Shaughnessy No.: 121601

Date out of EFGWB: MAY 9 1990

TO: R. Taylor/V. Walters
Product Manager #25
Registration Division (H7507C)

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)

Attached, please find the EFGWB review of ...

Reg./File #: 524-GUI

Chemical Name: 2-Chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide

Type Product: Selective preemergence herbicide

Common Name: Acetochlor

Company Name: Monsanto Company/ Monsanto Agricultural Products Co.

Purpose: Review of Anaerobic soil metabolism, Leaching & adsorption/ desorption, and Rotational crop studies

Date Received: 1 May 1990 Date Completed: 7 May 1990

Action Code: 161

EFGWB #(s): 90-0347/90-0348

Total Reviewing Time: 1.5 days

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:

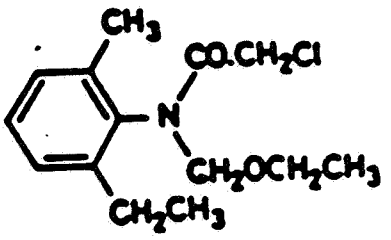
Chemical name: 2-Chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide

CAS no.: 34256-28-1

Common name: Acetochlor

Trade name: MON 8437, Harness

Chemical structure:



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

Molecular weight: 269.8

Formulation: Acetochlor.....81.15%
Inert Ingredients.....18.85%

Physical/Chemical properties of active ingredient:

Physical characteristics: Colorless thick liquid, aromatic odor

Vapor Pressure: 4.4×10^{-5} mm Hg

Solubility: 233 mg/L at 25°C

Octanol/water partition coefficient: $1 \times 10^{2.6}$

2. TEST MATERIAL:

See individual DER's.

3. STUDY/ACTION TYPE:

Review of Anaerobic soil metabolism, Leaching & adsorption/desorption, and Rotational Crop studies.

4. STUDY IDENTIFICATION:

Campbell, D.H. and Hamiltion, D.E. ANAEROBIC SOIL METABOLISM STUDIES OF ACETOCHLOR. Submitted and Performed by Monsanto Agricultural Company, St. Louis, MO under Lab. project no. MSL-9183; Study completed August 1980; Received by EPA 19 Dec. 1989; MRID No. ~~40198501~~ 41338501.

Campbell, D.H. and Hamilton, D.E. LEACHING AND ADSROPTION/DESORPTION STUDIES OF ACETOCHLOR. Submitted and Performed by Monsanto Agricultural Company, St. Louis, MO under Lab. project no. MSL-9184; Study completed August 1980; Received by EPA 19 Dec. 1989; MRID No. 40198502.

Lauer, R. and Mayonado, N.J. ACETOCHLOR RESIDUES FROM TWO METABOLITE CLASSES IN ROTATIONAL CROPS AND ACETOCHLOR PARENT IN SOIL FOLLOWING PREEMERGENT APPLICATION OF TOP-HAND TO CORN, THE PRIMARY CROP. Submitted and Performed by Monsanto Agricultural Company, St. Louis, MO under Laboratory Project Number/R.D. No. MSL-8845; Study completed May 1989; Received by EPA 19 Dec 1989; MRID No. 41338503.

5. REVIEWED BY:

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

Signature: Gail Maske
Date: 8 May '90

6. APPROVED BY:

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

Signature: Emil Regelman
Date: MAY 9 1990

7. CONCLUSIONS:

a. The anaerobic soil metabolism study is acceptable to meet Subdivision N data requirement. No further anaerobic soil metabolism data for acetochlor is required at this time.

Acetochlor demonstrated a half-life of 17.3 days, 19.3 days, and 20.4 days when applied to Ray, Drummer, and Spinks loam soils under anaerobic conditions, respectively. Microbial metabolism appears to be the major degradation pathway in the environment for acetochlor. Numerous metabolites are formed under anaerobic conditions which continue to degrade into a variety of metabolites due to microbial modifications.

b. The Leaching, adsorption/desorption studies are acceptable to meet Subdivision N data requirement. No further leaching, adsorption/desorption data for acetochlor is required at this time.

Unaged soils column experiments were conducted using Ray silt loam, Drummer silty clay loam, Spinks sandy loam, and Lintonia sandy soil. Freundlich adsorption coefficients were 0.4, 1.1, 1.6, and 2.7 for Lintonia, Ray, Spinks, and Drummer soils, respectively. The aged acetochlor leaching experiment was conducted in Ray soil which indi-

cated the major soil metabolites of acetochlor had greater mobility in soil than acetochlor. Soil thin-layer chromatography demonstrated acetochlor was mobile to very mobile in soils with organic matter content <2%. There appeared to be a correlation between organic matter content of the soils and the strength of binding, as well. The desorption phase demonstrated that acetochlor is reversibly bound.

c. This field rotational crop study will not be reviewed at this time. The review will be postponed until completion of the confined rotational crop study. The field rotational crop study will be retained in the file for review at the completion of an acceptable confined rotational crop study review.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

a. The anaerobic soil metabolism study is acceptable to meet Subdivision N data requirement. No further anaerobic soil metabolism data is required at this time.

b. The leaching, adsorption/desorption study is acceptable to meet Subdivision N data requirement. No further leaching, adsorption/desorption data is required at this time.

c. This field rotational crop study will not be reviewed at this time. The review will be postponed until completion of the confined rotational crop study.

