

US EPA ARCHIVE DOCUMENT



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

1 MAR 1993

March 1, 1993

MEMORANDUM

Subject: Metolachlor RED Candidate

From: Henry Jacoby, Chief  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

To: Lois Rossi, Chief  
Reregistration Branch  
Special Review and Reregistration Division (H7508W)

Fred Betz, Acting Chief  
Science Analysis and Coordination Staff  
Environmental Fate and Effects Division (H7507C)

Attached is the Environmental Fate and Ground Water package for the List A RED. This package contains reviews of all data (DER's included) received prior to 25 February 1993 and an Environmental Fate assessment. Only two guidelines are not considered fully satisfied at this time (terrestrial field dissipation [164-1] and confined rotational crops [165-1] data requirements).

In the environmental fate and transport assessment of metolachlor, the chemical has been identified as a potential leacher to ground water. The chemical is listed in the Pesticides in Ground-Water Database as being detected in ground water. Further evaluation of the ground water contamination issue will be scheduled with the Ground-Water Technology Section of the EFGWB for review. A projected due date will be given as GWTS evaluates the degree of difficulty and its present priorities.

The additional data requested for terrestrial field dissipation studies (164-1) will help determine the efficiency and precision of extraction and analysis for metolachlor and several of its degradates in field studies. This information will not qualitatively change the assessment of the persistence and mobility of metolachlor. It will, however, better quantitate the rates of metolachlor dissipation through degradation and movement down the soil profile. These data will also be essential to validate input

parameters and results of any higher tier EEC, ground water or surface water modeling that might be needed.

The additional information on the confined rotational crop study (165-1) will confirm the application rate and allow EFGWB to determine residue levels in rotated crops at the maximum rate of metolachlor application.

**ENVIRONMENTAL FATE AND GROUND WATER BRANCH**

**Review Action**

To: Walt Waldrop, PM #71 and Connie Childress, PM# 74  
 ReRegistration Division (H7508W) Registration Division (H7505C)

From: Paul Mastradone, Ph.D., Section Chief *Paul J Mastradone*  
 Environmental Fate Review Section #1  
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief *Henry Jacoby*  
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

DP Barcode:	D185152, D172022		
Common Name:	Metolachlar	Trade name:	DUAL
Company Name:	Ciba Corporation		
ID #:	108801		
Purpose:	List A RED		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
Herbicide	606,627,660	90-0286,0546,0567,0605;920308,930187	80 days

**STATUS OF STUDIES IN THIS PACKAGE:**

Guideline	#MRID	Status of Data Requirement <sup>2</sup>
161-1	42999901	S
161-2	40430202	S
161-3	40430203	S
162-1	41309801A,41309801	S
162-2	41309801B	S
163-1	40494602-40494606	S
163-2	40494606	S
164-1	41484201-41484206	N
	41309802-41309805	
	41335701,41335702	
165-1	41470601	N

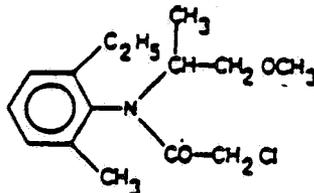
Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved.

1.0 CHEMICAL:

Common name: Metolachlor

Chemical name: 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide

Chemical Structure:



2.0 TEST MATERIAL: <sup>14</sup>C-Metolachlor and unlabeled Metolachlor

3.0 STUDY/ACTION TYPE: RED and review environmental studies submitted for registration

4.0 STUDY IDENTIFICATION:

Spare, William, C. 1987. Leaching Characteristics of Parent Metolachlor. Study Conducted by Agrisearch Incorporated, Frederick, Md. for the Agricultural Division of Greensboro, N.C. MRID No. 404946-02.

Spare, William, C. 1987. Determination of the Hydrolysis Rate Constants of Metolachlor. Study Performed by Agrisearch Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404302-01.

Spare, William, C. 1987. Determination of the Solution Photolysis Rate Constant and Photodegradation Products of Metolachlor under Natural and Artificial Light. Study Conducted by Agrisearch Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404302-02.

Spare, William, C. 1987. Soil Photolysis of Metolachlor under Natural and Artificial Light. Study Conducted by Agrisearch Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404302-03.

Spare, William, C. 1987. Leaching Characteristics of Aged Metolachlor. Study Conducted by Agrisearch Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404946-03.

Spare, William, C. 1987. Determination of Adsorption/Desorption Constants of Metolachlor. Study Conducted by Agriseach Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404946-04.

Spare, William, C. 1988. Determination of Adsorption Constants of CGA-51202. Study Conducted by Agriseach Incorporated, Frederick, Md. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404946-05.

Spare, William, C. 1987. The Volatilization of Metolachlor from Soil. Study Conducted by Agriseach Incorporated, Frederick, Md. for Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. 404946-06.

Spare, William, C. 1989. Identification of Unknown Metabolites of Metolachlor in Aerobic Soil Metabolism. Report No. ABR-89093. Study Performed and Submitted by Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41309801-A.

Spare, William, C. 1989. Soil Metabolism of Metolachlor under Aerobic, Aerobic/Anaerobic, and Sterile Conditions. Agriseach Project No. 1258. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro N.C. MRID No. 41309801-B.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site A. Agriseach Project No. 1264-A. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41309802.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site A. Amendent to MRID No. 41309802. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484201.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site A. Agriseach Project No. 1265-A. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41309803.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site A. Amendment to MRID No. 41309803. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484202.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site B. Agriseach Project No. 1264-B. Study Performed by Agriseach Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41335701.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site B. Amendment to MRID No. 41335701. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484203.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site B. Agrisearch Project No. 1265-B. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. 41335702.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in Iowa-Site B. Amendment to MRID No. 41335702. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484204.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in California-Site C. Agrisearch Project No. 1264-C. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41309804.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in California-Site C. Amendment to MRID No. 41309804. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484205.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in California-Site C. Agrisearch Project No. 1265-C. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41309805.

Merricks, D.L. 1989. Metolachlor Field Dissipation Study in California-Site C. Amendment to MRID No. 41309805. Study Performed by Agrisearch Incorporated, Frederick, Md. for Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41484206.

Thede, B. 1990. Uptake of <sup>14</sup>C-Metolachlor in Rotational Crops Grown in Soil which has been Previously Used for Growing Potatoes. Laboratory/Study No. ABR-90037. Study Performed and submitted by Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 41470601.

5.0 REVIEWED BY:

George Tompkins  
Entomologist, Review Section 1  
EFGWB/EFED

Signature: *George Tompkins*  
Date: **E** 1 MAR 1990

6.0 APPROVED BY:

Paul Mastradone  
Section Chief, Review Section 1  
EFGWB/EFED

Signature: *Paul Mastradone*  
Date: **E** 1 MAR 1993

## 7.0 CONCLUSIONS:

The LUIS report (dated 18 June 1992) indicates that metolachlor has terrestrial food crop, terrestrial food+feed crop, terrestrial feed crop, and terrestrial non-food crop use sites. The sites listed are for alfalfa, cabbage, peppers (chili type), potato, legume vegetables, lupine, peanuts, peas, safflower, sorghum, soybean, corn, cotton, commercial/industrial lawns, golf course turf, nonagricultural rights-of-way/fencerows/hedgerows, ornamental and/or shade trees, ornamental herbaceous plants, ornamental lawns and turf, and ornamental woody shrubs and vines. It may be applied preplant, preemergence, or postplant. It is listed that it can be applied by aerial means, ground, granule applicator, spreader, pneumatic applicator, or center pivot irrigation.

