Date Out: APR 22 1997
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DP Barcode:D232589
Chemical Code: 108800

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: J. Miller
Registration Division (7505C

From: Paul Mastradone, Section Chief
Chemistry Review Section 1
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Betsy Behl, Acting Branch Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Common Name:	CGA-77102	**Trade name:**	DUAL II Magnum
Company Name:	Ciba-Geigy Corporation		
ID #:	108800		
Purpose:	To review bridging environmental fate data (soil photolysis, mobility, aerobic soil metabolism, unaged leaching, adsorption/desorption, and aged soil column leaching) submitted in support of registration		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
Herbicide	101		15 days

STATUS OF STUDIES IN THIS PACKAGE:
ADDRESSED IN THIS PACKAGE:

Guideline #	MRID	Status[1]
161-3	43928935	U
162-1	43928936	U
163-1	43928937	A
163-1	43928938	A

STATUS OF DATA REQUIREMENTS

Guideline #	Status[2]
161-3	N
162-1	N
163-1	S

[1]Study Status Codes: A=Acceptable U=Upgradeable C=Ancillary I=Invalid.
[2]Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved W=Waived

1. CHEMICAL:

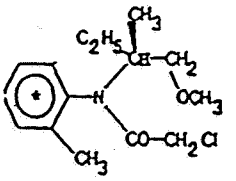
Chemical name: (S)-2-chloro-N-(2-ethyl-6-methyl-phenyl)-N-(2-methoxy-1-metnyl-ethyl)acetamide

CAS no.:

Common name: Stereoisomer Metolachlor

Trade name: Dual Magnum, Dual II Magnum, Bicep Magnum

Chemical structure:



Formulation: CGA-77102(highest conc.).....83.7%
Inert Ingredients.....17.6%

Physical/Chemical properties of active ingredient CGA-77102:

Physical characteristics:	Pale yellow, light brown clear liquid with weak odor
Molecular formula:	$C_{15}H_{22}NClO_2$
Molecular weight:	283.5
Vapor Pressure:	2.8×10^{-5} mm Hg @ 25°C
Solubility:	0.480 g/L at 25°C
Octanol/water partition coefficient:	1117

2: TEST MATERIAL:

See individual DERs attached.

3. STUDY/ACTION TYPE:

To review bridging environmental fate data (soil photolysis, aerobic soil metabolism, unaged leaching, adsorption/desorption, and aged soil column leaching) submitted in support of registration.

4. STUDY IDENTIFICATION:

Merritt. A. PHOTODEGRADATION OF ^{14}C-METOLACHLOR AND ^{14}C-CGA-77102 ON SOIL UNDER ARTIFICIAL LIGHT. Sponsored, Performed, and Submitted by Ciba Crop Protection, Environmental Fate and Effects Department, Ciba-Geigy Corporation, Greensboro, NC; Performed under Laboratory Project ID. ABR-95128 and Ciba Study Number 53-95; Study completed on 21 December 1995; Received by EPA 26 January 1996; MRID 43928935.

Clark, A.O. COMPARATIVE AEROBIC SOIL METABOLISM OF PHENYL-^{14}CGA-77102 AND PHENYL-^{14}C-METOLACHLOR. Sponsored and Submitted by Ciba Crop Protection, Ciba- Geigy Corporation, Greensboro, NC; Performed by Ciba Crop Protection, EFED, Ciba-Geigy Corporation, Greensboro, NC and Agrisearch Incorporated, Frederick, MD under Ciba Study Number

338-94 and ABR-95102; Study completed on 18 December 1995; Received by EPA 26 January 1996; MRID 43928936.

Spare, W.C. ADSORPTION/DESORPTION OF ^{14}C-CGA-77102 BY THE BATCH EQUILIBRIUM METHOD ON REPRESENTATIVE AGRICULTURAL SOILS. Sponsored and Submitted by Ciba-Geigy Protection, Ciba-Geigy Corporation, Greensboro, NC under Ciba-Geigy Study No. 71-95 and Agrisearch Project No. 12218; Study completed on 11 July 1995; Received by EPA 26 January 1996; MRID 43928937.

Spare, W.C. LEACHING CHARACTERISTICS OF AGED ^{14}C-CGA-77102 IN FOUR SOIL TYPES. Sponsored and Submitted by Ciba-Geigy Protection, Ciba-Geigy Corporation, Greensboro, NC under Study No. 72-95; Performed by Agrisearch Incorporated, Frederick, MD under Agrisearch Project No. 12216; Study completed on 22 December 1995; Received by EPA 26 January 1996; MRID 43928938.

5. REVIEWED BY:

Gail Maske
Chemist, Review section #1
OPP/EFED/EFGWB

Signature: [signature]
Date: [date]

6. APPROVED BY:

Paul Mastradone, Chief
Review section #1
OPP/EFED/EFGWB

Signature: [signature]
Date: 4/23/97

7. CONCLUSIONS:

The registrant (Ciba-Geigy Corporation) submitted environmental fate studies (soil photodegradation, aerobic soil metabolism, unaged leaching, adsorption/desorption, and aged soil column leaching) to support registration of CGA-77102 the stereoisomer metolachlor. These environmental fate data evaluation recorders are attached. In addition, the environmental fate of CGA-77102 in aquatic and soil environments is assessed.

ENVIRONMENTAL FATE ASSESSMENT SUMMARY

Based on present data which is acceptable and supplemental laboratory and field data (including bridging data) submitted for CGA-77102 and metolachlor, only a tentative environmental fate assessment can be made at this time. The bridging data indicate that the environmental fate of the two is basically the same. The major route of degradation appears to be microbial mediated processes (biphasic half-lives for aerobic soil metabolism = 8.8/67.9 days and 7.5/ 69.7 days for CGA-77102 and metolachlor, respectively). CGA-77102 and metolachlor appear to be mobile in silt and sandy soils, moderately mobile in clay soil, and very mobile in sand soil (K_d values = 1.1 to 2.4 for silt and sandy loam soils, ≈4 for clay soil, and <1 for sand soil).

In addition, previous metolachlor and present bridging data indicate that both CGA-77102 and metolachlor are stable to hydrolysis (stable with <5% of applied degrading) and photolysis (aqueous photolysis half-life = 70 days for metolachlor, soil photolysis half-lives vary from 8 to 95 days). Upgradable terrestrial field data confirm the laboratory data (half-lives in Iowa varied from 7 days to 159 days, in California varied from 128 to 292 days with detections not reported >0.7 ppm below the 48 inch soil

depth). Even though major environmental fate data is supplemental and there are discrepancies in previous and present data for CGA-77102 and metolachlor, it is believed that the major routes of dissipation will not change. However, there may be significant changes in reported rates of degradation.

Review of Submitted Studies:

a. Photodegradation on soil (161-3)
MRID 43928935

The photodegradation on soil study is scientifically valid, and can be used as supplemental data. However, it is not acceptable to fulfill the photodegradation on soil data requirement (161-3) for the following reasons:

a. There is a discrepancy in previous metolachlor soil photolysis data (GT;02/25/93) and these bridging soil photolysis data for metolachlor (half-life = 8 days vs 78.8 days, respectively).

b. There is a discrepancy in these bridging soil photolysis data (half-lives = 78.8 and 95.1 days for metolachlor and CGA-77102, respectively) and the bridging aerobic soil metabolism data (half-life = ≈8 days for metolachlor and CGA-771020). All these half-lives were based on days 0 to 21 test samples or data.

Therefore, additional data addressing these discrepancies are needed to clarify the environmental fate of CGA-77102 and metolachlor and to make a more complete environmental fate assessment.

These photodegradation data indicate that CGA-77102 and metolachlor do not degrade when exposed to an artificial light source. Half-lives reported for light exposed samples were 78.8 and 95.1 days for metolachlor and CGA-77102, respectively. The half-lives reported for dark control samples were 40.9 and 50.2 days for metolachlor and CGA-77102, respectively. Therefore, since the half-lives reported for the light exposed samples were greater than the half-lives reported for the dark control samples, photolysis appears not to be a significant route of degradation for metolachlor or CGA-77102. In addition, data for test material under the same conditions were not widely disparate. Light exposed samples of metolachlor and CGA-77102 decreased to 74.43% and 78.64% of applied dose, respectively, and dark control samples of metolachlor and CGA-77102 decreased to 59.99% and 66.86% of applied dose, respectively, by day 30 posttreatment.

The degradation pathways and qualitative and quantitative profiles for light exposed and dark control samples of metolachlor and CGA-77102 were similar. In day 30 light exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 7.20% & 7.19% and 0.91% & 0.73% of applied dose, respectively. In day 30 dark exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 9.85% & 9.01% and 6.21% & 3.83% of applied dose, respectively. In addition, trace amounts of CGA-40919, CGA-46129, CGA-48087, and CGA-50720 were discernible.

See attached DER for details.

b. Aerobic soil metabolism (162-1)
MRIDs 43928936

The aerobic soil study is scientifically valid, and can be used as supplemental data. However, it is not acceptable to fulfill the aerobic soil metabolism data requirement (162-1) for the following reasons:

a. There is a discrepancy in the half-life reported in the previous metolachlor data (GT;02/25/93) and these bridging data. A half-life of 67 days was reported in previous metolachlor data. These data reported biphasic half-lives of 8/67.9 and 7.8/69.7 days for metolachlor and CGA-77102.

b. There is a discrepancy in these bridging aerobic soil metabolism data and the bridging soil photolysis data. For the 0 to 21 day data, the bridging soil photolysis data reported a half-life of 78.8 and 95.1 days for metolachlor and CGA-77102. The aerobic soil metabolism data reported a half-life of 8 days for the 0 to 21 days data.

c. Biphasic half-lives were not reported in previous metolachlor data.

Therefore, additional data addressing these discrepancies are needed to clarify the environmental fate and to make a more complete environmental fate assessment of metolachlor and CGA-77102.

The aerobic soil study is scientifically valid, and can be used as supplemental data. However, it is not acceptable to fulfill the aerobic soil metabolism data requirement (162-1). There are discrepancies between the half-lives for the soil photolysis data and these aerobic soil metabolism data (78.8 and 95.1 days vs biphasic 8/67.7 days) and between these aerobic soil metabolism data and previous metolachlor. Biphasic half-lives were not calculated in previous metolachlor aerobic soil metabolism data. Therefore, additional data addressing these discrepancies are needed at this time.

Aerobic metabolism appears to be a major route of degradation for metolachlor and CGA-77102. Biphasic half-lives of 8.8/67.9 days and 7.5/69.7 days were reported for CGA-77102 and metolachlor, respectively. Calculated rate constants of -0.8 $days^{-1}$ and -0.9 $days^{-1}$ for the primary phase (0-21 days posttreatment samples) were reported, as well. These data indicate that metolachlor and CGA-77102 not only degrade by microbial mediated processes but at almost the same rate.

The major degradation pathway for metolachlor and CGA-77102 appear to involve chlorination and subsequent hydroxylation which was followed by progressive oxidation. The degradation pathway involved the same degradation products. In addition, the reported quantitation data of the degradation products were close.

During the degradation process, there was a steady generation of carbon dioxide(average of 19.8% and 20.2%). In addition, there were two major non-volatile metabolites, CGA-354743 and CGA-51202, formed at maximum concentrations of >10% of applied radioactivity. Three degradation products, CGA-40172, CGA-50720, an unidentified degradate, were discernible at concentrations >5% of applied material. However, the unidentified degradate was determined to be comprised of two components when analyzed by MS. Other discernible products, CGA 46129 and additional unidentified degradates, were reported to reached maximum concentrations of <5% of applied radioactivity. Identified degradation products were confirmed by MS analysis.

See attached DER for details.

c. Mobility, unaged leaching, adsorption/desorption and aged leaching soil column (163-1)
MRIDs 43928937 and 43928938

Leaching, adsorption/desorption (unaged)
MRID 43928937

The adsorption/desorption mobility study is scientifically valid. In addition, it can be used to fulfill the unaged mobility data requirement (163-1). No further unaged mobility data for CGA-77102 are needed. The aged mobility data (MRID 439289938-see attached DER) requirement is fulfill by additional submitted data, as well. Therefore, no further mobility data for CGA-77102 are needed at this time.