d. The status of the Environmental Fate Data Requirements for registration of 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 (HLM;03/05/81)	00064805
161-2 Photodegradation in water	Fulfilled (PRD;03/23/88)	00131388
161-3 Photodegradation on soil	Fulfilled (PRD;03/23/88)	00131388
Metabolism Studies-Lab		
162-1 Aerobic (Soil)	Fulfilled (HLM;03/05/81)	00064805
162-2 Anaerobic (Soil)	This review	41338501

Mobility Studies

163-1	Leaching, Adsorption/ Desorption	This review	41338502
163-2	Volatility-lab	Not Required (PRD;04/24/89)	

Dissipation Studies-Field

164-1	Terrestrial	Not Fulfilled (PRD;04/24/89)	40811901

Accumulation Studies

165-1	Rotational crops-confined protocol	Not Fulfilled (PRD;03/23/88) (MIR;04/16/90)	00131390
165-2	Rotational crops-field	Postponed review until 165-1 is completed	41338503
165-4	In fish	Fulfilled (NKW;01/25/84)	00131388

9. BACKGROUND:

General Background

Acetochlor, a chloroacetamide, is used as a preemergent corn herbicide. Harness (MON 8437), which has acetochlor as its active ingredient, is an emulsifiable herbicide used to control yellow nutsedge, many annual grass and broadleaf weed species on corn, soybean, peanuts, and sunflowers.

Harness is applied either as a surface application after planting or shallowly incorporated prior to planting to blend the acetochlor into the upper 1 to 2 inches of soil. The seedbed should be fine, firm, and free of clods and thrash. Harness is not applied to coarse textured soils or to medium and fine textured soils which has less than 1.5% organic matter content. When applied to coarse textured or to medium and fine textured soils which has less than 1.5% organic matter content, acetochlor may cause damage to the crop. The broadcast rate varies according to the organic matter content and type of soil to be treated.

ICI Agricultural Products, Wilmington, DE is requesting registration of acetochlor for noncrop use and use on corn crops. ICI began developing acetochlor use for registration as a herbicide in 1988.

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

5

Environmental Fate Background

Degradation:

Acetochlor in deionized water, sterile lake water, and in sterile buffer solutions at pH 3, 6, and 9 did not show any significant degradation. A half-life of greater than 24 months was estimated. Therefore, acetochlor should not hydrolysis under environmental conditions.

Acetochlor was stable when exposed to irradiation in water and on soil.
Metabolism:

Under aerobic conditions in viable soil at 22°C the half-life of acetochlor in Ray soil was 8 days, in Drummer soil was 10 days, and in Spinks soil was 12 days. Data from the sterile soil studies indicated that microbial metabolism is the dominant degradation pathway for acetochlor in soil.

Nineteen metabolites were identified in the study. The three major metabolites were unambiguously identified as derivatives of methyloxanilic acid, sulfinylacetic acid, and sulfoacetanilide. None of the metabolites accounted for more than 18% of the applied acetochlor. Therefore, acetochlor degrades fairly rapidly under aerobic soil conditions yielding several metabolites.

Rapid microbial degradation took place under anaerobic soil conditions. Numerous degradates were formed which continued to be broken down into a wide array of degradates.

Mobility:

Soil adsorption and desorption of acetochlor were studied using Lintonia, Ray, Spinks, and Drummer soils having organic matter content of 0.7%, 1.4%, 2.4%, and 3.4%, respectively. Soils with a higher organic matter content bound acetochlor more tightly than those with lower organic matter content. The four soils (Lintonia, Ray, Spinks, and Drummer) had adsorption coefficients of 0.4, 1.1, 1.6, and 2.7, respectively.

Soil column studies of aged and unaged acetochlor reflected the correlation between organic matter content and adsorption seen in the previous adsorption studies. Therefore, soil adsorption/desorption and column leaching studies indicate that acetochlor is moderately mobile when applied to soils with higher organic matter content (approximately 3.4%). Acetochlor appears to be very mobile when applied to soils with lower organic matter content (approximately 0.7%).

Dissipation:

Acetochlor when applied to California soil, which was sandy with less than 1% organic matter content and very low field moisture capacity (worst-case scenario), demonstrated a half-life of <3 days. Only trace levels of acetochlor were found to occur in depths below 6 inches. Soil samples taken at from 8 foot soil core at 258 days demonstrated complete dissipation with undetectable acetochlor residues levels (<0.005 ppm).

From observations of the 2.0 lb/A treatment acetochlor residues in soil, significant residues in soil from typical acetochlor at 60 days posttreatment or at a depth of 6 inches would not be expected.

Accumulation:

Uptake of acetochlor into soybean was 1.2 ppm in foliage and 0.2 ppm in grain when harvested at maturity. When harvested at 30 days posttreatment, residues in the forage were 13.2 ppm from the carbonyllabelled acetochlor and 1.99 ppm from the phenyllabelled acetochlor.
Residues in follow crops were 0.2 ppm and 0.4 to 1.13 ppm in barley grain and straw, respectively. In cabbage the residues ranged from 0.09 to 0.2 ppm and 0.03 to 0.04 ppm 0.16 to 0.18 ppm in radishes, radishes greens, respectively. The amount of acetochlor uptake decreased as time of posttreatment planting increased. Five month rotational crops have residues which ranged from 0.03 to 1.13 ppm from all experiments, while those from the 1 year rotational crops ranged from 0.01 to 0.63 ppm.