### 7.1 Status of Data requirements:

<u>Data requirements</u>	<u>MRID No.</u>	<u>Terrestrial Food/Non-Food</u>
Hydrolysis (161-1)	404302-01	Satisfied
Aqueous Photolysis (161-2)	404302-02	Satisfied
Soil Photolysis (161-3)	404302-03	Satisfied
Aerobic Soil Metabolism (162-1)	41309801-A 41309801-B	Satisfied
Anaerobic Soil Metabolism (162-2)	41309801-B	Satisfied
Anaerobic Aquatic Metabolism (162-3)	411857-01	Satisfied
Aerobic Aquatic Metabolism (162-4)	411857-01	Satisfied
Leaching/Adsorp/Desorp (163-1)	404946-02 404946-04, 404946-03, 404946-05	Satisfied
Laboratory Volatility (163-2)	404946-06	Satisfied
Terrestrial Field Dissipation (164-1)	41309802 41484201, 41309803, 41484202, 41335701, 41484203, 41335702, 41484204, 41309804, 41484205, 41309805, 41484206	Not satisfied/ upgradeable
Confined Crop Accumulation (165-1)	41470601	Not satisfied/ upgradeable
Accumulation in Fish (165-4)	411542-01	Satisfied

Since metolachlor can be applied by aerial application it would trigger the following spray drift data requirements:

Droplet Size Spectrum (201-1)

Drift Field Evaluation (202-1)

Since Ciba-Geigy Corporation is a member of the Spray Drift Task Force, the data requirements for these data requirements are reserved.

7.2. EFGWB concludes that the following studies for registration of metolachlor for Terrestrial Food Crop, Terrestrial Food + Feed

Crop, Terrestrial Feed Crop and Terrestrial Non-Food Crop uses are acceptable and satisfy the data requirements:

a). Hydrolysis (161-1), MRID No. 404302-01. Metolachlor is stable to hydrolysis at pH 5.0, 7.0, and 9.0. The study information indicated that no significant degradation of metolachlor from hydrolysis occurred during the 30 day test period. No calculation of rate constant or half-life were performed.

b). Photodegradation in Water (161-2), MRID No. 404302-02. Metolachlor had a reported half-life of 70 days when exposed to natural sunlight and 0.17 day when exposed to an artificial light source (450 watt medium pressure mercury arc lamp with a light intensity of 4500-4800 uW/cm<sup>2</sup>). Numerous degradation products (see Fig. 1 for structure and nomenclature) were isolated and the ones in greatest quantities after 30 days from natural sunlight exposure were CGA-41638 (3.63%), CGA-51202 (3.54%), CGA-46129 (3.42%), CGA-50720 (3.20%), and parent metolachlor remaining was 62.92%. After 8 hours exposure to artificial light the identifiable degradates occurring in greatest quantities were CGA-48081 (8.64%), CGA-51202 (5.59%), and CGA-46129 (5.02%) with 36.13% parent metolachlor remaining.

c). Photodegradation on Soil (161-3), MRID No. 404302-03. Metolachlor had a reported half-life of 8 days when exposed to natural sunlight and when exposed to artificial light conditions (mercury arc lamp with intensity of 1600-2400 uW/cm<sup>2</sup>) the half-life was 37 days. The major degradates after 21 days exposure to natural light were CGA-51202 (a maximum of 3.4% of applied radiocarbon), CGA-37735 (maximum of 9.0%), CGA-41638 (maximum of 5.7%), CGA-40172 (6.2%), and CGA-37913 (7.3% of applied radiocarbon). After 30 days exposure to artificial light the major degradates reported were CGA-41638 (a maximum of 6.4% of applied radiocarbon) and CGA-13656 (1.7% of applied radiocarbon).

d). Unaged Leaching and Adsorption/Desorption (163-1), MRID No. 404946-04 and 404946-02. Unaged metolachlor was shown to range from being highly mobile in a sand soil ( $K_d$  of 0.08) to moderately mobile ( $K_d$  value of 4.81) in a sandy loam soil from column leaching studies using four soils. In these studies the leachate contained from 15.03% to 82.91% of the applied radioactivity (75.50% of the applied radioactivity was parent metolachlor, 1.14% was CGA-51202, 3.69% was CGA-37735, and 2.26% was CGA-41638). In batch equilibrium studies employing the same four soils the reported Freundlich adsorption ( $K_{ad}$ ) values ranged from 0.108 to 2.157 and the reported desorption constants ranged from 0.38 to 3.59. These results indicated that metolachlor has the potential to be a moderately mobile material in the clay soil and sandy loam soil used and the potential to be highly mobile in the loam soil and sand soil used.

e). Aged Leaching and Adsorption/Desorption (163-1), MRID No. 404946-03 and 404946-05. The reported cumulative  $K_d$  for aged metolachlor and its degradates in columns of an Iowa sandy loam soil was 2.01, indicating that metolachlor and its identified degradates (CGA-51202, CGA-37735, and CGA-41638) have the potential to be mobile. It is to be noted that in other studies (MRID Nos. 404946-02, 404946-04, and 404946-05) metolachlor and its CGA-51202 degradate leached the slowest in the Iowa sandy loam soil in comparison to their leaching rate in the other three soils tested. In batch equilibrium studies the CGA-51202 degradate was shown to have the potential to be an extremely mobile. The reported Freundlich adsorption ( $K_{ad}$ ) values for CGA-51202 ranged from 0.04 in the Maryland sand soil to 0.171 in the Iowa sandy loam soil indicating that this metolachlor degradate has the potential to be extremely mobile in the four soils tested.

f). Laboratory Volatility (163-2), MRID No. 404946-06. Metolachlor in the granular (Dual 25G) and emulsifiable concentrate (Dual 8E) forms did not dissipate very rapidly from the soil and it appears that volatility was not a significant mode of dissipation of metolachlor from the soil used. When nitrogen with 0 percent humidity was purged through the soil, no detectable (detection limit was 0.035% of the dose per day) metolachlor was found to volatilize from the soil. When the humidity was increased to 100% in the nitrogen and purged through the soil, approximately 0.05% of the metolachlor dose was volatilized per day.

g). Aerobic Soil Metabolism (162-1), MRID No. 41309801-A and 41309801-B. Metolachlor degraded under aerobic conditions with a reported half-life of 67 days in a sandy loam soil. The major metabolite was CGA-51202 (maximum of 28.09% of the applied radioactivity at 90 days posttreatment). Other identified metabolites were CGA-37735 (a maximum of 1.27% at 30 days), CGA-50720 (maximum of 14.85% of applied at 272 days), CGA-41638 (maximum of 2.06% at 90 days), and CGA-13656 (maximum of 1.02% immediately posttreatment). Other metabolites that were detected but not quantifiable were CGA-40172, CGA-41507, CGA-40919, and CGA-37913.

h). Anaerobic Soil Metabolism (162-2), MRID No. 41309801-B. Metolachlor degraded with a reported half-life of 81 days in a sandy loam soil that was incubated under anaerobic conditions for 60 days at approximately 25°C following 30 days of aerobic incubation. The major degradate in both the soil and flood water was CGA-51202 (at a maximum of 23.33% of the applied at 29 days after anaerobic conditions were established). Other identified degradates were CGA-37735 (maximum of 1.25% of the applied radioactivity at 29 days), CGA-41638 (maximum of 8.30% at 60 days), CGA-13656 (maximum of 1.46% at 29 days), and CGA-50720 (maximum of 7.34% at 60 days).

