

DATA EVALUATION RECORD
STUDY 3

5/31/1994

CHEM 090501

Alachlor

§164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 42528001

Schott, M.L., and M.A. Schlicher. 1990. Terrestrial field dissipation of alachlor at two sites in California. Laboratory Project No. MSL-10395. Unpublished study performed by Monsanto Agricultural Company, St. Louis, MO, Pan-Agricultural Laboratories, Inc., Madera, CA, and Chemtec, Inc., Chico, CA; and submitted by Monsanto Agricultural Company, St. Louis, MO.

STUDY ID 42528002

Schlicher, M.A., and M.L. Schott. 1991. Terrestrial field dissipation of alachlor metabolites in Chico, California. Laboratory Project No. MSL-10844. Unpublished study performed by Monsanto Agricultural Company, St. Louis, MO, Pan-Agricultural Laboratories, Inc., Madera, CA, and Chemtec, Inc., Chico, CA; and submitted by Monsanto Agricultural Company, St. Louis, MO.

STUDY ID 42528003

Schneider, D.A. 1991. Storage stability of alachlor and alachlor metabolites in soil. Laboratory Project No. MSL-11592. Unpublished study performed and submitted by Monsanto Agricultural Company, St. Louis, MO.

STUDY ID 42528004

Kludas, R.S. 1991. PANAG Laboratory quality assurance and site information, terrestrial field dissipation of alachlor at two sites in California. Laboratory Project No. 0624-89-1. Unpublished study performed by Pan-Agricultural Laboratories, Inc., Madera, CA, and Chemtec, Inc., Chico, CA; and submitted by Monsanto Agricultural Company, St. Louis, MO.

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REVIEWED BY: M. Dillman
EDITED BY: K. Ferguson
W. Martin
APPROVED BY: W. Spangler

TITLE: Staff Scientist
TITLE: Task Leader
Asst. Task Leader
TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: José Luis Meléndez
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 703-305-7495

SIGNATURE:

José Luis Meléndez
5/31/94

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study can be used towards the fulfillment of data requirements.
2. Alachlor (Lasso 4-EC; 2-chloro-2',6'-diethyl-N-methoxymethyl-acetanilide; 4 lb ai/gallon EC), applied once at 4 lb ai/A, dissipated with an observed half-life of approximately 11 days from a plot of loam/sandy clay loam soil in California that was planted to corn immediately after treatment. Alachlor did not appear to leach into the soil below 18 inches. The degradates [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid (oxanilic acid), [N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl]sulfinylacetic acid (sulfinylacetic acid), and [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (sulfonic acid) were detected primarily in the upper 12 inches of the soil. The degradate [(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid) was detected only intermittently in the soil to a depth of 36 inches.
3. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the dissipation of alachlor and four of its degradates from field plots of loam/sandy clay loam soil in California that were treated with the emulsifiable concentrate formulation of alachlor at the proposed use rate of 4 lb ai/A.
4. This study may be used to support the registration of alachlor at an application rate of ≤ 4 lb ai/A for the emulsifiable concentrate formulation; additional data may be required for sites at which the proposed use rate is greater.

Ancillary Study - Freezer Storage Stability

1. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) was stable in sandy loam soil fortified at 0.05 ppm and stored frozen at $<0^{\circ}\text{C}$ for 194 days. The sodium salts of the alachlor degradates [(2,6-diethylphenyl)amino]-2-oxoacetic acid (alachlor DM-oxanilic acid), [N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl]sulfinylacetic acid (alachlor sulfinylacetic acid), and [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid) were stable in sandy loam soil fortified at 0.05 ppm and stored frozen at $<0^{\circ}\text{C}$ for 566 days. Data submitted for [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid) showed higher variability, but it suggests that the chemical is stable.

METHODOLOGY:

Alachlor (Lasso 4-EC; 2-chloro-2',6'-diethyl-N-methoxymethyl-acetanilide; 4 lb ai/gallon EC, Monsanto) was broadcast applied and

