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**Alachlor
Terrestrial Field Dissipation
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Schneider, Ronald W. 1995. "Terrestrial Field Dissipation of Alachlor and its Metabolites at Hickman, California." Unpublished study performed by Environmental Science Department, Monsanto Company, St. Louis, MO, and ABC Laboratories, Inc., Columbia, MO, and Stewart Agricultural Research Services, Inc., Macon, MO, and Hulst Research Farm Service, Inc., Hughson, CA; and submitted by Monsanto Company, St. Louis, MO

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CONCLUSIONS:

This study is acceptable and can be used to partially satisfy the Terrestrial Field Dissipation data requirement. Taken together with a previously reviewed study conducted in Chico, California, the studies satisfy the Terrestrial Field Dissipation data requirement. No additional data are required.

Alachlor (Lasso® E.C.), applied once at 4 lb a.i./A, dissipated with a registrant-calculated half-life of 6.2 days from the 0-6 inch soil depth of a bareground plot of sandy loam soil in Hickman, California. The field was bareground to simulate preemergent application to a crop. In the 0-6 inch soil depth, alachlor averaged 1.363-1.458 ppm at 0-1 days posttreatment, 0.932 ppm on day 7 after application, and 0.220 ppm on day 21 after application. Alachlor remained mostly in the 0-6 inch soil depth. Detections averaging 0.018-0.046 ppm were reported in the 6-12 inch soil depth on days 0 and 1 after application.

The following degradates were detected in the soil:

[(2,6-diethylphenyl)amino]-2-oxoacetic acid (alachlor DM-oxanilic acid), which was detected in the 0-6 inch soil depth from day 1 through day 366 after treatment at average levels from 0.006-0.048 ppm (no clear pattern of formation or decline). The chemical was detected in the 6-12 inch soil depth only on day 182 after application, with an average value of 0.004 ppm.

[2-(2,6-diethylphenyl)methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid), which was detected in the 0-6 inch soil depth from day 0 through day 366 after application at average levels from 0.005 to 0.058 ppm, with no clear pattern of formation and decline. At three test intervals, detections were reported in the 6-12 inch soil layer. On days 0, 125, and 182, the oxanilate levels were 0.004, 0.004, and 0.013 ppm, respectively. The chemical was also detected in the 12-18 and 18-24 inch soil layers on day 182 after application, with average values of 0.007, and 0.008, respectively.

[N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl] sulfinylacetic acid (alachlor sulfinylacetic acid), which was observed at low levels in the 0-6 inch soil layer from day 1 to 182 after application, at average levels ranging from 0.002 to 0.017 ppm. In addition, the chemical was detected in the 6-12 and 18-24 inch soil layers on day 182 after application, with average values of 0.004 ppm in both cases,

and,

[2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid or ESA), which was observed at low levels from day 0 through day 366 after application at average levels ranging from 0.003-0.010 ppm. Detections were also reported in the 6-12 inch soil depth on days 182 and 366 after application, with average values of 0.004 and 0.008 ppm, respectively. Furthermore, the chemical was detected in the 12-18 inch soil depth on day 182 after application, with an average value of 0.003 ppm

PROCEDURES:

The procedures followed for this study appear in the report (MRID# 43774701), pages 14-20. The study protocol appears in pages 38-76 (Appendix-A). Some details about the procedure are sketched below:

Procedures followed in the field:

1. Five samples of soils from the field were used to characterize the physical and chemical properties of the soil in the site (% clay, % sand, % silt, %OM, bulk density, pH, CEC, and moisture capacity).

