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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:

44107107 Horton, S. (1996) Storage Stability of Acetochlor Residues in Alfalfa and Clover Raw Agricultural Commodities: Lab Project Number: MSL-14134: 95-27-R-1: RES-074-93. Unpublished study prepared by Monsanto Co. 110 p.

## EXECUTIVE SUMMARY:

In a storage stability study, control samples of homogenized alfalfa forage and clover hay were fortified separately with ethyl methyl aniline (EMA)- and hydroxyethyl methyl aniline (HEMA)-producing metabolites of acetochlor, each at 0.10 ppm. The stored samples were fortified at various intervals over an 11-month period, and then analyzed on a single date, along with duplicate freshly fortified samples. The storage intervals for the frozen samples were 1, 27, 57, 85, 113, 145, 176, 204, 238, 265, 302, and 330 days.

A High Performance Liquid Chromatography/Oxidative Coulometric Electrochemical Detection (HPLC/OCED) method was used to determine residues containing the EMA and HEMA moieties in alfalfa forage and clover hay. The method, which is equivalent to the current tolerance enforcement method, was adequately validated in conjunction with the analysis of samples from the storage stability study. The LOQ for both EMA and HEMA is 0.01 ppm, or 0.02 ppm expressed in acetochlor equivalents. The LOD was not reported.

The storage stability data are adequate and indicate that EMA and HEMA type metabolites are stable in alfalfa forage and clover hay for at least 11 months.



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## 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 ethyl methyl aniline (EMA)- and hydroxyethyl methyl aniline (HEMA)-producing metabolites, 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#6F4791) proposing the use of acetochlor (EC) on sweet corn and requesting tolerances on sweet corn commodities and tolerances for inadvertent residues in rotated non-grass animal feeds.

**TABLE A.1. Acetochlor Nomenclature**

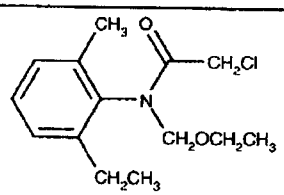
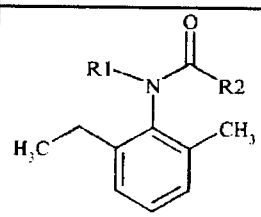
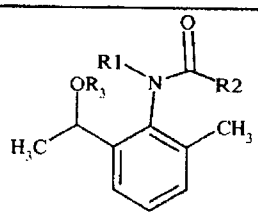
| | |
|---|---|
| Chemical structure |  |
| Common name | Acetochlor |
| Molecular Formula | $C_{14}H_{20}ClNO_2$ |
| Molecular Weight | 269.8 |
| IUPAC name | 2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide |
| CAS name | 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide |
| CAS # | 34256-82-1 |
| 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 ($4.5 \times 10^{-5}$ 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 | |

**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 alfalfa forage and clover hay were fortified separately with the

ethyl methyl aniline (EMA)- and hydroxyethyl methyl aniline (HEMA)-producing metabolites of acetochlor, each at 0.10 ppm. At about four-week intervals over a period of eleven months, unfortified samples were thawed, fortified and immediately returned to frozen storage. All the fortified stored samples were extracted and analyzed on a single date, and duplicate concurrent samples were fortified separately and analyzed with the frozen fortified samples. Storage intervals for the frozen samples were 1, 27, 57, 85, 113, 145, 176, 204, 238, 265, 302, and 330 days after fortification.

### B.2. Analytical Methodology

Samples of alfalfa and clover forage and hay 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. The method LOQ for both EMA and HEMA is 0.01 ppm, or 0.02 ppm expressed in acetochlor equivalents. The LOD was not reported.