Adsorption/desorption data, using four test soils with varying organic matter content (0.3 to 2.2%) and soil texture (sand, sandy loam, silt loam, and clay), indicate that CGA-77102 is mobile in sandy loam and silt loam soils (Kds=1.4 and 1.1, respectively), moderately mobile in clay soil (Kd=4.7), and highly mobile in sand soil (Kd=0.3). Calculation of the K_{oc} values (adsorption constants based on organic carbon) yielded values ranging from 110 for sand soil to 369 for clay soil. Kd values for the desorption phase ranged from 1.3 to 8.0 (1.3 for sand, 3.7 for silt loam, 4.1 for sandy loam, and 8.0 for clay soils). The correlation coefficients for the adsorption and desorption phases ranged form 0.9964 to 0.9999.

Freundlich adsorption/desorption data was reported for CGA-77102 based on the stability (no degradation in TLC or HPLC analysis) of parent CGA-77102 during the testing period and the linear logarithmic plots of data. These data indicate that CGA-77102 did adsorb to the test soils. In addition, based on the Kd values for adsorption, CGA-77102 does have the potential to move through most soil profiles.

See attached DER for details.

Leaching soil column (aged)
MRID 43928938

The aged mobility study is scientifically valid. In addition, it can be used to fulfill the aged mobility data requirement (163-1). No further aged mobility data for CGA-77102 are needed at this time. The unaged (adsorption/desorption) mobility portion of the mobility data requirement (MRID 439289937-See attached DER) is fulfilled, as well. Therefore, no further mobility data for CGA-77102 are needed at this time.

Parent CGA-77102 and its degradation products do appear to move through the soil profile when applied to different soil textures. Aged CGA-77102 and its metabolites appear to be mobile in sandy loam and silt loam soils, moderately mobile in clay soil, and very mobile in sand soil. K_d values for aged CGA-77102 (at its soil metabolic half-life) were reported to be 2.3 for silt loam soil, 2.4 for sandy loam soil, 4.1 for clay soil, and 0.8 for sand soil. Reported Koc values for sandy loam soil were 200 to 208, for silt loam soil were 226 to 243, for clay soil were 311 to 324, and for sand soil were 455 to 468. The average radioactivity in the leachates were reported to be 16.8% for the clay soil columns, 24.4% for the sandy loam soil columns, 27.3% for the silt loam soil, and 58.2% for sand soil columns. Parent CGA-77102 was detected in all the leachates (0.2% in clay, 36.3%, in sand, 2.3% in sandy loam, and 4.3% in silt loam soils). Three degradates (CGA-51202, CGA-50720, and CGA-46129) were identified at approximately 5.5 to 11.0%, 1.1 to 6.9%, and 0.4 to 1.5% of applied radioactivity in

the leachates. There were approximately 8 other degradation products discernible in the leachates, but the total maximum concentration of these degradation products was 5.0% of applied radioactivity. Therefore, the average amount of radioactivity that remained in the soil columns was 77.9% for clay soils, 70.6% for silt loam soils, and 69.5% for sandy loam soils, and 33.7% for sand soils. CGA-77102 was the primary radioactivity extracted from the soil column sections. Minor degradation products (≤ 2.6% of applied radioactivity) were identified as CGA-51202, CGA-50720, CGA-41507, CGA-41638, CGA-40919, CGA-354743, and CGA-40172.

See attached DER for details.

ENVIRONMENTAL FATE ASSESSMENT

Based on the present environmental fate data only a tentative environmental fate assessment can be made at this time. However, acceptable (hydrolysis, aqueous photodegradation, and mobility) and supplemental (soil photodegradation, aerobic metabolism (aqueous and soil), anaerobic soil (aqueous and soil) metabolism, and terrestrial field) laboratory and field data (including bridging data) indicate that the major route of dissipation is microbial mediated processes (biphasic half-lives for aerobic soil metabolism = 8.8/67.9 days and 7.5/ 69.7 days for CGA-77102 and metolachlor, respectively). CGA-77102 and metolachlor appear to be moderately mobile in silt and sandy loam soils, mobile in clay soil, and very mobile in sand soil (K_d values = 1.1 to 2.4 for silt and sandy loam soils, ≈4 for clay soil, and <1 for sand soil).

In addition, previous metolachlor and present bridging data indicate that both CGA-77102 and metolachlor are stable to hydrolysis (stable with <5% of applied degrading) and photolysis (aqueous photolysis half-life=70 days for metolachlor, soil photolysis half-lives vary from 8 to 95 days). Upgradable terrestrial field data confirm the laboratory data (half-lives in Iowa varied from 7 days to 159 days, in California varied from 128 to 292 days with detections not reported >0.7 ppm below the 48 inch soil depth). Since major environmental fate data are supplemental and there are discrepancies in previous and present data for CGA-77102 and metolachlor, this environmental fate may be subject to significant changes. Even though there are discrepancies in bridging data and previous metolachlor, the bridging data indicate that the environmental fate of the two is basically the same.

Since this is bridging data for CGA-77102 and metolachlor, attached is the previous environmental fate assessment of metolachlor (GT;02/25/93). Due to the discrepancies found in the bridging data submitted for CGA-77102 which included metolachlor photolysis and metabolism data and previous metolachlor data, the attached environmental fate assessment for metolachlor can only be considered tentative at this time:

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 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 e dependent on microbially mediated (aerobic soil metabolism $t_{½}$=67 days, anaerobic soil metabolism $t_{½}$=81 days) and abiotic processes (photodegradation in water $t_{½}$=70 days under natural sunlight and photodegradation on soil $t_{½}$=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 0.1 to 1.9). Upgradeable field dissipation studies indicate that metolachlor is non-persistent to persistent in the surface soil ($t_{½}$ ranging from 7 days to 292 days in 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 to 36 inch soil depth (MRID No. 41335701); CGA-40172 was detected as far as the 36 to 48 inch depth (MRID No. 41309802); CGA-40919 was detected in the 36 to 48 inch depth (0.21 ppm in MRID No. 41309802); and CGA 50720 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 ^{14}C-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 ppm in beet tops and roots, respectively; 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.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

a. There are discrepancies in the previous metolachlor photodegradation on soil and aerobic soil metabolism data (MRIDs 40430203 and 41309801 A-B)and in previous and present metolachlor data. Even though the previous photodegradation on soil methodology used different light sources (natural sunlight and mercury arc lamp), the discrepancy between the half-lives for the soil photolysis and the aerobic soil metabolism was not addressed if metolachlor is considered stable to photolysis. In addition, in the previous aerobic soil metabolism study, biphasic half-lives were not calculated. Additional data addressing these discrepancies are needed at this time.

b. The photolysis (aquatic and soil), aerobic and anaerobic (aquatic and soil) metabolism studies reviewed in 1993 (GT;02/25/93) are considered supplemental at this time. The status of these data requirements may be changed depending on the additional data submitted addressing the discrepancies in these studies. It should be noted that biphasic half-lives were not calculated for the terrestrial field dissipation data, as well.

c. The bridging mobility (uaged and aged) studies for CGA-77102 are acceptable to fulfill the data requirement. However, according to the registrant, mobility data on a major degradate, CGA-354743 will be submitted in the future.

d. A detailed review of the bridging data and of previous metolachlor data changes the status of the data requirements stated in the new chemical screen memorandum (JAH;09/17/96). The soil photolysis and aerobic metabolism data can not be used as bridging data until the discrepancies are addressed satisfactory. Until these discrepan-

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cies are satisfactory addressed, the aqueous photolysis, anaerobic metabolism, and aerobic aquatic data requirements are considered not fulfilled.

e. The status of the environmental fate data requirements needed to support the registration of CGA-77102 for use on terrestrial food and feed crops indoor uses is as follows:

Environmental Fate Data Requirements		Status of Data Requirement	MRID No.
Degradation Studies-lab			
161-1	Hydrolysis	Fulfilled[1] (GT;02/25/93)	40430201
161-2	Photodegradation in water	Not Fulfilled[9] (GT;02/25/93)	40430202
161-3	Photodegradation on soil	Not Fulfilled[2] (GT;02/25/93) (GML;04/ /97)	40430203 43928935
161-4	Photodegradation in air	Waived[3]	
Metabolism Studies-lab			
162-1	Aerobic soil	Not Fulfilled[2] (GT;02/25/93) (GML;04/ /(97)	41309801A 41309801B 43928936
162-2	Anaerobic soil	Not Fulfilled[7] (GT;02/25/93)	41309801B
162-3	Anaerobic aquatic	Not Fulfilled[7] (GT;02/25/93)	41185701
162-4	Aerobic aquatic	Not Fulfilled[7] (GT;02/25/93)	41185701
Mobility Studies			
163-1	Leaching, Adsorption/ Desorption	Fulfilled[2&8] (GT;02/25/93) (GML;04/ /97)	40494602 40494603 40494604 40494605 43928937 43928938
163-2	Volatility-Lab	Waived[3]	
163-2	Volatility-Field	Waived[3]	
Dissipation Studies-field			
164-1	Soil, terrestrial & turf	Not Fulfilled[1,4,5] (GT;02/25/93	41309802 41309803 41309804 41309805 41335701 41335702 41484201 41484202 41484203 41484204 41484205 41484206
Accumulation Studies			
165-4	in Fish	Fulfilled[1]	41154201

Con't--

Environmental Fate Data Requirements	Status of Data Requirement	MRID No.
Spray Drift Studies		
201-1 Droplet size spectrum	Not Submitted[6]	
202-1 Drift field evaluation	Not Submitted[6]	

[1] These data requirements are supported by previous submitted metolachlor environmental fate data.

[2] The status of these data requirements are based on both CGA-77102 environmental fate bridging data and previous metolachlor environmental fate data.

[3] Based on the vapor pressure (2.8×10^{-5} mm Hg @ 25°C) and laboratory data, these data requirements are waived at this time. Generally the volatility and air photolysis data requirements are waived for pesticides with vapor pressures $<10^{-4}$ mm Hg.

[4] Additional field dissipation data are needed to support registration of metolachlor and CGA-77102. Previous Data Evaluation Records for the above field dissipation MRIDS should be reexamined prior to submitting the additional data for the field dissipation data requirement. It should be noted that field data should reflect the different application methods, treatment sites, and maximum application rates. It should also be noted that previous field data did not calculate biphasic half-lives.

[5] Turf field dissipation data are needed to support turf uses. It is presently understood that an application for turf uses may be submitted in the future.

[6] Based on possible aerial applications, these data requirements are needed to make a more complete environmental fate assessment.

[7] These data requirements were considered fulfilled under the previous metolachlor data review. However, based on the new CGA-77102 and metolachlor bridging data, these data requirements can not be considered fulfilled at this time. Supporting data are needed to determine if there are anaerobic soil and aquatic and aerobic aquatic biphasic half-lives, as well. If additional data indicate that metolachlor anaerobic metabolism and/or aerobic aquatic metabolism is not biphasic, these data can be used to fulfill the respective data requirements.

[8] A number of mobility studies (MRID 40449602, 40449603, 40449604, and 40449605) for metolachlor have been submitted and reviewed (GT; 02/25/96). A review of these data indicate that MRIDs 40449602 and 40449604 fulfill the unaged metolachlor mobility data requirement. However, the remaining studies (MRIDs 40449603 and 40449605) only partially fulfill the aged mobility data requirement. Only one concentration of test material was used in the column leaching study, and mobility data is not available for all the major metolachlor degradation products (CGA-50720 and CGA-354743) which reached maximum concentrations >10% of applied (≈14% and ≈12% or applied radioactivity, respectively).

[9] Based on previous soil photolysis data and these bridging data, the status of the aqueous photolysis data is considered supplemental and the data requirement not fulfilled at this time. After additional data addressing the discrepancies in the previous metolachlor

data and in these bridging data, the status of this data requirement will be reevaluated.

