

US EPA ARCHIVE DOCUMENT



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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:**

45322110 Anderson, L., Walter, J. and Spillner, C. (1997) Residue Levels in Processed Commodities of Sunflowers Planted as a Rotational Crop Following Corn from a Trial Carried Out in the United States of America During 1996: Lab Project Number: ACET-95-PR-02: RJ2568B. Unpublished study prepared by Zeneca Agrochemicals. 89 p.

#### **EXECUTIVE SUMMARY:**

In a field trial conducted during 1996 in SD, acetochlor (6,4 lb/gal EC) was applied to a primary crop of field corn as a preemergence application at 15 lb ai/A. The corn was grown and harvested following common agricultural practices, and a rotational crop of sunflowers was planted 338 days after treatment (DAT). Single bulk control and treated samples of sunflower seeds were later harvested at commercial maturity, 139 days after planting (477 DAT), and were processed using simulated commercial procedures into meal and oil. Samples of seed were stored frozen for up to 5 months prior to analysis and samples of meal and oil were stored frozen for ~1 month prior to analysis; these storage intervals and conditions are supported by available storage stability data.

Samples of sunflower weed, meal and oil were analyzed for residues of acetochlor (converted to EMA) and its metabolites convertible to ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) using a GC/mass selective detector (MSD) method (RAM 280/02. In each sunflower commodity, 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.



Combined residues of EMA and HEMA were 0.20 ppm in seeds collected from the field (RAC), 0.16 ppm in seeds from the processor, 0.18 ppm in meal, and <0.04 ppm in oil. Based on the combined residues in the field-sampled seeds (RAC), combined acetochlor residues were reduced in both sunflower meal (0.9x) and oil (<0.2x).

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in this study, the sunflower seed processing 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:**

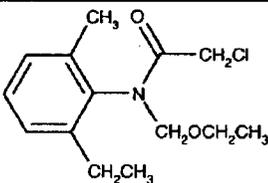
Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.



## 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 EMA or HEMA, to be analyzed as acetochlor, and 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 <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>
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



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)	Acetochlor HED Chapter of the 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 $\mu$ Hg ( $4.5 \times 10^{-5}$ 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	

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



## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

**TABLE B.1.1. Trial Site Conditions.**

Trial Identification (City, State, Year)	Soil characteristics			
	Type	%OM	pH	CEC (meq/g)
Lake Preston, SD	Silt Loam	NR	NR	NR

**TABLE B.1.2. Study Use Pattern to Primary Corn Crop.**

Location (County, State) Year, Trial ID	End-use Product	Application information				Rotational Crop
		Method <sup>1</sup> ; Timing	Vol. (GPA)	Application Rate (lb ai/A)	PBI <sup>2</sup> (days)	
Lake Preston, SD 1996 34-SD-96-446	6.4 lb/gal EC	Broadcast Soil: preemergence	14	15	338	Sunflowers

<sup>1</sup> The application was made using ground equipment.  
<sup>2</sup> Plantback Interval.

### B.2. Sample Handling and Preparation

Single bulk samples of control and treated sunflower seeds (50 lbs) were harvested at commercial maturity, 139 days after planting (477 DAT). Samples were frozen within 30 minutes of sampling and shipped by ACDS freezer truck to the processing laboratory, Texas A&M University Food Protein Research and Development Center, TX. Sunflower seed were processed into meal and oil using simulated commercial procedures. Single treated and control samples were collected of seed from the field, seed at the processing facility, meal and oil. Samples were frozen and then shipped frozen to the analytical laboratory, Jealott's Hill Research Station (Berkshire, UK), where samples were stored at ~ -18 °C prior to analysis. Samples of seed were stored frozen from collection to analysis for up to 5 months prior to the analysis, and meal and oil samples were stored for ≤1 month.

### B.3. Analytical Methodology

Samples of sunflower seed, meal and oil 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, therefore, not appropriate for use in risk assessment or for tolerance setting purposes. Further, since these data generated from analytical method RAM 244 are not of utility for regulatory purposes, they are not included in this document.

Additionally, samples of sunflower seed, meal and oil 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 heptafluorobutyric 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

Prior to analysis, samples of seed were stored frozen for up to 5 months and meal and oil samples were stored frozen for ~1 month (Table C.1). Adequate storage stability data are available (Acetochlor HED Chapter of the TRED, 3/1/06) indicating that acetochlor and its metabolites are stable up to 24 months in soybeans. These data will support the frozen storage intervals for seeds in this trial. As meal and oil samples were analyzed within ~1 month, no supporting storage stability data are required for these commodities.