preplant incorporated at 4 lb ai/A to a plot (80 x 100 feet) of loam/sandy clay loam soil (0- to 18-inch depth: 42-56% sand, 22-30% silt, 22-28% clay, 1.0-2.4% organic matter, pH 6.5-6.6, CEC 16.8-19.8 meq/100 g) near Chico, California, on June 22, 1989. The plot was then planted to corn. An untreated plot (20 x 100 feet) located 75 feet from the treated plot was maintained as a control. Soil samples were collected from the treated and control plots prior to treatment, at 0, 1, 3, 7, 11, 14, 18, 21, 44, and 78 days, and approximately 3, 4, 6, 9, and 12 months posttreatment. For the purpose of sampling, the treated plot was divided into three subplots (each 20 x 100 feet) separated by 10-foot borders. At each sampling interval, five 4-foot soil cores were randomly collected from each subplot of the treated plot and from the control plot. The upper soil cores (0- to 6-inch depth) were collected by the can excavation technique, and the lower cores (6- to 48-inch depth; 1.5-inch diameter) were collected with continuous corers equipped with plastic sleeves. The lower soil cores were divided into 6- to 12-, 12- to 18-, 18- to 24-, 24- to 36-, and 36- to 48-inch segments. The soil segments from the treated plot were composited by subplot, soil depth, and sampling interval; the soil segments from the control plot were composited by soil depth and sampling interval. The composited samples were thoroughly homogenized, then stored frozen at -20 to 32°F for up to 3 and 17 months prior to extraction for alachlor and its degradates, respectively. Extracts were stored for up to 17 days prior to analysis.

For the analysis of alachlor, subsamples (50 g) of the soil were extracted with methanol:water (9:1, v:v) by shaking on a reciprocating shaker for 30 minutes. After the extraction, the slurries were allowed to settle for >30 minutes; an aliquot of the supernatant was removed, diluted with water, and then applied to a C-18 solid-phase extraction column. Alachlor was eluted from the columns with ethyl acetate:isooctane (20:80, v:v), and the eluate was filtered through sodium sulfate. Aliquots of the filtered eluate were analyzed by GC with electron-capture detection. The identification and quantitation of alachlor in the extracts were achieved by comparison to an alachlor reference standard. The detection limit was 0.005 mg/kg. The average recoveries from soil samples fortified with alachlor were 91.3-100% (Master Summary Table of MRID 42528001). The results of the analysis of the soil samples were corrected for the average recovery and were expressed on a dry soil basis.

For analysis of the sodium salts of the alachlor degradates [(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid), [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid (oxanilic acid), [N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl]sulfinylacetic acid (sulfinylacetic acid), and [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (sulfonic acid), subsamples (50 g) of the soil were extracted with acetonitrile:water (50:50, v:v; 60:40 if high clay content) by shaking for 30 minutes. After the extraction, the slurries were

centrifuged and the supernatants were decanted. The extracts were diluted with water, then applied to C-18:Florisil:activated carbon amine solid-phase extraction columns. The eluates were collected, and the columns were rinsed with acetonitrile:water (50:50, v:v); the eluates and rinsates were combined. The combined solutions were concentrated on a water bath at 40-50 C, then acidified with dilute phosphoric acid. The acidified solutions were diluted with acetonitrile, filtered (0.2 um), and concentrated by rotary evaporation. The residues were dissolved in acetonitrile:pH 6 potassium phosphate buffer (15:85, v:v), and the solutions were filtered (0.2 um). Aliquots of the filtrates were analyzed by HPLC using a Zorbax or Supelco C-18 column eluted with an acetonitrile:-potassium phosphate buffer (pH 6) gradient; the column was equipped with UV (219 nm) detection. Compounds were identified by comparison to reference standards of the four degradates. The detection limit for each degradate was 0.01 mg/kg. The average recoveries from soil samples fortified with alachlor DM-oxanilic acid, alachlor oxanilic acid, alachlor sulfinylacetic acid, or alachlor sulfonic acid were 82.0-94.8%, 76.9-90.7%, 83.6-98.7%, and 84.9-103%, respectively (Raw Data Table of MRID 42528002). The results of the analysis of the soil samples were corrected for the average recovery for each analyte, and were expressed on a dry soil basis in alachlor equivalents.

Freezer Storage Stability:

Portions of sandy loam soil (56% sand, 34% silt, 10% clay, 0.7% organic matter, pH 7.0, CEC 5.9 meq/100 g) were fortified at 0.05 ppm with alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; purity 99.7%, Monsanto) dissolved in ethanol. Additional portions of the soil were fortified with a mixture of the sodium salts of the alachlor degradates [(2,6-diethylphenyl)amino]-2-oxoacetic acid (alachlor DM-oxanilic acid), [2-(2,6-diethylphenyl)(methoxymethyl)-amino]-2-oxoacetic acid (alachlor oxanilic acid), [N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl]sulfinylacetic acid (alachlor sulfinylacetic acid), and [2-(2,6-diethylphenyl)-(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid), each at 0.05 ppm; the degradates were dissolved in ethanol. The fortified soil samples were stored frozen at <0°C; duplicate samples were removed for analysis at intervals up to 194 days posttreatment for alachlor and 566 days for alachlor degradates. The recoveries from soil samples fortified with alachlor were 78.3-85.9%. The recoveries from soil samples fortified with alachlor DM-oxanilic acid, alachlor oxanilic acid, alachlor sulfinyl acetic acid, or alachlor sulfonic acid were 86.2-87.7%, 125-156%, 80.6-83.6%, and 86.6-87.3%, respectively.

