

Cover Sheet for

## **ENVIRONMENTAL CHEMISTRY METHOD**

***Pesticide Name:*** Metalaxyl

***MRID #:*** 409854-01

***Matrix:*** Soil

***Analysis:*** GC/NPD

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Submitted To:

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P.O. Box 5126  
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Study Title

Analysis of Soil Samples in the Field Dissipation Study  
of Ridomil<sup>®</sup> SG on Bare Ground  
Hollandale, Minnesota

Data Requirement

FIFRA Guideline: Subdivision N, 164-1

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87031

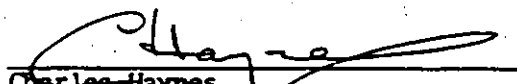
Report Completion Date

July 29, 1988

Analysis of the Soil Samples in the Field Dissipation Study  
of Ridomil<sup>R</sup> 5G on Bare Ground  
Hollandale, Minnesota

Quality Assurance Monitoring Statement

This report has been audited, confirmed with the raw data and found to be in compliance with the specifications for acceptance by Quality Assurance. This study has been reviewed for compliance with TL policies, specific protocols and all applicable Federal regulations pertaining to GLPs.

  
\_\_\_\_\_  
Charles Haynes  
Quality Assurance

8/26/88  
\_\_\_\_\_  
Date

Good Laboratory Practice Statement

This study "Analysis of the Soil Samples in the Field Dissipation Study of Ridomil<sup>®</sup> 5G on Bare Ground, Hollandale, Minnesota" was conducted to the best of my knowledge according to EPA Good Laboratory Practice Standards, 40 CFR 160.

The raw data for this study will be stored in the archives of Tegeris Laboratories, 9705 N. Washington Blvd., Laurel, MD 20707 for five years after the completion of the final report. At that time, Ciba-Geigy will be notified as to the disposition of the raw data.

Anthony F. Grigor  
Anthony F. Grigor  
Technical Director of Chemistry

8/26/88  
Date

Approved by:

John Yarko  
John Yarko  
Director of Chemistry

8/26/88  
Date

Andrew S. Tegeris  
Andrew S. Tegeris  
President

Aug 26, 1988  
Date

Project Personnel:

Below are listed the Tegeris Laboratories personnel who were involved in various phases of the project.

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Lloyd Palmer	Lab Technician	LP (b, 02A)
Ruth Ramseur	Lab Technician	RMR
Shirley Wilkens	Lab Technician	SW (b, 02A)
Joyce Johnson	Lab Technician	JJ
Debbie Sellards	Lab Technician	DS (b, 02A)
Ilo Uche	Lab Technician	I. U. (b, 02A)
William Wassell-Bridger	Chemist	WLB
Tarun Mehta	Chemist	TM (b, 02A)
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STUDY IDENTIFICATION

Field Dissipation Study on Ridomil<sup>R</sup> SG for Terrestrial Uses on Bare Ground  
Hollandale, Minnesota

Landis Associates, Inc.

164-87-71-07-15B-01

Study Location:

Hollandale, Minnesota

Test Material:

Ridomil<sup>R</sup> SG  
N-(2, 6-dimethylphenyl)-N-(methoxyacetal)  
alanine methyl ester

Sponsor:

CIBA-GEIGY CORPORATION  
P.O. Box 18300  
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Study Timetable:

Starting Date:

July 15, 1987

Termination Date:

August 5, 1988

### Abstract

The purpose of this study was to analyze soil samples for metalaxyl (CGA-48988) and its major metabolite CGA-62826. The soil samples were generated from the field dissipation study of Ridomil<sup>R</sup> 5G on bare ground at a test site in Hollandale, Minnesota.

Pre-sectioned soil samples of depths 0-6", 6-12", 12-18", 18-24", 24-36" and 36-48" for -2, 0, 1, 10, 14, 31, 67, 95, 127, 278 and 364 days were received from Agri-Growth Research (subcontractor for Landis Associates) and analyzed.