2. Samples were taken from the treated and check plots at regular intervals (approximately -1, 1, 3, 7, 14, 21, 30, 60, 120, 180, 365, and 545 days).
3. Six samples were collected from each of the three treated subplot and six samples were collected from the control plot. Check samples were collected first. Core holes were refilled with soil from a nontreated area. The samples were frozen immediately after collection (within four hours).
4. Four foot deep soil samples were collected from the check plot. For the treated plot a preexcavation of the 0-6 inch depth was performed, followed by sampling to a depth of 4 feet.
5. For each of six inch depth intervals three composited samples were made from the 18 soil cores. Each composited sample was made from two randomly selected cores from each subplot.
6. Weather data, including maximum and minimum air temperatures, and daily rainfall or irrigation were recorded.
7. The protocol provided form the analysis of parent alachlor and four major degradates (procedures discussed later): alachlor DM-oxanilate, alachlor oxanilate, alachlor sulfinyl acetate, and alachlor sulfonate.
8. A method validation (of the analytical procedures) was conducted by the analytical contract laboratory (ABC Laboratories, Inc., Columbia, MO). The soil used for this method validation was taken from Hickman, California.
9. During the analysis, laboratory fortifications were also tested, covering the range of validation. Calibration samples cover the following ranges for parent alachlor: 0.0025-0.1 $\mu\text{g}/\text{mL}$; for the metabolites: 0.05-1.00 $\mu\text{g}/\text{mL}$. For the fortified samples recoveries should lie in the range of 70-120%, after background correction.
10. Duplicate moisture analyses were conducted on check and treated samples.
11. The history of the test site was known and it had not been treated with Lasso® (alachlor) herbicide or related chemistry during the five years preceding the study.
12. The test substance, Lasso® herbicide, was applied using a tractor mounted broadcast sprayer, at a target application rate of 4.0 lb a.i./A.
13. To verify the application rate, polyurethane foam deposition plates were placed on the ground.

14. To maintain the field weed free, another maintenance herbicide, Roundup, was applied.

Procedure for moisture determination:

1. A 100 mL beaker was weighed and approximately 25 g of soil are weighed into the beaker. The beaker is placed in an oven at 110°C overnight.
2. The container is removed and allowed to cool to room temperature. The beaker is reweighed and the percent moisture is calculated.

Procedure used for the analysis of parent alachlor in soil:

1. Samples were received by the analytical laboratory in bags containing approximately 300-1400g of homogenized soil. While the samples were not in use they were stored in a freezer at -20°C.
2. Alachlor was extracted from the soil samples (~50 g) with a 9:1 mixture of methanol and water (100 mL), shaking for 30 minutes.
3. 20 mL of the supernatant are removed and placed in a 500 mL round bottom flask and 200 mL of water added and mixed.
4. A C18 solid phase extraction column is precleaned with 2-5 mL portions of ethyl acetate. Then it is activated with 5 mL 1:1 methanol/water, followed by 5 mL water.
5. The alachlor sample is aspirated (with the aid of a vacuum) through the SPE column.
6. The alachlor was eluted from the columns with 3 mL portions of 20% ethyl acetate/isooctane into 10 mL centrifuge tubes. Then the tubes are filled to the mark with 20% ethyl acetate/isooctane. Sodium sulfate is added. Dilutions are performed if necessary to obtain a peak within the expected range.
7. The alachlor samples are placed in GC vials. The test substance is quantitated by gas chromatography using a ⁶³Ni electron capture detector. A capillary column was used. Column temperature had a programmed ramp from 170°C to 250°C. The carrier gas is helium. (A second set of analysis conditions was also described to be used if the first set failed.) A calibration curve was generated for every set of samples run. Alachlor standards are prepared at five levels. These standards are distributed randomly throughout the actual samples.
8. It was observed that the untreated check soil samples did not have major interferences for this method. Similarly solvents and reagents had high purity and

did not constitute interferences as well.