## C. RESULTS AND DISCUSSION

Duplicate samples of alfalfa forage and clover hay were fortified separately with the EMA and HEMA metabolites of acetochlor at 0.10 ppm and analyzed after frozen (ca. -20°C) storage intervals of 0, 1, 27, 57, 85, 113, 145, 176, 204, 238, 265, 302, and 330 days. Concurrent fresh recoveries were determined prior to the analysis of stored samples. All analyses were conducted on a single day, with stored samples fortified over an 11-month period. The data indicate that residues of EMA and HEMA type metabolites are stable in/on alfalfa forage and clover hay for up to 330 days (Table C.1). The mean corrected recoveries of alfalfa forage and clover hay samples ranged from 86-109% at all storage intervals.

**TABLE C.1. Stability of EMA and HEMA Type Metabolites in Alfalfa Forage and Clover Hay Following Frozen (ca. - 20°C) Storage.[1]**

| Matrix | Spike level (ppm) | Storage interval (days) | EMA | | | HEMA | | |
|---|---|---|---|---|---|---|---|---|
| | | | Average Concurrent Recovery (%) | Residues in Stored Samples (ppm)[1] | Mean Corrected Recovery (%)[2] | Concurrent Recovery (%) | Residues in Stored Samples (ppm)[1] | Mean Corrected Recovery (%)[2] |
| Alfalfa forage | 0.10 | 0 | 92[3] | 0.0920 | 100 | 70[3] | 0.0714 | 100 |
| | | 1 | | 0.0917 | 100 | | 0.0767 | 107 |
| | | 29 | | 0.0958 | 104 | | 0.0778 | 109 |
| | | 57 | | 0.0911 | 99 | | 0.0753 | 105 |
| | | 85 | | 0.0883 | 96 | | 0.0748 | 105 |
| | | 113 | | 0.0877 | 95 | | 0.0762 | 107 |
| | | 145 | | 0.0929 | 101 | | 0.0765 | 107 |
| | | 176 | | 0.0893 | 97 | | 0.0754 | 106 |
| | | 204 | | 0.0937 | 102 | | 0.0781 | 109 |
| | | 239 | | 0.0927 | 101 | | 0.0774 | 108 |
| | | 267 | | 0.0917 | 100 | | 0.0762 | 107 |
| | | 302 | | 0.0898 | 98 | | 0.0766 | 107 |
| | | 330 | | 0.0787 | 86 | | 0.0676 | 95 |
| Clover hay | 0.10 | 0 | 84[3] | 0.0872 | 100 | 69[3] | 0.0721 | 100 |
| | | 1 | | 0.0889 | 102 | | 0.0728 | 101 |
| | | 27 | | 0.0917 | 105 | | 0.0747 | 104 |
| | | 57 | | 0.0932 | 107 | | 0.0752 | 104 |
| | | 85 | | 0.0881 | 101 | | 0.0739 | 102 |
| | | 113 | | 0.0884 | 101 | | 0.0719 | 100 |
| | | 145 | | 0.0865 | 99 | | 0.0710 | 98 |
| | | 176 | | 0.0910 | 104 | | 0.0752 | 104 |
| | | 204 | | 0.0887 | 102 | | 0.0735 | 102 |
| | | 238 | | 0.0902 | 103 | | 0.0768 | 107 |
| | | 265 | | 0.0895 | 103 | | 0.0736 | 102 |
| | | 302 | | 0.0869 | 100 | | 0.0718 | 100 |
| | | 330 | | 0.0850 | 97 | | 0.0709 | 98 |

1 Residues of EMA and HEMA are reported in acetochlor equivalents.
2 Results were corrected using the average concurrent recoveries. Stored samples were fortified over 11 months and all analyzed on one date, with freshly fortified samples. Results were rounded to the nearest whole percentage by the reviewer.
3 The results are the average of two concurrent recovery samples.

## D. CONCLUSION

The storage stability data are adequate and indicate that EMA- and HEMA-type metabolites are stable in alfalfa forage and clover hay for at least 11 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): 6F4791
DP Barcode(s): D230310 and D275019
PC Code: 121601