7.3. EFGWB concludes that the following studies submitted for registration of metolachlor are upgradeable and require further information from the registrant (see 10.0-Discussion of Individual Studies):

a). Terrestrial Field Dissipation (164-1), MRID No. 41309802, 41484201, 41309803, 41484202, 41335701, 41484203, 41335702, 41484204, 41309804, 41484205, 41309805, and 41484206. Metolachlor (Dual 8E) surface applied at 4.0 lb ai/A and 6 lb ai/A to a silt loam soil in one site in Iowa had a reported half-lives in the top 0-6 inch soil layer ranging from 7 to less than 28 days. Metolachlor was reported at a maximum concentration of 1.52 ppm in the 6-12 inch soil layer (22 days posttreatment and concentrations of  $\leq 0.09$  ppm at depths below 12 inches. The metabolite CGA-51202 was a maximum of 0.15 ppm at the 6-12 inch soil depth and  $< 0.05$  ppm below 18 inches. CGA-40172 and CGA-40919 were detected at 0.07 ppm and 0.21 ppm in the 36-48 inch soil layers. CGA-50720 was not detected ( $< 0.07$  ppm) in any soil sampled at any interval.

Metolachlor (Dual 25G) applied at 4.0 lb ai/A and 6.0 lb ai/A to the same type of silt loam soil had reported half-lives of 141 days in the 0-6 soil layer in the plot planted to corn and 159 days in the bareground plot. Metolachlor was detected in the 36-48 inch soil layer. The field test sites received over 40 inches of water during the study period.

In a second test site in Iowa (silty clay loam soil) Dual 8E and Dual 25G were applied at 4 lb ai/A and 6 lb ai/A and the reported half-life in the upper 6 inches of soil ranged from 117 days to 144 days in both the bare ground plots and plots planted to soybeans immediately after posttreatment. Metolachlor was detected ( $< 0.09$  ppm) below 24 inches (up to 48 inches). The test site received over 40 inches of water during the test period.

In California field dissipation studies conducted in loamy sand soil, the half-life of metolachlor (Dual 8E) applied at 4 lb ai/A and 6 lb ai/A ranged from 97 to 132 days from the upper 6 inches. Metolachlor was reported to be  $\leq 0.07$  ppm below 18 inches (up to 36 inches). Metolachlor (Dual 25G) applied at 4 and 6 lb ai/A in the same loamy sand soil in California had a reported half-life of 193 to 292 days from the upper 6 inch soil layer. Metolachlor was primarily found in the 6-12 and 12-18 inch soil layers and reportedly  $\leq 0.07$  ppm below 18 inches (up to 36 inches). In both studies conducted in California the total water applied during the study totaled 16.9 inches.

b). Confined Accumulation in Rotational Crops (165-1), MRID No. 41470601. Metolachlor residues accumulated in lettuce, beets, and wheat planted 115 days after [ $^{14}$ C]metolachlor was applied at approximately 3.0 lb ai/A to a loamy sand soil

subsequently planted to potatoes. At mature harvest, total [<sup>14</sup>C]residues were 0.32 ppm in lettuce; 0.66 and 0.86 ppm in beet tops and roots; and 2.86, 0.14, and 1.17 ppm in wheat stalks, grain, and hulls, respectively. Metolachlor, CGA-13656, CGA-40172, CGA-41638, CGA-42444, CGA-37913, and CGA-118243 were detected in all crops.

#### ENVIRONMENTAL FATE ASSESSMENT

Although the environmental fate data base is not complete the information from all acceptable and upgradeable environmental fate data from the 1980 Registration Standard to present indicate that parent metolachlor appears to be moderately persistent to persistent. It also ranges from mobile to highly mobile in different soils and it has been detected in ground water. Metolachlor is stable to hydrolysis under normal environmental conditions of pH 5.0, 7.0, and 9.0. Metolachlor degradation appears to be dependent on microbially mediated (aerobic soil metabolism  $t_{1/2}$ =67 days, anaerobic soil metabolism  $t_{1/2}$ =81 days) and abiotic processes (photodegradation in water  $t_{1/2}$ =70 days under natural sunlight and photodegradation on soil  $t_{1/2}$ =8 days under natural sunlight). The major degradates were identified as CGA-51202, CGA-50720, CGA-41638, CGA-37735, and CGA-13656 (see Table 1 for structures).

Depending on the soil characteristics metolachlor has the potential to range from a moderately mobile to a highly mobile material ( $K_d$  values ranging from 0.08 to 4.81). Upgradeable field dissipation studies indicate that metolachlor is persistent in the surface soil ( $t_{1/2}$  ranging from 7 days to 292 days the upper 6 inch soil layer). Metolachlor was reportedly detected as far as the 36 to 48 inch soil layer in some of the studies. The degradate CGA-51202 was detected (0.11 ppm) as far as the 30-36 inch soil depth (MRID No. 41335701); CGA-40172 was detected as far as the 36-48 inch depth (MRID No.41309802); CGA-40919 was detected in the 36-48 inch depth (0.21 ppm in MRID No.41309802), and CGA-50720 was not detected (0.07 ppm) in any soil segment at any interval.

Metolachlor appears to have a low potential to bioaccumulate in fish with a reported whole body bioconcentration factor of 69 and a whole body elimination of 93% after 14 days depuration. In an upgradeable confined accumulation in rotational crop study <sup>14</sup>C-metolachlor residues accumulated in lettuce, beets, and wheat planted 115 days after metolachlor was applied. Total <sup>14</sup>C residues were 0.32 ppm in lettuce; 0.66 and 0.86 in beet tops and roots; and 2.86 ppm, 0.14 ppm and 1.17 ppm in wheat stalks, grain, and hulls, respectively.

The pesticide in ground water data base indicates that residues of metolachlor were detected in wells in 20 states. Levels exceeded the Health Advisory level (100 mg/l) in 3 wells located in Wisconsin, New York, and Montana. In 8 other states concentrations in some well waters exceeded 10% of the HA.

