Shaughnessy No.: 121601

Date out of EFGWB: JAN 18 1991

TO: J. Miller/J. Mayes
Product Manager #23
Registration Division (H7505C)

FROM: Emil Regelman, Supervisory Chemist
Chemistry Review Section #2
Environmental Fate and Ground Water Branch

THRU: Hank Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Hank Jacoby

Attached, please find the EFGWB review of ...

Reg./File #: 010182-EUP-LU

Chemical Name: 2-Chloro-2'-methyl-6'-N-ethoxymethylacetanilide

Type Product: Herbicide

Common Name: Acetochlor

Company Name: ICI Americas Inc.

Purpose: Review of application for EUP on corn

Date Received: 20 September 1990 Date Completed: 17 Oct. 1990

Action Code: ____

EFGWB #(s): 90-0890

Total Reviewing Time: 1.0 day

Deferrals to: ___Ecological Effects Branch, EFED
___Science Integration and Policy Staff, EFED
___Non-Dietary Exposure Branch, HED
___Dietary Exposure Branch, HED
___Toxicology Branch

1. CHEMICAL:

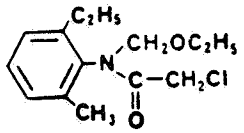
Chemical name: 2-Chloro-2'-methyl-6'-N-ethoxymethylacetanilide

CAS no.: 34256-28-1

Common name: Acetochlor

Trade name: ICIA5676

Chemical structure:



Formulation:	Acetochlor	70.9%
	Inert Ingredients	29.1%

Physical/Chemical properties of active ingredient:

Physical characteristics: Colorless thick liquid, aromatic odor

Molecular formula: $C_{14}H_{20}ClNO_2$

Molecular weight: 269.8

Vapor Pressure: 4.4×10^{-5} mm Hg

Solubility: 233 mg/L at 25°C

Octanol/water partition coefficient: 3.0

2. TEST MATERIAL:

N/A

3. STUDY/ACTION TYPE:

Review of application for ICIA5676 Experimental Use Permit (EUP) on corn.

4. STUDY IDENTIFICATION:

Kaminski, B. CORRESPONDENCE TO J. MILLER: ICIA5676 6.4EC HERBICIDE (CONTAINING ACETOCHLOR) APPLICATION FOR EXPERIMENTAL USE PERMIT. ICI Agricultural Products, Wilmington, DE; 2 July 1990; Received by EPA on 10 July 1990.

5. REVIEWED BY:

Gail Maske
Chemist, Review section #2
OPP/EFED/EFGWB

Signature: Gail Maske
Date: 17 Oct 90

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review section #2
OPP/EFED/EFGWB

Signature:
Date: JAN 18 1991

7. CONCLUSIONS:

a. There is insufficient environmental fate data to support the Experimental Use Permit (EUP) request (use of ICIA5676 on corn) for the following reasons:

1. The aerobic soil metabolism study for acetochlor did not fulfill the data requirement.

2. Studies have not been submitted to fulfill the accumulation in confined rotational crops and accumulation in fish data requirements for acetochlor.

3. Data are still needed to evaluate the environmental fate of the [redacted] for the proposed use on corn, Data needed to support the proposed EUP are:

161-1	Hydrolysis
162-1	Aerobic soil metabolism
163-1	Leaching, adsorption/ desorption
163-2	Volatility-lab
165-1	Rotational crops-confined
165-4	Accumulation in fish

The following studies are reserved (depending on results of 163-2):

161-4	Photodegradation in air
163-3	Volatility-field

b. The hydrolysis study is acceptable to meet Subdivision N Data Requirement. No further hydrolysis data for acetochlor is required at this time.

There was no detectable hydrolytic decomposition during the 31 day test period in the pH 5, 7, and 9 sterile buffered solutions. Recovery of acetochlor in samples analyzed at 31 days posttreatment was ≥ 96.6% of applied material .

INERT INGREDIENT INFORMATION IS NOT INCLUDED

c. The aerobic soil metabolism study is not acceptable to meet Subdivision N Data Requirement for the following reasons:

> One-dimensional TLC was not adequate to separate, quantify, and identify all degradation products. Nine to eleven degradates (G1, G3/G4, F1/F2, F4, F5, F6, F7, F8, and F9), each detected at concentrations ranging from 0.04 to 0.23 ppm, were not identified in the study. [There was no other analytical method used in the study. Therefore, degradates, that appeared to be > 0.01 ppm, were not identified in the study.]

The registrant must address these deficiencies for this study to fulfill the data requirement. If the registrant does not satisfactorily address the above deficiencies, a new aerobic soil metabolism study is required.

Acetochlor degraded in silty clay loam soil with an aerobic soil half-life of 13.5 days. N-(ethoxymethyl)·N-(2-ethyl-6-methylphenyl) oxalic acid and N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid were identified as the major degradates. These metabolites reached maximum levels of 20% and 13% of applied radioactivity after 60 and 180 days, respectively. Both degradates declined to 8% of the applied radioactivity after 1 year. Carbon dioxide accounted for at least 8 to 11% of the applied radioactivity over the 365 day test period.

d. The batch equilibrium study for acetochlor is acceptable to meet Subdivision N Data Requirement. No further leaching, adsorption/desorption data for acetochlor is required for unaged acetochlor, N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) oxamic acid, and N-(ethoxymethyl)-N-2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid at this time.