The acetochlor bioconcentration factor (BCF) for whole fish is 84, for fillet 35, and for viscera 150. These values are consistent with the low octanol/water partition coefficient which is $1 \times 10^{2.6}$. Depuration at 14 days for whole fish was 85%, for fillet was 52%, and for viscera was 90%.

Acetochlor should not accumulate in fish.

10. DISCUSSION:

See individual DER's.

11: COMPLETION OF ONE-LINER:

See attached one-liner.

12: CBI APPENDIX:

The information is considered to be CBI by the registrant, and should be treated as such.

DATA EVALUATION RECORD

Shaughnessy No. 121601 STUDY 1 PM 25

CHEMICAL 2-Chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide

BRANCH Environmental Fate and Ground Water; 162-2

FORMULATION Radiolabelled active ingredient

MRID NO. 40198501

Campbell, D.H. and Hamilton, D.E. ANAEROBIC SOIL METABOLISM STUDIES OF ACETOCHLOR. Sponsored and Submitted by Monsanto Agricultural Company, St. Louis, MO under Lab. Project No. MSL-9183; Study Completed August 1980, Received by EPA 19 Dec. 1989.

SUBST. CLASS: Herbicide

REVIEWED BY: Gail Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: (703)557-9734

SIGNATURE:

CONCLUSIONS:

The anaerobic soil metabolism study is acceptable to meet Subdivision N data requirement. No further anaerobic soil metabolism data for acetochlor is required at this time.

Acetochlor demonstrated a half-life of 17.3 days, 19.3 days, and 20.4 days when applied to Ray, Drummer, and Spinks loam soils under anaerobic conditions, respectively. Microbial metabolism appears to be the major degradation pathway in the environment for acetochlor. Numerous metabolites are formed under anaerobic conditions which continue to degrade into a variety of metabolites due to microbial modifications.

MATERIALS AND METHODS

Test materials: Radiolabelled [^{14}C-carbonyl]acetochlor (9.89mCi/mmole) with a radiochemical and chemical purity of 95% as determined by GLC/RAD and GLC, respectively. This material was synthesized by R.C. Freeman in several steps from chloroacetyl chloride-[1-^{14}C], ethyl-6-methylaniline and chloromethyl ethyl ether.

Radiolabelled [^{14}C-phenyl]acetochlor (11.35 mCi/mmole) was used with a radiochemical and chemical purity of 98% as determined by GLC/RAD and GLC, respectively. This material was synthesized by R.C. Freeman in several steps from chloroacetyl chloride, ethyl-6-methylaniline[phenyl uniformly ring labelled ^{14}C], and chloromethyl ethyl ether.

Radiolabelled [^{14}C-carbonyl]acetochlor (8.29 mCi/mmole) was used for the repeat experiment. The chemical purity was 99% as determined by GLC. The radiolabelled purity was not determined. The material was synthesized by R.C. Freeman in the same manner as described for the main experiment.

Radiolabelled [^{13}C-carbonyl]acetochlor was prepared by D.H. Campbell. The chemical purity was 98% as determined by GC.

Standards: The standards of acetochlor metabolites were prepared by E.J. Breaux and K.C. Erickson.

Soil: Three viable soils (Ray silt loam, Drummer silty clay loam, and Spinks sandy loam) were used in the study. See Table 9 for the analytical analysis and content of each soil.

Equipment: See Figure 12.

Sampling: Samples were taken in the main experiment and analyzed at 30, 60, and 90 days after treatment or 0, 30, and 60 days of anaerobic incubation.

Samples were taken in the repeat experiment at 60, 90, 120 days after treatment or 0, 30, 60, 90, and 120 days of anaerobic incubation.

Samples were taken in the large-scale experiment after 62 days of anaerobic incubation.

Experimental procedure: The soil was sieved to 16 mesh and placed in the incubation flask (50 g dry weight). The dosing solution was applied in water. For the main experiment, [^{14}C-carbonyl]acetochlor at 9.89 mCi/mmole was used. For the repeat experiment, [^{14}C-carbonyl]acetochlor at 8.29 mCi/mmole was used. For the large-scale anaerobic experiment, a 52.8:47.2 ratio of [^{13}C-carbonyl]acetochlor/[^{14}C-phenyl]-acetochlor at 11.35 mCi/mmole was used. The mixture was prepared by combining 2.93 mg of [^{14}C-phenyl]acetochlor with 3.28 mg of [^{13}C-carbonyl]acetochlor. Following application of radiolabelled acetochlor, the flasks were agitated to distribute the acetochlor evenly throughout the soil. The moisture content of the soil was adjusted to 75% of field capacity. During the 30-day aerobic incubation period, trapping towers were used to trap volatiles and $^{14}CO_2$. The towers consisted of two pieces. The lower

piece of the trapping tower was plugged with a foam plug and filled with indicator Drierite. The upper part of the trapping tower was layered sequentially from the bottom with a foam plug, 15 g of Ascarite (1:1 mixture of 8-20 mesh and 20-110 mesh), a foam plug, 15 g of Ascarite, a foam plug, layer of Drierite, and a foam plug. The trapping tower was placed on top of each incubation flask using a Telfon sleeve. Trapping towers were changed weekly during the aerobic incubation period. The flasks for the main experiment were incubated at 22°C, while the flasks for the repeat experiment were incubated at 30°C.