9. BACKGROUND:

CGA-77102 is a stereoisomer of metolachlor. CGA-77102 and metolachlor are chloracetanilide selective herbicides which are preplant surface applied, preplant incorporated, or preemergence treatment in water of fluid fertilizer. CGA-77102 and metolachlor are used to control annual grasses and broadleaf weeds in corn, cotton, peanuts, pod crops, potatoes, safflower, grain, forage sorghum, and soybeans. There are five end product formulations, which are all liquid formulation, registered at this time. Other EC formulations, a granular formulation, and turf applications are expected to be registered in the future.

Even though the stereoisomer of metolachlor, CGA-77102 is reported to be applied at an application rate of ≈62.5% that of metolachlor which is a 37.5% decrease in active ingredient, the releasable data summaries did not totally confirm a 37.5% decrease in the concentration of CGA-77102 residues. These releasable data did not clarify whether this was due to hot spots or inaccurate application rates of test material. CGA-77102 is applied by surface ground equipment, preplant incorporation equipment, and aerial application equipment. The application rate is dependent on soil organic matter content and soil texture. However, the application rates for metolachlor appear to range from 0.75 lb a.i./A to 4 lbs a.i./A for single applications and 6 lbs a.i./A (on corn) for total seasonal application. For CGA-77102 the application rates range from 0.48 lb a.i./A to 2.48 lbs a.i./A for single and 3.72 lbs a.i./A (on corn) for total seasonal application.

Metolachlor appears to be toxic to birds. The toxicity to birds is reported in Farm Chemical Handbook.

10. DISCUSSION:

See individual DERs.

11. COMPLETION OF ONE-LINER:

There is no one-liner at this time.

12: CBI APPENDIX:

N/A

DATA EVALUATION RECORD

STUDY 1

CHEM 108800 Stereoisomer Metolachlor CGA-77102 §161-3

STUDY ID 43928935

Merritt. A. PHOTODEGRADATION OF ^{14}C-METOLACHLOR AND ^{14}C-CGA-77102 ON SOIL UNDER ARTIFICIAL LIGHT. Sponsored, Performed, and Submitted by Ciba Crop Protection, Environmental Fate and Effects Department, Ciba-Geigy Corporation, Greensboro, NC; Performed under Laboratory Project ID. ABR-95128 and Ciba Study Number 53-95; Study completed on 21 December 1995; Received by EPA 26 January 1996.

DIRECT REVIEW TIME = 1.8 days

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: OPP/EFED/EFGWB
TEL: 305-5245

SIGNATURE:

APPROVED BY: Paul Mastradone, Chief
Supervisory Chemist
Review section #1
OPP/EFED/EFGWB

Signature: Paul J. Mastradone

Date: 4/23/97

CONCLUSIONS:

Degradation - Photodegradation, soil

The photodegradation on soil study is scientifically valid, and can be used as supplemental data. However, it is not acceptable to fulfill the photodegradation on soil data requirement (161-3) for the following reasons:

a. There is a discrepancy in previous metolachlor soil photolysis data (MRID 40430203) and these bridging soil photolysis data for metolachlor (half-life = 8 days vs 78.8 days, respectively).

b. There is a discrepancy in these bridging soil photolysis data and the bridging (MRID 43928936) aerobic soil metabolism data (half-life = 78.8/95.1 days vs 8 days for 0 to 21 days, respectively) for metolachlor and CGA-77102.

Therefore, additional data addressing these discrepancies are needed to clarify the environmental fate of CGA-77102 and metolachlor and to make a more complete environmental fate assessment.

These photodegradation data indicate that CGA-77102 and metolachlor do not degrade when exposed to an artificial light source. Half-lives reported for light exposed samples were 78.8 and 95.1 days for metolachlor and CGA-77102, respectively. The half-lives reported for dark control samples were 40.9 and 50.2 days for metolachlor and CGA-77102, respectively. Therefore, since the half-lives reported for the light exposed samples were greater than the half-lives reported for the dark control samples, photolysis appears not to be a significant route of degradation for metolachlor or CGA-77102. In addition, data for test material under the same conditions were not widely disparate. Light exposed samples of metolachlor and CGA-77102 decreased to 74.43% and 78.64% of applied dose, resp-

ectively, and dark control samples of metolachlor and CGA-77102 decreased to 59.99% and 66.86% of applied dose, respectively, by day 30 posttreatment.

The degradation pathways and qualitative and quantitative profiles for light exposed and dark control samples of metolachlor and CGA-77102 were similar. In day 30 light exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 7.20% & 7.19% and 0.91% & 0.73% of applied dose, repectively. In day 30 dark exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 9.85% & 9.01% and 6.21% & 3.83% of applied dose, respectively. In addition, trace amounts of CGA-40919, CGA-46129, CGA-48087, and CGA-50720 were discernible.

MATERIALS AND METHODS:

Test Material: [^{14}C]phenyl radiolabelled metolachlor was obtained from Ciba-Geigy Chemical Synthesis Group. A specific activity of 85.1 μCi/mg was reported. In addition, radiochemical and chemical purities of 98.8% and 99.9%, respectively, were reported.

[^{14}C]phenyl radiolabelled CGA-77102 was obtained from Ciba-Geigy Chemical Synthesis Group. A specific activity of 84.4 μCi/mg was reported. In addition, radiolabelled and chemical purities of 97.6% and 99.9% were reported.

See Figures 1 and 9.

Reference Standards: Unlabeled reference standards were obtained from Ciba-Geigy Corporation. The stability of the reference standards were verified by consistent TLC R_f. See Figure 3 for structures and names of reference standards (See Table XIX).

Chemical purities of reference standards were reported as follows:

metolachlor	99.3%
CGA-77102	99.4%
CGA-50720	>99.9%
CGA-41638	93.9%
CGA-51202	99.3%
CGA-40172	99.6%
CGA-48087	>99.9%
CGA-46129	>99.9%
CGA-40919	>99.9%
CGA-42446	98.2%
CGA-37735	99.5%
CGA-13656	99.7%
CGA-37913	99.5%

Stock Solution: Each test material was separately dissolved in 1.0 mL of acetonitrile.

Test Substance: An aliquot (490 μL) of the stock solution was transferred to a vial and diluted to 5.0 mLs of acetonitrile.

The standard dilution for reference standards were prepared by weighing a quantity of the desired reference in a vial. An appropriate volume of solvent was then added.

Soil: A sequatchie sandy loam soil was collected from the Buckeystown, Frederick County, MD. The soil was transferred to the Agrisearch Inc. facility where it was screened through a 2 mm sieve and stored in the dark at 25 ± 1°C. Characterization of the test soil was performed by Agvise (See Table 1A).

Water: The water used to adjust the soil moisture was filtered through a 0.2 μm filter and processed through a Hydro Picotech system which exceeds all ASTM Type 1 standards.

Light Source: A Heraeus Suntest Unit with an Xenon arc lamp was used for the light source. Borosilicate flasks and a pyrex filter were used to filter out UV output below 290 nm. The intensity of the artificial light was adjusted to the same intensity as natural sunlight (See Figures 5 and 8).

Sampling: Duplicate light exposed and dark control samples were collected at 0 (immediately following application of test material), 1, 7, 14, 21, and 30 days posttreatment. Samples from the volatile traps of test samples were collected at 3, 7, and 14 days posttreatment.

Test System: See Figures 4, 5, and 6.

METHODOLOGY:

Prior to initiation of the study, the agar media, utensils, and the glassware used for the dosing and incubation of samples were sterilized in an autoclave. Agar media was sterilized at 121°C for 15 minutes while glassware and utensils were sterilized at 121°C for 30 minutes.

Approximately 3.6 grams of Sequatchie sandy loam soil (test soil), which equalled a 2 mm soil layer, was transferred to each test flask. After the soil moisture was adjusted to 75% at 1/3 bar, 30 μL of test material, which is equilvalent to 1.3 ppm of the test material, was topically applied to each test flask. In addition, for each test substance three soil samples in test vials were dosed. One test vial from each test set was for storage stability analysis. The other two test vials from each set were for 0 day (immediately posttreatment) sample analysis.

The dark exposed test samples were wrapped in aluminum foil and placed in an aluminum foil covered box. The aluminum foil covered test samples were incubated for 30 days posttreatment with the temperature monitored during the entire testing period.

After being weighed down with lead strips and two rubber bands, the light exposed test samples were placed in a waterbath controlled at 25 ± 1°C. A pyrex plate was then placed over the borosilicate test flask to filter out the UV light (≤290 nm wavelengths). Following adjustment of the height of the water bath, the test samples were exposed to a Heraeus Suntest Unit with a total natural sunlight intensity of 410 W/m^2. The total intensity (300 nm to 800 nm) of natural sunlight was measured and adjusted to that of natural sunlight (See Figure 8) in Greensboro, NC during the month of September. The light exposed test samples were exposed to a intermediate light cycle (12 hours light on and 12 hours dark). The temperature of the light exposed test samples was monitored during the entire testing period, as well.

During the testing period, ^{14}C-Volatiles were trapped or collected from the headspace of the soil sample flask. The organic volatiles were collected in

ethylene glycol traps and carbon dioxide was collected in two KOH traps by applying a negative pressure to the trap series.

Duplicate light exposed and dark control samples were collected at 0 hours (immediately posttreatment), 1, 7, 14, 21 and 30 days posttreatment (See Table II). Volatile and storage stability samples were not collected at 0 hours posttreatment. However, at day 3 posttreatment volatile samples were collected and 100 µL aliquots were radioassayed. All soil samples were weighed, air-dried, and extracted. Each extract was radioassayed and the final residue combusted to determine radio chemical balance.

To aliquots of homogenized (mortar and pestle) 0 hour and day 14 test samples and direct transferred day 21 and day 30 test samples, approximately 7 mLs of an acetonitrile:water (80:20,v/v) solution was added and mixed for 30 minutes. The soil samples were then centrifuged and the supernatant decanted. Three soil samples were again extracted with acetonitrile:water solution, centrifuged, and the supernatant decanted. The supernatants from the same soil samples were combined and aliquots were radioassayed. If the extracted soil contained >10% of applied radioactivity, the soil samples was further extracted by reflux.

Two soil samples, day 21 and day 30, were further extracted with 7 mLs methanol:water reflux (50:50,v/v). The day 14 soil samples were accidently refluxed with 1N NaOH:methanol solvent (50:50,v/v). The refluxed samples were centrifuged, supernatants decanted, combined (for soil samples extracted/refluxed twice), and radioassayed. The remaining soil residues were air-dried, weighted, and oxidized to determine the amount of radioactivity remaining in the soil samples. The day 14 and Day 30 refluxed samples required further extraction to achieve solubization of 90% of the total radioactivity applied. These soil samples were refluxed with 7 mLs of 1M NaOH/methanol (50:50,v/v) for 1 hour, centrifuged, supernatant decanted, air-dried, weighed, and oxidized to determine the amount of radioactivity remaining in the samples. In addition, the day 21 soil samples required further extraction using 7 mLs of 12.5M NaOH. Concentrated NaOH solution was used accidently instead of the 1M NaOH:methanol (50:50,v/v) solution. The soil samples were then centrifuged, supernatants decanted, air-dried weighed, and oxidized to determine the amount of radioactivity remaining in the soil sample.

The soil extracts and refluxes, except for 0 hour, were concentrated for chromatography (TLC and HPLC). TLC and HPLC were used for characterization and quantitation. The TLC plates were developed using single and two dimensional chromatograms. The solvent systems used were chloroform:methanol:NH_4OH:water (80:30:4:2,v/v/v/v) and toluene:acetone:formic acid (75:25:4,v/v/v). Reference standards were used for comparison with single and two dimensional chromatograms spotted in a similar manner. Reverse phase HPLC was used to characterize and quantitate selected samples, as well. Aliquots of selected reference standards were co-injected and co-chromatographed on HPLC chromatograms. The LOQ (limit of quantitation) for metolachlor and CGA-77102 was 2.0 ppb in ethylene glycol trap radioassays. For other radioassays the LOQ ranged from 2.2 to 7.3 ppb.