Acetochlor and its metabolites, N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) oxamic acid and N-(ethoxymethyl)-N-(2-ethyl-6-methyl phenyl)acetamide-2-sulphonic acid, are classified as very mobile to moderately mobile. The Kd values for the parent, acetochlor, were 0.05 to 0.26 for the coarse sand soil, 0.53 to 3.34 for the loamy sand soil, 1.14 to 3.02 for the sandy loam soil, 3.77 to 4.93 for the clay soil, 0.93 to 5.48 for the sand soil, and 7.90 to 37.8 for the sandy loam soil. The Kd values for the oxamic acid metabolite and sulphonic acid metabolite ranged from 0.05 to 0.21 and 0.06 to 0.26 for the coarse sand soil, 0.15 to 0.68 and 0.17 to 0.71 for the loamy sand soil, 0.17 to 0.51 and 0.19 to 0.90 for the sandy loam soil, 0.25 to 0.62 and 0.35 to 1.1 for the clay soil, 0.19 to 0.38 and 0.20 to 0.38 for the sand soil, and 0.70 to 0.99 and 0.73 to 1.1 for the sandy loam soil, respectively. The Kd values for acetochlor and the two metabolites did appear to correlate to the organic matter content and the pH of the soil. Adsorption for all three compounds is shown to be favored in soil which are acid and have high organic matter content.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

8. RECOMMENDATIONS:

The registrant should be informed of the following:

a. There is insufficient environmental fate data to support the proposed EUP for use of acetochlor and [redacted] on corn. The environmental fate data for acetochlor and [redacted] should be submitted simultaneously in order that a complete environmental fate assessment of ICIA5676 can be made.

b. The hydrolysis and the leaching, adsorption/desorption studies for acetochlor are acceptable to meet Subdivision N Data Requirements.

c. The aerobic soil metabolism study for acetochlor is not acceptable to meet the Subdivision N Data Requirement. The registrant must address the above deficiencies (Conclusions, part c) to fulfill the data requirement. If the registrant does not satisfactorily addressed these deficiencies, a new aerobic soil metabolism study is required.

d. The status of the EUP Environmental Fate Data Requirements for acetochlor for terrestrial food use is as follows:

Environmental Fate Data Requirements	Status of Data Requirement	MRID No.
Degradation Studies-Lab		
161-1 Hydrolysis	Fulfilled This review	41565144
Metabolism Studies-Lab		
162-1 Aerobic (Soil)	Not Fulfilled This review	41565147
Mobility Studies		
163-1 Leaching, Adsorption/ Desorption	Fulfilled This review	41565149
163-2 Volatility-lab	Not Required (PRD;04/24/89)	
Accumulation Studies		
165-1 Rotational crops-confined	Not Submitted[1]	
165-4 In fish	Not Submitted[2]	

INERT INGREDIENT INFORMATION IS NOT INCLUDED

e. The status of the EUP Environmental Fate Data Requirements for [redacted] for terrestrial food use is as follows:

Environmental Fate Data Requirements	Status of Data Requirement	MRID No.
Degradation Studies-Lab		
161-1 Hydrolysis	Not Submitted	
Metabolism Studies-Lab		
162-1 Aerobic (Soil)	Not Submitted	
Mobility Studies		
163-1 Leaching, Adsorption/ Desorption	Not Submitted	
163-2 Volatility-lab	Not Submitted	
Accumulation Studies		
165-1 Rotational crops-confined	Not Submitted[1]	
165-4 In fish	Not Submitted[2]	

[1]: Confined accumulation study is required when it is reasonably foreseeable that any food or feed corp may be subsequently planted on the site of pesticide application.

[2]: The fish accumulation study is required if significant concentrations of the active ingredient and/or its principal degradation products are likely to occur in aquatic environments and may accumulate in aquatic organisms.

9. BACKGROUND:

The purpose of this submission is to obtain an EUP for use of ICIA5676 on corn.

ICI Agricultural Products, Wilmington, DE will be requesting registration of acetochlor for terrestrial food (corn) and terrestrial non-food crops. ICI began developing acetochlor use for registration as a herbicide in 1988.

A new chemical screen for ICI's acetochlor for terrestrial noncrop use was just completed (November 1990). The acetochlor new chemical package did not pass the new chemical screen. Since the EUP request was submitted with the new chemical package, the hydrolysis, aerobic soil metabolism, and the adsorption/desorption studies were reviewed (see attached DER's).

INERT INGREDIENT INFORMATION IS NOT INCLUDED

General Background

ICIA5676 6.4 EC herbicide is a novel combination of the chloroacetamide, acetochlor, and the [redacted] The acetochlor will be used to control many annual grasses, yellow nutsedge and certain broadleaf weeds in transplanted junipers and yews and corn while the [redacted] acts as [redacted] used in pesticide formulations to attenuate the phytotoxicity of the pesticide's active ingredient (acetochlor)).

Acetochlor is toxic to aquatic life, but is less toxic to bees.

10. DISCUSSION:

In meeting the objectives of the proposed experimental program, a total of up to 10,000 pounds will be applied on up to 5,000 acres across the United States (see Table I) over a two year period which begins 1 February 1991 and ending 31 January 1993. During 1991 there will be a total of up to 3,340 pounds applied on up to 1,670 acres. In 1992 there will be up 6,600 pounds applied on up to 3,330 acres. The primary application season will be April, May, and June of each year.

Acetochlor, ICIA5676, will be applied at a rate of 0.75 to 2.5 lbs. ai/A (varying according to soil type and organic matter from site to site) with no more than one application per site per year. The application at a site could be make as early as 6 weeks prior to planting or as late as 1 day before emergence of the corn seedings.

ICIA5675 6.4 EC will be applied to the soil surface primarily using ground equipment. However, some material will be applied aerially. There will be no chemigation applications. If applied with dry bulk fertilizer, ICIA-5676 6.4 EC will be applied either as a liquid spray or impregnated on the dry fertilizer.

