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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:

45322104 Veal, P. and Spillner, C. (1997) Residue Levels on Dried Shelled Peas Planted as a Rotational Crop Following Corn From Trials Carried Out in the United States of America During 1995-1996: Lab Project Number: ACET-95-CR-02: RJ2262B. Unpublished study prepared by Zeneca Agrochemicals Ltd. 55 p.

EXECUTIVE SUMMARY:

Five field rotational trials were conducted on dry peas at field sites throughout the U.S. during 1995. At each site, acetochlor (6.4 lb/gal EC) was applied to a primary crop of field or sweet corn as a preplant incorporated or preemergence broadcast application at 3.0 lb ai/A. The corn was grown and harvested following common agricultural practices, and a rotational crop of dry peas was planted 296-336 days after treatment (DAT). Single control and duplicate treated samples of dried peas were harvested from each test at commercial maturity, 107-125 days after planting (412-444 DAT). Samples were stored frozen for up to 4 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.

A GC/mass selective detector (MSD) method (RAM 280) was used to determine residues of acetochlor and it metabolites convertible to ethyl methyl aniline (EMA) and hydroxyethyl methyl aniline (HEMA) in dried peas. The extraction scheme employed for analytical method RAM 280 is substantially similar to the current enforcement method; therefore, HED concludes that the method is adequate to recover weathered residues from field samples. Additionally, the method has been adequately validated as a data collection method in conjunction with the analysis of field trial 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.

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

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 dry pea 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

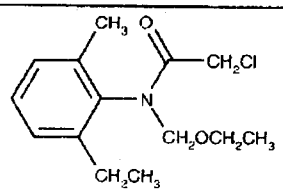
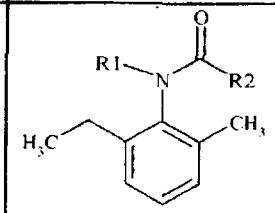
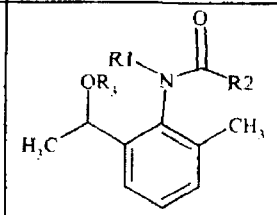
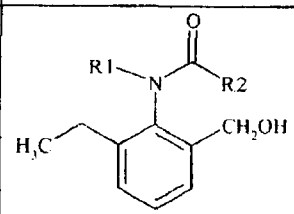
Chemical structure	
Common name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide
CAS name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS #	34256-82-1
PC Code	121601
End-use Product	6.4 lb/gal EC

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)	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 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

Five field rotational crop trials were conducted using dried peas at field sites throughout the US during 1995. 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 dried peas was planted 296-336 DAT (10-11 months).

Detailed soil characteristics and meteorological data were not provided, but maintenance pesticides and detailed plot history were provided. In addition, the study authors noted that weather patterns at all trial sites were typical of the growing regions. 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 (days)[3]	
Jerome, ID 1995 16-ID-95-715	6.4 lb/gal EC	Broadcast Soil: preplant incorporated	20.0	3	334	Peas
Jerome, ID 1995 16-ID-95-716	6.4 lb/gal EC	Broadcast Soil: preplant incorporated	20.0	3	327	Peas
Ephrata, WA 1995 94-WA-95-718	6.4 lb/gal EC	Broadcast Soil: preemergence	23.1	3	301	Peas
Mt. Vernon, WA 1995 15-WA-95-719	6.4 lb/gal EC	Broadcast Soil: preplant incorporated	16.9	3	336	Peas
Hermiston, OR 1995 15-OR-95-720	6.4 lb/gal EC	Broadcast Soil: preemergence	10.8	3	296	Peas

1 All applications were made using ground equipment.
2 Actual application rates were not reported, but application rates were reported to be ±10% of target.
3 Plant-back interval.