Mass spectral analysis was performed on each HPLC isolate. A Varian 3400 GC interfaced with Finnagan TSQ700 mass spectral was used for MS confirmation analysis.

Linear regression analysis was performed using the least squares method. The half-lives were then calculated using the equation $t_{1/2}=(LN\ 2)/k$.

DATA SUMMARY:

In the light exposed samples, metolachlor and CGA-77102 decreased to 74.43% and 78.64% of applied dose by day 30, respectively. The half-lives reported for light exposed samples of metolachlor and CGA-77102, using first order kinetics

calculations, were 78.8 days and 95.1 days, respectively. In the dark control samples, metolachlor and CGA-77102 decreased to 59.99% and 66.86% by day 30, respectively. The half-lives reported for metolachlor and CGA-77102 dark control samples were 40.9 days and 50.2 days, respectively (See Tables XX and XXI, Figures 51 and 52). The correlation coefficients for the best fit lines ranged from -0.9452 to -0.9801. For both test materials the half-lives valves for the light exposed samples were longer than for the dark control samples. Based on the test methodology, the study author assumed that the longer half-lives for the light exposed samples was a secondary result of the artificial light source (xenon arc lamp) on the soil microbial population. However, there appears to be no significant difference between the test materials under the same conditions, either light exposed or dark control. In addition, since the quantitative and qualitative profiles were basically the same, these data indicate that soil photolysis is not a significant route of degradation for metolachlor or CGA-77102 (See Tables VII thru XII and Figures 22 thru 29).

The degradation pathways were not widely disparate for metolachlor and CGA-77102. Only two degradation products, CGS-40172 and CGA-51202, reached concentrations >5.6% of applied radioactivity in some of the test samples. In day 30 light exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 7.20% & 7.19% and 0.91% & 0.73% of applied dose, respectively. In day 30 dark exposed samples of metolachlor and CGA-77102, CGA-40172 and CGA-51202 reached a reported 9.85% & 9.01% and 6.21% & 3.83% of applied dose, respectively. There were trace amounts of CGA-40919, CGA-46129, CGA-48087, and CGA-50720 discernible in some of the test samples (See Tables XIII thru XVIII).

In addition, only trace amounts of ^{14}C-volatiles were detected in the volatile collection traps. Therefore, volatiles did not significantly contribute to the radiochemical balance of ^{14}C-metolachlor or ^{14}C-CGA-77102 samples. Many radioassays of the ethylene glycol and KOH collected samples resulted in values <MQA (minimum quantifiable amount) which were replaced with values of zero for the radiochemical balance calculations. The total ^{14}C-radioactivity in the KOH traps ranged from <MQA to 0.14% of applied ^{14}C-metolachlor. The total radioactivity in the KOH traps ranged from <MQA to 0.27% of applied ^{14}C-CGA-77102. The total radioactivity in the ethylene glycol traps ranged from <MQA to 0.05% of applied radioactive metolachlor and from <MQA to 0.17% of applied radioactive CGA-77102. This gave a range of <MQA to 0.27% for all ^{14}C-volatiles. Since these volatiles values are considered negligible, volatiles were not further characterized during the analytical process.

To determine bound soil residues, the extracted soil samples were oxidized and bound soil residues calculated as percent of applied radioactivity. The mean bound radioactive carbon in extracted soil samples ranged from 2.62% to 8.75% of applied radioactivity. The amount of bound radioactive carbon in soil samples ranged from 2.34% to 9.11% of applied radioactivity.

The temperature of the light exposed and microbial viability samples was monitored during the testing period. The temperature of light exposed samples was maintained within a 25 ± 1°C range except on one occasion. On 17 March 1995 the temperature reached 23.9°C for no longer than 40 minutes. The temperature of the microbial viability samples ranged from 23.3°C to 26°C during the incubation period.

The artificial light source approximated the intensity and spectral distribution of the natural sunlight. The intensity of the artificial light source ranged from 410 to 433 W/m^2 (See Figure 8).

Since the day 3 and day 10 test samples were not needed to establish the half-lives, they were harvested on day 30, and served as microbial viability samples in the light exposed and dark control samples. The results indicate that both the light exposed and dark control samples were and remained viable during the

testing period (See Table 1). However, the viability data did indicate a decrease in the microbial populations during the testing period.

The mean application rates for ^{14}C-metolachlor and ^{14}C-CGA-77102 were 1.29 ppm and 1.35 ppm, respectively, with respect to the wet weight of the soil. The average wet weight of the soil for all samples was 3.6 grams. The radiochemical balance for metolachlor and CGA-77102 treated samples, light exposed and dark control samples ranged from 94.62% to 106.63%, respectively (See Tables III to VI).

COMMENTS:

1. No photodegradation in water data for CGA-77102 has been submitted. It is not clear whether these soil photolysis data are in agreement with the aqueous photolysis data. Discrepancies between previous metolachlor photolysis data and these bridging CGA-77102 and metolachlor data need to be addressed before a more complete environmental fate can be assessed. Half-lives of ≈70 days and 8 days were reported for aqueous photolysis and soil photolysis in previous metolachlor data. In addition, if metolachlor is considered stable to photolysis, there is a discrepancy in soil photolysis data and the aerobic metabolism data. Half-lives of 8 days and 67 days were reported for soil photolysis and aerobic soil metabolism, respectively.

2. There is a discrepancy in the photodegradation on soil for metolachlor using natural sunlight and these bridging soil photolysis data (8 days vs 78.8 days; MRID 40430203) (GT:02/25/93). The reason for this discrepancy is not clear at this time. Artificial light sources may have a greater effect on the microbial population than natural sunlight. The previous study did report a mercury arc lamp artificial light source resulted in a half-life of 37 days. However, data using mercury arc lamps have historically not been accepted to fulfill data requirements for photolysis. Microbial viability should be monitored during the entire photodegradation testing period to clarify the environmental fate assessment.

3. Even though the half-lives for photodegradation on soil using an artificial light source (xenon arc lamp) for metolachlor and CGA-77102 were not widely disparate (both >30 days; extrapolated=78.8 days vs 95.1 days), these data are not in agreement with the bridging aerobic soil metabolism data. Biphasic half-lives of 8 days for the 0 to 21 days posttreatment and 67.7 for the 0 to 6 month posttreatment calculations were reported for the bridging aerobic soil metabolism data. This discrepancy needs to be addressed to make an environmental fate assessment.

4. Based on soil moisture, metolachlor appears to be stable to hydrolysis. This is in agreement with previous metolachlor data.

5. The glassware used in the study was silicon treated by soaking it in a 10:90 (v/v) solution of dichlorodimethylsilane in hexane for 15 minutes. After rinsing the treated glassware with methanol and heating to 100°C for one hour, the glassware was washed to remove any residue.

6. The microbial activity of the test soil was reported for the light exposed and the dark control samples at initiation of the study and termination of the study. These data confirmed that the microbial populations for the light exposed samples decreased during the testing period. However, it is not clear if the decrease was significant in the longer half-lives calculated for the light exposed samples than for the dark control samples.

7. The microbial viability of the test soil was measured prior to treatment and at termination of the testing period for the both light exposed and dark control samples. EFGWB prefers that the soil viability be monitored during

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the testing period, as well. However, EFGWB believes that repeating the soil photolysis study would not significantly change the environmental fate assessment. In future photodegradation studies, soil viability should be monitored during the testing period for comparison of any changes in soil viability and photolysis data.

8. The author stated that the light exposure was intermittent (intermittent= 12 hours of light exposure and ≈12 hours of darkness) which reflects rather closely natural sunlight exposure which is intermittent. In addition, it appears the half-lives were based on an intermittent light cycle day (12 hour light exposure and 12 dark day).

9. The soil moisture content was monitored during the testing period. The moisture content was maintained at 75% of 1/3 bar. Water filtered through a Nalgene Filterware Unit which exceeds all ASTM Type 1 standards and through a 0.2 μm filter to sterilize the water was used to adjust the moisture content several times during the testing period.

EFED Review dated 4/22/1997

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DATA EVALUATION RECORD
STUDY 2

CHEM 108800 Stereoisomer Metolachlor CGA-77102 §162-1

STUDY ID 43928936

Clark, A.O. COMPARATIVE AEROBIC SOIL METABOLISM OF PHENYL-^{14}CGA-77102 AND PHENYL-^{14}C-METOLACHLOR. Sponsored and Submitted by Ciba Crop Protection, Ciba- Geigy Corporation, Greensboro, NC; Performed by Ciba Crop Protection, EFED, Ciba-Geigy Corporation, Greensboro, NC and Agrisearch Incorporated, Frederick, MD under Ciba Study Number 338-94 and ABR-95102; Study completed on 18 December 1995; Received by EPA 26 January 1996.

DIRECT REVIEW TIME = 2.8 days

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: OPP/EFED/EFGWB
TEL: 305-5245

SIGNATURE:

APPROVED BY: Paul Mastradone, Chief
Supervisory Chemist
Review section #1
OPP/EFED/EFGWB

Signature: Paul Mastradone

Date: 4/23/97

CONCLUSIONS:

Metabolism - Aerobic soil

The aerobic soil study is scientifically valid, and can be used as supplemental data. However, it is not acceptable to fulfill the aerobic soil metabolism data requirement (162-1) for the following reasons:

a. There is a discrepancy in the half-life reported in the previous metolachlor data (MRID 41309801A-B) and these bridging data. A half-life of 67 days was reported in previous metolachlor data. These data reported biphasic half-lives of 8/67.9 and 7.8/69.7 days for metolachlor and CGA-77102.

b. There is a discrepancy in these bridging aerobic soil metabolism data and the bridging soil photolysis data (MRID 43928935). For the 0 to 21 day data, the bridging soil photolysis data reported a half-life of 78.8 and 95.1 days for metolachlor and CGA-77102. The aerobic soil metabolism data reported a half-life of 8 days for the 0 to 21 days data.

c. Biphasic half-lives were not reported in previous metolachlor data.

Therefore, additional data addressing these discrepancies are needed to clarify the environmental fate and to make a more complete environmental fate assessment of metolachlor and CGA-77102.

Aerobic metabolism appears to be a major route of degradation for metolachlor and CGA-77102. Biphasic half-lives of 8.8/67.9 days and 7.5/69.7 days were reported for CGA-77102 and metolachlor, respectively. Calculated rate constants of -0.8 days^{-1} and -0.9 days^{-1} for the primary phase (0-21 days posttreatment samples) were reported, as well. These data indicate that metolachlor and CGA-77102 not only degrade by microbial mediated processes but at almost the same rate.

The major degradation pathway for metolachlor and CGA-77102 appear to involve chlorination and subsequent hydroxylation which was followed by progressive oxidation. The degradation pathway involved the same degradation products. In addition, the reported quantitation data of the degradation products were close.

During the degradation process, there was a steady generation of carbon dioxide (average of 19.8% and 20.2%). In addition, there were two major non-volatile metabolites, CGA-354743 and CGA-51202, formed at maximum concentrations of >10% of applied radioactivity. Three degradation products, CGA-40172, CGA-50720, an unidentified degradate, were discernible at concentrations >5% of applied material. However, the unidentified degradate was determined to be comprised of two components when analyzed by MS. Other discernible products, CGA 46129 and additional unidentified degradates, were reported to reached maximum concentrations of <5% of applied radioactivity. Identified degradation products were confirmed by MS analysis.

MATERIALS AND METHODS:

Test Material: [14C]phenyl-CGA-77102 was obtained from Ciba-Geigy Chemical Synthesis Group. The CGA-77102 radioactive test material was reported to have a specific activity of 84 4. μCi/mg, a radiochemical purity of 98.4% and a chemical purity of >99.9%.

[14C]phenyl-metolachlor was obtained from Ciba-Geigy Chemical Synthesis Group. The metolachlor radioactive test material was reported to have a specific activity of 85.8 μCi/mg, a radiochemical purity of 97.6%, and a chemical purity of >99.9%.

See Figure 1.