Although the primary application will be preplant surface, at some sites the material may be incorporated into the top 1 to 2 inches of soil. The incorporation will be done by using one of several implements such as a disk, field cultivator, rotary hoe, or other mechanical means to thoroughly distribute the ICIA5676 within the soil layer.

Two types of data will be collected. The first is efficacy or percent control versus a commercial standard and an untreated check. The percent may be arrived at by stand counts of weeds in each treatment compared to the standard and untreated check or it can be a visual estimation against the same criteria. The second type of data to be collected is phytotoxicity evaluations. This will be rating of hybrid lines by actual stand counts, or percent stunting, seeding vigor, chlorosis, and epinasty versus commercial standards and untreated checks.

In general there will be two types of tests. The most numerous will be small scale plots with 3 to 4 replicates per treatment covering approximately 1 acre. The second type and less numerous, but covering more total acreage, is large scale plots. The large scale plots will be non-replicated and cover more than an acre. The larger plots will be primarily those done by air and with dry bulk fertilizer. Those types of applications require larger equipment and acreages for a minimal loading.

Food or feed items grown under this EUP containing residues which do not exceed the established temporary tolerances would be sold through the normal channels of trade. Those food or feed items from plots, such as the phytotoxicity studies, which receive a rate higher than 2.5 lbs. ai/acre will be destroyed or used for research purposes and not allowed to enter human or animal diets.

11: COMPLETION OF ONE-LINER:

No one-liner is attached.

12: CBI APPENDIX:

N/A

TABLE 1

G2 STATES IN WHICH ICIA5676 6.4 EC HERBICIDE IS TO BE USED, AMOUNTS TO BE USED AND ACREAGES TO BE TREATED PER STATE.

Crops	Method of Application	Number of Applications	Applications Begin	End	Applications Rate Per Acre	State	Acres Needed 1991	1992	Amount Needed 1991	1992
Field Corn	Broadcast Air or Ground	1 Per Year	2/91	1/93	0.75 to 2.5 lbs a.i./acre	AL	30	60	60	120
						AZ	10	20	20	40
						AR	30	60	60	120
						CO	30	60	60	120
						CT	10	20	20	40
						DE	50	100	100	200
						FL	30	60	60	120
						GA	30	60	60	120
						ID	10	20	20	40
						IL	90	180	180	360
						IN	90	180	180	360
						IA	90	180	180	360
						KS	20	60	60	120
						KY	50	100	100	200
						LA	30	60	60	120
						MD	40	80	80	160
						MA	10	20	20	40
						MI	40	80	80	160
						MN	70	140	140	280
						MS	30	60	60	120
						MO	60	120	120	240
						MT	25	50	50	100
						NE	80	150	160	300
						NE	10	20	20	40
						NJ	20	40	40	80
						NM	20	40	40	80
						NY	50	100	100	200
						NC	60	120	120	240
						ND	30	60	60	120
						OH	60	120	120	240
						OK	30	60	60	120
						OR	20	40	40	80
						PA	40	80	80	160
						SC	30	60	60	120
						SD	50	100	100	200
						TN	50	100	100	200
						TX	60	120	120	240
						UT	10	20	20	40
						VA	50	100	100	200
						WA	20	40	40	80
						WV	20	40	40	80
						WI	50	100	100	200
						WY	25	50	50	100
TOTALS BY YEAR						TOTALS	1670	3330	3340	6660

DYNAMAC
CORPORATION

ACETOCHLOR

TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES

TASK 2: ENVIRONMENTAL FATE ASSESSMENT

November 14, 1990

FINAL REPORT

Contract No. 68D90058

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

ACETOCHLOR

Table of Contents

Page

Scientific Studies

DATA EVALUATION RECORD

STUDY 1

CHEM 121601 Acetochlor §161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41565144

Myers, H.W. 1989. ICIA-5676 Hydrolysis studies. Report Number WRC 88-70. Unpublished study performed and submitted by ICI Americas Inc., Richmond, California.

DIRECT REVIEW TIME = 12

REVIEWED BY: L. Parsons TITLE: Staff Scientist

EDITED BY: W. Martin TITLE: Staff Scientist
K. Patten Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: G. Maske-Love
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-9733

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

1. This study can be used to fulfill data requirements.

2. Acetochlor did not hydrolyze in sterile aqueous buffered solutions (pH 5, 7, and 9) that were incubated in the dark at 25 C for 31 days.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of acetochlor in sterile aqueous buffers at pH 5, 7, and 9.

4. No additional information on the hydrolysis of acetochlor is needed at this time.

METHODOLOGY:

Acetochlor (purity 99.5%) in acetonitrile was added at 83.0-85.3 ppm to sterile aqueous buffered solutions that had been adjusted to pH 5 (0.001 M sodium phthalate), 7 (0.001 M sodium phosphate), or 9 (0.001 M sodium borate/HCl). The final concentration of acetonitrile in the test solutions was 1% by volume. Aliquots of the test solutions were sealed in tubes with teflon closures and incubated in the dark at 25 C. Duplicate samples were removed for analysis at 1- to 3-day intervals until 31 days posttreatment.

The samples were extracted with toluene containing 9-phenylcarbazole as a GC standard. The extracts were stored over anhydrous sodium sulfate at -5 C until analysis by GC with nitrogen/phosphorus-selective thermionic detection. Total acetochlor concentration was determined by integrating the peak areas using 9-phenylcarbazole as an internal standard. Recovery efficiencies from solutions fortified at 88 mg/L ranged from 94.3 to 96.9%.