The method used to determine residues of acetochlor (converted to EMA) and its ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) type metabolites in sunflower seeds, meal and oil was adequately validated prior to and in conjunction with the analysis of treated samples (Table C.2). In the method validation trials, samples of sunflower seed were fortified with EMA and HEMA at 0.01 – 0.1 ppm and samples of meal and oil were fortified with EMA and HEMA at 0.02 – 0.1 ppm. EMA recoveries averaged 86% ( $\pm 10\%$ ), 80% ( $\pm 9\%$ ) and 104% ( $\pm 8\%$ ) for sunflower seed, meal and oil, respectively. HEMA recoveries average 90% ( $\pm 7\%$ ), 86% ( $\pm 9\%$ ) and 119% ( $\pm 3\%$ ) in sunflower seed, meal and oil respectively. Concurrent recovery samples were fortified with EMA and HEMA at 0.02 and 0.5 ppm. EMA recoveries averaged 98% ( $\pm 3\%$ ), 76% ( $\pm 2\%$ ) and 102% ( $\pm 5\%$ ) for sunflower seed, meal and oil, respectively. HEMA recoveries average 101% ( $\pm 3\%$ ), 78% ( $\pm 2\%$ ) and 110% ( $\pm 1\%$ ) in sunflower seed, meal and oil respectively. Adequate samples calculations were provided along with example chromatograms. Apparent residues of both analytes were <LOQ in all control samples.



Following an application of acetochlor (EC) to field corn at 15 lb ai/A (5x use rate), residues of EMA were 0.03 ppm in seeds (field and processor), 0.04 ppm in meal, and <0.02 ppm in oil. Residues of HEMA were 0.17 ppm in seeds from the field (RAC), 0.13 ppm in seeds from the processor, 0.14 ppm in meal, and <0.02 ppm in oil. Combined residues (EMA+HEMA) were 0.20 ppm in seeds from the field (RAC), 0.16 ppm in seeds from the processor, 0.18 ppm in meal, and <0.04 ppm in oil. Based on the combined residues in the field-sampled seeds (RAC), residues were reduced in both sunflower meal (0.9x) and oil (<0.2x).

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.

Matrix	Storage Temp. (°C)	Actual Storage Duration (days)	Limit of Demonstrated Storage Stability (months) <sup>1</sup>
Sunflower Seeds	-18	104-155	24
Sunflower Meal		20-34	
Sunflower Oil			

<sup>1</sup> Samples extracts were analyzed within 8 days of extraction.

<sup>2</sup> Acetochlor TRED, 3/1/06; storage stability data on soybean seeds.

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean √ std dev
<b>Concurrent Recovery</b>					
Seed	EMA	0.02-0.5	2	100, 96	98 ± 3
	HEMA		2	103, 99	101 ± 3
Meal	EMA	0.02-0.5	2	77, 74	76 ± 2
	HEMA		2	79, 76	78 ± 2
Oil	EMA	0.02-0.5	2	98, 105	102 ± 5
	HEMA		2	111, 109	110 ± 1
<b>Method Validation</b>					
Seed	EMA	0.01-0.1	8	95, 94, 91, 97, 69, 77, 83, 81	86 ± 10
	HEMA		8	97, 95, 94, 99, 84, 80, 87, 85	90 ± 7
Meal	EMA	0.02-0.1	8	89, 84, 82, 77, 82, 81, 83, 60	80 ± 9
	HEMA		8	94, 90, 86, 82, 92, 87, 91, 66	86 ± 9
Oil	EMA	0.02-0.1	6	109, 105, 110, 111, 91, 100	104 ± 8
	HEMA		6	12, 113, 119, 119, 120, 121	119 ± 3

Residues containing the EMA or HEMA moieties were determined using GC/MSD Method RAM 280/02.



**TABLE C.3. Residue Data from Sunflower Processing Study using Seed Grown from Sunflowers Rotated with Field Corn Treated with Acetochlor (6.4 lb/gal EC).**

RAC	Processed Commodity	Total Rate (lb ai/A)	DALA <sup>1</sup> (days)	Residues <sup>2</sup> (ppm)			Processing Factor
				EMA	HEMA	Combined Residues <sup>3</sup>	
Sunflower Seeds	RAC	15.0	477	0.03	0.17	0.20	NA
	RAC (Pre-Processing)	15.0	477	0.03	0.13	0.16	NA
	Meal	15.0	477	0.04	0.14	0.18	0.9x
	Oil	15.0	477	<0.02	<0.02	<0.04	0.2x

<sup>1</sup> DALA= Days After Last Application. The sunflower rotational crop was planted 338 DAT and mature seeds were harvested 139 days after planting.

<sup>2</sup> The LOQ is EMA and HEMA. The LOD was not reported.

<sup>3</sup> 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.

NA = not applicable.

#### D. CONCLUSION

The processing study on rotational sunflowers is adequately supported by field documentation and storage stability data and residue data were generated using a validated analytical method.

The data indicate that the processing factors for the combined acetochlor residues (EMA+HEMA) are 0.9x in sunflower meal and <0.2x in sunflower oil. No data were provided on residues of the hydroxymethyl ethyl aniline (HMEA) metabolites

#### 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 (3/27/06), M. Doherty (4/18/06).

Petition Number(s): 1F6263

DP Barcode(s): D230310 and D275019

PC Code: 121601