Reference Standards: The non-radioactive metolachlor standard used for the study was obtained from the Analytical and Product Chemistry Department, Ciba-Geigy Corporation. All other non-radioactive reference standards were obtained from Ciba Chemical Synthesis Group. They were stored in Environmental Fate Freezers at -5oC.

See Figures 1 and 2.

Stock Solution: Aliquots of the test materials (15.25 mg 14C-CGA-77102 and 8.38 mg 14C-metolachlor) were dissolved in separate flask containing 25 mL of acetonitrile. The purity of these stock solutions were determined by two dimensional TLC and by HPLC.

Soil: The test soil was obtained by Agrisearch, Inc. from a field in Buckeystown, MD. The moisture content of the test soil was adjusted to 75% of 1/3 bar and sieved through a 2mm mesh screen.

Characterization of the test soil was performed by Agvise Lab., Northwood, ND. In addition, viability of the test soil was monitored throughout the testing period at -0 (pretreatment), 1 month, 4 months, and 6 months posttreatment.

See Figure 3.

Sampling: Duplicate test samples (aerobic) were collected at 0 (immediately posttreatment), 1, 3, 5, 7, 10, 14, 21, 30 (1 month)

days posttreatment and at 2, 2.5, 3, 4, and 6 months posttreatment. In addition, duplicate sterile samples were collected at 0 (immediately posttreatment), 1, 4, and 6 months posttreatment.

Except for the 0 day samples, test samples were purged and volatiles collected immediately after samples until 1 month posttreatment. After the 1 month posttreatment samples were collected, test samples were purged and volatiles collected every 14 days and at each sample interval.

Test System: No picture was provided.

Foil-wrapped 250 mL Erlenmeyer flasks fitted with a 24/40 ground glass joint was used for the test chamber. Volatile traps (glass dispersion tubes) were fitted with impinges. All glassware was silylated and sterilized.

METHODOLOGY:

Prior to initiation of the aerobic soil metabolism study, the test soil was sieved through a 2mm sieve, and the soil microbial count for test soil used in aerobic portion of the study was determined (See Table IA). The test glassware was then silylated and sterilized for the study initiation.

After the pre-initiation steps were completed, the test flasks were inoculated with 3.6 mL or 14C-CGA-77102 or 6.5 mL of 14C-metolachlor. After inoculation the acetonitrile solvent was allowed to evaporate. Then 1650 grams (dry weight of test soil, Maryland sandy loam soil, was transferred to the test flask. The application rate verified by combustion and LSC using five replicate aliquots and the moisture level brought to 75% of 1/3 bar. The application rate established by LSC was approximately 1.3 and 1.4 for metolachlor and CGA-77102, respectively.

For the sterile soil samples, approximately 50 grams of test soil were transfer red to each sterile test flask. Prior to treatment the sterile test flasks were then autoclaved for one hour at 121oC for three consecutive days. After sterization of the sterile test flask containing test soil, 107 μL aliquots of 14C-CGA-77102 or 195 μL aliquots of 14C-metolachlor stock solution were transferred to the sterile test soil flask. The sterile test samples were then adjusted to 75% of 1/3 bar moisture capacity. The application rate established by LSC was 1.30 ppm and 1.32 ppm for CGA-77103 and metolachlor, respectively.

A silylated glass impinge with ground glass 24/40 joint was sealed to each test flask. The inlet side of the impinge was attached to the hydration vessel and the outlet side was attached to the traps. Traps were attached in series using foam plugs and a 10% KOH solution for trapping carbon dioxide. Approximately 50 mL of 10% KOH solution was added to each trap.

Duplicate test samples were collected at 0 (immediately after treatment), 1, 3, 5, 7, 10, 14, 21, 30 (1 month) days and 2, 2.5, 3, 4, and 6 months posttreatment The sterile test samples were collected at 0 (immediately after treatment), 1, and 6 months posttreatment. Except for the 1 and 10 days and the 2.5 month post treatment test samples and the 6 month posttreatment sterile samples, which wer not quantitated, all the test samples were characterized and quantitated by LSC TLC, and HPLC.

Volatiles were collected at each sampling time interval until 1 month posttreatment by purging the test samples immediately after being harvested. After 1 month posttreatment, all samples were purged every 14 days and on the sampling day. Each matrix was radioassayed at collection by LSC. Foam plugs were placed

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in scintillation vials containing cocktail and directly analyzed by LSC. Fresh foam plugs and KOH solutions were provided after each volatile sampling interval

Each test sample and sterile test sample were extracted by blending each sample with approximately 30 mLs of acetonitrile:water (80:20/v,v). The extracted (soil portion) samples were then centrifuged and the supernatant decanted to a separate vial. The soil portion of the extracted samples were extracted a second time. The supernatants from the two extractions were combined and radioassayed by LSC.

After the percent extractable radioactivity was determined, aliquots of the aqueous phases were concentrated for analysis. Quantitation and confirmation analysis wee performed using 2 dimensional TLC and HPLC, respectively.

The extracted soil test samples (not sterile samples) were refluxed for 1 hour with approximately 30 mLs of methanol:water (50:50/v,v). The samples were centrifuged and the supernatant transferred to separate test vessels. Aliquots of each test extract sample were then concentrated and quantitated by 2-dimensional TLC and HPLC.

From Day 3 through month 6 posttreatment test samples (except for Day 5) were further refluxed with 30 mL methanol:1M NaOH (50:50/v,v). The refluxed samples (1 to 2 hours) were centrifuged and the supernatant decanted. The percent extractable radioactivity was calculated using LSC data, and aliquots of each extract sample were concentrated and/or quantitated as above.

From Day 5 through month 6 posttreatment test samples were further refluxed for one hour with 1M NaOH. The refluxed samples were centrifuged and the supernatant transferred to separate test vessels. The percent extractable radioactivity was determined by using LSC data, and aliquots of each extract sample were concentrated and quantitated as above using TLC and HPLC.

The day 14 posttreatment test samples were further refluxed in 30 mLs for one hour with methanol:water:formic acid (50:50:2/v,v,v). The refluxed samples were centrifuged and the supernatant transferred to separate test vessels. The percent extractable radioactivity was determined by using LSC data.

Since there was very little radioactivity extracted with the methanol:water: formic acid reflux exercise, the day 14 posttreatment test samples were further refluxed for one hour with acetic acid:methanol:sodium acetate (8:1:1;v/v/v). This reflux exercise resulted in the release of very little radioactivity, as well.

The extracted and/or refluxed soil test samples were oxidized to determined the amount of bound radioactivity. The radioactive carbon dioxide was trapped in aliquots of Oxosol.

Spiked test samples were stored in freezers and monitored at the termination of the testing period. The soils were extracted with acetonitrile:water (80:20; v/v), concentrated if needed, and quantitated for HPLC analysis.

Two dimensional TLC was used for characterization, isolation of degradates, and quantitation on all test samples and reference standards. The solvent systems used were chloroform:methanol:ammonium hydroxide:water (80:30:4:2;v/v/v/v) and toluene:acetone:acetic acid (75:25:4;v/v/v). The non-radiolabelled reference standards were placed in the sample origin and margins created by solvent systems.

HPLC, using ammonium acetate buffer as the mobile phase, was used to isolate test material for mass spectral analysis. Non-radioactive reference standards were co-injected with selected samples for characterization of CGA-77102 and metolachlor residues and for calibration of instrument. Quantitation by reverse

phase HPLC was performed by the injection of a known amount of radioactive sample.

Mass spectral analysis (GC/MS/CI) was used for confirmation of TLC and HPLC analysis. The mobile phases utilized in GC/MS were methanol and ammonium formate.

Half-lives were determined by assuming first order reaction kinetics. The rate constant is calculated using the following equation: $\ln C = -kt + \ln C^{\circ}$ as ($y = mx + b$)

The detection limits were calculated based on 0.5 and 0.25 gm for soil combustions, on 0.25 mL for volatile trapping solutions, and a specific activity of 187368 dpm/μg for radioactive CGA-77102 or 190476 dpm/μg for radioactive metolachlor. The detection limits were determined to be 0.5 ppb for 0.5 gm soil combustion, 0.9 ppb for 0.25 gm soil combustion, and 0.7 ppb for volatile trapping solutions.

DATA SUMMARY:

Aerobic metabolism appears to be a route of degradation for CGA-77102 and metolachlor. Diphasic half-lives of 8.8 and 67.9 days were reported for CGA-77102, and biphasic half-lives of 7.5 and 69.7 days were reported for metolachlor (See Table XII). The first half-lives were based on data from 0 to 21 days posttreatment test samples, and the second half-lives were based on data from 21 days to 6 months posttreatment test samples. The rate constants for the primary half-lives were -0.08 $days^{-1}$ and -0.09 $days^{-1}$ for CGA-77102 and metolachlor, respectively, with correlation coefficients of -1.0 and -0.99 for CGA-77102 and metolachlor, respectively. The correlation coefficients for the secondary half-lives were -0.95 and -0.91 for CGA-77102 and metolachlor, respectively. These data indicate that metolachlor and CGA-77102 not only degrade under microbial mediated processes but at almost the same rate (See Tables III thru VIII).

There was a steady generation of carbon dioxide during the testing period. An average generation of 19.8% and 20.2% for metolachlor and CGA-77102 was reported. Two major non-volatile metabolites, CGA-354743 and CGA-51202, were reported. CGA-354743 was reported to reach a maximum concentration of 10.7% and 12.4% of applied radioactivity at day 60 posttreatment in the metolachlor and CGA-77102 test samples, respectively. CGA-51202 was reported to reach a maximum concentration of 10.3% and 10.9% of applied radioactivity at day 21 posttreatment in the metolachlor and CGA-77102 test samples, respectively. Both major metabolites declined to >6.7% of applied radioactivity by 6 months posttreatment. Another degradate which reached a total of 6.8% and 7.4% of applied radioactivity in metolachlor and CGA-77102 test samples was actually determine to be comprised of two components by MS analysis. Two other degradates confirmed by MS analysis at maximum levels of 6.2% and 8.2% of applied radioactivity were CGA-40172 and CGA-50720, respectively. Based on TLC and HPLC data and confirmed by MS in leaching data, degradate CGA-46129 appeared to be present at maximum levels of 3.9% to 4.1% of applied radioactivity, as well. Other discernible degradates were reported to only reached maximum concentrations of ≤3.7% of applied radioactivity. Therefore, they were not further characterized during this study.

The major degradation pathway for metolachlor and CGA-77102 appeared to involve dechlorination and subsequent hydroxylation which was followed by progressive oxidation. The degradation pathways indicates the formation of the same degradation products for metolachlor and CGA-77102. In addition, the quantitations for degradation products were very close. Sulfur addition was seen forming CGA-354743, the sodium salt.

CGA-77102 and metolachlor appeared to degrade only slightly under sterile conditions. The sterile test samples for metolachlor went from 91.4% of applied radio-

activity as parent at initiation of study to 77.1% at 4 months posttreatment while CGA-77102 went from 98.0% of applied radioactivity as percent at initiation of study to 86.0% at 4 months posttreatment. The total other radioactive components for CGA-77102 and metolachlor ranged from 1.0% to 8.5% and 1.0% to 13.1% during the testing period, respectively, with the largest individual component accounting for 1.8% in metolachlor sterile test samples and 1.7% in CGA-77102 sterile test samples. These data indicated that metolachlor and CGA-77102 were relatively stable when applied to sterile soil (See Table XI).

Storage stability data indicated that metolachlor and CGA-77102 are relatively stable when stored in freezer conditions (-5°C). At 6 months posttreatment storage conditions, metolachlor and CGA-77102 had reported recoveries of 92.5% and 89.0%, respectively, of the initial time 0 rates.

The average radiochemical balance for the test samples ranged between 90.6% and 102.2% for CGA-77102, and ranged between 91.3% and 100.8% for metolachlor (See Tables I-II and IX-X). The average radiochemical balance for the sterile test samples ranged between 99% to 101.6% for CGA-77102, and ranged between 98.6% and 100% for metolachlor (See Tables III-IV). These radiochemical balances were the summary of extracts, volatiles, and soil combustion radioactivity.