Residues of CGA-48988 and CGA-62826 were extracted from the soil with 50% aqueous methanol. The extract was diluted, basified and partitioned with dichloromethane. The dichloromethane phase containing CGA-48988 was further cleaned up (if necessary) on a basic alumina column and injected into a gas chromatograph equipped with a nitrogen-phosphorus detector. The aqueous phase (of the dichloromethane partitioning) which contains the CGA-62826 was acidified and extracted with dichloromethane. The extracted CGA-62826 was methylated with diazomethane and analyzed by gas chromatography under the same conditions as the CGA-48988.

The results (on a dry corrected basis) for the treated samples are summarized in Table I. The values shown are the averages of three samples for the three plots. At the 0-6" depth, the level of CGA-48988 residue decreased from a maximum of 1.051 ppm to 0.093 ppm at 364 days. For CGA-62826, at the 0-6" depth, the residue level showed a maximum of 0.181 ppm at 95 days decreasing to 0.075 ppm at 364 days.

No residues (average) of CGA-62826 were detected below the 6" depth at the screening level of 0.05 ppm. Two intervals (31 and 67 days) showed average residues of CGA-48988 above the screening level of 0.05 ppm. These average residues were 0.054 and 0.067 ppm.

Fortified samples run concurrently with the treated samples demonstrated very good recoveries at all depths for both CGA-48988 and CGA-62826. The average recoveries for CGA-48988 were 94% ± 17%, 83% ± 12%, 91% ± 14%, 97% ± 11%, 93% ± 15% and 84% ± 10% at 0-6", 6-12", 12-18", 18-24", 24-36" and 36-48", respectively. For CGA-62826, the average recoveries were 95% ± 16%, 95% ± 16%, 98% ± 11%, 96% ± 15%, 102% ± 11% and 94% ± 8% at the depths 0-6", 6-12", 12-18", 18-24", 24-36" and 36-48", respectively.

The contact person for this study is Anthony F. Grigor at (301) 776-8036.



## I. Introduction

This report describes the results of the analytical phase of the field dissipation study of Ridomil<sup>®</sup> 5G on bare ground conducted at a test site in Hollandale, Minnesota during 1987-1988. This study was conducted to satisfy the registration guideline requirements specified in subdivision N, 164-1 of FIFRA. The biology phase was conducted by Landis Associates, Inc., Valdosta, Georgia. Details of the biology phase of the study are provided by Landis Associates, Inc., Valdosta, Georgia.

Soil samples from the test site at depths of 0-6", 6-12", 12-18", 18-24", 24-36" and 36-48" were processed and analyzed by Tegeris Laboratories for metalaxyl (CGA-48988) and the major metabolite CGA-62826. The structures and nomenclature for metalaxyl and CGA-62826 are shown in Figure 1. The analyses were conducted using an analytical protocol developed by Tegeris Laboratories. Details of this protocol as well as a detailed description of the analytical method is provided in the Appendix of this report.

This report provides the results of the analyses of soil samples received thus far, namely for 364 days. Any additional analyses for later intervals, if necessary, will be provided as an addendum at a later date.

## II. Materials and Procedures

### A. Standards

CGA-48988, Lot # S85-0831, purity: 96.5%, received 5/28/87  
CGA-62826, Lot # S85-0650, purity: 98.1%, received 5/28/87

### B. Reagents

1. Alumina, Basic (Woelm) W200, activity Grade I (prepared by the addition of the 76 ml of water to 324g of Activity Grade Type I Alumina)
2. Diazomethane, ethyl ether solution, prepared according to Organic Syntheses, Coll. Vol. IV, 250 (1963).
3. Ethyl ether, anhydrous, reagent grade
4. Acetone, residue grade
5. Hexane, residue grade
6. Dichloromethane, residue grade
7. 7% (V/V) ethyl ether in hexane
8. 70% (V/V) ethyl ether in hexane
9. 1N Hydrochloric acid, reagent grade
10. 12N Sodium hydroxide, reagent grade
11. Methanol, residue grade
12. 50% (V/V) Methanol in water
13. Isooctane, residue grade

### C. Apparatus

1. Centrifuge bottle, 250 ml, polyethylene
2. Flask, round bottom, 250 ml
3. Separatory funnel, 500 ml
4. Filter paper, Whatman 1
5. Centrifuge, with head to accommodate 250 ml centrifuge bottles
6. Rotary evaporator, Buchi, or equivalent
7. Mechanical shaker
8. Disposable chromatographic columns, 8 ml
9. Vacuum manifold to accept disposable chromatographic columns
10. N-evap, Organamation or equivalent
11. Centrifuge tubes, graduated, 15 ml