The flasks were converted to anaerobic conditions by flooding the flasks with 100 mL of deionized water. Dried plant material was added to help maintain anaerobic conditions. The solution/soil mixtures were flushed with nitrogen by inserting a syringe needle into the sidearm septum to allow gas to escape at the same time that a syringe needle attached to a nitrogen line was inserted into other septum, followed by opening both stopcocks. The system was flushed with nitrogen for one hour. Trapping towers were assembled in syringe barrels to trap $^{14}CO_2$ during the anaerobic incubation period. Ascarite was sandwiched between two layers of glass wool and attached to the sidearm of the incubation flask using needle and rubber septum while the flask was purged with nitrogen. During the anaerobic incubation period of the main and repeat experiment the flasks were purged with nitrogen at weekly intervals which trapped the $^{14}CO_2$ in the towers. During the large-scale experiment, the flasks were purged every two weeks.

Analysis for the study were carried out by LSC, HPLC, GLC, GLC/RAD, and GLC/MS. Details are furnished for each in the study.

REPORTED RESULTS: The extraction, combustion, and CO_2 evolution data for the main experiment, conducted in three soils, are presented in Table 1. The data shows the continuous breakdown of acetochlor under anaerobic conditions with a corresponding loss in the amount of organic soluble material. There was a decrease in the amount of water soluble material in Ray and Drummer soils, but in Spinks soil the level remained nearly constant. The amount of $^{14}CO_2$ released per week dropped off dramatically after anaerobic conditions were introduced.

The total accountabilities for the main experiment were consistently high (Table 1). This probably was due to the fact that an unrepresentative sample of the soil was analyzed to define the soil-bound radioactivity. It was determined that in sampling the soil after extraction and centrifugation, an unrepresentative sample was being analyzed for bound residues. To obtain a sample for combus-

tion analysis, a portion of the soil was simply scraped from the residue in the centrifuge bottle, dried, and combusted. It became apparent that this was not a good way to sample, since a higher percentage of the very light and fine high organic content soil particles which centifuged down last make up a disproportionate portion of the sample that was removed. After developing this understanding for the high levels of soil-bound radioactivity and recoveries, the entire soil sample after centrifugation was homogenized before sampling. After this error in sampling was discovered, the Ray soil anaerobic study was repeated. In the repeat experiment the percent of soil bound radioactivity was consistently around 20% and the total recoveries were in the range of 80 to 90% as shown in Table 2. The repeat experiment was conducted over a longer period to determine if additional metabolism was occurring after longer incubation periods. In the repeat experiment only minor changes were seen in the distribution of metabolites between water- and organic-soluble materials. However, this study was conducted at 30°C as opposed to 22°C for the main experiment. At the higher temperature, the metabolism of acetochlor was much faster during the aerobic period, so that little remained to be metabolized when the anaerobic aging was initiated.

Most of the metabolites seen in the anaerobic study were formed during the aerobic portion of the experiment and were identified by comparison with the metabolite fractions from a large scale aerobic study in which a mix of $^{12}C/^{13}C/^{14}C$ acetochlor was used. Standards were used for comparison.

The large quantities used in the large-scale experiment were used in identification and characterization experiments. The chromatographic distribution of the metabolites from the main anaerobic experiment was determined, and then the corresponding metabolites were isolated from the large-scale experiment, characterized and in most cases identified.

The soils from the main, repeat, and large-scale experiments were extracted with an acetonitrile/water mixture. The extractable metabolites were partitioned between organic soluble metabolites and water soluble metabolites by extraction of the soil extract with methylene chloride. The methylene chloride fraction was analyzed by GC. The water soluble fraction was analyzed by HPLC. Radioactivity in the metabolite fractions was quantified. These results applied radioactivity between water soluble and organic soluble fractions is summarized in Tables 1 and 2. In all samples, water soluble metabolites accounted for more of the applied radioactivity than organic soluble metabolites. Table 8 and Figure 13 contain chemical names and structures of all compounds determined.

The organic soluble fraction from the soil extracts accounted for up to 25% of applied radioactivity. Table 3 gives a summary of the levels of organic soluble metabolites as determined by GLC/RAD. Unmetabolized acetochlor **X** was present in this fraction. At the end of the 30 day aerobic aging period, acetochlor represented 6.6, 14.0, and 12.6% of the applied radioactivity in Ray, Drummer, and Spinks soils, respectively. During the first 30 days of the anaerobic phase of the study, most of the acetochlor was metabolized, indicating rapid microbial degradation of acetochlor under anaerobic conditions.

Most of the metabolites identified in the organic soluble material were formed during the aerobic aging period and were gradually metabolized further during the anaerobic phase. No organic soluble accounted for more than 4% of the applied activity at any time. Organic soluble metabolites present at the end of the aerobic aging period included the sec-amide methyl sulfone **V**, the tert-amide nor chlor acetochlor **XI**, the tert-amide alcohol **XV**, the tert-amide methyl sulfone **XIV**, the tert-amide methyl sulfoxide **XIII**. Also present were the acetanilide **XXI**, the dione **XXII**, the sec-amide nor-chlor acetochlor **II**, and the tert-amide methyl sulfide **XII**.