Analytical method for the determination of alachlor's four major degradates:

1. Soil samples were stored frozen until time for analysis. Subsamples of the soil are taken for moisture determination.
2. 50.0 g soil samples were weighed into a 250 mL centrifuge bottle (fortifications were made at this time if applicable). Then 200 mL of 50% acetonitrile-water was added to the bottle. After shaking for approximately 30 minutes, the sample is centrifuged at -5 to +5°C.
3. The sample was then aspirated through a solid phase extraction column (10 g amine SPE column to which it is added 10.5 g of a mixture containing Florisil®, C₁₈, and decolorizing carbon). The column was previously conditioned with water, and 50% acetonitrile-water.
4. When the sample was passed through the SPE column, the eluant is collected in a 400 mL beaker. The eluate is quantitatively transferred to a round bottom flask and its contents is evaporated to approximately 1-2 mL at bath temperature between 40 and 50°C.
5. After the sample is cool, 4 drops of 8.5% phosphoric acid were added, 30 mL of acetonitrile, and, after swirling the flask, it is filtered (using a disposable syringe). The sample was evaporated to dryness by rotary evaporation.
6. The samples were dissolved in 3 mL of 15% acetonitrile-0.02 M potassium phosphate buffer (pH=6). The samples were filtered through a 0.2 µ. HPLC filter, and analyzed by HPLC using a C18 column and a UV detector (219 nm). A solvent gradient of acetonitrile-0.02 M potassium phosphate buffer (pH=6) was used. The system temperature was 45°C.

Analytical method for the determination of alachlor in rate verification samples (polyurethane foam pads):

1. The polyurethane foam pads dimensions were 12x12x0.5 inch. These pads were used to trap alachlor during the application of the herbicide.
2. Foam pads were kept frozen in metal cans until needed for analysis.
3. One liter of acetonitrile was added to the foam pads and allowed to soak for 2-3 minutes.

4. Using safety gloves, the foam pad was soaked in solvent, and the procedure was repeated. The foam pad was discarded.
5. 1.0 mL of the extract was pipetted to a 125 mL separatory funnel containing 50 mL of 20% ethyl acetate/iso-octane (v/v) and 50 mL of deionized water. The organic (upper) layer was saved and added 25 mL of 3 M NaCl (aq) and the extraction was repeated.
6. The organic extract was further diluted as necessary with 20% ethyl acetate in iso-octane (v/v).
7. The sample was analyzed by GC, equipped with a fused silica capillary column and a ⁶³Ni electron capture detector, with column temperature varying from 170 to 250°C.

RESULTS (as described by the registrant):

1. The test field had a sandy loam soil in the 0-6 inch soil depth, with a pH of 5.0 and 2.2% OM.
2. Temperatures were approximately within the normal range of historical air temperature data. Rainfall plus irrigation was higher than the average rainfall.
3. The lowest limit of method validation (LLMV) for parent alachlor was 0.005 ppm. The limit of detection (LOD) and the limit of quantitation (LOQ), based on the recoveries from samples fortified at the lower limit of method validation (LLMV) are as follows:

<u>Analyte</u>	<u>LOD (ppm)</u>	<u>LOQ (ppm)</u>
alachlor	0.002	0.008
alachlor DM-oxanilate	0.004	0.013
alachlor oxanilate	0.003	0.009
alachlor sulfinyl acetate	0.002	0.008
alachlor sulfonate	0.003	0.010

4. During method development, the recoveries of exogenous fortifications of alachlor in soil ranged from 94-119% using normal analysis conditions, and 85-116% for the alternate method.
5. For the validation of recoveries of alachlor degradates, the following ranges were observed:

alachlor DM oxanilic acid	71.5-85.5%
alachlor oxanilic acid	83.5-104%

alachlor sulfonic acid	86.7-110%
alachlor sulfinylacetic acid	88.5-96.6%

6. Polyurethane foam pads were fortified at rates equivalent to 1.4-5.0 lb/A. The recoveries ranged from 88.9-117.3%. The lower limit of method validation (LLMV) was 15,000 μg (corresponding to approximately 1.4 lb/A). The analysis of the samples in the field (six samples) yielded an average application rate of 4.10 lb a.i./A (target 4.0 lb a.i./A). The values ranged from 3.33 to 5.10 lb a.i./A.