DATA SUMMARY:

Acetochlor (purity 99.5%), at 83.0-85.3 ppm, did not hydrolyze in sterile buffered pH 5, 7, and 9 solutions that were incubated in the dark at 25 C for 31 days. At 31 days posttreatment, the acetochlor concentration measured in the test solutions was 84.0-86.0 ppm (Tables II-IV). During the study, acetochlor ranged from 79.3 to 86.3 ppm in all test solutions with no discernible pattern.

COMMENTS:

The pH and sterily of the test solutions at the completion of the test period were not reported.

RIN 2556-94 ACETOCHLOR REVIEW (121601)

Page_____ is not included in this copy.

Pages 14 through 20 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

____ The document is a duplicate of page(s) __________.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

STUDY 2

CHEM 121601 Acetochlor §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41565147
Skidmore, M. 1989. The metabolism of $[^{14}C]$acetochlor in silty clay loam soil under aerobic conditions. Unpublished study performed by Huntingdon Research Centre, Ltd., Cambridgeshire, UK, and submitted by ICI Americas, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 20

REVIEWED BY: L. Parsons TITLE: Staff Scientist

EDITED BY: W. Martin TITLE: Staff Scientist
K. Patten Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
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TEL: 468-2500

APPROVED BY: G. Maske-Love
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-9733

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study cannot be used to fulfill data requirements at this time.

2. Acetochlor, at 4.5 ppm, degraded with a half-life of 13.5 days in silty clay loam soil incubated in the dark at 19.5 C and 81% of 0.33 bar moisture capacity. In contrast, acetochlor, at an increased application of 41 ppm, degraded with a half-life of 55 days in silty clay loam soil incubated under similar conditions. Nonvolatile degradates identified were N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid and N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid.

3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reasons:

   the analytical method (TLC) failed to adequately separate all minor degradates; and

   up to eleven degradates, each present at >0.01 ppm (0.225% of the applied radioactivity), were not identified.

4. In order for this study to fulfill the aerobic soil metabolism data requirement, degradates G3/G4 and F1/F1 should be individually quantified, and all degradates present at >0.01 ppm (0.225% applied radioactivity)--specifically G1 at 1.7%, G3/G4 at 7.0%, F1/F2 at 5.2%, F4 at 1%, F5 at 4.5%, F6 at 3.8%, F7 at 2.8%, F8 at 2.0%, and F9 at 1.4%--must be identified.

METHODOLOGY:

Samples of sieved (2 mm) silty clay loam soil (31% clay, 67% silt, 2% sand, 4.1% organic matter, pH 6.9, CEC 23.6 meq/100 g) were weighed into glass crystallizing dishes and treated at 4.5 ppm with uniformly ring-labeled [^{14}C]acetochlor (radiochemical purity 96%, specific activity 2.93 x 10^7 dpm/mg, Amersham) dissolved in acetone. The treated soils were moistened to 81% of 0.33 bar with deionized water, then mixed. The dishes were placed in a steel rack inside two sealed glass chambers (Figure 1) and incubated in the dark at 19.5-25.0 C. Humidified air was pumped continuously (flow rate not specified) through the chambers and vented through a series of traps containing 2-ethoxyethanol, aqueous sodium hydroxide, and ethanolamine:2-ethoxyethanol. Duplicate samples were removed for analysis at 0, 1, 3, 7, 14, 30, 60, 90, 120, 275, and 365 days posttreatment. Trapping solutions were removed for analysis and replaced with fresh solutions at intervals until 365 days posttreatment. Periodically, the plastic tubing connecting the column and the traps was rinsed with acetone; at 365 days posttreatment, the glass columns and racks were rinsed with methanol:water (1:1, v:v).

Soil samples were extracted 1-2 times with acetonitrile by shaking for 30 minutes, 1-2 times with acetonitrile:water (7:3, v:v) by shaking for 30 minutes, and once with acetonitrile:water (7:3, v:v) by Soxhlet for 8 hours. The acetonitrile extracts were pooled and acetonitrile:water extracts were pooled; each set of extracts was analyzed separately. The combined extracts were analyzed for total radioactivity by LSC, and for specific compounds using normal-phase TLC on Kieselgel 254F plates developed with chloroform:methanol:acetic acid (70:30:3, v:v:v, solvent system G) and reverse-phase TLC on octadecyl silane plates developed in acetonitrile:water:acetic acid (45:50:5, v:v:v, solvent system F). Reference standards (Figure 2) were cochromatographed with the extracts. The unlabeled reference standards were located by UV fluorescence quenching; radioactive areas were located by

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autoradiography and radioscanning. The extracted soils were air-dried, and subsamples were analyzed for unextracted radioactivity by LSC following combustion.

The plastic tubing, glass columns, and racks rinsate were analyzed by LSC. Aliquots of the trapping solutions were analyzed by LSC; methanol was added to the ethanolamine/2-ethoxyethanol mixture prior to LSC. Also, the sodium hydroxide trapping solution was measured for CO_2 using barium chloride precipitation techniques.

In order to identify degradates, an ancillary experiment was performed at a higher application rate. Uniformly ring-labeled [^{14}C]acetochlor (radiochemical purity 97%, specific activity 1.53 X 10^7 dpm/mg, Amersham) plus nonradiolabeled acetochlor (purity not reported), dissolved in acetone, was added at 40.9 ppm to silty clay loam soil. The soil was incubated, sampled, and analyzed as described above. The acetonitrile:water extracts from the 180-day sampling interval were pooled, and the acetonitrile was removed by rotary evaporation. An aliquot of the resulting aqueous solution was chromatographed on an Amberlite XAD-2 column eluted with methanol and acetonitrile:water (7:3, v:v). The eluants were pooled and evaporated to dryness (method not reported), and the residues were redissolved in methanol. The methanol solution was analyzed by TLC using solvent system G. The radioactive areas were scraped from the plate and eluted in methanol; the extract was concentrated under a nitrogen stream and diluted with methylene chloride, and an aliquot of this extract was again analyzed by TLC using solvent system G. The remainder of the extract was analyzed by HPLC using a silica gel column eluted with methylene chloride:methanol (4:1, v:v). The major peak from the HPLC was concentrated under a nitrogen stream and analyzed by MS; aliquots of the major peak were also analyzed by TLC developed in either solvent system G or chloroform:methanol:formic acid:water (70:25:3:3, v:v:v:v, solvent system J).

