

US EPA ARCHIVE DOCUMENT



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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:**

45322111 Anderson, L., Walter, J. and Spillner, C. (1997) Residue Levels in Processed Commodities of Potatoes Planted as a Rotational Crop Following Corn from a Trial Carried Out in the United States of America During 1996: Lab Project Number: ACET-96-PR-01: RJ2567B. Unpublished study prepared by Zeneca Agrochemicals. 60 p.

#### **EXECUTIVE SUMMARY:**

In a field trial conducted during 1996 in WA, acetochlor (6.4 lb/gal EC) was applied to the primary crop of field corn at a rate of 15 lb ai/A. The corn was grown and harvested following common agricultural practices, and a rotational crop of potatoes was planted 377 days after treatment (DAT). Single bulk control and treated samples of potatoes were harvested at commercial maturity, 132 days after planting (509 DAT), and processed into peel, chip and flakes using simulated commercial procedures. Tuber samples were stored frozen for up to 5 months prior to analysis, an interval supported by available storage stability data.

A GC/mass selective detector (MSD) method (RAM 280) was used to determine residues acetochlor (converted to EMA) and its metabolites convertible to ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) in potato samples. 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.



Following a 15 lb ai/A (equivalent to a 5x treatment rate based on currently registered uses of acetochlor) application of acetochlor (EC) to a primary corn crop, residues in mature potato tubers planted 377 DAT were <LOQ (<0.02 ppm acetochlor equivalents) each for EMA and HEMA. Combined residues were <0.04 ppm (EMA plus HEMA, expressed in acetochlor equivalents). As residues were non-quantifiable in whole tubers (RAC) from a 5x-treatment (based on currently registered uses), no analysis of processed fractions was conducted. The data indicate that acetochlor residues are unlikely to be detectable in potato processed fractions.

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 potato 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:**

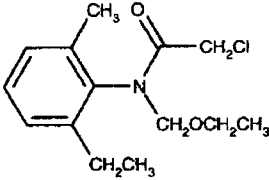
Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.



## 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).

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 <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)
Ephrata, WA 1996	Sandy Loam	NR	NR	NR

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)	
Ephrata, WA 1996 15-WA-96-421	6.4 lb/gal EC	Broadcast Soil: Seed	18	15	377	Potatoes

<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 potatoes (300 lbs) were harvested at commercial maturity, 132 days after planting (509 DAT), and a subsample of potatoes was collected. The remaining bulk samples were transported directly to Englar Food Laboratories (Moses Lake, WA). A second subsample of whole tubers was collected at the processing facility, and the remaining bulk samples were processed into chips, flakes, and peels using simulated commercial procedures. After processing, samples were frozen and shipped on dry ice by overnight courier to the processing laboratory, Zeneca Ag Products at the Western Research Center, CA, where sample were stored frozen (~ -18°C). Samples were later shipped frozen to the analytical laboratory, Jealott's Hill Research Station (Berkshire, UK) and stored frozen (-18°C) until analysis. Samples were stored frozen from collection to analysis for up to 5 months.

### B.3. Analytical Methodology

Samples of potato tubers 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 the data generated from analytical method RAM 244 are not of utility for regulatory purposes, they are not included in this document.



Additionally, samples of potato tubers 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 280/01 (D. Davis, 44107103.der).

For Method RAM280/01, 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, potato samples were stored frozen for a maximum of 5 months (Table C.1). Adequate storage stability data are available (D. Davis, 45483301.der) indicating that acetochlor and metabolites of EMA and HEMA are stable up to 9 months in potato tubers. These data will support the frozen storage intervals in this trial.

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 potato tubers were adequately validated prior to and in conjunction with the analysis of treated samples (Table C.2).

In the method validation trials, recoveries from tubers fortified at 0.01 and 0.10 ppm averaged  $97 \pm 6\%$  for EMA, and  $94 \pm 7\%$  for HEMA. Concurrent recoveries from tubers fortified at 0.02-0.05 ppm averaged  $89 \pm 6\%$  for EMA, and  $86 \pm 1\%$  for HEMA. The LOQ is 0.02 ppm acetochlor equivalents each for EMA and HEMA; the LOD was not reported. Adequate samples calculations were provided along with example chromatograms. Apparent residues of both analytes were <LOQ in all control samples.

Following application of acetochlor to primary corn crops at 15 lb ai/A (5x), residues of acetochlor were <0.1 ppm and residues of EMA and HEMA were each <0.02 ppm in whole potato tubers collected from either the field or processing facility. Combined residues were <0.04 ppm (EMA plus HEMA, expressed in acetochlor equivalents). As residues were non-quantifiable in tubers (RAC) from a 5x-treatment, no analysis of processed fractions was conducted.



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	Storage Temp. (°C)	Actual Storage Duration (months) <sup>1</sup>	Limit of Demonstrated Storage Stability (months) <sup>2</sup>
Potato tubers	-18	5	9

<sup>1</sup> Samples extracts were analyzed within 2 days of extraction.  
<sup>2</sup> D. Davis, 45483301.der.

**TABLE C.2. Summary of Method Recoveries of Acetochlor, HEMA and EMA from Potato Samples.**

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev
<b>Concurrent Recovery</b>					
Potato	EMA	0.02-0.5	3	85, 87, 96	89 ± 6
	HEMA	0.02-0.5	3	97, 95, 97	86 ± 1
<b>Method Validation</b>					
Potato	EMA	0.01-0.10	8	96, 92, 91, 90, 103, 101, 105, 101	97 ± 6
	HEMA		8	103, 101, 95, 104, 89, 90, 87	94 ± 7

<sup>1</sup> Residues containing the EMA or HEMA moieties were determined using GC/MSD Method RAM 280/02.

**TABLE C.3. Residue Data from Potato Processing Study using Tubers Grown from Potatoes 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 <sup>3</sup>	
Potatoes	Tubers Field-sampled (RAC)	15.0	509	<0.02	<0.02	<0.04	NA
	Tubers Processor-sampled	15.0	509	<0.02	<0.02	<0.04	NA

DALA= Days After Last Application  
<sup>2</sup> The LOQ is 0.02 ppm for EMA and HEMA (acetochlor equivalents). 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; as residues were <LOQ in the RAC from a 5x application, the processed fractions were not analyzed.





#### **D. CONCLUSION**

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

EMA and HEMA residues were all <LOQ in/on tubers harvested from potatoes planted 377 days after a 15 lb ai/A treatment (equivalent to a rate of 5x based on the currently registered uses) to the primary corn crop. As residues were non-quantifiable in whole tubers (RAC) from a 5x-treatment, no analysis of processed fractions was conducted. The data indicate that acetochlor residues are unlikely to be detectable in potato processed fractions. 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