifying EMA and HEMA, respectively. Residues are quantified by comparison to external standards. The LOQ is 0.01 ppm for both EMA and HEMA, or 0.02 ppm when expressed as acetochlor equivalents. The LOD was not reported.

Method RAM 280 employs an extraction scheme substantially similar to that used in the current enforcement method; therefore, HED considers that this method is adequate to recover weathered residues from field samples. Additionally, the method has been adequately validated as a data collection method based on the results of concurrent fortification sample spiked with HEMA- or EMA-type compounds.

C. RESULTS AND DISCUSSION

Samples were stored frozen for a maximum of 5-6 months (Table C.1). Adequate storage stability data are available (Acetochlor TRED, 3/1/06) indicating that acetochlor and its metabolites are stable up to ≥2 years in cereal grain and soybean commodities. These data will support the frozen storage intervals in this trial.

The method used to determine residues of acetochlor (converted to EMA) and its metabolites convertible to EMA and HEMA in sunflower seeds was adequately validated prior to and in conjunction with the field sample analyses (Table C.2). Method validation and concurrent recovery samples fortified with EMA yielded recoveries within the 70% to 120% acceptable range with the exception of one method validation sample fortified at 0.10 ppm with a recovery of 69%. Method validation and concurrent recovery samples fortified with HEMA yielded recoveries within the 70% to 120% acceptable range with the exception of one concurrent fortification sample fortified at 0.10 ppm with a recovery of 65%. Adequate samples calculations were provided along with example chromatograms. Apparent residues of EMA and HEMA were <LOQ in all control samples.

Residues of EMA and HEMA were each <LOQ (<0.02 ppm acetochlor equivalents) in all seed samples, for combined residues of <0.04 ppm. As the GC/MSD method would result in the conversion of acetochlor to EMA, combined residues are the sum of EMA and HEMA residues, expressed in acetochlor equivalents.

No data were provided on residues of the hydroxymethyl ethyl aniline (HMEA) metabolites. Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

TABLE C.1. Summary of Storage Conditions

Matrix	Analyte	Storage Temp. (°C)	Actual Storage Duration (days) [1]	Limit of Demonstrated Storage Stability (months) [2]
Sunflower seeds	EMA/HEMA	-18	139-175	13

1 Samples extracts were analyzed within 8 days of extraction.
2 Acetochlor TRED, 3/1/06; storage stability data on soybean seeds.

TABLE C.2. Summary of Method Recoveries of EMA and HEMA from Sunflower Seeds.[1]

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev
Method Validation[2]					
Seeds	EMA	0.01	4	95, 94, 91, 97	95 ± 1.4
		0.10	4	69, 77, 83,81	77 ± 6.2
	HEMA	0.01	4	97, 95, 94, 99	96 ± 2.2
		0.10	4	84, 80, 87, 85	84 ± 2.9
Concurrent Recovery[3]					
Seeds	EMA	0.02	3	86, 84, 82	84 ± 2.0
		0.10	3	79, 74, 85	79 ± 5.5
	HEMA	0.02	3	72, 95, 80	82 ± 12
		0.10	3	65, 88, 80	78 ± 12

[1] Residues containing the EMA or HEMA moieties were determined using GC/MSD Method RAM 280
[2] Concentrations are for EMA/HEMA.
[3] Concentrations are expressed as parent equivalents.

TABLE C.3. Residues of EMA and HEMA in Rotational Sunflower seeds.

Location (County, State, Year)	EPA Region	Variety	Total Rate (lb ai/A)	PBI[1] (days)	Harvest DALA[2]	Residues (ppm)[3]		
						EMA	HEMA	Combined[4]
Brownton, MN 1996 36-MN-96-431	5	IS 7000	3	346	492	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Grove City, MN 1996 36-MN-96-432	5	IS 7000 (Payco)	3	350	481	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Doran, MN 1996 36-MN-96-433	5	IS 7000 (Payco)	3	357	499	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Washburn, ND 1996 34-ND-96-434	7	Pioneer 6340	3	379	505	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Kulon, ND 1996 34-ND-96-435	7	Mycogen 98338	3	371	500	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Mansfield, SD 1996 34-SD-96-436	7	DK3868	3	371	503	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Madrid, NE 1996 48-NE-96-437	7	Triumph 546	3	373	495	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Eaton, CO 1996 48-CO-96-438	8	Triumph	3	380	519	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

1 PBI = Plant Back Interval.
2 DALA= Days after last application.
3 The LOQ is 0.02 ppm for EMA and HEMA. The LOD was not reported.
4 As acetochlor is converted to EMA by the GC/MSD method, the combined total residues are the sum of EMA and HEMA residues, expressed in acetochlor equivalents.

TABLE C.4. Summary of Residue Data in Rotational Sunflowers.

Commodity	Total Rate (lb ai/A)	PBI (days)	Residue Levels (ppm) [1]						
			n	Min.	Max.	HAFT[2]	Median (STMdR[3])	Mean (STMR[3])	Std. Dev.
EMA									
Sunflower seed	3.0	346-380	16	<0.02	<0.02	<0.02	0.01	0.01	NA
HEMA									
Sunflower seed	3.0	346-380	16	<0.02	<0.02	<0.02	0.01	0.01	NA
Combined Residues [4]									
Sunflower seed	3.0	346-380	16	<0.04	<0.04	<0.04	0.02	0.02	NA

1 LOQ is 0.02 ppm acetochlor equivalents each for EMA and HEMA. The LOD was not reported.
2 HAFT = Highest Average Field Trial.
3 STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue. For calculation of the median, mean and standard deviation, ½ the LOQ (0.01 ppm) was used for residues reported at <LOQ.
4 As acetochlor is converted to EMA by the GC/MSD method, the combined total residues are the sum of EMA and HEMA residues, expressed in acetochlor equivalents.

D. CONCLUSION

The submitted field rotational crop data on sunflowers are adequately supported by field documentation and storage stability data. The residue data were generated using a validated analytical method.

Residues in sunflower seeds planted 11 – 13 months following application of acetochlor to a primary crop of corn at 3 lbs ai/A were each <LOQ (<0.02 ppm acetochlor equivalents). Combined residues were <0.04 ppm expressed as acetochlor equivalents.

No data were provided on residues of HMEA-type residues.

E. REFERENCES

DP Barcode:	D292336
Subject:	**ACETOCHLOR**. Revised HED Chapter of the Tolerance Reassessment Eligibility Decision (TRED) Document.
From:	A. Protzel
To:	F. Fort
Dated:	3/1/06
MRID(s):	None

F. DOCUMENT TRACKING

RDI: D. Davis (3/21/06), T. Goodlow (3/28/06)
Petition Number(s): 1F6263
DP Barcode(s): D230310 and D275019
PC Code: 121601