7. The stability of the test substance was determined. After shipping and storage, a QC sample was retested. Results were as follows:

	(average wt. % alachlor 3,000 ppm, respectively)
QC sample prior to shipment	45.40
returned QC sample	53.67

The registrant suspects that the cap of the QC container was not sealed properly. As possible evidence for this, the registrant noted that the returned QC sample had only 83% of the volume remaining after shipping and storage.

8. Using a first-order spatial variability model of Gustafson and Holden (1990), the following results were obtained:

DT_{50} =6.23 days
 DT_{90} =28.7 days

The registrant indicates that the half-life observed in this study compares with previously reported studies. An acceptable study previously reviewed had shown an observed half-life of 11 days. The study was conducted in Chico, California.

9. Alachlor was a maximum of 1.458 ppm on day 1 after application in the 0-6 inch soil layer, it was 0.287 ppm on day 14 after application and 0.015 ppm on day 85 after application. Alachlor was last observed on day 182, when the average value was 0.002 ppm.

10. Alachlor was confined only to the 0-6 and 6-12 inch soil layers. Detections in the 6-12 inch soil layer were reported, averaging 0.046 ppm on day 0 and 0.018 ppm on day 1 after treatment

11. Alachlor DM-oxanilate was observed from day 1 to day 366 after application, with average values ranging from 0.006 to 0.048 ppm. There is no clear pattern of formation-decline for this degradate.

12. Alachlor oxanilate was observed from day 0 to day 366 after application at average levels ranging from 0.005 to 0.058 ppm. There is no clear pattern of formation and

decline for this degradate. The oxanilate was observed in the 6-12 inch soil layer on days 0, 125, and 182 (average values ranging from 0.004-0.013 ppm). On day 182 the degradate was observed at low levels (0.007-0.008) ppm in the 12-18 and 18-24 inch soil depth.

13. Alachlor sulfinyl acetate was observed at low levels from day 1 to day 182 after application (average values 0.002-0.017 ppm), with no clear pattern of formation and decline. The chemical was observed in the 6-12 and the 18-24 inch soil depths at very low values (average 0.004 ppm).
14. Alachlor sulfonate was observed at very low levels from day 0 to 366 after application. The average values ranged from 0.003 to 0.010 ppm. The chemical was observed in the 6-12 inch soil layer on days 182 and 366 after application (average 0.004 and 0.008 ppm, respectively). It was also observed in the 12-18 inch soil layer on day 182 after application (average 0.003 ppm).

COMMENTS:

1. All soil samples were kept frozen; however, for samples from day 366 after application, the temperature rose above 32°F when samples were removed from the freezer. Samples remained frozen.
2. The plot had been planted to tomatoes, dry beans, potatoes, and cabbage during the five years prior to treatment with alachlor. Various pesticides were applied.
3. Analysis of the soil characterization of the soils in the field show a soil series Hanford and soil texture sandy loam through 0-48 inch soil depth. The % organic matter decreased gradually from 2.2% in the 0-6 inch soil depth to 0.3% in the 42-48 inch soil depth.
4. During the study, the maintenance pesticide Roundup was applied to the plots on seven occasions.
5. The depth to the water table at the test site was 40-45 ft.. The plot area slope is 0.5%.
6. The target application rate at the treated plot was 4.0 lb a.i./A
7. The first significant rainfall/irrigation event after application of alachlor occurred on day 2, with 0.70 inch water applied. Artificial irrigation was applied to the test site by a sprinkler and/or flood type system.
8. In order to obtain a better picture of the pattern of decline of alachlor, there would be a need for a sampling interval between day 30 and day 85 after application.

There is a sharp decrease in the concentration of alachlor between these two test intervals (from 0.167 to 0.015 ppm).

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Alachlor EFED Review

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Pages 10 through 20 are not included.

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