DATA SUMMARY:

Alachlor (Lasso 4-EC; 2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; 4 lb ai/gallon EC), at 4 lb ai/A, dissipated with a registrant-calculated half-life of 6 days and an

observed half-life of approximately 11 days from a plot of loam/sandy clay loam soil in Chico, California that was treated in June 1989 and immediately planted to corn. In the 0- to 6-inch soil depth, alachlor averaged 0.781-0.798 ppm at 0 and 1 days posttreatment, 0.641 ppm at 7 days, 0.350 ppm at 11 days, 0.244 ppm at 14 days, 0.082 ppm at 21 days, and ≤ 0.039 ppm at 44 through 389 days (Table 1 of MRID 42528001). In the 6- to 12-inch soil depth, alachlor averaged 0.029-0.231 ppm at 7-18 days posttreatment, and < 0.005 ppm at all other sampling intervals; in the 12- to 18-inch soil depth, alachlor averaged 0.007-0.051 ppm at 11-18 days posttreatment, and < 0.005 ppm at all other sampling intervals; in the 18- to 24-inch depth, alachlor averaged 0.045 ppm at 14 days posttreatment, and ≤ 0.006 ppm at all other sampling depths; and in the 24- to 36- and 36- to 48-inch depths, alachlor averaged ≤ 0.007 ppm at all sampling intervals. Two samples showed ≥ 0.124 ppm at 14 days both in the 12- to 18- and 18- to 24-inch soil depths. In addition, five minor detections occurred at 24- to 36- and 36- to 48-inch soil depths, at ≤ 0.016 ppm at 11-18 days. The degradates detected in the soil were [2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid),

[N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxoethyl]sulfinylacetic acid (alachlor sulfinylacetic acid),

[2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (alachlor sulfonic acid), and

[(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid).

In the 0- to 6- and 6- to 12-inch soil depths, alachlor oxanilic acid averaged ≤ 0.047 ppm through 44 days posttreatment; alachlor sulfinylacetic acid averaged ≤ 0.039 ppm through 44 days; alachlor sulfonic acid averaged ≤ 0.027 ppm through 44 days; and DM-oxanilic acid averaged ≤ 0.020 ppm at 0 through 78 days (Tables 1-4 of MRID 42528002). The degradates were not detected in the upper 12-inches of soil after 44-77 days posttreatment and, with the exception of sporadic detections apparently due to contamination, were not detected below the 12-inch soil depth at any sampling interval.

Rainfall plus irrigation totaled 4 inches through 9 days posttreatment, 6 inches through 18 days, and 37 inches throughout the entire study. The air temperatures ranged from 26 to 108 F. The soil temperatures were not provided. The depth to the water table was 10-30 feet, and the slope of the plot was $< 1\%$.

Freezer Storage Stability Data:

Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; purity 99.7%) was stable in sandy loam soil fortified at 0.05 ppm and stored frozen at < 0 C for 194 days. Throughout the study, recoveries of alachlor were 80-98% (0.040-0.049 ppm; Table 3); there was no discernable pattern of decline.

[(2,6-Diethylphenyl)amino]-2-oxoacetic acid (alachlor DM-oxanilic acid; purity 89.7%),
[N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxoethyl]sulfinylacetic acid (alachlor sulfinylacetic acid; purity 94.3%), and
[2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (alachlor sulfonic acid; purity >95%)
were stable in sandy loam soil fortified at 0.05 ppm and stored frozen at <0°C for 566 days. Throughout the study, the recoveries of alachlor DM-oxanilic acid, alachlor sulfinylacetic acid, and alachlor sulfonic acid were 68-90% (0.034-0.045 ppm), 66-96% (0.033-0.048 ppm), and 70-96% (0.035-0.048 ppm), respectively (Table 4).

Recoveries of

[2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid; purity 94.8%)
were 90-172% (0.045-0.086 ppm) in sandy loam soil fortified at 0.05 ppm and stored at <0°C for 566 days, with no discernible pattern of decline.