Also, the acetonitrile:water extracts from the 365-day sampling interval were pooled and the acetonitrile was removed by rotary evaporation. The resulting aqueous solution was acidified with HCl and partitioned twice with diethyl ether. The diethyl ether phase was partitioned twice with 0.01 M sodium hydroxide; the aqueous phases were combined, acidified with HCl, and partitioned twice with diethyl ether. An aliquot of the organic phase was evaporated to dryness and analyzed by direct insertion probe MS. The remainder of the organic phase was derivatized to the methyl or trimethylsilyl derivatives and analyzed by MS. Aliquots of the extract were also analyzed by TLC using solvent system G or J.

DATA SUMMARY:

Uniformly ring-labeled [^{14}C]acetochlor (radiochemical purity 96%), at 4.5 ppm, degraded with a calculated half-life of 13.5 days in silty clay loam soil that was incubated in the dark at 19.5 C and 81% of

0.33 bar moisture. Acetochlor was an average of 92.7% of the applied radioactivity immediately posttreatment, 48.8% at 14 days, 19.1% at 30 days, and 0.6% at 365 days posttreatment (Table IX). Two degradates were identified:

> N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (G2), which was a maximum of 22.9-28.3% of the applied at 30-60 days posttreatment and 7.2-8.6% at 365 days (Table XII); and
>
> N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (G5), which was a maximum of 13.4% at 180 days and 7.4-7.9% at 365 days.

Unidentified nonpolar [^{14}C]degradates were F1/F2, present at up to 5.2% of the applied; F4 at 1%; F5 at 4.5%; F6 at 3.8%; F7 at 2.8%; F8 at 2.0%; and F9 at 1.4% (Table XI). Unidentified polar [^{14}C]degradates were G1, present at 0.3-1.7% of the applied, and G3/G4 at 0.2-7.0% (Table XII). Volatile [^{14}C]residues totaled 8.6-10.9% of the applied radioactivity (Table I). Unextracted [^{14}C]residues increased from an average of 2.5% of the applied radioactivity immediately posttreatment to 34.2-34.7% at 365 days posttreatment (Table I). The material balances were 91.2-114.5% from 0-30 days posttreatment, 82.9-85.4% at 60 days and 76.6-77.1% at 365 days (Table I). It was suggested that the poor material balance was due to inefficient trapping of CO_2.

In contrast, [^{14}C]acetochlor, at 41 ppm, degraded with a half-life of 55 days in silty clay loam soil that was incubated under similar conditions (Table IX). The material balances were 87.4-89.7%.

COMMENTS:

1. The analytical method that was used by the study author, one-dimensional TLC, failed to adequately separate several of the minor degradates (specifically F1/F2 and G3/G4). These degradates appear to have each been present at >0.01 ppm, and therefore may require identification. Additional analytical techniques, such as two-dimensional TLC or HPLC, should have been tried in an attempt to get satisfactory resolution of these degradates.

2. Up to eleven nonvolatile degradates (G1, G3/G4, F1/F2, F4-F9), each detected at maximum concentrations of 1.0-5.2% of the applied (0.04-0.23 ppm), were not identified (Tables XI and XII). Subdivision N guidelines specify that all compounds present at ≥0.01 ppm must be identified.

3. The material balances were acceptable (98.1-99.9% of the applied radioactivity) at 30 days posttreatment, but were lower (76.6-77.1% applied radioactivity) at 365 days posttreatment. The material balances were acceptable for two half-lives of the parent before they declined to an unacceptable level.

To characterize the radioactivity lost in the main study, the trapping system was modified to include foam plugs (material not described), and ethyl digol and ethanolamine:2-ethoxyethanol traps. It appeared that the loss of radioactivity may have been due to inefficient trapping of CO_2; the material balances for the modified 90-day study were >90% of the applied. However, the study was terminated too soon to confidently assume the pattern would continue until 365 days, the length of the original study.

4. When the application rate was increased from 4.5 to 41 ppm, the measured half-life of acetochlor in the soil increased from 13.9 to 55 days. No explanation for this increase was provided by the study author. The 41 ppm application rate is 10x the proposed application rate, and was used primarily for ease of degradate identification.

5. The study author reported that N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (G5) eluted as two peaks upon HPLC analysis in the system described above. However, "subsequent TLC analysis showed that both fractions contained the same metabolite". Only the "major peak" was concentrated and analyzed by MS.

6. The calculations used to equate the approximate field application rate (4.0 lb ai/A) and the concentration of acetochlor (4.5 mg/kg) used in this study were not reported.

RIN 2556-94 ACETOCHLOR REVIEW (121601)

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DATA EVALUATION RECORD

STUDY 3

CHEM 121601 Acetochlor §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41565149
Robbins, A.J., and M.W. Hatfield. 1990. Acetochlor and its two major metabolites: adsorption/desorption in soil. Unpublished study performed and submitted by ICI Americas, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 20

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CONCLUSIONS:

Mobility - Adsorption/Desorption

1. This study can be used to fulfill data requirements.

2. Acetochlor and the degradates N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (oxamic acid), and N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (sulphonic acid) are mobile to very mobile in clay, loamy sand, sandy loam, sand, and coarse sand soils with Freundlich K_{ads} values of 0.19-20.0.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (batch equilibrium) of unaged acetochlor, oxamic acid, and sulphonic acid in clay, loamy sand, two sandy loams, sand, and coarse sand soils.