## ENVIRONMENTAL FATE SUMMARY

Metolachlor appears to be stable to hydrolysis at pH's of 5, 7, 9 without significant degradation of parent material after 30 days. The aqueous photolysis half-life was 70 days when exposed to natural sunlight and 0.17 day when exposed to artificial sunlight (450 watt mercury arc lamp with light intensity of 4500-4800 uW/cm<sup>2</sup>). After 30 days exposure to natural sunlight the degradation products (see Table 1 for structure) were CGA-41638 (3.63% of applied radiocarbon), CGA-51202 (3.54%), CGA-46129 (3.42%), CGA-50720 (3.20%), and parent metolachlor remaining was 62.92%. The soil photolysis half-life of metolachlor when exposed to natural sunlight was 8 days, and when exposed to artificial light conditions (mercury arc lamp with intensity of 1600-2400 uW/cm<sup>2</sup>) the half-life was 37 days. The major degradates reported after 21 days exposure to natural sunlight were CGA-51202 (maximum of 3.4% of applied radiocarbon), CGA-37735 (9.0%), CGA-41638 (5.7%), CGA-40172 (6.2%), and CGA-37913 (maximum of 7.3% of applied radiocarbon).

Under aerobic soil conditions metolachlor degraded with a half-life of 67 days in a sandy loam soil. The major metabolite was CGA-51202 (maximum of 28.09% of applied radioactivity at 90 days posttreatment). Other identified metabolites were CGA-37735 (maximum of 14.85% at 272 days), CGA-41638 (maximum of 2.06% at 90 days), and CGA-13656 (maximum of 1.02% immediately posttreatment). Other metabolites that were detected but not quantifiable were CGA-40172, CGA-41507, CGA-40919, and CGA-37913. The aerobic aquatic metabolism half-life of metolachlor was 47 days. The major metabolites in the sediment were CGA-41507 (3.34% of applied radiocarbon at 29 days), CGA-50720 (1.17%), CGA-40172 (1.13%), CGA-46127 (1.54%) and parent metolachlor was 34.56%. In the water fraction after 29 days incubation parent metolachlor was 30.90% and the metabolite CGA-41507 was 1.21% and CGA-51202 was 1.99%.

Under anaerobic soil conditions metolachlor degraded with a half-life of 81 days in a sandy loam soil that was incubated under anaerobic conditions for 60 days at 25°C following 30 days of aerobic incubation. The major degradate in both the soil and flood water was CGA-51202 (maximum of 23.33% of applied radiocarbon at 29 days after anaerobic conditions were established); and other reported degradates were CGA-37735 (1.25% at 29 days), CGA-41638 (8.30% at 60 days), CGA-13656 (1.46% at 29 days), and CGA-50720 (maximum of 7.34% at 60 days). The anaerobic aquatic metabolism half-life for metolachlor was 78 days. In the anaerobic waters the major degradates were CGA-40172 (maximum of 5.64% at 12 months), CGA-37913 (maximum of 4.28% at 6 months), CGA-46127 (maximum of 4.69% at 12 months) and CGA-41507 (maximum of 4.85% at 6 months). The major degradates in the sediment were CGA-41507 (maximum of 15.88% of applied radiocarbon at 12 months), CGA-40172 (maximum of 3.18% at 12 months), CGA-46127 (maximum of 13.02% at 12 months), CGA-50720 (maximum of 1.67% at 29 days), and CGA-37913 (maximum of 2.33% at 6 months), and after 12 months the sediment contained 1.47% parent metolachlor.

In the unaged portion of the leaching and adsorption and desorption study metolachlor was shown to range from being highly

mobile in a sand soil ( $K_d$  value of 0.08) to being moderately mobile ( $K_d$  value of 4.81 in a sandy loam soil) from column leaching studies using four soils. The leachate contained from 15.03% to 82.91% (comprised of 75.5% parent metolachlor, 1.14% of CGA-51202, 3.69% of CGA-37735, and 2.26% CGA-41638) of the applied radioactivity. In batch equilibrium studies employing the same four soils, the Freundlich adsorption ( $K_{ad}$ ) values ranged from 0.108 to 2.157. This data indicates that metolachlor has the potential to range from being a moderately mobile material (clay soil and sandy loam soil) to being a highly mobile material (loam soil and sand soil). In the aged leaching portion of the leaching and adsorption and desorption study the reported cumulative  $K_d$  for aged metolachlor and its degradates in columns of an Iowa sandy loam soil was 2.01. This indicates that metolachlor and its identified degradates (CGA-51202, CGA-37735, and CGA-41638) have the potential to be mobile since in other studies it was shown that metolachlor and its CGA-51202 degrade leached the slowest in the Iowa sandy loam soil compared to their leaching rate in the other three soils tested. Batch equilibrium studies showed that CGA-51202 has the potential to be extremely mobile with reported Freundlich adsorption ( $K_{ad}$ ) values ranging from 0.04 in the Maryland sand to 0.171 in the Iowa sandy loam soil. Laboratory volatility studies indicated that volatility is not a significant mode of dissipation for metolachlor from the soil. The maximum dissipation was 0.05% of the metolachlor dose volatilizing per day.

In numerous terrestrial field dissipation studies using metolachlor (Dual 8E and Dual 25G) both applied at 4 and 6 lb ai/A the half-life of metolachlor in the 6-12 inch soil layer ranged from 7 days (Iowa) to 292 days (California) with a range of the total water applied ranging from 16.97 inches to >40 inches during the study period. Detections of metolachlor were made as far as the 36-48 inch soil layer in some of the tests. The degrade CGA-40172 (0.07 ppm) and CGA-40919 (0.21 ppm) were detected in the 36-48 inch soil layers in one Iowa site. CGA-50720 was not detected (<0.07 ppm) in any soil sampled at any interval.

Metolachlor appears to have a low potential to bioaccumulate in fish with a reported whole body bioconcentration factor of 69X and a whole body elimination of 93% after 14 days depuration. The confined accumulation in rotational crop data indicates that metolachlor residues accumulated in lettuce, beets, and wheat planted 115 days after metolachlor was applied. Total  $^{14}C$  residues were 0.32 ppm in lettuce; 0.66 and 0.86 in beet tops and roots; and 2.86 ppm, 0.14 ppm and 1.17 ppm in wheat stalks, grain, and hulls, respectively.

## 8.0 RECOMMENDATIONS:

The environmental fate data base is not complete at this time. However, the additional information that would be supplied for the  
164-1 Terrestrial Field Dissipation, and  
165-1 Confined Rotational Crop  
studies is unlikely to change the overall environmental fate assessment for metolachlor.

Parent metolachlor has been found to be persistent and mobile in acceptable laboratory studies. Metolachlor degradation products were also found to be mobile in laboratory studies.

The additional data requested for terrestrial field dissipation studies (164-1) will help determine the efficiency and precision of extraction and analysis for metolachlor and several of its degradates in field studies. This information will not qualitatively change the assessment of the persistence and mobility of metolachlor. It will, however, better quantitate the rates of metolachlor dissipation through degradation and movement down the soil profile. These data will also be essential to validate input parameters and results of any higher tier EEC, ground water or surface water modeling that might be needed.