### D. Analytical Method

#### 1. Principle

Residues of CGA-48988 and CGA-62826 were extracted from soil with 50% aqueous methanol. An aliquot of the extract was diluted with water and basified with sodium hydroxide. Residues of the parent CGA-48988 were partitioned into dichloromethane. If necessary, the dichloromethane extract was cleaned up by column chromatography on a basic alumina column and an appropriate aliquot was injected into a gas chromatograph equipped with a nitrogen-phosphorus detector. Residues of the acid metabolite, CGA-62826, were extracted from the initial alkaline aqueous solution by acidification with hydrochloric acid and partitioning with dichloromethane. After evaporation of the solvent, the CGA-62826 was reacted with diazomethane to form the methyl derivative of CGA-62826. The derivative, present as the parent CGA-48988, was cleaned up by column chromatography (if necessary) and analyzed by gas chromatography under the same conditions as the original CGA-48988. A flow diagram of the procedure is depicted in Figure 2.

#### 2. Procedure

##### a. Extraction

A 50 g soil was extracted using 200 ml of 50% aqueous methanol on a mechanical shaker for 90 minutes. After centrifugation for 20 minutes at 2500 rpm, the supernatant was filtered and basified to pH 10 with 12N NaOH.

##### b. Partition of CGA-48988

The aqueous solution was partitioned with three 50 ml portions of dichloromethane (DCM) which were filtered through a cotton plug and sodium sulfate into a 250 ml round bottom flask. The aqueous layer was saved for CGA-62826 analysis. The combined DCM extract was taken to

dryness on a rotary evaporator with a water bath at 35<sup>o</sup>-40<sup>o</sup>C. The residue was transferred with two 3 ml portions of hexane to either an alumina cleanup column (see below) or to a graduated centrifuge tube for GC analysis.

- c. Cleanup of CGA-48988 (if necessary)  
If gas chromatographic analysis indicated that additional cleanup were necessary, the extract from the partition step was subjected to column chromatography. A cleanup column was prepared adding 3.0 g of 16% basic Super I Alumina to a disposable 8 ml chromatographic column. The column was placed on a vacuum manifold and 10 ml of hexane was passed through the column. The two 3 ml portions of hexane extract from the partitioning step were transferred to the column. Five ml of 7% ether was then passed through column and discarded. The CGA-48988 was then eluted with 10 ml of 70% ether in hexane. The eluate was transferred to a graduated centrifuge tube for GC analysis.
- d. Partitioning of CGA-62826  
The aqueous extract of the DCM partitioning step was acidified to pH 3.0 with 1N HCl and extracted with three 50 ml portions of DCM. The combined DCM extracts were filtered through a cotton plug into a 250 ml round bottom flask and taken to dryness on a rotary evaporator at 35<sup>o</sup>-40<sup>o</sup>C.
- e. Derivatization of CGA-62826  
Five ml of methanol and approximately 5 ml of diazomethane ethyl ether solution was added to the residue and the solution allowed to stand for at least 20 minutes with occasional swirling. The diazomethane reagent was added to maintain a yellow color indicating excess diazomethane reagent. The solution was evaporated to dryness on a rotary evaporator at 35<sup>o</sup>-40<sup>o</sup>C. The residue was then dissolved in two 3 ml portions of hexane which were then subjected to column cleanup as described in 2.c. or transferred to a graduated centrifuge tube.
- f. Gas chromatographic analysis  
The extract contained in the graduated centrifuge tube from one of the above steps was evaporated to dryness on an N-evap under a stream of nitrogen. After the residue was reconstituted with isoctane to the appropriate volume, usually 1.5 ml, the solution was subjected to gas chromatography using one of the following systems:

(1) Instrument: Tracor 560 NPD  
Packing: 3% OV/17 on Chromosorb W-HP 80/100  
Length: 6 ft x 4 mm  
Temp: Column: 205°C  
Injector: 250°C  
Detector: 250°C  
Gas Flow: He: 65 ml/min  
Air: 125 ml/min  
H<sub>2</sub>: 6.8 ml/min  
Attn: 01  
Min. Det. Sens: 0.5 ng

