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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). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

45483301 White, B. (2001) Acetochlor and the EMA and HEMA Metabolite Class Storage Stability in Potato Tubers and Sugar Beet Tops Stored Deep Frozen for up to 9 Months: Lab Project Number: 99JH224: 852-560: RJ3114B. Unpublished study prepared by Syngenta Jealotts Hill International Research Centre. 43 p. (OPPTS 860.1380)

EXECUTIVE SUMMARY:

In a storage stability study, control samples of homogenized potato tubers and sugar beet tops were fortified separately with acetochlor, and ethyl methyl aniline (EMA)- and hydroxyethyl methyl aniline (HEMA)-type metabolites, each at 0.20 ppm. Samples of each commodity were stored frozen (<-18°C) for up to 9 months, with analyses at 0, 3, 7 or 8, and 9 months. At each interval, duplicate stored samples of potato tubers and sugar beet tops were analyzed along with duplicate freshly fortified samples and a control sample.

A GC/nitrogen-phosphorus detection (GC/NPD) method (RAM 244/02) was used to determine residues of acetochlor, *per se*. HED notes that while RAM 244/02 is adequate for data collection to support this storage stability study, the registrant has not demonstrated that the method can extract weathered residues; therefore, this methodology may have limited utility with respect to analysis of field trial data. Additionally, a GC/mass selective detector (MSD) method (RAM 280/02) was used to determine residues of EMA and HEMA type metabolites in tubers and tops. This method has been adequately validated as data collection methods in conjunction with the storage stability study. For Method RAM 244/02 the LOQ for acetochlor is 0.01 ppm; the LOD was not reported. For Method RAM 280/02 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 storage stability data are adequate and indicate that acetochlor and its EMA and HEMA type metabolites are stable in frozen potato tubers and sugar beet tops for at least 9 months.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the storage stability 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

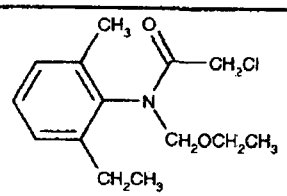
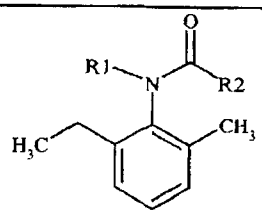
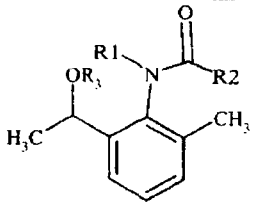
Chemical structure	
Common name	Acetochlor
Molecular Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
IUPAC name	2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide
CAS name	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
CAS #	34256-82-1
PC Code	121601
End-use Product	6.4 lb/gal EC

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	

B. EXPERIMENTAL DESIGN

B.1. Sample Preparation

Homogenized control samples of potato tubers and sugar beet tops were fortified separately with acetochlor. and EMA- and HEMA-producing metabolites, each at 0.20 ppm. A single untreated and duplicate fortified subsamples of each matrix were then extracted and analyzed to establish

day zero recoveries; the remaining samples were stored frozen (< - 18 °C) for up to 9 months. At each sampling interval, a single control samples and duplicate freshly fortified samples were analyzed along with duplicate frozen stored samples. Stored samples were analyzed at 0, 3, 7 (acetochlor only), 8 (EMA and HEMA only), and 9 months.

B.2. Analytical Methodology

Samples of potato tubers and sugar beet tops were analyzed for residues of acetochlor, *per se*, using GC/NPD Method RAM 244/02 (D. Davis, D44107102), and for residues of EMA and HEMA type metabolites using GC/MSD Method RAM 280/01 (D. Davis, D44107103).