The additional information on the confined rotational crop study (165-1) will confirm the application rate and allow EFGWB to determine residue levels in rotated crops at the maximum rate of metolachlor application.

#### 9.0 BACKGROUND:

#### 10.0 DISCUSSION OF INDIVIDUAL STUDIES:

Twelve field dissipation studies were submitted to support the registration of metolachlor. Each was scientifically valid, yet they did not fulfill the 164-1 data requirement because the control samples fortified at 0.05 to 5.0 ppm (all degradates) or up to 10.0 ppm (metolachlor) carried through the procedure with test samples indicated a wide variation in the recovery efficiencies. For example in one study the recovery efficiencies varied from 24 to 211% of the applied metolachlor and additionally extremely wide variations in the recovery efficiencies of the degradates were observed (see Individual DERs). It was requested for the registrant to submit a written explanation specifying these variations in recovery for each field dissipation study. Upon receipt of an explanation regarding the wide variations in the recovery results, each study will be reevaluated.

The confined accumulation in rotational crops (MRID No. 41470601) study is considered supplemental but upgradeable. The data from analysis of day 0 was not provided and thus the application rate could not be confirmed. Information regarding the immediate posttreatment soil data is requested. Upon receipt of that data the study will be reevaluated.

#### 11.0 COMPLETION OF ONE-LINER:

#### 12.0 CBI APPENDIX:

## DATA EVALUATION RECORD

### STUDY IDENTIFICATION:

Spare, W.C. 1987. Determination of the Hydrolysis Rate Constants of Metolachlor. Study performed by Agrisearch Incorporated, Frederick, MD. for Ciba-Geigy Corporation, Agricultural Division, Greensboro, NC. MRID No. 404302-01.

TYPE OF STUDY: Hydrolysis (161-1)

### REVIEWED BY:

George Tompkins, Entomologist  
Review Section 1, EFGWB, EFED

Signature: *George Tompkins*  
Date: 25 FEB 1993

### APPROVED BY:

Paul J. Mastradone, Section Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: 25 FEB 1993

### CONCLUSIONS:

1. This study is satisfactory and satisfies the hydrolysis data requirements.
2. The study information indicates that metolachlor is stable to hydrolysis at pH 5.0, 7.0, and 9.0. A rate constant or a half-life calculation were not made.
3. The material balance at each pH tested was >96%.

### MATERIALS AND METHODS:

Analytical [U-ring-<sup>14</sup>C]-metolachlor (specific activity 26.2 uCi/mg, 99.7% purity) was used in this study and several standards (see Table 1) were used to monitor any degradation. The water solubility of metolachlor is 530 ppm at 20°C. All glassware used in the study was sterilized by autoclaving and the buffer solutions sterilized by filtration through a 0.22 µ filter. The buffer solutions (pH 5.0 was 0.01 M sodium acetate; pH 7.0 was a phosphate buffer; and the pH 9.0 was 0.025 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) were prepared using distilled, deionized water.

The test systems used were 25 ml screw capped glass scintillation vials with teflon lined screw caps. The <sup>14</sup>C-metolachlor (specific activity 26.2 uCi/mg) was dissolved with 5 ml acetone. Of this radioactive solution, 6.5 µl were removed and mixed with 20 ml of buffered solution to achieve a final

theoretical dose of 10 ppm. Two replicates of 20 ml each of each buffer solution were prepared in 25 ml glass vials. Sampling intervals for the hydrolysis studies were: 0, 1, 3, 7, 14, and 30 days. At the final sampling, microbial plating check was performed to confirm the sterility of all solutions.

At each sample interval duplicate 25 ul aliquots of each <sup>14</sup>C-metolachlor solution were radioassayed by LSC immediately after sampling. All prepared solutions were maintained in the laboratory in an incubator at 25±1°C and were covered with foil to maintain darkness. Aliquots of each hydrolysis solution were analyzed by single dimension TLC and each sample spot was overspotted with non-labeled metolachlor. All standards were chromatographed next to samples. The TLC plates were developed in either of 2 single dimension solvent systems: 1) chloroform/methanol/formic acid/water (75/20/4/2, v/v/v/v), or 2) dichloromethane/ethyl acetate (9/1, v/v). The plates were developed to a solvent front of 15 cm, air dried, and visualized at 254 nm.

#### REPORTED RESULTS:

1. Analysis of the percent of parent metolachlor from each sampling at each pH showed that metolachlor did not hydrolyze during the study (Table 4).
2. The material balance of total radioactivity during the study varied from 99.69-103.51% at pH 5.0, 97.16-104.26% at pH 7.0, and 96.77-105.94% at pH 9.0 (Table 3).
3. The pH remained relatively constant for all three concentrations (Table 2), with a variation of 4.98-5.10 for the pH 5 solution, 6.92-6.99 for the pH 7 solution, and 8.96-9.01 for the pH 9 solution.

#### DISCUSSION:

It appeared that no significant degradation of metolachlor from hydrolysis occurred during the 30 day test period. Therefore no calculations of rate constant and half-life were performed. At pH ranges normally found in the environment it appears from the study data that metolachlor does not degrade from hydrolysis.

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3/1/93 EFED memo

Metatackler

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## DATA EVALUATION RECORD

STUDY IDENTIFICATION: Spare, William, C. 1988. Determination of Adsorption Constants of CGA-51202. Study Conducted by Agrisearch Incorporated, Frederick, MD. for the Agricultural Division of Ciba-Geigy Corporation, Greensboro, N.C. MRID No. 404946-05.

TYPE OF STUDY: Leaching/Adsorption/Desorption (163-1)

REVIEWED BY:

George Tompkins, Entomologist  
Review Section 1, EFGWB, EFED

Signature: *George Tompkins*  
Date: 25 FEB 1993

APPROVED BY:

Paul J. Mastradone, Section Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: 25 FEB 1993

CONCLUSIONS:

1. EFGWB concludes that this study is acceptable and partially satisfies the leaching/adsorption/desorption data requirements by providing information from batch equilibrium studies on the potential of CGA-51202 (N-(2'-methoxy-1'-methylethyl)-2-ethyl-6-methyl-oxalic acid anilide) to leach in four soils. This study combined with three other leaching/adsorption/desorption studies (MRID Nos. 404946-02, 404946-03, and 404946-04) fulfills the leaching/adsorption/desorption data requirement.
2. It can be concluded that CGA-51202 has the potential to be an extremely mobile material in the four soils tested. The reported Freundlich adsorption ( $K_{ad}$ ) values were 0.04 in the Maryland sand soil, 0.079 in the Maryland clay soil, 0.086 in the Mississippi loam soil, and 0.171 in the Iowa sandy loam soil. The reported desorption constants ranged from 9.49 to 9.99.

MATERIALS AND METHODS:

Chemical: [phenyl ring-<sup>14</sup>C]-CGA-51202, specific activity of 13.1 uCi/mg, radiopurity 97.9%, and analytical standard of CGA-51202.

