

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:**

45322112 Manning, M.J. (1997) Acetochlor Residues in Oat Rotational Crop Processed Commodities Following Application of Acetochlor Herbicide to Corn: Lab Project Number: MSL-14118: 94-27-R-5. Unpublished study prepared by Monsanto Co. and American Agricultural Services, Inc. 228 p.

#### **EXECUTIVE SUMMARY:**

In two field trials conducted during 1995 in IL, acetochlor (6.4 lb/gal EC) was applied to the primary crop of sweet or field corn as a single preplant or preemergence broadcast application at 15 lb ai/A. The corn was grown and harvested following common agricultural practices. At each site, a rotational crop of oats was planted 285 or 299 days after treatment (DAT). Single bulk control and treated samples of oat grain were harvested at commercial maturity, 126-129 days after planting (414-425 DAT). The grain (RAC) was processed using simulated commercial procedures into hull, flour, and groats. Samples were stored frozen for up to 27 days prior to analysis, an interval supported by available storage stability data.

A High Performance Liquid Chromatography/Oxidative Coulometric Electrochemical Detection (HPLC/OCED) method was used to determine residues containing the EMA and HEMA moieties in oat grain, hulls, flour, and groats. The method, which is equivalent to the current tolerance enforcement method, was adequately validated in conjunction with the analysis of processing study samples. For oat commodities, the LOQs are 0.017 and 0.018 ppm for EMA and HEMA, respectively, and the LOD is 0.005 ppm for both analytes.

Combined residues of EMA and HEMA in mature oat grain from the 15 lb ai/A application (5X rate based on currently registered uses) were 0.048 ppm from the IL1 test site and 0.018 ppm (<LOQ) from the IL2 test site. For the IL1 site, combined residues following processing were



0.020 ppm (<LOQ) in hulls and non-detectable (<0.01 ppm) in flour and groats. For the IL2 site, combined residues following processing were 0.039 ppm in hulls, 0.012 ppm (<LOQ) in flour and non-detectable (<0.01 ppm) in groats. The average processing factors for combined residues from the two tests were 1.3x for hulls, 0.5x for flour and <0.4x for groats.

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 oat processing study 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:**

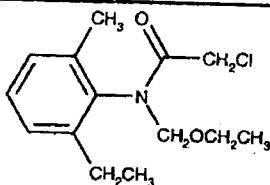
Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.



## 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.

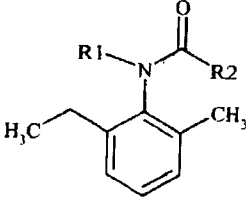
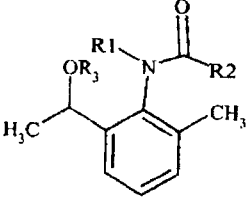
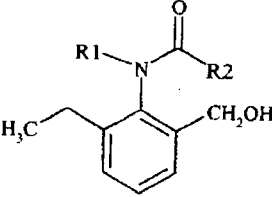
The ARP has submitted a petition (PP#1F6263) proposing tolerances for inadvertent residues of acetochlor in rotated dried peas and beans (subgroup 6C), sugar beets, sunflowers, potatoes, cereal grains (group 15, except corn and rice), and the forage, fodder, and straw of cereal grains (group 16, except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

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	



Parameter	Value	Reference
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 <sub>a</sub>	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

Trial Identification (City, State, Year)	Soil characteristics			
	Type	%OM	pH	CEC (meq/g)
Monmouth, IL 1995 95-27-R-5-IL1	Silty Clay Loam	3.6	4.9	16.1
Jerseyville, IL 1995 95-27-R-5-IL2	Silt Loam	3.2	6.6	19.3

Location (County, State) Year, Trial ID	End-use Product	Application				Rotational Crop
		Method <sup>1</sup> ; Timing	Vol. (GPA)	Application Rate (lb ai/A)	PBI <sup>2</sup> (days)	
Monmouth, IL 1995 95-27-R-5-IL1	6.4 lb/gal EC	Broadcast Soil: Preplant- incorporated	18.5	15.32	299	Oats
Jerseyville, IL 1995 95-27-R-5-IL2	6.4 lb/gal EC	Broadcast Soil: Preemergence	19.2	14.39	285	Oats

<sup>1</sup> All applications were made using ground equipment.  
<sup>2</sup> Planthack interval.

### B.2. Sample Handling and Preparation

Single bulk samples of control and treated grain (~60 lbs) were harvested at commercial maturity, 126-129 days after planting (414-425 DAT). Subsamples of grain from the field were collected, and the bulk grain samples were shipped to the processing facility, Texas A&M, Food Protein Research and Development Center, Bryan, TX. The oat grain was processed using simulated commercial procedures into hulls, groats, and flour. Samples of grain and each processed fractions were frozen and shipped by overnight courier to the analytical laboratory, Monsanto Company (St. Louis, MO) and stored frozen at ~ -18°C prior to analysis. Samples were stored frozen from collection to analysis for up to 27 days (oat grain from field), 19 days (oat grain from processor), 9 days (hulls), 7 days (flour), and 16 days (groats).