For Method RAM 244/02, residues of acetochlor are extracted with methanol, filtered, and concentrated. Residues are then diluted with a sodium chloride solution and partitioned into toluene. Residues are cleaned up using NH_2 and silica gel columns eluted with ethyl acetate:hexane (40:60, v/v). Residues are then analyzed by GC/NPD and quantified using external standards. Mass selective detection (MSD) was used for confirmation in selected samples. The LOQ for acetochlor residues is 0.01 ppm; the LOD was not reported. HED notes that while RAM 244/02 is adequate for data collection to support this storage stability study, the registrant has not demonstrated that the method can extract weathered residues; therefore, this methodology may have limited utility with respect to analysis of field trial data.

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 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. This method has been adequately validated as data collection method.

C. RESULTS AND DISCUSSION

Duplicate samples of potato tubers and sugar beet tops were fortified separately with acetochlor and the EMA and HEMA metabolites of acetochlor at 0.20 ppm, and analyzed after frozen (<-18°C) storage intervals of 0, 3, 7 or 8, and 9 months. At each sampling interval duplicate frozen stored samples were analyzed along with duplicate freshly fortified samples and a control sample. However, individual values for the freshly fortified samples were not reported. The study authors only reported the overall average fresh recovery of acetochlor (89%), EMA (82%) and HEMA (76%).

Compared to residues found at Day 0, recoveries from frozen potatoes and sugar beet tops during frozen storage were 86-105% for acetochlor, 95-110% for EMA, and 90-100% for HEMA (Table

C.1). The data indicate that residues of acetochlor, and its EMA and HEMA type metabolites are stable at -18°C in potato tubers and sugar beet tops for up to 9 months.

TABLE C.1 Stability of Acetochlor, and EMA and HEMA Type Metabolites in Potato Tubers and Sugar Beet Tops Following Frozen (<- 18°C) Storage.

Matrix	Spike level (ppm)	Storage interval (days)	Concurrent Recovery [1] (%)	Residues in Stored Samples (ppm) [2]	Mean Recovery (%) [3]
Acetochlor					
Potato tubers	0.20	0	89	0.20, 0.21 (0.21) [3]	100
		98		0.20, 0.20 (0.20)	95
		216		0.20, 0.20 (0.20)	95
		295		0.21, 0.20 (0.21)	100
Sugar beet tops	0.20	0		0.22, 0.21 (0.22)	100
		98		0.19, 0.21 (0.20)	91
		216		0.20, 0.17 (0.19)	86
		294		0.22, 0.23 (0.23)	105
EMA					
Potato tubers	0.20	0	82	0.20, 0.20 (0.20)	100
		104		0.24, 0.19 (0.21)	105
		251		0.19, 0.20 (0.20)	100
		286		0.22, 0.21 (0.22)	110
Sugar beet tops	0.20	0		0.22, 0.21 (0.22)	100
		104		0.20, 0.21 (0.21)	95
		251		0.21, 0.20 (0.21)	95
		286		0.21, 0.21 (0.21)	95
HEMA					
Potato tubers	0.20	0	76	0.20, 0.20 (0.20)	100
		104		0.20, 0.20 (0.20)	100
		251		0.18, 0.19 (0.19)	95
		286		0.20, 0.19 (0.20)	100
Sugar beet tops	0.20	0		0.21, 0.20 (0.21)	100
		104		0.21, 0.20 (0.21)	100
		251		0.20, 0.19 (0.20)	95
		286		0.18, 0.20 (0.19)	90

1 Duplicate freshly fortified samples were analyzed along with the stored samples at each interval; however, only the average fresh recovery was reported.

2 Residues of EMA and HEMA are reported in acetochlor equivalents. The average of the two recovery samples are in parentheses.

3 The average recovery of the stored samples was corrected by the reviewer by dividing by the residues found at Day 0.

D. CONCLUSION

The storage stability data are adequate and indicate that acetochlor and its EMA and HEMA type metabolites are stable in frozen potato tubers and sugar beet tops for at least 9 months.

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 (3/13/06); T. Goodlow (3/20/06)
Petition Number(s): 1F6263
DP Barcode(s): D230310 and D275019
PC Code: 121601