Four soils (a Maryland clay, a Maryland sand, a Mississippi loam, and an Iowa sandy loam soil, see Table 1 for characterization) were sieved through a 2 mm mesh sieve prior to use. The soils were oven dried at 90°C for 24 hr and autoclaved for 60 min at 121°C prior to use in the study. For the preliminary and definitive test, stock solutions of the radioactive compound and non-labeled compound were prepared in acetonitrile. A 305 ul volume of the nonradioactive stock and 100

ul of the radioactive stock were diluted to 160 ml using deionized, distilled and boiled water containing 0.01 N calcium ion to obtain a final nominal concentration of 10 ug/ml. Aqueous dilutions of this nominal 10 ug/ml solution were prepared in sterile solution containing 0.01 N calcium ion to provide the following concentrations for the study: 10 ug/ml, 5 ug/ml, 1 ug/ml, 0.5 ug/ml, 0.2 ug/ml and control concentration of 0.00 ug/ml.

The test system for this study was each capped centrifuge tube of soil, solution and CGA-51202. Prior to initiating the study, a test for potential interferences due to the test container was conducted. Two types of containers (polypropylene and borosilicate glass) were checked for absorbance of CGA-51202. Prior to the definitive testing, each soil was tested to establish the ratio of soil to stock solution and equilibration time for use in the adsorption and desorption phases of the study. The range finding test was performed in duplicate using the highest concentration (10 ug/ml) of CGA-51202 to be tested. After the equilibration shaking time and solution to soil ratios were determined, the adsorption phase of the study was performed.

Samples of prepared soil (5 gm each) were placed in 50 ml polypropylene centrifuge tubes in duplicate for each test solution concentration. Twenty five ml of CGA-51202 stock solution at 0.00, 0.2, 0.5, 1.0, 5.0, and 10.0 ug/ml was transferred to appropriate containers and capped. The sample set was shaken for 18 hrs. Following centrifugation (1000 x g for 15 min), the equilibrium concentrations ( $C_e$ ) of CGA-51202 were determined. Solutions remaining after adsorption were decanted and residual soils were used for the desorption phase of the study. Twenty five ml of calcium ion solution, at 0.01 N without CGA-51202 was added to the soils. Prior to the addition of the calcium ion solution, all soil samples (wet) were re-weighed to correct for remaining adsorption solution in the final calculations. The entire sample set was shaken for 4 hrs and samples were centrifuged (1000 x g for 15 min) and the supernatant analyzed by LSC to determine  $C_e$ . All solutions were analyzed by direct LSC. Soils were oxidized and generated  $^{14}\text{CO}_2$  was trapped.

#### REPORTED RESULTS:

1. The reported Freundlich adsorption ( $K_{ad}$ ) values for CGA-51202 were 0.040 in the Maryland sand soil, 0.79 in the Maryland clay soil, 0.086 in the Mississippi loam soil, and 0.171 in the Iowa sandy loam soil (Table 9). The reported desorption constants ranged from 9.49 to 9.99.
2. Results of the preliminary study indicated that solution equilibrium was achieved by 2 hours.
3. The radiocarbon balance from the range finding study averaged 97.9% (Table 4).

## DISCUSSION:

1. LSC analysis of control samples showed that less than 10% of CGA-51202 was lost after 72 hr due to adsorption to polypropylene or borosilicate glass centrifuge tubes.

2. Results of TLC analyses of aliquots of the highest solution concentration from adsorption showed that no degradation of CGA-51202 was observed. The results demonstrated that CGA-51202, with reported Freundlich adsorption constants ( $K_{ads}$ ) ranging from 0.04 to 0.171, has the potential to be an extremely mobile material in the soils tested.

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Metelachlor

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## DATA EVALUATION RECORD

STUDY IDENTIFICATION: Spare, W. C. 1987. Determination of Adsorption/Desorption Constants of Metolachlor. Study Conducted by Agriseach Incorporated, Frederick, MD. for Ciba-Geigy Corporation, Agricultural Division, Greensboro, N.C. MRID No. 404946-04.

TYPE OF STUDY: Leaching/Adsorption/Desorption (163-1)

REVIEWED BY:

George Tompkins, Entomologist  
Review Section 1, EFGWB, EFED

Signature: *George Tompkins*  
Date: 25 FEB 1993

APPROVED BY:

Paul J. Mastradone, Section Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: 25 FEB 1993

CONCLUSIONS:

1. EFGWB concludes that this study is acceptable and partially satisfies the unaged portion of the leaching and adsorption/desorption data requirements. This study provides information on the potential of metolachlor to leach in four soils from batch equilibrium studies. This study combined with three other leaching/adsorption/desorption studies (MRID Nos. 404946-02, 404946-03, and 404946-05) fulfills the leaching/adsorption/desorption data requirement.

2. It can be concluded that metolachlor has the potential to be a very mobile material in the soils tested with reported Freundlich adsorption ( $K_{ad}$ ) values of 0.108 in the Maryland sand soil, 0.773 in the Mississippi loam soil, 1.869 in the Maryland clay soil, and 2.157 in the Iowa sandy loam soil. The reported desorption constants ranged from 0.38 to 3.59 in these same four soils..

MATERIALS AND METHODS:

Chemical: [phenyl ring-<sup>14</sup>C]-Metolachlor (CGA-24705), specific activity 26.2 uCi/mg, radiopurity 97.8%.

Four soils (a Maryland clay, a Maryland sand, a Mississippi loam, and an Iowa sandy loam, see Table 1 for characteristics) were sieved through a 2 mm mesh screen, oven dried at 90°C for 24 hours, and then autoclaved at 121°C prior to use in this study. In the preliminary study the stock solutions of the radioactive compound and non-labeled compound were prepared in acetone. These solutions were then diluted using deionized, distilled and boiled

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water containing 0.01 N calcium ion to a concentration of 10 ug/ml. The same stock solutions were used for the definitive study. A portion of the radioactive stock was mixed with 0.2 um membrane filtered sterilized, deionized, distilled water and boiled water containing 0.01 N calcium ion in autoclaved glassware. The final metolachlor nominal concentration was 10 ug/ml (ppm). Aqueous dilutions of this nominal 10 ug/ml solution were prepared in sterile solution containing 0.01 N calcium ion to provide the following concentrations for the study: 10 ug/ml, 5 ug/ml, 1 ug/ml, 0.5 ug/ml, and 0.2 ug/ml.

The test system for the study was each capped centrifuge tube of soil, solution and metolachlor. All test systems were shaken in the laboratory at 24-26°C and all solutions were analyzed within a few hours of sampling. Prior to the definitive testing each soil was tested to establish the ratio of soil to stock solution and equilibration time for use in the adsorption and desorption phases of the study. In the adsorption phase 5 gm samples of prepared soil were placed in 50 ml polypropylene centrifuge tubes in duplicate for each test solution concentration. Twenty five ml of 0.0, 0.2, 0.5, 1.0, 5.0, and 10.0 ug/ml metolachlor stock solution was transferred to appropriate containers and capped. The sample set was shaken for 24 hr and after centrifugation (1000 x g for 15 min), the equilibrium concentrations ( $C_e$ ) of metolachlor were determined in all solutions. Solutions remaining after adsorption were decanted and residual soils were combusted to determine the actual concentration of metolachlor adsorbed.