4. No additional information on the mobility of acetochlor, oxamic acid, and sulphonic acid is needed at this time. However, information on the mobility of any other degradates of concern that may be identified in future studies will be required.

METHODOLOGY:

Clay, loamy sand, two sandy loam, sand, and coarse sand soils (Table 2) were air-dried, sieved (2 mm), and irradiated (28 KGys for 12 hours). The soils were equilibrated with sterile 0.01 M $CaCl_2$ solution for 24 hours prior to the addition of a mixture of acetochlor, N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (oxamic acid), and N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (sulphonic acid). Based on a preliminary study using a sandy loam soil (East Jubilee), an equilibration time of 2 hours and a 1:4 soil:water ratio were selected for all soils.

Uniformly ring-labeled [^{14}C]acetochlor, [^{14}C]oxamic acid, and [^{14}C]sulphonic acid (radiochemical purities $\geq 97\%$, specific activities and source not reported), dissolved in ethanol and diluted with 0.01 M $CaCl_2$ solution, were added to self-sealing teflon tubes containing the soils. The respective concentrations of acetochlor, oxamic acid and sulphonic acid studied were, respectively, 0.25:0.2:0.2 ug/cm3, 0.5:0.4:0.4 ug/cm3, 1.0:0.8:0.8 ug/cm3, 2.0:1.0:1.0 ug/cm3, and 4.0:1.0:1.0 ug/cm3. The soil:solution slurries (5 g soil:20 ml solution) were shaken at 20 C for 2 hours. Following equilibration, the tubes were centrifuged. The supernatant was decanted and aliquots were analyzed by LSC.

To determine desorption potential, the supernatant was replaced with pesticide-free 0.01 M $CaCl_2$ solution. The soil slurries were agitated for 2 hours at 20 C, then centrifuged and analyzed by LSC.

The mass balance was determined for the clay soil (Old Paddock) by centrifuging the slurry, pipetting off the supernatant, and calculating the volume by weight. The remaining soil was shaken with acetonitrile:water (50:50) for 1 hour. The slurries were filtered, the soil was freeze-dried and samples analyzed by LSC following combustion. The organic extract was concentrated (method not described) and the residue diluted with ethanol. An aliquot of the ethanol solution was analyzed by LSC. A second aliquot was concentrated (method not described) and analyzed by TLC on Camlab sil g25/UV254 plates developed with ethyl acetate:n-propanol:water (60:40:10). The radioactive areas were located by autoradiography and radioscanning.

DATA SUMMARY:

Based on batch equilibrium experiments, uniformly ring-labeled

[^{14}C]acetochlor,

[^{14}C]N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (oxamic acid), and

[^{14}C]N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (sulphonic acid)

(radiochemical purities $\geq$97%) were mobile to very mobile in clay, loamy sand, two sandy loam, sand, and coarse sand soil:$CaCl_2$ slurries (1:4) containing 0.25-4.0 ug/mL acetochlor, 0.2-1.0 ug/mL oxamic acid, and 0.2-1.0 ug/mL sulphonic acid that were equilibrated for 2 hours at 20 C.

The Freundlich K_{ads} values for acetochlor were 7.5 for the clay soil, 0.81 for the loamy sand soil, 5.9 and 20 for the sandy loam soils, 1.9 for the sand soil, and 1.9 for the coarse sand soil; respective K_{oc} values were 239, 389, 422, 216 and 428 (Table 4). K_{des} values ranged from 8.5-35 for the clay soil, 22-70 for the loamy sand soil, 1.9-8.0 and 40-112 for the sandy loam soils, 51-160 for the sand soil, and 3.5-8.4 for the coarse sand soil (Table 7).

The Freundlich K_{ads} values for oxamic acid were 0.77 for the clay soil, 0.19 for the loamy sand soil, 1.2 and 0.91 for the sandy loam soils, 0.27 for the sand soil, and 0.55 for the coarse sand soil; respective K_{oc} values were 24, 17, 20, 31 and 124 (Table 5). K_{des} values ranged from 0.73-1.2 for the clay soil, 2.5-5.1 for the loamy sand soil, 0.48-1.4 and 6.4-11.2 for the sandy loam soils, 6-19 for the sand soil, and 0.04-2.0 for the coarse sand soil (Table 8).

The Freundlich K_{ads} values for sulphonic acid were 1.6 for the clay soil, 0.23 for the loamy sand soil, 6.4 and 1.1 for the sandy loam soils, 0.27 for the sand soil, and 0.30 for the coarse sand soil; respective K_{oc} values were 52, 21, 430, 24, 31, and 68 (Table 6). K_{des} values ranged from 0.76-1.6 for the clay soil, 3.1-5.6 for the loamy sand soil, 0.53-1.6 and 8.1-12 for the sandy loam soils, 8-27 for the sand soil, and 0.01-2.3 for the coarse sand soil (Table 9).

The material balance for total radioactivity (acetochlor, oxamic acid, plus sulphonic acid) in the clay soil (Old Paddock) was 84-104%. (Appendix II).

COMMENTS:

1. The study author conducted this study using acetochlor and two of its soil degradates, oxamic acid, and sulphonic acid, apparently in lieu of performing an aged acetochlor mobility study. However, the use of

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a mixture of parent acetochlor, oxamic acid, and sulphonic acid required the quantitation of residues from TLC plates, and did not address the mobility of other degradates that may be of interest.