The tert-amide methyl sulfide **XII** was the more abundant during the anaerobic soil study than during the aerobic soil metabolism study, where it was only detected as a minor metabolite as a shoulder on the peak for **XXI**. Metabolite **XII** probably accounted for most of the metabolite. However, the retention times were so close separation was not possible. The GC/CI mass spectrum of **XII** is shown in Figure 8. The organic soluble metabolites are numerous. No organic soluble metabolite of acetochlor accounted for more than 4% of the applied activity.

The water soluble fraction from the soil extracts accounted for a significant portion of the applied radioactivity after the 30 day aerobic aging period as shown in Tables 1 and 2. During the anaerobic incubation period, a slow loss of water soluble radioactivity was noted in the Ray and Drummer soils, but little change was seen in the Spinks soil. The water soluble metabolites were quantified by HPLC/RAD, and the results are summarized in Tables 4 and 5 for the main and repeat experiments. Three major metabolites formed under aerobic conditions decreased with time under anaerobic conditions. These three metabolites are the tert-amide oxanilic acid **XVII**, the tert-amide sulfinylacetic acid **XVII**, and the tert-amide sulfonic acid **XIX**. Also present in the water soluble fraction at the end of the aerobic aging period were acetic acid **VII**, the sec-amide oxanilic acid **VIII**, and the sec-amide sulfonic acid **IX**. The levels of the sec-amide oxanilic acid **VIII** and

the sec-amide sulfonic acid **IX** remained relatively constant during the anaerobic incubation period. Two metabolites increased significantly under anaerobic incubation. The tert-amide thioacetic acid **XX** was not observed as an early aerobic soil metabolite. Under anaerobic conditions, **XX** becomes a significant metabolite, accounting for 5.6% of the applied activity after 30 days of incubation under anaerobic conditions in Drummer soil, with somewhat lesser amounts in Ray and Spinks soils. On further aging the amount of thioacetic acid **XX** decreased with time. A CI mass spectrum was obtained by GLC/MS and is shown in Figure 10. Acetic acid (**VII**), is also formed from acetochlor under anaerobic conditions. In the soil extracts, there was a metabolite fraction that eluted near the void volume under the normal HPLC conditions used for metabolite quantification. When this fraction was isolated and reanalyzed under different conditions, one very polar metabolite accounted for as much as 90% of the total polar faction. Other minor metabolites were present in the polar fraction, which made quantification of **VII** difficult. An attempt to isolate this metabolite from the large scale experiment failed because the ^{14}C-label in the large scale experiment was located in the phenyl ring. The metabolite was isolated from the main experiment and the crude isolated material was derivatized with p-bromoaniline.

The data shows that acetochlor was rapidly degraded on a variety of soil types under anaerobic conditions, and that the aerobic soil metabolites of acetochlor were further degraded under anaerobic conditions. Acetochlor should not persist in the soil and does not appear to pose a hazard to the environment as it undergoes rapid microbial degradation under both aerobic and anaerobic conditions.

The half-life of acetochlor can be estimated by first-order kinetics. Figures 5, 6, and 7 contain plots of ln (% DPMA as acetochlor) versus days of anaerobic incubation for Ray, Drummer, and Spinks soils, respectively. The data for these calculations was taken from the main experiment, where acetochlor was quantified at 0, 30, and 60 days of anaerobic incubation (see Table 6). The half-life of acetochlor under anaerobic conditions was observed to range from 17 to 20 days, compared to the half-life of 8 to 12 days observed in soil under aerobic conditions. The half-lives of acetochlor in Ray silt loam, Drummer silty clay loam, and Spinks sandy loam were 17.3, 19.3, and 20.4 days, respectively.

The half-life of the three major aerobic soil metabolites of acetochlor present after the 30 day aerobic incubation phase were determined. The three metabolites present after 30 days of incubation were the tert-amide oxanilic acid **XVII**, the tert-amide sulfinylacetic acid **XVIII**, and the tert-amide sulfonic acid **XIX**. The half-live values for

XVII, XVIII, and XIX were estimated by first order kinetics. Of the three aerobic soil metabolites, the tert-amide sulfinylacetic acid XVIII had the shortest half-life, ranging from 28 to 59 days. The tert-amide oxanilic acid XVII had a half-life ranging from 59 to 100 days. The tert-amide sulfonic acid XIX had a half-life ranging from 51 to 88 days.

REVIEWER'S COMMENTS:

1. The recoveries ranged from 81.5% to 89.5% of applied radioactivity. There were numerous metabolites formed which continued to break down further into other metabolites. The continuous formation of metabolites could account for the low recoveries.

2. Other experiments were undertaken to verify the results of the main experiment due to sampling error. The results of further testing gave better recovery values and verified the initial data.

3. Volatiles formed other than CO_2 were not identified. However, volatiles other than CO_2 only made up 0.2 to 0.5% of the applied radioactivity.

4. The soil was sieved through a 16 mesh screen which is 1 mm instead of the 2mm required by the guidelines. However, in the anaerobic soil metabolism study this should not be of significants.

5. The location from which the soils were obtained was not given.

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

Page_____ is not included in this copy.

Pages 15 through 36 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

Shaughnessy No. 121601 STUDY 2 PM 25

CHEMICAL 2-Chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide

BRANCH Environmental Fate and Ground Water; 163-1

FORMULATION Radiolabelled active ingredient

MRID NO. 40198502

Campbell, D.H. and Hamilton, D.E. LEACHING AND ADSORPTION/DESORPTION STUDIES OF ACETOCHLOR. Sponsored and Submitted by Monsanto Agricultural Company, St. Louis, MO under Lab. Project No. MSL-9184; Study Completed August 1980, Received by EPA 19 Dec. 1989.