COMMENTS:

1. The half-life reported in a previous submitted aerobic soil metabolism study (GT;02/25/93;MRID 41309801A & B) was 67 days. No biphasic half-lives were reported in the previous submitted aerobic soil metabolism study. There was no discussion concerning the discrepancy in half-lives between the previous study and this study. It should be noted that the degradation pathways were basically the same in the two studies. However, the discrepancy in half-lives (67 vs 8/67.9 days) needs to be addressed at this time.

2. There appears to be discrepancies in the soil photolysis data and the aerobic soil metabolism data (78.8 and 95.1 days vs biphasic 8/67.7 and 7.8/69.7 days, respectively). The half-life for the soil photolysis and the first phase of aerobic soil metabolism data were calculated on ≈the first 21 days posttreatment data. These discrepancies need to be addressed so a more complete environmental fate assessment can be made.

3. The sterile test samples in the previous aerobic soil metabolism study (41309801A-B) had similar results to the sterile data in this study. There was a decline of approximately 10% of the initial time 0 parent material reported for both studies (41309801A-B and 43928936).

4. These data appear to be in agreement with other laboratory environmental fate data (hydrolysis and mobility). These data indicated that metolachlor and CGA-77102 are relatively stable to hydrolysis, and degradation pathways for the aged mobililty study were in agreement.

5. The same or similar (from the same area) sandy loam soil used for the aerobic soil metabolism study that was used for the photodegradation on soil study and in the leaching, adsorption/desorption study. The characterization of the sandy loam soil in the photodegradation on soil was slightly different than that for the sandy loam in the other laboratory studies. Using the same or similar soil for appropriate laboratory studies allows for better comparison and validation of data.

EFED Review dated 4/22/1997

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DATA EVALUATION RECORD

STUDY 3

CHEM 108800 | Stereoisomer Metolachlor CGA-77102 | 163-1

STUDY ID 43928937

Spare, W.C. ADSORPTION/DESORPTION OF ^{14}C-CGA-77102 BY THE BATCH EQUILIBRIUM METHOD ON REPRESENTATIVE AGRICULTURAL SOILS. Sponsored and Submitted by Ciba-Geigy Protection, Ciba-Geigy Corporation, Greensboro, NC under Ciba-Geigy Study No. 71-95 and Agrisearch Project No. 12218; Study completed on 11 July 1995; Received by EPA 26 January 1996.

DIRECT REVIEW TIME = 2.8 days

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: OPP/EFED/EFGWB
TEL: 305-5245

SIGNATURE:

APPROVED BY: Paul Mastradone, Chief
Supervisory Chemist
Review section #1
OPP/EFED/EFGWB

Signature: Paul J Mastradone

Date: 4/23/97

CONCLUSIONS:

Mobility- Adsorption/desorption

The adsorption/desorption mobility study is scientifically valid. In addition, it can be used to fulfill the unaged mobility data requirement (163-1). No further unaged mobility data for CGA-77102 are needed. The aged mobility data (MRID 439289938-see attached DER) requirement is fulfill by additional submitted data, as well. Therefore, no further mobility data for CGA-77102 are needed at this time.

Adsorption/desorption data, using four test soils with varying organic matter content (0.3 to 2.2%) and soil texture (sand, sandy loam, silt loam, and clay), indicate that CGA-77102 is mobile in sandy loam and silt loam soils (Kds=1.4 and 1.1, respectively), moderately mobile in clay soil (Kd=4.7), and highly mobile in sand soil (Kd=0.3). Calculation of the K_{oc} values (adsorption constants based on organic carbon) yielded values ranging from 110 for sand soil to 369 for clay soil. Kd values for the desorption phase ranged from 1.3 to 8.0 (1.3 for sand, 3.7 for silt loam, 4.1 for sandy loam, and 8.0 for clay soils). The correlation coefficients for the adsorption and desorption phases ranged form 0.9964 to 0.9999.

Freundlich adsorption/desorption data was reported for CGA-77102 based on the stability (no degradation in TLC or HPLC analysis) of parent CGA-77102 during the testing period and the linear logarithmic plots of data. These data indicate that CGA-77102 did adsorb to the test soils. In addition, based on the Kd values for adsorption, CGA-77102 does have the potential to move through most soil profiles.

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MATERIALS AND METHODS:

Test Material: [^{14}C]phenyl radiolabelled CGA-77102 was obtained from Ciba-Geigy Chemical Synthesis Group. A specific activity of 84.4 μCi/mg and a radiolabelled purity of 98.4% was reported for the test material (See Figure 1).

Reference Standards: Non-radiolabelled CGA-77102 was obtained from Ciba-Geigy Corporation. A chemical purity of 99.4% was reported (See Figure 1).

Calcium Chloride solution: The aqueous calcium chloride solution (0.01 M) was prepared by adding 7.75 grams of calcium chloride dihydrate to 4 liters of water (1.94 gms CaCl/L of water). The 0.1 M CaCl solution was sterilized by filtration through a 0.2 micro membrane filter. The final pH of the solution was 7.02. Test water (see below) was used to prepared the solutions.

Stock Solutions: The 15 mgs of radioactive CGA-77102 was completely dissolved in 25 mL of acetonitrile (0.6 mg/mL). The stock solution was determine to be within 3% of the mean using LSC.

Test Solutions: Preliminary phase-

A 3.3 mL aliquot of the radioactive CGA-77102 stock solution (0.6 mg/mL) was transferred to a sterile flask. After evaporation of the solvent, acetonitrile, 200 mL of prepared sterile 0.01 M calcium ion solution was used to dilute the CGA-77102. The final CGA-77102 concentration was 9.827 μg/mL. The final CGA-77102 concentration for the repeated preliminary phase was 10.300 μg/mL.

Definitive phase-

A 4.8 mL aliquot of the radioactive CGA-77102 stock solution (0.6 mg/mL) was transferred to a sterile flask. After evaporation of the solvent, acetonitrile, 275 mL of prepared sterile 0.01 M calcium ion solution was used for dilution of the CGA-77102. A set of 5 dilutions were prepared for the definitive phase of the study. The final concentrations for the definitive phase of the study were: 0.0, 0.203, 0.513, 1.034, 4.971, and 10.068 μg/mL.

Test Soil: Four test soils (sandy loam, silt loam, clay, sand) were used for the study. See Table I for soil characteristics. The sandy loam soil, which was the same soil used for the aerobic soil metabolism study, was collected from Maryland. The silt loam and sand soils wee collected from Maryland, as well. The clay soil was collected from Mississippi. All four soils were air-dried and sieved through a 2 mm sieve prior to characterization and initiation of study.

Test Water: The test water was from Frederick County, Maryland. The test water was considered drinking water which was filtered, deionized, boiled, and distilled.

METHODOLOGY:

Four representative soils (sandy loam, silt loam, clay, and sand) were collected for the study. Three soils (sandy loam, silt loam, and sand) for the study were collected in Maryland. The fourth soil, clay soil, was collected in Mississippi. Prior to characterization and initiation of study, the four test soils were air dried and sieved through a 2 mm sieve. After sieving the test soils, an aliquot of each was sent to Agvise Laboratory, Northwood, ND for characterization and determination of soil texture (See Table I). In addition, the microbial viability of the test soil, incubation temperatures, and pHs were evaluated and reported in Tables II, III, and IV, respectively.

Prior to initiation of the study a preliminary test was initiated to establish adsorption equilibrium time and the optimum ratio of soil to test solution for the definitive adsorption/desorption phases or study. Adsorption of test material to the test container or cap was determined during the preliminary test, as well.

For the preliminary phase, duplicate soil samples of each test soil was treated with CGA-77102 at 9.827 ppm in aqueous 0.01M $CaCL_2$ solution. The test tubes contained 1 gm. of the appropriate test soil. Twenty mL each of the test solution was transferred to each test tube, capped, and shaken in the dark at 25 ± 1°C. The test samples for the preliminary phase was collected at 0 (analysis of test solution directly), 2, 4, 8, and 24 hours posttreatment. The collected test samples were centrifuged for 15 minutes and the supernatant removed and analyzed by LSC. In addition, bound residues were determined at the final equilibrium analysis by combustion. The stability of radioactive CGA-77102 in aqueous $CaCl^2$ solution was evaluated by HPLC analysis.

Since the soil combustion analysis indicated that soil bound radioactivity was 0.7% to 15.7% of applied radioactivity which is not within the specified 20% to 80% range, a repeated preliminary phase was initiated to better evaluate equilibrium time and test solution to soil ratios. Therefore, for the repeated preliminary phase of the study, the ratio of solution to soil was changed and the soil-less blanks were not repeated. Approximately 10 gms of sandy loam, silt loam, and sand soils were used per 20 mLs of 0.01M $CaCl_2$ solution and 4 gms of clay soil was used per 20 mLs of 0.01M $CaCl_2$ solution which resulted in a 2:1 ratio of solution to soil for sandy loam, silt loam, and sand soils and 5:1 ratio for clay soil. These soil to calcium ion solutions resulted in reported bound radioactivity residues of 10.0% to 45.4%.

Based on the equilibrium time and calcium solution to test soil ratio data provided by the repeat preliminary phase, a 2:1 ratio for solution to soil for the Maryland sand and silt loam soils and a 5:1 ratio for solution to soil for the Maryland sandy loam and Mississippi Clay soils were used in the definitive phase of the study. Duplicate test samples of each test soil were treated at ^{14}C-CGA-77102 concentration levels of 0.0, 0.203, 0.513, 1.034, 4.971, and 10.068 ppm (See Tables VIII thru XI). The pH of each test solution was determined and the test samples were shaken in the dark for 4 hours at 25 ± 1°C. At 4 hours the test samples were centrifuged for 15 minutes, the supernatant decanted, and aliquots analyzed by LSC.

The desorption phase was then initiated by adding 0.01M $CaCl_2$ solution (same amount as was used in the adsorption phase) to the soil portion of the adsorption test samples. These samples were then mixed, shaken for four hours, centrifuged, and supernatant decanted. Triplicate 2 mL aliquots of each supernatant were removed and analyzed by LSC. Desorption soil concentration were determined by combustion of the soil portion of the desorption samples. The soil portion of the test samples that were treated at the 10.068 ppm concentration level, and were extracted with a 1:1 solution of 80:20 acetonitrile/water and shaken for 30 minutes. The samples were then centrifuged and the extract decan-

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ted. The soil samples were again extracted and the extracts from the same soil sample were combined and analyzed by LSC.

The material balances of the test samples for each sample was calculated using total radioactivity in the aqueous phase plus total radioactivity in the soil phase. The target recovery of applied radioactivity was ≥90% to ≤110%.

The supernatant from one test sample treated at the 10.068 ppm level was analyzed by TLC and HPLC. Additionally the desorption supernatant from one replicate per soil type treated at the 10.068 ppm level was analyzed by TLC and HPLC.

TLC plates were developed using two solvent systems. The first dimension used chloroform/methanol/ammonium hydroxide/water (80:30:4:2;v/v/v/v) for the solvent system. The second dimension used toluene/acetone/formic acid (70:25:4;v/v/v) for the solvent system. The TLC test samples were air-dried and then eluted to 15 cm above the origin. The TLC plates were evaluated using an radioactivity scanner. For additional verification, at least 10% of the TLC plates were evaluated by LSC.

Solvent systems used for HPLC were 0.05M ammonium acetate buffer and acetonitrile. The CGA-77102 analytical standard was co-chromatographed with each test sample analyzed by HPLC.

The detection limits were determined for soil combustions, preliminary phase solutions, adsorption solutions, and desorption solutions. Detection limits calculations were based on a 2 mL volume for desorption, 0.5 mL volume for adsorption, 0.1 mL volume for preliminary phase, an average soil sample weight of 0.22 gms for combustion, and a specific activity of 1873868 dpm/μg for ^{14}C-CGA-77102.