2. This study was poorly written. For example, the pesticide desorption conditions and protocol used for the mass balance determination were not clearly stated.

3. The soils were sterilized by gamma irradiation. Gamma irradiation is the most acceptable way to sterilize soil since it is the least likely to alter soil structure and chemistry.

4. The test soils were not classified according to the USDA Soil Classification System, and the classification system used by the authors cannot be readily converted to the USDA system. In the USDA system. the sand fraction includes particles that are 0.05-2 mm in diameter. The study authors classified the test soils using a system that included particles as part of the silt fraction that would be considered sand in the USDA system.

5. There is an apparent typographical error in Appendix II. The value in the column "dps in Aqueous Phase" should read 83048 instead of 830449 for the 4.0 ug/cm3 concentration.

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RIN 2556-94 ACETOCHLOR REVIEW (12/6/01)

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EXECUTIVE SUMMARY

The following findings are derived from those reviewed studies which have met the requirements of 40 CFR Part 158.290 and the guidance of Subdivision N, and were also deemed acceptable.

Hydrolysis studies

(Myers, 41565144)

Acetochlor (purity 99.5%), at 83.0-85.3 ppm, did not hydrolyze in sterile buffered pH 5, 7, and 9 solutions that were incubated in the dark at 25 C for 31 days. At 31 days posttreatment, the acetochlor concentration measured in the test solutions was 84.0-86.0 ppm (Tables II-IV). During the study, acetochlor ranged from 79.3 to 86.3 ppm in all test solutions with no discernible pattern.

Leaching and adsorption/desorption studies

(Robbins and Hatfield, 41565149)

Based on batch equilibrium experiments, uniformly ring-labeled [^{14}C]acetochlor, [^{14}C]N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (oxamic acid), and [^{14}C]N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (sulphonic acid) (radiochemical purities $\geq$97%) were mobile to very mobile in clay, loamy sand, two sandy loam, sand, and coarse sand soil:$CaCl_2$ slurries (1:4) containing 0.25-4.0 ug/mL acetochlor, 0.2-1.0 ug/mL oxamic acid, and 0.2-1.0 ug/mL sulphonic acid that were equilibrated for 2 hours at 20 C.

The Freundlich K_{ads} values for acetochlor were 7.5 for the clay soil, 0.81 for the loamy sand soil, 5.9 and 20 for the sandy loam soils, 1.9 for the sand soil, and 1.9 for the coarse sand soil; respective K_{oc} values were 239, 389, 422, 216 and 428. K_{des} values ranged from 8.5-35 for the clay soil, 22-70 for the loamy sand soil, 1.9-8.0 and 40-112 for the sandy loam soils, 51-160 for the sand soil, and 3.5-8.4 for the coarse sand soil.

The Freundlich K_{ads} values for oxamic acid were 0.77 for the clay soil, 0.19 for the loamy sand soil, 1.2 and 0.91 for the sandy loam soils, 0.27 for the sand soil, and 0.55 for the coarse sand soil; respective K_{oc} values were 24, 17, 20, 31 and 124. K_{des} values ranged from 0.73-1.2 for the clay soil, 2.5-5.1 for the loamy sand soil, 0.48-1.4 and 6.4-11.2 for the sandy loam soils, 6-19 for the sand soil, and 0.04-2.0 for the coarse sand soil.

The Freundlich K_{ads} values for sulphonic acid were 1.6 for the clay soil, 0.23 for the loamy sand soil, 6.4 and 1.1 for the sandy loam soils, 0.27 for the sand soil, and 0.30 for the coarse sand soil; respective K_{oc} values were 52, 21, 430, 24, 31, and 68. K_{des} values ranged from 0.76-1.6 for the clay soil, 3.1-5.6 for the loamy sand soil, 0.53-1.6 and 8.1-12 for the sandy loam soils, 8-27 for the sand soil, and 0.01-2.3 for the coarse sand soil.

The following findings are derived from the single reviewed study which has <u>not</u> met the requirements of 40 CFR 158.290 and/or the Subdivision N Guidelines, but which has been deemed a good study following generally sound scientific practice. It thereby provides <u>supplemental</u> information on the fate of the pesticide.

<u>Aerobic soil metabolism studies</u>

(Skidmore, 41565147)

Uniformly ring-labeled [^{14}C]acetochlor (radiochemical purity 96%), at 4.5 ppm, degraded with a calculated half-life of 13.5 days in silty clay loam soil that was incubated in the dark at 19.5 C and 81% of 0.33 bar moisture. Acetochlor was an average of 92.7% of the applied radioactivity immediately posttreatment, 48.8% at 14 days, 19.1% at 30 days, and 0.6% at 365 days posttreatment. Two degradates were identified: N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid (G2), which was a maximum of 22.9-28.3% of the applied at 30-60 days posttreatment and 7.2-8.6% at 365 days; and N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid (G5), which was a maximum of 13.4% at 180 days and 7.4-7.9% at 365 days. Unidentified nonpolar [^{14}C]degradates were F1/F2, present at up to 5.2% of the applied; F4 at 1%; F5 at 4.5%; F6 at 3.8%; F7 at 2.8%; F8 at 2.0%; and F9 at 1.4%. Unidentified polar [^{14}C]degradates were G1, present at 0.3-1.7% of the applied, and G3/G4 at 0.2-7.0%. Volatile [^{14}C]residues totaled 8.6-10.9% of the applied radioactivity. Unextracted [^{14}C]residues increased from an average of 2.5% of the applied radioactivity immediately posttreatment to 34.2-34.7% at 365 days posttreatment. The material balances were 91.2-114.5% from 0-30 days posttreatment, 82.9-85.4% at 60 days and 76.6-77.1% at 365 days. It was suggested that the poor material balance was due to inefficient trapping of CO_2.