SUBST. CLASS: Herbicide

REVIEWED BY: Gail Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: (703)557-9734

SIGNATURE: Gail Maske 7 May '90

CONCLUSIONS:

The leaching adsorption/desorption studies are acceptable to meet Subdivision N data requirement. No further leaching adsorption/desorption data for acetochlor is required at this time.

Unaged soils column experiments were conducted using Ray silt loam, Drummer silty clay loam, Spinks sandy loam, and Lintonia andy soil. Freundlich adsorption coefficients were 0.4, 1.1, 1.6, 2.7 for Lintonia, Ray, Spinks, and Drummer soils, respectively. The aged acetochlor leaching experiment was conducted in Ray soil which indicated the major soil metabolites of acetochlor had greater mobility in soil than acetochlor. Soil thin-layer chromatography (TLC) demonstrated that acetochlor was mobile to very mobile in soils with organic matter content <2%. There appears to be a correlation between organic matter content of the soils and the strength of binding, as well. The desorption phase demonstrated that acetochlor was reversibly bound.

MATERIALS AND METHODS

Test materials: Radiolabelled [^{14}C-carbonyl]acetochlor (8.29 mCi/mmole) with a chemical purity of 99% as determined by GLC, was used for the unaged soil column experiments, adsorption/desorption experiments, and the thin-layer chromatography experiments. This material was synthesized by R.C. Freeman.

Radiolabelled [^{14}C-phenyl]acetochlor (11.35 mCi/mmole) with a radiochemical and chemical purity of 98% as determined by GLC/RAD and GLC, respectively, was used for the aged soil column experiments. This material was synthesized by R.C. Freeman in several steps from chloroacetyl chloride, ethyl-6-methylaniline[phenyl uniformly ring labelled ^{14}C], and chloromethyl ethyl ether.

The [^{13}C-carbonyl]acetochlor was prepared by D.H. Campbell. The chemical purity was 98% as determined by GC.

Standards: The standards of acetochlor metabolites were prepared by E.J. Breaux and K.C. Erickson.

Soil: Three viable soils (Ray silt loam, Drummer silty clay loam, and Spinks sandy loam) were used in the study. See Table 9 for the analytical analysis and content of each soil.

Equipment: See Figure 12.

Sampling:

Experimental procedure: A stock solution of [^{14}C-carbonyl]acetochlor was prepared in 0.01 N $CaSO_2$ for the adsorption/desorption studies. From this solution four solutions containing 21.0, 15.2, 7.4, and 3.5 ppm [^{14}C-carbonyl]acetochlor (8.29 mCi/mmole) in 0.01 N $CaSO_2$ were prepared. Into duplicate 16 x 125 mm glass tubes with Teflon-lined screw caps was placed 2.5 g (air-dried, <500 micron) of the appropriate soil and 10 mL of one of the acetochlor solutions. Tubes were also prepared without soil to determine applied activity. The tubes were shaken overnight at room temperature. The solution and soil were separated by centrifugation, and the amount of supernatant determined after decanting. Aliquots of the aqueous solution were taken in duplicate for LSC analysis.

The soils remaining after the adsorption step were subjected to four desorption cycles using 10 mL of a 0.01 N $CaSO_2$ solution which had been equilibrated with the appropriate soil. The solutions were shaken, ceantrifuged, and analyzed by LSC analysis.

For the soil column experiments, the experiment was conducted where the applied material was rapidly eluted, with no aerobic aging period. These experiments were conducted on Ray, Drummer, Lintonia, and Spinks soils. The soils were air dried and sieved to 1 mm. Water content was determined by lyophilization. Glass columns were constructed from 15 sections of glass tubing which were 1.5 inches in diameter and 2 cm long. The tubing was held together with pressure tape to insure a water tight seal. The columns were topped with a 10 cm section of glass tubing. At the lower end of all columns was secured a 43-mm I.D. Coors funnel by means of pressure tape. Glass wool was placed on the bottom of the columns and then the appropriate soil was added. Two columns were prepared for each soil. The soil was lightly tamped to insure uniform packing up to the top of the fifteen 2 cm sections. The total weight of the soil used ranged from 300 to 450 gms. (dry weight). Water was added to each of the columns to bring the moisture content to 75% of field capacity.

An aqueous solution of [^{14}C-carbonyl]acetochlor (8.29 mCi/mmole) was prepared which was 108.9 ug acetochlor/mL. A portion of this dosing solution, 2.25 mL, was added to the top of each column, which was equivalent to a 1.78 lbs/A treatment rate. After ten minutes, 580 mL of water was added to each column as rapidly as elution occurred. This is equivalent to 20 inches of rainfall.

The total effluent from each rapidly eluted column was measured, aliquoted, and analyzed by LSC. The effluent was extracted with methylene chloride. Aliquots of the aqueous and the organic layers were analyzed by LSC. The organic soluble fraction was analyzed by GLC/RAD. The aqueous fraction was frozen and lyophilized. The residue was dissolved in about 2 mL water and analyzed by HPLC/RAD.