After adsorption, desorption was performed on the soil samples remaining from adsorption. Twenty five ml of calcium ion solution at 0.01 N without metolachlor was added to the soils. The sample set was shaken for 24 hr and samples were centrifuged (1000 x g for 15 min) and the supernatant analyzed by LSC to determine the  $C_e$ . Following desorption all soil samples were combusted to determine actual metolachlor concentration. Following completion of the adsorption and desorption phases of the study, aliquots of the highest solution concentrations were analyzed by TLC.

#### REPORTED RESULTS:

1. The reported Freundlich adsorption ( $K_{ad}$ ) values for metolachlor were 0.108 in the Maryland sand soil, 0.773 in the Mississippi loam, 1.869 in the Maryland clay, and 2.157 in the Iowa sandy loam soil. The reported desorption constants ranged from 0.3 to 3.6.
2. Results of the preliminary study indicated that solution equilibrium was achieved in 24 hours (Table 2).
3. Analysis of the highest solution concentrations following completion of the adsorption and desorption phases of the study indicated that only metolachlor was found and no degradation observed.

DISCUSSION:

The results demonstrated that metolachlor is mobile in the four soils tested and is not strongly adsorbed onto the soil. The Freundlich adsorption constants ranged from 0.108 to 2.157 and the desorption constants ranged from 0.38 to 3.59. These values indicate that metolachlor has the potential to be a highly mobile material in the soils tested.

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3/1/93 EFE Memo

Metolachlor

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## DATA EVALUATION RECORD

### STUDY IDENTIFICATION:

Spare, W.C. 1987. The Volatilization of Metolachlor from Soil. Study Conducted by Agrisearch Incorporated, Frederick, MD. for Ciba-Geigy Corporation, Agricultural Division, Greensboro, N.C. MRID No. 404946-06.

TYPE OF STUDY: Laboratory Volatility (163-2)

### REVIEWED BY:

George Tompkins, Entomologist  
Review Section 1, EFGWB, EFED

Signature: *George Tompkins*  
Date: 25 FEB 1993

### APPROVED BY:

Paul J. Mastradone, Section Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: 25 FEB 1993

### CONCLUSIONS:

1. EFGWB concludes that the study submitted is scientifically valid and satisfies the environmental fate data requirements for a laboratory volatility study.
2. It can be concluded that metolachlor did not volatilize very rapidly from the soil. When nitrogen with 0 percent humidity was purged through the soil at 300 ml/min, no detectable metolachlor was found to volatilize from the soil (detection limit 0.035% of dose per day). When the humidity was increased to 100% in the nitrogen, approximately 0.05% of the metolachlor dose was volatilized per day (slightly above the detection limit).

### MATERIALS AND METHODS:

Metolachlor in both the granular (Dual 25G) and emulsifiable concentrate (Dual 8E) were used in this study to determine the volatility of the end use products. A sandy loam soil from Des Moines, Iowa (same soil sample collection used in the soil metabolism study of metolachlor) was used (See Table 1 for soil characterization). The soil was air dried and sieved through a 2 mm screen before being autoclaved at 121°C for 60 min and then oven dried at 110°C for more than 24 hr. Two 400 g aliquots of soil were used so that one received a theoretical 4 mg (10 ppm of metolachlor a.i.) of Dual 8E and the second the same weight of Dual 25G. The soil was mixed and two 10 g subsamples were then removed for zero time analysis. The remaining soil was divided into two replicates and transferred to gas saturation vessels

fitted with traps containing polyurethane plugs, then placed in an incubator maintained at  $25 \pm 0^\circ\text{C}$ . The assembled vessels were purged with nitrogen at either 0% relative humidity or 100% relative humidity at a flow rate of 300 ml/min for 12 days. The polyurethane plugs were replaced at 6 intervals during the study (0-1 day, 1-2, 2-4, 4-6, 6-8, and 8-12 days). These plugs had been pre-extracted with 100% dichloromethane, followed by 100% acetone and then 100% hexane and air dried prior to use. Two foam plugs were used for each collection time period. When the polyurethane foam plugs were removed they were placed into 25 ml glass scintillation vials with a teflon cap liner. Fresh foam plugs were placed into the upper gas trapping cylinder and the nitrogen flow resumed.

The polyurethane foam plugs were immediately extracted by adding 20 ml of hexane:acetone (2:1, v:v) to the glass vials in which the plug had been collected. A glass rod was used to squash the plug several times in the extraction solvent. The samples were then sonicated for 30 min and then shaken for 30 min by a reciprocal shaker, and then allowed to equilibrate for 24 hr. The extract was stored at  $-20^\circ\text{C}$  for 48 hr and then a subsample of the extraction solvent was removed for injection on the gas chromatograph.

All soil samples (day 0 and 12) were immediately stored at  $-20^\circ\text{C}$  until extraction and analysis. Day 0 and day 12 (0% humidity soils) were stored for 8 days, while the day 12 100% humidity soils were stored for 50 days. Soil samples were extracted by using a mixture of hexane:acetone (2:1, v:v). The soil to solvent ratio was adjusted to 1:10 (w/v). Prior to addition of solvent to soils flushed with 0% humidity nitrogen the soil was moistened with 10% water (1 ml/10 g soil). Ten gram soil samples were extracted by sonication for 30 min, followed by shaking for thirty min in a glass bottle with a teflon screw cap. Subsamples of the extraction solvent were then analyzed directly by GC.

#### REPORTED RESULTS:

1. No detectable metolachlor was found to volatilize from the soil through which nitrogen at 0% relative humidity was passed (less than 0.07%, Table 3).
2. When nitrogen with 100% relative humidity was passed through the soil, approximately 0.05% of the metolachlor dose was volatilized per day. At a flow rate of 300 ml/min,  $0.432 \text{ m}^3$  of nitrogen passed through the soil per day. The range of the metolachlor concentration in the air was 2.34 to  $2.59 \text{ ug/m}^3$  with a volatility of  $2.14$  to  $2.38 \times 10^{-3} \text{ ug/cm}^2/\text{hr}$  (Table 3).
3. The spiked soil samples had a 97.2 to 104.8% recovery with a 101.3% average. The spiked polyurethane foam plugs had a recovery range of 97.8 to 118.2% with an average of 104.8% (Table 4).

## DISCUSSION:

1. Previous storage stability studies conducted on the same soil showed recoveries of 122% at 1 ppm and 93% at 5 ppm after 60 days storage.

2. Analysis of the formulation after dosing demonstrated that the concentration of each formulation was 102% (Dual 8E) and 92% (Dual 25G) of expected. Therefore, the actual doses used in the study were 10 ppm (Dual 8E) and 9.2 ppm (Dual 25G).

3. The detection limit was 0.035% of dose per day. No detectable metolachlor was found to volatilize from the soil through which 0% humidity nitrogen was passed. When nitrogen with 100% humidity was passed through the soil approximately 0.05% of the metolachlor dose was volatilized per day. By increasing the humidity to 100% in the nitrogen passed through the soil, the volatility was increased to be just over the detection limit. The results of these studies indicate that metolachlor does not volatilize rapidly under the test conditions and that volatility was not a significant mode of dissipation of metolachlor from the soil used.