(2) Instrument: Shimadzu GC-9A NPD  
Packing: 3% SP 2250 on Supelcoport 100/120  
Length: 2.6m x 1.6 mm  
Temp: Column: 210°C  
Injector: 250°C  
Detector: 250°C  
Gas Flow: He: 37 ml/min  
H<sub>2</sub>: 2.7 ml/min  
Air: 135 ml/min  
Attn: 1  
Min. Det. Sens: 0.5 ng

(3) Instrument: Hewlett Packard 5890A with NPD  
Column: Methyl Silicone, 530 u ID  
Length: 5 m x 530 u  
Temp: Column: 165°C  
Injector: 180°C  
Detector: 220°C  
Gas Flow: He: 20 ml/min  
Air: 100 ml/min  
H<sub>2</sub>: 3.5 ml/min  
Attn: 0  
Min. Det. Sens: 0.5 ng

For the CGA-48988 analyses, typical chromatograms for the standard and untreated control, fortified and treated samples are shown in Figure 3, 4, 5 and 6, respectively. The typical CGA-62826 chromatograms for the standard and untreated control, fortified and treated samples are provided in Figures 7, 8, 9 and 10. It should be mentioned, that these chromatograms are

actually of the methylated derivative of CGA-62826 (or CGA-48988). All injected volumes are 2 ul. The final volume of extract is 1.5 ml for all samples except the recovery samples (Figures 5 and 9) where the final volume is 3.0 ml.

#### E. Calculations

Standards were injected into the gas chromatograph and peak heights obtained from a Hewlett Packard 3390A, Shimadzu C-R6A or Hewlett Packard 3393A integrator. From the amount the standard injected and the corresponding peak heights, a linear regression analysis was made to determine the amounts of CGA-48988 and CGA-62826 (as CGA-48988). The concentration in parts per million (ppm) of CGA-48988 and CGA-62826 were calculated as follows:

$$\text{ppm (dry)} = \frac{\text{amount residue found(ng)}}{\text{mg soil injected}} \times \frac{100}{100-M} \times \frac{100}{100-R}$$

where M is the moisture remaining after air drying and R is average recovery for the recovery samples. If R was greater than 100, R was taken as 100. That is, the procedural recovery was only used to correct the found values for recoveries less than 100%.

Since residues of CGA-62826 were determined as CGA-48988 in both samples and standards no stoichiometric correction feature was required to convert residues determined as CGA-62826 to equivalents of CGA-48988.

The concentration of CGA-48988 or CGA-62826 as received (or wet basis) was determined by the following equation:

$$\text{ppm (as received)} = \text{ppm(dry)} \times \frac{100-M'}{100}$$

where M' is the moisture as received.