Immediately after leaching was complete the soil segments from each column were separated, frozen, and lyophilized. The ^{14}C content of each segment was determined by combustion analysis. The three lower soil segments of each column were combined. These were the segments with the maximum activity. From the mixture a 50 g aliquot was taken and extracted four times with 100 mL of 30% acetonitrile/70% water. The extracts were combined and extracted with 180 ml methylene chloride. Aliquots of each layer were taken and counted by LSC. The methylene chloride layers were concentrated and analyzed by GLC/RAD. The water layers were frozen, lyophilized and analyzed by HPLC/RAD.

Soil column experiments were conducted where the applied material was aged under aerobic conditions for 30 days prior to elution of the columns with water. These experiments were conducted on Ray silt loam soil. The soils were air dried and sieved to 1 mm. Water content was determined by lyophilization. Glass columns were as described for the unaged soil columns. For the aged experiment, the upper section of the glass column was topped with a 34/45 outer joint that was equipped with a side arm containing a stopcock. Two columns were prepared for Ray soil.

An aqueous solution of [^{14}C-phenyl]acetochlor (11.35 mCi/mmole) was prepared that was 41.2 ug acetochlor/mL. A portion of this dosing solution, 5 mL, was added to the top of each column, which was equivalent to a 1.5 lbs/A treatment rate. These columns were immediately topped with a trapping towers which were used to trap volatiles a $^{14}CO_2$. The towers were constructed using two pieces. The lower piece of the trapping tower was plugged with a foam plug and filled with indicator, Drierite. The upper part of the trapping tower was layered sequentially from the bottom with a foam plug, 15 gms of Ascarite, a foam plug, 15 gms of Ascarite, a foam plug, Drierite, and a foam plug. The columns were allowed to age for 30 days. The Ascarite towers were changed at 15 day intervals throughout the study and analyzed for $^{14}CO_2$. After the aging period, water was added twice a week to the columns for 6.5 weeks at the rate of 0.5 inches of rainfall per day. The eluents were collected separately for each addition, generally for one to two days after each addition. There was no water eluted from either column after the first addition.

The individual fractions from the columns were measured, aliquoted and counted by LSC. The eluents were extracted with methylene chloride. Aliquots of both the water and methylene chloride layers were taken for LAC. The methylene chloride layers were concentrated and analyzed by GLC/RAD. The organics from the aged acetochlor columns were combined into early, middle, and late eluting fractions before analysis by GLC/RAD. The water layers were combined as groups of three into five fractions before analysis.

Immediately after leaching was complete the soil segments from each column were separated, frozen, and lyophilized. The ^{14}C content of each segment was determined by combustion analysis. The three upper segments of the aged acetochlor columns were combined. These were the segments with the maximum activity. From the mixture a 50 g aliquot was taken and extracted four times with 100 mL of 30% acetonitrile/70% water. The extracts were combined and extracted with 180 mL methylene chloride. Aliquots of each lay-

er were taken and counted by LSC. The methylene chloride layers were concentrated and analyzed by GLC/RAD. The water layers were frozen, lyophilized, and analyzed by HPLC/RAD.

For the soil thin-layer chromatography experiments, the four soil types were air dried and sieved to < 500 microns for Spinks and Lintonia soils and <250 microns for Ray and Drummer soils. Soil and distilled water were placed in a 1000 mL flask and shaken well. Water was added to form a free flowing slurry. Using a Shandon unoplane leveler and a Shandon adjustable spreader, the slurry was spread onto five glass TLC plates to a thickness of 0.030 inches. The plates were 20 cm by 20 cm. After drying well the soil was trimmed from the plates as shown below.

Radiolabelled glyphosate and propachlor were used as reference compounds. Stock solutions of these reference standards and acetochlor were prepared which contained approximately 100 ug/mL of the radiolabelled herbicide. Using a 10 uL syringe 10 one uL drops were applied to a 2 cm wide band. The plates were allowed to dry and were then placed in individual chromatography chambers. The soil TLC plate was connected to the development trough through a paper towel wick weighed down with a glass strip to insure good contact with the soil. The glass cover of the chromatography chamber was replaced, and the system was allowed to equilibrate for 15 minutes. Deionized water (75 mL) was then poured into the development trough through a hole in the glass cover. When the solvent front had completely moved across the soil, the TLC plate was removed and allowed to air dry horizontally overnight. The TLC plate was placed under a detector. The position of the solvent front and origin were marked with ^{14}C markers. Frontal R_f's of the standards were determined and found to agree reasonably well with previous data. Frontal R_f's of acetochlor were also determined on the four soils.

REPORTED RESULTS: The experimental data for the adsorption studies is presented in Tables 1 and 4 and Figures 1 to 4. The soil after desorption was not combusted, so total recovery (mass balance) data is not available.

The adsortion equilbria for acetochlor with these soils were evaluated using the Freundlich equation. C_s represented the amount of adsorbed acetochlor per unit amount of soil, and C_e represented the equilibrium solution concentration of acetochlor. The Freundlich adsorption were determined from the plot were $K = C_s$ when $C_e = 1$ ppm. The Freundlich adsorption coefficients obtained for the Lintonia, Ray, Spinks, and Drummer soils were 0.4, 1.1, 1.6, and 2.7, respectively. These Freundlich adsorption coefficients indicated that increases in the value of K

increased adsorption of the chemical. As a result it can be seen that soils containing a higher level of organic matter bind the acetochlor very tightly. Since acetochlor is intended for use primarily on high organic soils it can be concluded that acetochlor should be thightly bound under planned use conditions.