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3/1/93 EFED memo

Mitchell

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Pages 56 through 68 are not included.

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## DATA EVALUATION RECORD

### STUDY IDENTIFICATION:

Spare, W. C. 1987. Determination of the Solution Photolysis Rate Constant and Photodegradation Products of Metolachlor Under Natural and Artificial Light. Study conducted by Agrisearch Incorporated, Frederick, MD. for Ciba-Geigy Corporation, Agricultural Division, Greensboro, N.C. MRID No. 404302-02.

TYPE OF STUDY: Aqueous Photolysis (161-2)

### REVIEWED BY:

George Tompkins, Entomologist  
Review Section 1, EFGWB, EFED

Signature: *George Tompkins*  
Date: 23 FEB 1993

### APPROVED BY:

Paul J. Mastradone, Section Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: 25 FEB 1993

### CONCLUSIONS:

1. EFGWB concludes that this study is acceptable and fulfills the data requirements for aqueous photolysis.
2. It can be concluded from data presented in this study, that metolachlor photolyzed in aqueous solution exposed to natural sunlight with a calculated half-life of approximately 70 days. EFGWB does not accept the artificial light data because the wave length of the mercury arc lamp may not simulate that of natural sunlight as is evident from the discrepancy in the results (70 day half-life by natural sunlight versus 0.17 day by artificial light).
3. Numerous photolysis products from metolachlor were isolated from either natural sunlight or artificial light exposure. The degradates after 30 days exposure to natural sunlight that occurred in greatest quantities were CGA-41638 (3.63% of applied radiocarbon), CGA-51202 (3.54%), CGA-46129 (3.42%), CGA-50720 (3.20%), and parent metolachlor remaining was 62.92% of applied.

### MATERIALS AND METHODS:

Analytical grade [U-ring-<sup>14</sup>C]-metolachlor (specific activity of 26.2 uCi/mg, radiopurity 97.8%) was dissolved with 5.0 ml of acetone and to a sterile erlenmeyer flask, 7 ul of <sup>14</sup>C-metolachlor was mixed with 21 ml of pH 7 buffer. The final theoretical dose was calculated to be 10 ppm.

The test systems utilized were quartz test tubes with teflon coated stoppers. One tube was covered with aluminum foil to serve

as a dark control. In the natural light exposure the photolysis reactor was the sun and the tubes were held at an angle of approximately  $45^{\circ}$  to the sun on a wire rack with a dark background approximately one foot from the tubes. Light measurements were made using a Blak-Ray Long Wave Ultraviolet Meter and ranged from  $1600 \text{ uW/cm}^2$  to greater than  $6000 \text{ uW/cm}^2$ . Exposure was on the roof at Agrisearch Incorporated,  $39^{\circ}25'$  North Latitude and  $77^{\circ}24'$  West Longitude. Test solutions for natural exposure were prepared on 22 April 1987 and exposure commenced on that date. The sampling intervals were at 0, 0.5 day, 1, 2, 4, 7, 14, 21, and 30 days for natural sunlight exposure. At each sampling interval 10 ul aliquots of exposed and dark samples were directly spotted for TLC. Additional 10 ul aliquots were directly counted by LSC. Weather observations and temperatures were recorded during the exposure.

The photolysis reactor for artificial light was equipped with a 450 watt medium pressure mercury arc Conrad-Hanovia lamp and a 290 nm and lower wavelength cut-off sleeve. The lamp and sleeve were inserted into a water jacketed quartz immersion well which fit into the reactor vessel and maintained at  $25^{\circ}\text{C}$  during the study period. Exposure was continuous for 24 hours. The exposure intensity of the lamp varied from 4300 to  $4500 \text{ uW/cm}^2$ . The artificial light exposure solutions were dosed on 4 June 1987 and aliquots were taken at 0, 1, 2, 4, 8, and 24 hrs after continuous exposure and also from the dark control solution.

Duplicate samples of the buffers from each exposure period from both natural and artificial light were spotted on TLC plates. Standards were chromatographed adjacent to sample spots. The plates were developed in either: 1) dichloromethane:ethyl acetate (9:1, v/v), or 2) chloroform:methanol:formic acid:water (75:20:4:2, v/v/v/v). Two dimensional TLC was also performed using the same solvent systems. All plates were developed to a solvent front of 15 cm, air dried and visualized under short wave UV light (254 nm). All solutions were analyzed by direct LSC.

#### REPORTED RESULTS:

1. The half-life of metolachlor in aqueous solution exposed to natural sunlight was approximately 70 days. For artificial light the half-life was approximately 4 hours.
2. After 30 days exposure to natural sunlight the percent parent metolachlor remaining decreased to approximately 73% (Table 6). The dark control after 30 days had approximately 99.5% of parent metolachlor remaining. After 24 hours continuous exposure to the artificial light source the average parent metolachlor remaining ranged from 2.25 to 9.82% (Table 6).
3. Numerous photolysis products from metolachlor solutions were isolated by TLC analysis. Fourteen photolysis products were observed from either artificial or natural light exposure (Table 9) ranging from 0.99% to 8.64% of applied dose. The degradates after 30 days from natural sunlight exposure occurring in

greatest quantities were CGA-41638 (3.63%), CGA-51202 (3.54%), CGA-46129 (3.42%), and CGA-50720 (3.20%), and parent metolachlor remaining was 62.92%. After 8 hours exposure to artificial light the identifiable degradates occurring in greatest quantities were CGA-48081 (8.64%), CGA-51202 (5.59%), and CGA-46129 (5.02%) and parent metolachlor remaining was 36.13%.

4. The radiocarbon balance of the solution exposed to natural sunlight ranged from 89.8% (day 30) to 94.8% (day 14) of the 1 hr exposed solutions. The dark controls ranged from 94.1% (day 30) to 100.9% (day 7). The radiocarbon balance for the solutions exposed to artificial light ranged from 99.8% (24 hr) to 111.6% (4 hr).

5. The temperature readings recorded under natural sunlight varied from 8 to 45°C. The temperature of the solution exposed to artificial light was maintained at 25°C.

#### DISCUSSION:

1. The total intensity over the time exposed in either the natural sunlight or the artificial light source was not provided. The light intensity was recorded up to 6000 uW/cm<sup>2</sup> (Table 3) but it appears that the measuring device was probably not capable of accurately giving readings above this reported value, even though numerous readings were simply expressed as >6000 uW/cm<sup>2</sup>.

2. Although on page 10 it is mentioned that the artificial light source was 2 to 3 times the intensity of the natural sunlight, this doesn't appear to be always the case. The light intensity under natural sunlight (Table 3) was shown to range from 300 to >6000 uW/cm<sup>2</sup> whereas the light intensity for artificial conditions (Table 4) was 4500-4800 uW/cm<sup>2</sup>.

3/1/93 EFED memo

M. Tolachko

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Pages 72 through 86 are not included.

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