COMMENTS:

1. A similar study was conducted at a second site (Madera, CA) at 4 lbs ai/A, but the concentrations of alachlor in the soil at time 0 were too low (<0.1 ppm) to accurately assess the dissipation of alachlor under these test conditions. According to the study authors, no explanation was found for the low residue levels. Sampling at the Madera site was discontinued at 180 days posttreatment and apparently no attempts were made to isolate degradates from the soil.
2. Close examination of the soil composition reveals an increasing amount of clay content as the soil depth increases (pages 3.11B to 3.11D). There was a 28% clay in the 0- to 6-inch soil depth, it increases to 42% at 18- to 24-inch soil depth, and to 56% in the 36- to 48-inch soil depth. This increasing clay effectively reduces the flow of water in the soil, decreasing the possibility of leaching of both parent alachlor and its degradates. It is possible that under conditions that would favor the flow of water in the soil, alachlor would have been detected in deeper soils.
3. Alachlor data were variable at individual sampling intervals (e.g. 0.251-1.20 ppm at time 0, 0- to 6-inch depth); nonetheless, average results demonstrated a reasonable pattern of dissipation of alachlor over the course of the study. Similar variability was observed for each of the degradates. Additionally, the degradate DM-oxanilic acid was observed intermittently in the samples collected from the control plot at up to 0.026 ppm.
4. Although the samples for this field study were stored frozen at -24 to 32°F, the freezer storage stability study was conducted at <0 F. The stability study should have been conducted under conditions which more closely paralleled those employed in the actual field study.

5. Field data for irrigation and rainfall for this test site reported in MRID 42528001 differ markedly from the data provided in MRID 42528004. Because the irrigation data reported in MRID 42528001 were provided by the field office, the Dynamac reviewer has assumed that these data are correct. Additionally, the rainfall data provided in MRID 42528001, collected at Beale AFB in California, are assumed to be correct; the source of the rainfall data in MRID 42528004 was not specified.
6. Upon review of the field information provided in Appendix C, it appears that the descriptions of the two test sites provided within the main body of the original document ("Results and Discussion") were reversed.
7. Prior to alachlor application, the test plots were cultivated and fertilized. Before planting, the corn seeds were treated with captan and thiram. The test plots were cultivated and disced intermittently throughout the study, and the corn was harvested on December 4, 1989. Apparently, no additional pesticides were applied during the study.
8. The pesticide treatment history was provided for the 3 years preceding this study. In 1986 and 1987, the plots were planted to walnuts; in 1986, Roundup liquid (glyphosate), Surflan liquid (oryzalin), and Goal liquid (oxyfluorfen) were applied at 2 pints/A (three applications), 4 quarts/A (two applications), and 4 quarts/A, respectively; in 1987, Diazinon WP, Ridomil liquid (metalaxyl), Aliette WP (fosetyl-AI), and Roundup liquid were applied at 1 quart/A, 2.5 gallons/A, 2.5-7.5 lbs/A (three applications), and 2 pints/A (two applications), respectively. In 1988, the site was fallow, and no chemicals were applied.
9. At the time of application, wind speeds were ≤ 1 miles/hour from the west, the cloud cover was 0%, the air temperature was 61.6 F, and the soil temperature was 72.8°F and 71.6°F at a 1- and 2-inch depth, respectively; additionally, the soil was dry.
10. The study authors stated that samples were not collected within 6 feet of the edge of each treatment area.
11. Examination of the equation used to determine the percent moisture reveals that it was determined on the basis of the "wet" weight $[(\% \text{moisture} = \text{weight of wet sample} - \text{dried weight}) / \text{weight of wet sample}] \times 100$. Generally, the % moisture is determined on the "dried" weight basis (dividing by the "dried" weight). Reviewer estimation indicates that the use of this equation leads to values up to about 7% smaller than the actual ones, depending on the % moisture.

Freezer Storage Stability Data:

1. Data for alachlor oxanilic acid (applied at 0.05 ppm) was variable. Throughout the study, alachlor oxanilic acid results varied by as much as 0.041 ppm, with no discernible pattern of decline. According

to the study author, the abnormally high recoveries of alachlor oxanilic acid were due to an interference in the sample matrix that could only be partially separated from alachlor oxanilic acid during chromatographic analysis.

2. The study author stated that statistical analysis of the storage stability data for the degradates alachlor sulfinylacetic acid and alachlor oxanilic acid showed significant increases in concentration over time. The magnitude of the increase was 130% of the initial concentration for alachlor oxanilic acid and 120% for alachlor sulfinylacetic acid at 480 days posttreatment. This would suggest an overestimation of the residue levels reported in the field dissipation study.
3. The soil samples fortified in this study were collected from the 0- to 6- soil depths at a test site in Chico, California, that had been used for a terrestrial field dissipation study. The soil at this depth was classified as a sandy loam.
4. The reported results for the storage stability samples were not corrected for recoveries of analytical check standards.