The Freundlich equation was used for calculation of the K_d values. The values of ln C_e verses ln x/n were plotted for adsorption and desorption. The K_d constants K_d and n were determined from the slope (1/n) and intercept (ln K_d) of the resultant straight line using linear regression. In addition, K_{oc} values were calculated. For data reduction, mathematical methods of linear regression, means, percent variance, sums, and logs were used in calculations.

DATA SUMMARY:

Preliminary phase-

The preliminary phase testing period was terminated at 24 hours. Based on only slight changes in the concentrations of test material in the aqueous portion of the study, equilibrium appeared to be reached at 4 hours (See Table V).

Kd values (See Table VI) calculated for the preliminary phase indicated that the Kd values for the Mississippi Clay and Maryland sandy loam soils would range from >1 to <10 and for Maryland sand and silt loam soils would be ≤1. These data were used to establish the solution to soil ratios of 5:1 for the clay and sandy loam soil samples and 2:1 for the sand and silt loam soil samples in the definitive phase of the study.

Mass radioactive balance was determined for the repeated preliminary phase of the study by summation of radioactivity detected in the aqueous equilibrium sample plus radioactivity detected in the combusted soil sample. The mass balance reported for the repeated preliminary phase samples ranged 94.3% to 102.1% of applied radioactivity (See Table VII).

In addition, the 0 time (no test soil added) test tubes indicated that there was no significant adsorption of CGA-77102 to the test tubes. The reported recovery

data for the aqueous solutions was 97.6% to 101.1% of applied radioactivity for 24 hours equilibrium test samples.

Definitive Phase-

Linear regression was used to calculate the Freundlich adsorption soil constants (K_d values) (See Table XIII and XIV). K_d values for the four test soils ranged from 0.3 to 4.7 (0.3 for sand, 1.1 for silt loam, 1.4 for sandy loam, and 4.7 for clay soils). K_{oc} values (adsorption coefficients based on organic matter) for the four test soils ranged from 110 (for silt loam soil) to 369 (for clay soil). Therefore, based on the K_d and K_{oc} values reported for the test soils, CGA-77102 appears to be mobile in sandy loam and silt loam soils, moderately mobile in clay soil, and highly mobile in sand soil. The correlation coefficient and 1/n slope for the adsorption portion of the study ranged from 0.9991 to 0.9999 and 0.909 to 0.934, respectively (See Figure 2).

Linear regression was used to calculate the Freundlich desorption soil constants, ($K_{des}s$) as well (See Table XIV). The desorption soil constants for four test soils ranged from 1.3 to 8.0 (1.3 for sand, 3.7 for silt loam, 4.1 for sandy loam, and 8.0 for clay soils). K_{oc} values for (desorption coefficients based on organic matter) for the four test soils ranged from 357 for Maryland sandy loam to 740 for Maryland sand. Based K_d and K_{oc} values reported for the test soils, CGA-77102 appears to have slightly less mobility than the adsorption coefficients indicated. However, CGA-77102 still appears to have the potential to move in the soil profile. The correlation coefficient and 1/n slope for the desorption portion of the study ranged from 0.9964 to 0.9999 and 0.918 to 1.003.

Material balances for the test samples averaged 99.0% of applied radioactivity with a range of 86.1% to 113.7% (See Tables XII thru XV). Extractability of test samples appeared to vary. Extractability was reported to range from 77.8% to 97.0% of available radioactivity. Combustion of the extracted soil samples accounted for the remaining radioactivity.

Detection limit calculations for soil combustions, preliminary phase solution, adsorption solutions, and desorption solutions ranged from 0.0001 to 0.0017 ppm. The detection limit for soil combustion was 0.0011 ppm, for preliminary phase solution 0.0017 ppm, for adsorption solution was 0.0003 ppm, and for desorption solution was 0.0001 ppm.

The test material, CGA-77102, appeared to be stable (≤0.27% of applied radioactivity) during the adsorption and desorption phases (See Tables XVI to XIX). HPLC and TLC analyses verified the radioactivity present as parent CGA-77102. There was no degradation products discernible during adsorption and desorption phases of the study.

COMMENTS:

1. These adsorption/desorption data for CGA-77102 appear to be in agreement with previous adsorption/desorption data for metolachlor. The K_d values for metolachlor ranged from 0.01 to 2.2 in previous submitted data (MRID 404496-04). There is some difference in the K_d values for the clay soils (1.9 vs 4.7, however, the clay soils did have characterization differences and both K_d values indicate that metolachlor is mobile. Therefore, metolachlor has the potential to move downward through most soil profiles. Both CGA-77102 and metolachlor are considered to be moderately mobile to highly mobile when applied to soil.

2. These unaged adsorption/desorption data using the same four test soils with varying organic matter content (0.3 to 2.2%) and soil texture (sand, sandy loam, silt loam, and clay), are in agreement with the aged adsorption/desorption data with both indicating that CGA-77102 is moderately mobile to

very mobile. The Kd values reported for the aged adsorption/desorption study were 2.3, 2.4, 4.1, and 0.8 for sandy loam, silt loam, clay, and sand soils, respectively. In addition, the calculated K_{oc} values ranged from 200 for sandy loam soil to 468 for sand soil.

3. Mobility data on one of the major degradates, CGA-51202, has been submitted and reviewed (GT;02/25/93). It appears that CGA-51202 is more mobile than the parent metolachlor (K_d values ranging from 0.3 to 4.7 for parent and 0.04 to 0.17. Mobility data on the other major degradate, CGA-354743, is presently underway and will be submitted when completed.

4. 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.

5. For determining the soil to 0.01M $CaCl_2$ ratio, the protocol specified soil bound residues was 20% to 80% of applied radioactivity. In the repeat preliminary phase of the study, the reported radioactive soil bound residues was 10% to 45.4% of applied radioactivity. Only the sand soil was not within the protocol specifications. Based on the data provided for the four test solution concentrations, EFGWB does not believe repeating the sand soil adsorption/desorption data would provide further significant data or change the environmental fate assessment.

EFED Review Dated 4/22/1997

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DATA EVALUATION RECORD

STUDY 4

CHEM 108800 Stereoisomer Metolachlor CGA-77102 163-1

STUDY ID 43928938

Spare, W.C. LEACHING CHARACTERISTICS OF AGED ^{14}C-CGA-77102 IN FOUR SOIL TYPES. Sponsored and Submitted by Ciba-Geigy Protection, Ciba-Geigy Corporation, Greensboro, NC under Study No. 72-95; Performed by Agrisearch Incorporated, Frederick, MD under Agrisearch Project No. 12216; Study completed on 22 December 1995; Received by EPA 26 January 1996.

DIRECT REVIEW TIME = 2.8 days

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: OPP/EFED/EFGWB
TEL: 305-5245

SIGNATURE:

APPROVED BY: Paul Mastradone, Chief
Supervisory Chemist
Review section #1
OPP/EFED/EFGWB

Signature: Paul Mastradone

Date: 4/23/97

CONCLUSIONS:

Mobility- Aged Leaching

The aged mobility study is scientifically valid. In addition, it can be used to fulfill the aged mobility data requirement (163-1). No further aged mobility data for CGA-77102 are needed at this time. The unaged (adsorption/desorption) mobility portion of the mobility data requirement (MRID 439289937-See attached DER) is fulfilled, as well. Therefore, no further mobility data for CGA-77102 are needed at this time.

Parent CGA-77102 and its degradation products do appear to move through the soil profile when applied to different soil textures. Aged CGA-77102 and its metabolites appear to be mobile in sandy loam and silt loam soils, moderately mobile in clay soil, and very mobile in sand soil. K_d values for aged CGA-77102 (at its soil metabolic half-life) were reported to be 2.3 for silt loam soil, 2.4 for sandy loam soil, 4.1 for clay soil, and 0.8 for sand soil. Reported Koc values for sandy loam soil were 200 to 208, for silt loam soil were 226 to 243, for clay soil were 311 to 324, and for sand soil were 455 to 468. The average radioactivity in the leachates were reported to be 16.8% for the clay soil columns, 24.4% for the sandy loam soil columns, 27.3% for the silt loam soil, and 58.2% for sand soil columns. Parent CGA-77102 was detected in all the leachates (0.2% in clay, 36.3%, in sand, 2.3% in sandy loam, and 4.3% in silt loam soils). Three degradates (CGA-51202, CGA-50720, and CGA-46129) were identified at approximately 5.5 to 11.0%, 1.1 to 6.9%, and 0.4 to 1.5% of applied radioactivity in the leachates. There were approximately 8 other degradation products discernible in the leachates, but the total maximum concentration of these degradation products was 5.0% of applied radioactivity. Therefore, the average amount of radioactivity that remained in the soil columns was 77.9% for clay soils, 70.6% for silt loam soils, and 69.5% for sandy loam soils, and 33.7% for sand soils. CGA-77102 was the primary radioactivity extracted from the soil column sections. Minor

degradation products (≤ 2.6% of applied radioactivity) were identified as CGA-51202, CGA-50720, CGA-41507, CGA-41638, CGA-40919, CGA-354743, and CGA-40172.

MATERIALS AND METHODS:

Test Material: [^{14}C]phenyl radiolabelled CGA-77102 was obtained from Ciba-Geigy Chemical Synthesis Group. A specific activity of 84.4 μCi/mg and a radiolabelled purity of 98.4% was reported for the test material (See Figures 1 and 2).

Reference Standards: Non-radiolabelled CGA-77102 was obtained from Ciba-Geigy Corporation. A chemical purity of 99.4% was reported (See Figure 1 and Table III).

Stock Solutions: The 15 mgs of radioactive CGA-77102 was completely dissolved in 25 mL of acetonitrile (0.6 mg/mL). The stock solution was determine to be within 3% of the mean using LSC.

Test Solutions: A 427 μL aliquot of stock solution was transferred to four test flask and the solvent evaporated. Once 200 gms of test soil (dry weight) was added the approximate fortification level was 1.3 ppm.

Calcium Chloride solution: The aqueous calcium chloride solution (0.01 M) was prepared by adding 7.75 grams of calcium chloride dihydrate to 4 liters of water (1.94 gms CaCl/L of water). The 0.1 M CaCl solution was sterilized by filtration through a 0.2 micro membrane filter. The final pH of the solution was 7.02. Test water (see below) was used to prepared the solutions.

Test Soil: Four test soils (sandy loam, silt loam, clay, sand) were used for the study. See Table I for soil characteristics. The sandy loam soil, which was the same soil used for the aerobic soil metabolism study, was collected from Maryland. The silt loam and sand soils wee collected from Maryland, as well. The clay soil was collected from Mississippi. All four soils were air dried and sieved through a 2 mm sieve prior to characterization and initiation of study.

Test Water: The test water was from Frederick County, Maryland. The test water was considered drinking water which was filtered, deionized, boiled, and distilled.

Test System: See Figures 3 and 4.

METHODOLOGY:

Prior to initiation of the aged column leaching study, the test soils were sieved through a 2mm sieve, and the soil microbial count for test soils used in aged leaching study were determined (See Table II). The test glassware was then silylated and sterilized for the study initiation.

A total of four test soils (Maryland sand, Maryland sandy loam, Maryland silt loam, and Mississippi clay) were used for the aged column leaching study. The organic matter content of the test soils range 0.3% for sand soil to 2.2% for clay soil, and the pHs ranged from 6.1 to 7.2 (See Table I). These test soils were collected in Maryland and Mississippi, and are the same soils used in the

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unaged mobility (adsorption/desorption) study and other environmental fate laboratory studies (soil photolysis and aerobic soil metabolism).

The calcium chloride solution (0.01M) was prepared by transferring 7.75 gms of dihydrated calcium chloride to a flask. The flask used for the calcium chloride solution contained four liters of Frederick County drinking water which had been filtered, deionized, and distilled. The pH of the 0.01M calcium chloride solution was reported to be 6.4.