The desorption of acetochlor from the four soils is summarized in Tables 5 to 20, and show that with all four soil types less than 10% of the applied acetochlor remained bound to the soil after four extractions with 16 equivalents water. As shown in the adsorption study, Drummer silty clay loam soil bound the acetochlor more tightly than the other soils which is reflected in the Freundlich desorption constants given in Table 21. Therefore, soils with higher organic content not only will bind acetochlor tighter but release it slower.

The results of the unaged soil column experiments are given in Tables 22 to 25. Total recoveries averaged 90.9 $\pm$ 6.0% for the eight soil columns conducted. The level of applied activity remaining in each column is illustrated in Figure 5. The amount of radioactivity is shown to increase linearly down through the column. The Drummer soil retained more, approximately 57%, of the applied acetochlor than the Spinks soil and the Ray soil which retained approximately 44% and 35%, respectively. The Lintonia soil column retained only 4% of the applied acetochlor which was spread uniformly through the column.

The major organic soluble component in all soils was acetochlor. The tert-amide nor-chloro acetochlor **XI** made up 2.5 to 5.5% of the eluted ^{14}C-activity, Tert-amide alcohol made up 1.0 to 3.0% of the eluted ^{14}C-activity. The remainder of the organic soluble material consisted of several minor impurities present in the organic acetochlor. The water soluble soil metabolites found in the column eluent were the tert-amide oxanilic acid **XVII**, the tert-amide sulfonic acid **XIX**, the tert-amide sulfinylacetic acid **XVIII**, and the tert-amide thioacetic acid **XX**.

The radioactive material remaining on the soil was determined and found to closely paralled that found in the leachates. These findings supported the conclusion that only very limited metabolism occurred in the short time the acetochlor was on the soil columns.

The results of the aged soil column experiment are summarized in Table 27 and Figure 6. Total recoveries were 94.6 and 87.7% for the two soil columns. The distribution of the organic and water soluble portions is described in Table 27. The level of organic soluble materials remained relatively constant. However, the first fractions to elute contained a relatively high percentage of water soluble

material which dropped to a very low level in the final fractions. The water soluble fraction contained three major soil metabolites: tert-amide oxanilic acid **XVII** (14.6% of applied activity), tert-amide sulfinylacetic acid **XVIII** (7.1% of applied activity), and tert-amide sulfonic acid **XIX** (10.5% of applied activity). Low levels, less than 2%, of several other metabolites where found which were not identified. These distributions are shown in Table 28.

Very low levels of organic soluble ^{14}C activity eluted through the column. Only 0.5% of the applied activity eluted through the column as unchanged acetochlor. Two organic soluble metabolites (tert-amide methyl sulfoxide **XIII** and tert-amide methyl sulfone **XIV**) were found to elute and accounted for 0.2% and 1.1% of the applied ^{14}C activity, respectively. These two metabolites were found in later fractions collected from the aged column, as well.

Combustion analysis of soil from the column demonstrated that the ^{14}C radioactivity was concentrated in the top three soil sections (See Table 29 and Figure 7). It was determined that only 44% of the ^{14}C-radioactivity present in the soil could be extracted. After extractable radioactivity was partitioned between water and organic solvent, 14.6% was water soluble and 29.4% was organic soluble. Several metabolites, each accounting for <1% of the applied radioactivity, were also identified in the organic fraction. These metabolites were sec-amide nor-chloro acetochlor **II**, 2-chloro-2'ethyl-6'-methylacetanilide **I**, tert-amide alcohol **XV**, and tert-amide methyl sulfone **XIV**. Examination of the water soluble metabolites extracted from the top three sections showed that the same group of meta bolites were present. No single metabolite accounted for more than 3% of the applied radioactivity.

The results from the soil thin-layer chromatography experiments compared very well with the results obtained from the unaged soil column experiments. The results are given in Table 26.

On reviewing the acetochlor soil TLC data with Drummer silty clay loam and Spinks sandy loam soil acetochlor falls in the intermediated mobility class. Acetochlor would be classified as being mobile on Ray silt loam and very mobile on Lintonia sandy soils. This is the same trend that was demonstrated in the earlier adsorption/desorption and the soil column studies, and further supports the correlation between Freundlich adsorption coefficient, organic matter, and soil mobility. The Freundlich K values and % of material leached beyond 30 cm were 2.7 and 29.7, 1.6 and 42.4, 1.1 and 55.3, 0.4 and 96.0 for Drummer, Spinks, Ray, and Lintonia, respectively.

REVIEWER'S COMMENTS:

1. Only one soil was used for the aged soil column experiment. The worst-case scenario would be the soil with the lowest organic matter content which was the Lintonia sand. However, the organic matter content of the Ray silt soil was 1.2 which should give significant data of the environmental fate of acetochlor in nature.

2. The location from which the soils were obtained was not given.

3. The soil was sieved through a 16 mesh screen which is 1 mm instead of the 2 mm required by the quidelines. However, acetochlor and degradates were found to be mobile to very mobile on the 1 mm sieved soil. Therefore this mesh size is sufficient for acetochlor.

4. The soils after the desorption phase of the study was not combusted, so total recovery data was not furnished in data presented in Tables 1 to 4.

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