### B.3. Analytical Methodology

Samples of oat grain, hulls, flour and groats were analyzed for residues of metabolites containing the EMA and HEMA moieties using the current tolerance enforcement method, which is an HPLC/OCED Method (RES-074-93).

For this method, residues are extracted with acetonitrile:water (4:1 v:v), filtered, 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 methylene chloride. HEMA is methylated using acidic methanol and residues of EMA and methylated HEMA (MEMA) are separated and determined using HPLC/OCED. Residues of EMA and HEMA are expressed in



acetochlor equivalents and the method LOQ for EMA and HEMA are 0.017 ppm and 0.018 ppm, respectively, for all oat commodities. The LOD for both EMA and HEMA is 0.005 ppm.

The HPLC-OCED method was validated concurrently with the analysis of processing study samples using control samples of grain, hull, flour and groats fortified with EMA and HEMA producing metabolites at 0.01-1.0 ppm.

### C. RESULTS AND DISCUSSION

Samples of each commodity were stored frozen for a maximum of 27 days prior to analysis (Table C.1). Adequate storage stability data are available (Acetochlor TRED, date) indicating that acetochlor metabolites are stable for up to 24 months in wheat grain. These data will support the frozen storage intervals in this trial.

The HPLC/OCED method used to determine EMA and HEMA residues in oat grain, hulls, flour and groats is adequate for data collection. Concurrent recoveries of EMA averaged  $114 \pm 4\%$  in oat grain,  $121 \pm 8\%$  in hulls,  $117 \pm 3\%$  in flour and  $102 \pm 1\%$  in groats (Table C.2); concurrent recoveries of HEMA averaged  $95 \pm 9\%$  in oat grain,  $102 \pm 7\%$  in hulls,  $98 \pm 4\%$  in flour and  $88 \pm 5\%$  in groats. Apparent residues of EMA and HEMA were <LOD in all the control samples. Adequate sample calculations and chromatograms were provided.

Following application of acetochlor to primary corn crops at 15 lb ai/A (5x), combined residues of EMA and HEMA in grain from rotational oats planted 9-10 month after treatment were 0.048 ppm from the IL1 test site and 0.018 ppm (<LOQ) from the IL2 test site (Table C.3). For the IL1 site, combined residues following processing were 0.020 ppm (<LOQ) in hulls and non-detectable (<0.01 ppm) in flour and groats. For the IL2 site, combined residues following processing were 0.039 ppm in hulls, 0.012 ppm (<LOQ) in flour and non-detectable (<0.01 ppm) in groats. The processing factors for the IL1 site were 0.4x for hulls, and <0.2x for flour and groats. The processing factors for the IL2 site were 2.2x for hulls, 0.7x for flour, and <0.6x for groats. The average processing factors for combined residues from the two tests were 1.3x for hulls, 0.5x for flour and <0.4x for groats.

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 for Oat Commodities.**

Matrix	Storage Temp. (°C)	Actual Storage Duration (days)	Limit of Demonstrated Storage Stability (days) <sup>1</sup>
Grain (field)	-18	27	382
Grain (processor)	-18	19	
Hulls	-18	9	
Flour	-18	7	
Groats	-18	16	

Acetochlor HED Chapter of the TRED, 3/1/06; storage stability data on wheat grain.

**TABLE C.2. Summary of Concurrent Method Recoveries of HEMA and EMA from Oat Processed Samples.**

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev
Oat grain	EMA	0.01-0.10	8	104-117	113 ± 4
	HEMA		8	85-108	95 ± 9
Hulls	EMA	0.01-0.10	4	110-127 (3) <sup>1</sup>	121 ± 8
	HEMA		4	93-108	102 ± 7
Flour	EMA	0.01-0.04	4	113-120	117 ± 4
	HEMA		4	95-104	98 ± 4
Groats	EMA	0.01-0.08	4	101-104	102 ± 1
	HEMA		4	83-95	88 ± 5

Values in parentheses indicate number of recoveries outside the acceptable 70-120% range

**TABLE C.3. Residue Data from Two Oat Field Rotational Crop Processing Studies 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	
Oats	Oat Grain (field)	15.3	425	0.034	(0.014)	0.048	NA
		14.4	414	(0.012)	(0.006)	(0.018)	NA
	Oat Grain (Processor)	15.3	425	0.033	0.022	0.055	NA
		14.4	414	(0.016)	(0.007)	(0.023)	NA
	Hulls	15.3	425	(0.013)	(0.007)	(0.020)	0.4x
		14.4	414	0.028	(0.011)	0.039	2.2x
	Flour	15.3	425	ND	ND	ND	<0.2x
		14.4	414	(0.006)	(0.006)	(0.012)	0.7x
	Groats	15.3	425	ND	ND	ND	<0.2x
		14.4	414	ND	ND	ND	<0.6x

DALA: Days After Last Application





<sup>2</sup> The LOQ is 0.017 ppm for EMA and 0.018 ppm for HEMA, for a combined LOQ of 0.035 ppm. The LOD is 0.005 for both analytes, for a combined LOD of 0.010 ppm. Values between the LOD and LOQ are in parenthesis  
ND = not detected

#### D. CONCLUSION

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

On average, combined residues concentrated slightly in oat hulls (1.3x), but were reduced by 0.5x in oat flour and 0.4x in groats. 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