In contrast, [^{14}C]acetochlor, at 41 ppm, degraded with a half-life of 55 days in silty clay loam soil that was incubated under similar conditions. The material balances were 87.4-89.7%.

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of acetochlor. The submission of data required for an Experimental Use Permit (EUP) for acetochlor on field and vegetable crop use sites is summarized below:

The following data are required:

<u>Aerobic soil metabolism studies</u>: One study (Skidmore, 41565147) was reviewed. This study is scientifically sound, but does not meet Subdivision N guidelines because the analytical method (TLC) failed to

adequately separate all minor degradates, and up to eleven degradates, each present at >0.01 ppm (0.225% of the applied radioactivity), were not identified.

Confined accumulation studies on rotational crops: No data were reviewed.

Laboratory studies of pesticide accumulation in fish: No data were reviewed.

The following data requirements are fulfilled:

Hydrolysis studies: One study (Myers, 41565144) was reviewed. This study is acceptable and fulfills data requirements by providing information on the hydrolysis of acetochlor in sterile aqueous buffers at pH 5, 7, and 9.

Leaching and adsorption/desorption studies: One study (Robbins and Hatfield, 41565149) was reviewed. This study is acceptable and fulfills data requirements by providing information on the mobility (batch equilibrium) of unaged acetochlor, oxamic acid, and sulphonic acid in clay, loamy sand, two sandy loams, sand, and coarse sand soils.

The following data requirements are not required for the EUP, are deferred, or are not required for presently registered uses:

Photodegradation studies in water: No data are required for the EUP; however, data will be required prior to full registration of acetochlor.

Photodegradation studies on soil: No data are required for the EUP; however, data will be required prior to full registration of acetochlor.

Photodegradation in air studies: No data were reviewed. The data requirement is deferred pending the receipt of acceptable laboratory volatility studies.

Anaerobic soil metabolism studies: No data are required for the EUP; however, data will be required prior to full registration of acetochlor.

Anaerobic aquatic metabolism studies: No data were reviewed. No data are required because the test substance is not registered for aquatic or forestry uses, or any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites.

Aerobic aquatic metabolism studies: No data were reviewed. No data are required because the test substance is not registered for aquatic uses or any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites.

Laboratory volatility studies: No data are required for the EUP; however, data will be required prior to full registration of acetochlor if the pesticide presents a significant inhalation exposure to workers.

Field volatility studies: No data were reviewed. The data requirement is deferred pending the receipt of acceptable laboratory volatility studies.

Terrestrial field dissipation studies: No data are required for the EUP; however, data will be required prior to full registration of acetochlor.

Aquatic field dissipation studies: No data were reviewed. No data are required because the test substance is not registered for aquatic food crop, aquatic nonfood (including antifouling paints, ditchbanks, and shorelines), or aquatic impact uses involving direct discharge of treated water into outdoor aquatic sites.

Forestry dissipation studies: No data were reviewed. No data are required because the pesticide has no forestry use.

Dissipation studies for combination products and tank mix uses: No data were reviewed; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed, but all data may be required if the results from the field dissipation/aerobic soil metabolism studies demonstrate that residues do not reach 50% dissipation in soil prior to the recommended subsequent application.

Field accumulation studies on rotational crops: No data were reviewed. The data requirement is deferred pending the receipt of acceptable accumulation studies in confined rotational crops.

Accumulation studies on irrigated crops: No data were reviewed; however, no data are required because the test substance is not intended for aquatic food crop or aquatic nonfood uses, for uses in and around holding ponds used for irrigation purposes, or for uses involving effluents or discharges to water used for crop irrigation.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed. No data are required because the test substance is not registered for forestry, aquatic nonfood, or aquatic impact uses.

REFERENCES

Myers, H.W. 1989. ICIA-5676 Hydrolysis studies. Report Number WRC 88-70. Unpublished study performed and submitted by ICI Americas Inc., Richmond, California. (41565144)

Robbins, A.J., and M.W. Hatfield. 1990. Acetochlor and its two major metabolites: adsorption/desorption in soil. Unpublished study performed and submitted by ICI Americas, Inc., Wilmington, DE. (41565149)

Skidmore, M. 1989. The metabolism of [^{14}C]acetochlor in silty clay loam soil under aerobic conditions. Unpublished study performed by Huntingdon

Research Centre, Ltd. Cambridgeshire, UK, and submitted by ICI Americas, Inc., Wilmington, DE. (41565147)

APPENDIX

ACETOCHLOR AND ITS DEGRADATES

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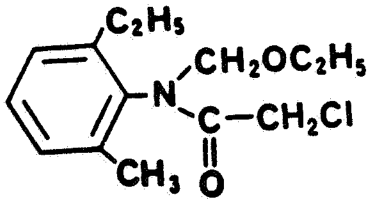
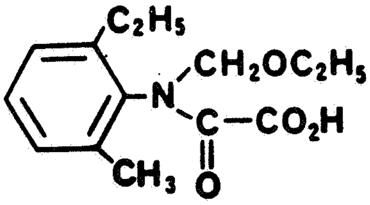


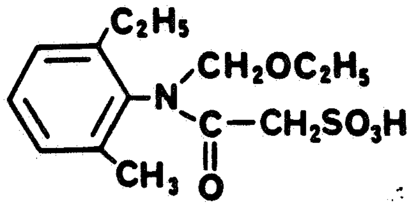
2-Chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide

(Acetochlor)



N-(Ethoxymethyl)-N-(2-ethyl-6-methylphenyl)oxamic acid

(Oxamic acid, G2)



N-(Ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide-2-sulphonic acid

(Sulphonic acid, G5)