TABLE B.1.2. Trial Numbers and Geographical Locations.			
NAFTA Growing Zones[1]	Dried Peas		
	Submitted	Requested	
		Canada	US
1	--	NA	--
2	--	NA	--
3	--	NA	--
4	--	NA	--
5	--	NA	--
6	--	NA	--
7	--	NA	--
8	--	NA	--
9	--	NA	--
10	--	NA	--
11	4	NA	5
12	1	NA	
Total	5	NA	5[2]

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

[2] Number of dried pea field trials required to support a crop group tolerance. Agency guidance does not recommend specific regions for dry pea field trials; however, 97% of dry peas are grown in Regions 11 and 12.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples of dried peas (≥ 2 lbs) were harvested at commercial maturity, 107-125 days after planting (412-444 DAT). After collection, samples were placed in frozen storage at the test facility within 1 hour of collection, and then shipped frozen to the analytical laboratory, Jealott's Hill Research Station, Berkshire, UK, where samples were stored frozen (~ -18E C) until analysis. Samples were stored frozen from collection to analysis for up to 120 days (4 months) prior to the analysis of EMA and HEMA.

B.3. Analytical Methodology

Samples of dried peas were analyzed for residues of acetochlor, *per se*, using GC/NPD Method RAM 244/02 (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.

Additionally, samples of dried peas 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 4 months (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 ≥2 years in cereal grain and soybean commodities. These data will support the frozen storage intervals in this trial.

The method used to determine acetochlor (converted to EMA) and its EMA and HEMA-type metabolites in dried peas was adequately validated in conjunction with the field sample analyses (Table C.2). Concurrent recovery samples of dried peas were fortified with EMA and HEMA at 0.02-0.10 ppm acetochlor equivalents. In all four samples, recoveries of EMA and HEMA were within the acceptable range of 70% to 120%. Adequate samples calculations were provided along with example chromatograms. Apparent residues of all three analytes were <LOQ in all control samples.

Residues of EMA and HEMA were each <LOQ (<0.02 ppm) in all seed samples, for combined residues of <0.04 ppm (Tables C.3 and C.4). 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 are provided for the hydroxymethyl ethyl aniline (HMEA)-type 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]
Dried peas	EMA/HEMA	-18	95-120	13

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

TABLE C.2. Summary of Concurrent Method Recoveries of HEMA and EMA from Dried Peas.

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev
Peas	EMA	0.02	2	71, 79	n/a
		0.10	2	103, 127	n/a
	HEMA	0.02	2	80, 79	n/a
		0.10	2	99, 109	n/a

TABLE C.3. Residues of EMA and HEMA in Rotational Dry Peas.

Location (County, State, Year)	EPA Region	Variety	Total Rate (lb ai/A)	PBI [1] (days)	Harvest DALA [2]	Residues (ppm) [3]		
						EMA	HEMA	Combined Residues [4]
Jerome, ID 1995 16-ID-95-715	11	Asgrow Cabree	3	334	444	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Jerome, ID 1995 16-ID-95-716	11	Asgrow Cabree	3	327	433	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Ephrata, WA 1995 94-WA-95-718	11	Columbian	3	301	426	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Mt. Vernon, WA 1995 15-WA-95-719	12	SS Alaska	3	336	443	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Hermiston, OR 1995 15-OR-95-720	11	Fraser	3	296	412	<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 Dry Peas.

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									
Dried Pea	3.0	296-336	10	<0.02	<0.02	<0.02	0.01	0.01	NA
HEMA									
Dried Pea	3.0	296-336	10	<0.02	<0.02	<0.02	0.01	0.01	NA
Combined Residues [4]									
Dried Pea	3.0	296-336	10	<0.04	<0.04	<0.04	0.02	0.02	NA

[1] LOQ is 0.02 ppm each for EMA and HEMA expressed as acetochlor equivalents. 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 dried peas are adequately supported by field documentation and storage stability data. Residue values were generated using a validated analytical method.

Residues of EMA and HEMA were each <0.02 ppm acetochlor equivalents in all samples of dried peas planted 10 – 11 months after acetochlor was applied to a primary crop of corn at 3 lbs ai/A. Combined residues were <0.04 ppm (EMA plus HEMA, expressed in acetochlor equivalents) in dried peas.

No data are provided for residues of HMEA-type 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 (3/21/06), T. Goodlow (3/28/06).
Petition Number(s): 1F6263
DP Barcode(s): D230310 and D275019
PC Code: 121601