After preparation of the stock solution (25 mL of acetonitrile was added to the 15 mg of test material = 0.6 mg/mL), an aliquot (427 μL) was transferred to each of the test flask. The test solution was then distributed on the flask walls and the solvent was allowed to evaporate. To each treated test flask which was labelled for the appropriate test soil, an aliquot (200 gms) of the appropriate dried soil was transferred and mixed. Therefore, each test flask containing the appropriate test soil was treated at an application rate of approximately 1.3 ppm (1.333 ppm for clay, 1.252 ppm for sand, 1.257 ppm for sandy loam, and 1.284 ppm for silt loam). The exact application rate was determined by radioactivity analysis (combustion of three random samples).

The treated soils were then transferred to 500 mL test flask which were equipped with volatile traps. Each test flask was brought to 75% of 1/3 bar moisture capacity and placed in an incubator at 25 ± 1°C for 30 days. During incubation moist air was flushed through the series of volatile traps (duplicate polyurethane form and KOH) for one hour under negative pressure at 2, 5, 7, 9, 14, 19, 22, or 33 days post-incubation (See Figure 3 and Tables IV and VI). To monitor the moisture content of the test soils, the flasks were weighed at each volatile sampling interval (See Table V). At termination of the 30 day incubation period, the radioactivity of the 30 day aged treated soils were determined by combustion of triplicate aliquots of test samples. Aliquots of each aged soil were extracted and characterization of CGA-77102 residues determined prior to initiation of the soil column leaching phase.

Prior to completion of the aging process of the treated soils, duplicate soil columns were prepared for each soil texture. Each column was prepared in a manner that soil particles were not loss during leaching. The 4.2 cm diameter x eighteen inch height acetate leaching columns were packed with twelve inches of soil which was approximately 400 to 650 gms of test soil. The soil in the test columns was gently tamped to a uniform density. The test columns were then immersed in 0.01M calcium chloride solution such that the water rose above the test soil level. The saturated test columns were then weighed to determine the void volume, the columns were drained till the soil field capacity for moisture was reached.

To the prepared soil columns, 10 gms of the appropriate aged soil was transferred to the top portion of the column and covered with a thin layer of untreated soil. To minimized the disturbance of the soil and to provide a more uniformly distribution of the leaching solution (See Figure 4), a layer of glass fiber filter paper and a small quantity of glass wool were then placed on top of the thin untreated layer.

Each soil column which contained a layer of homogeneous aged treated test soil (See Table XI) was leached with a volume 0.01M calcium chloride solution equal to at least twenty inches times the cross sectional area of the column. Monitored with a peristaltic pump, an infiltration rate of ≤1 inch/hour was controlled during the leaching period. During the leaching period, the leachate was collected, measured, and analyzed by LSC. At the termination of the leaching period, triplicate soil samples of each section were combusted for radioactivity analysis, and the test columns were frozen at -20°C for overnight. After LSC analysis of the leachates and soil segments and the freezing of the soil columns, the radioactivity residues in the leachate were characterized, and the frozen

soil columns were sectioned into 6 parts (the treated soil layer and five 6 cm segments) for extraction and characterization.

The aerobic aged and column section soil samples which had radioactive concentrations >1% of applied radioactivity were extracted twice with acetonitrile/water (8:2;v/v) and the aqueous phases combined (See Figure 5 for analytical diagram). After determining the radioactivity balance, the soil portion from samples with reported radioactivity balances of <95% were reextracted twice by reflux for one hour with methanol/water (1:1;v/v). The extracts were combined and the radioactivity measured by LSC. In addition, the radioactivity in the soil portion was determined. If the soil radioactivity was determined to be ≥10% of applied radioactivity, the sample was reflux for two hours using 1N NaOH/water (8:2;v/v). The extracts from the first extraction and reflux were analyzed using TLC and/or HPLC which were co-chromatorgraphied with reference standards. Reflux 2 extracts were fractionated into humic acid, fulvic acid, and soil humin.

Two dimensional TLC was used for characterization, isolation of degradates, and quantitation on all test samples and reference standards. The solvent systems used were chloroform:methanol:ammonium hydroxide:water (80:30:4:2;v/v/v/v) and chloroform:methanol:formic acid/water (75:20:4:2;v/v/v). The non-radiolabelled reference standards were placed in the sample origin and margins created by solvent systems.

HPLC, using ammonium acetate/acetonitrile buffer (95:5;v/v) as the mobile phase, was used to isolate test material for mass spectral analysis. Non-radioactive reference standards were co-injected with selected samples for characterization of CGA-77102 residues and for calibration of instrument. Quantitation by reverse phase HPLC was performed by the injection of a known amount of radioactive sample. In an attempt to better resolve the numerous CGA-77102 degradation products that were polar, a modified elution gradient (ammonium acetate/acetonitrile buffer at 83:17;v/v) was developed with a column oven (See Figure 6).

Mass spectral analysis (GC/MS/CI) was used for confirmation of TLC and HPLC analysis. The mobile phases utilized in GC/MS were methanol and ammonium formate (See Figure 6).

Half-lives for the aged aerobic soil metabolism portion was estimated by linear regression. The natural log of the percent of initially applied CGA-77102 recovered from the soil was regressed against incubation time.

The distribution coefficient (K_d) values were estimated using the formula $K_d = [Vp/Vv - 1] \times Vv/W$. The adsorption distribution coefficients were calculated based on organic carbon .

The detection limits were calculated based on 0.225 gm for soil combustions, on 0.25 mL for volatile trapping solutions, 3 mL for leachate samples, and a specific activity of 187368 dpm/μg for radioactive CGA-77102. The detection limits were determined to be 1.7 ppb for 100 μL of soil extract, 1.0 ppb for 0.225 gm of combusted soil, 0.1 ppb for 3 mL of leachate, and 0.7 ppb for 0.25 mL of volatile trapping solutions.

DATA SUMMARY:

Half-lives for the 30 days aerobic soil metabolism studies were calculated and reported for each test soil. The reported half-lives were 22 days for clay soil, 53 days for sand soil, 8 days for sandy loam soil, and 7 days for silt loam soil with corresponding rate constants (k) of 3.09×10^{-2} days^{-1}, 1.31×10^{-2} days^{-1}, $8.76\ 10^{-2}$ days^{-1}, and 9.81×10^{-2} days^{-1}, respectively (See Table IX). At termination of the aerobic metabolism (aging) portion of the study, CGA-77102 made up 51.3% to 67.1% of applied radioactivity. Four degradation were identified in the aged soil which was transferred to the soil columns. These four degradates

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were reported as CGA-51202, CGA-46129, CGA-41507, and CGA-354743. In addition, there were four unidentified degradates reported which were named A2, A4, A8, and A9 (See Table X). Funic acid, humic acid, and humin made up a total concentration of 11.8% to 16.2% in clay, sandy loam, and silt loam test soils. Funic acid, humic acid, and humin were not detected in the sand soil (See Table XX). There were no organic volatiles detected in the polyurethane foam traps during the soil aging phase. However, the KOH traps accounted for 0.6%, 0.2%, 0.6%, and 1.1% of applied radioactivity in the clay, sand, sandy loam, and silt loam soils, respectively (See Table VI and X). Other TLC and HPLC analysis performed during the testing period to monitor and validate the study are reported in Tables VII and VIII. The radioactivity balance during aging averaged 99.8%, 102.8%, 106.2%, and 110.5% for the clay, sand, sandy loam, and silt loam soils, respectively (See Table VI).

Based on the reported distribution of radioactivity in the soil columns, calculated K_d and K_{oc} values of 2.3 and 226 to 243 for silt loam, 2.4 and 200 to 208 for sandy loam, 4.1 and 311 to 324 for clay, and 0.8 and 455 to 468 for sand, respectively, were reported by the study author. These K^d and K^{oc} values were calculated for soil columns treated at 0.963 to 1.160 ppm total CGA-77102 residues (See Table XI). Total radioactive material recovery in leachate varied significantly for the soil textures. The clay and sand leachates contained 16.8% and 58.2% of the applied radioactivity, respectively. However, the silt loam and sandy loam soil were similar with 27.3% and 24.4% of applied radioactivity, respectively. The distribution of CGA-77102 of radioactivity recovered from each test column and leachate is reported in Table XII which shows radioactivity material recoveries ranging from 91.9% to 97.9% of applied. These data indicate that CGA-77102 residues are moderately mobile in sandy loam and silt loam soils, mobile in clay soil, and very mobile in sand soil.

Characterization of the radioactivity material in the soil columns and leachates by TLC and HPLC indicated that parent CGA-77102 represented 19.2 to 53.2% of the applied radioactivity on the soil columns and 0.2% to 36.3% of applied radioactivity in the leachates. The major metabolites were identified as CGA-50202 and CGA-50720 which reached reported maximum concentrations of 5.5% to 11.0% and 1.1% to 6.9% of applied radioactivity in leachates and maximum concentrations of 0.3% to 1.0% and 0.1% to 0.3% of applied radioactivity on soil columns, respectivity. Other degradation products (CGA-354743, CGA-46129, and CGA-41507) were reported at maximum concentrations of approximately 5% (maximum concentrations of 4.1% in leachates and 1.4% on soil columns) of applied radioactivity. Three minor metabolites, CGA-40919/40172/41638, made up a total of 5.2% of the applied radioactivity on soil columns and 3.2% of applied radioactivity in leachates (See Tables XV, XVI, and XVII). There were a couple of other minor degradation products (37735 and 212248) identified at maximum concentrations of 1.0 and 0.4% of applied radioactivity, respectively. In addition to these major and minor degradation products, there were four unidentified degradation products which reached maximum concentrations of 0.1 to 3.2% of applied radioactivity on the test soil columns and/or their leachate during the column leaching period. HPLC and MS confirmation of these results are given in Tables XIII thru XIX and XXI.

For the soil column leaching study, approximately 83.2% to 94.0% of the applied radioactivity was characterized. In addition, the radioactivity material balances for the soil columns portion of the study ranged from 91.5% to 96.7% of applied radioactivity.

COMMENTS:

1. For determining the soil to 0.01M $CaCl_2$ ratio, the protocol specified soil bound residues was 20% to 80% of applied radioactivity. In the repeat preliminary phase of the study, the reported radioactive soil bound residues was 10% to 45.4% of applied radioactivity. Only the sand soil was not within the protocol specifications. Based on the data provided for the four

test solution concentrations, EFGWB does not believe repeating the sand soil adsorption/desorption data would provide further significant data or change the environmental fate assessment.

2. These adsorption/desorption data for CGA-77102 appear to be in agreement with the adsorption/desorption data for metolachlor. The K_d values for metolachlor ranged from 0.1 to 2.2. Therefore, metolachlor has the potential to move downward through most soil profiles. Both CGA-77102 and metolachlor are considered to be moderately mobile to highly mobile when applied to soil.

3. These aged soil column data using the same four test soils with varying organic matter content (0.3 to 2.2%) and soil texture (sand, sandy loam, silt loam, and clay), are in agreement with the unaged adsorption/desorption data with both indicating that CGA-77102 is moderately mobile to very mobile. The Kd values reported for the unaged adsorption/desorption study were 1.4, 1.1, 4.7, and 0.3 for sandy loam, silt loam, clay, and sand soils, respectively. In addition, the calculated K_{oc} values ranged from 110 for sand soil to 369 for clay soil.

4. Based on laboratory data submitted for CGA-77102 and metolachlor which idicate that the degradation products for CGA-77102 and metolachlor are the same, the aged mobility data for metolachlor and CGA-77102 should be similar. The aged mobility data for CGA-77102 confirmed previous laboratory data. The mobility profile, degradation pathway, and quantitation data indicated no significant differences.

5. Mobility data on one of the major degradates, CGA-51202, has been submitted and reviewed (GT;02/25/93). It appears that CGA-51202 is more mobile than the parent metolachlor (K_d values ranging from 0.3 to 4.7 for parent and 0.04 to 0.17. Mobility data on the other major degradate, CGA-354743, is presently underway and will be submitted when completed.

6. Ethylene glycol traps were used in the adsorption/desorption system. However, discernible concentrations of radioactivity were not found in the traps. Therefore, only data for the polyurethane foam and aqueous KOH traps were reported for the soil column study, as well.

7. 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.

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