#### F. Method Validation

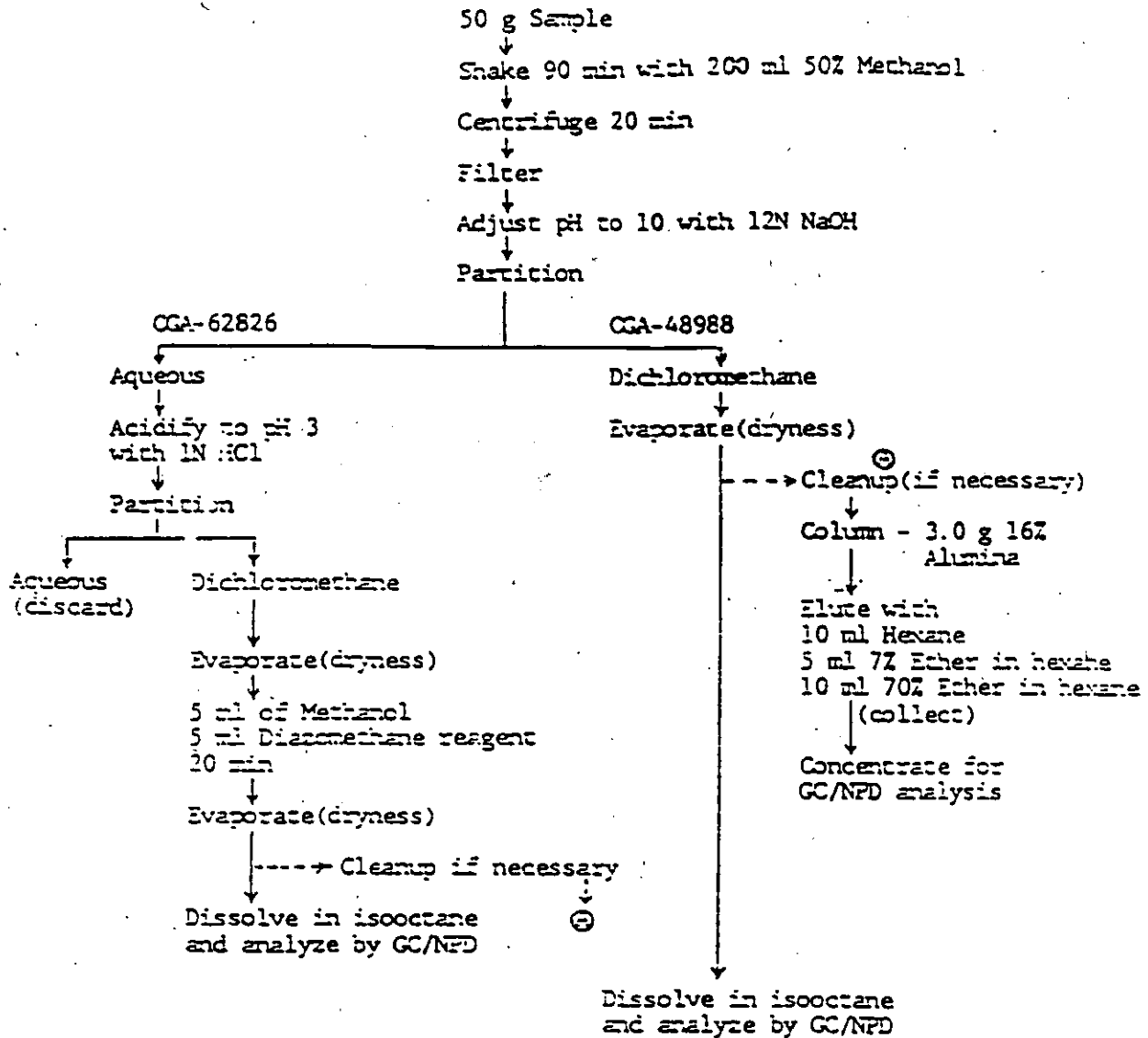
The method described above was validated by fortifying Minnesota soil samples from the 0-6" and 12-18" depths with CGA-48988 and CGA-62826 at 0.05, 0.20 and 2.0 ppm. The results of this method validation are summarized in Table II.

The average recoveries for CGA-48988 were  $83\% \pm 13$  (n=6) at the 0-6" depth and  $79\% \pm 11$  (n=6) at the 12-18" depth. For CGA-62826, the average recoveries were  $102\% \pm 18$  (n=6) and  $109\% \pm 11$  (n=6) at the 0-6" and 12-18" depths, respectively. No GC peaks for CGA-48988 nor CGA-62826 down to the detection limit of 0.025 ppm were detected in the control.

Table II. Method Validation Recoveries for CGA-48988 and CGA-62826

	Fortification Level (ppm)		Recovery (%)	
	CGA-48988	CGA-62826	CGA-48988	CGA-62826
Soil (0-6") (1)	0.05	0.05	76	89
Soil (0-6") (2)	0.05	0.05	639 ← ?	87
Soil (0-6") (1)	0.20	0.20	90	89
Soil (0-6") (2)	0.20	0.20	79	122
Soil (0-6") (1)	2.00	2.00	99	127
Soil (0-6") (2)	2.00	2.00	93	99
	Average		83 ± 13	102 ± 18
Soil (12-18") (1)	0.05	0.05	84	115
Soil (12-18") (2)	0.05	0.05	88	122
Soil (12-18") (1)	0.20	0.20	71	118
Soil (12-18") (2)	0.20	0.20	61	88
Soil (12-18") (1)	2.00	2.00	88	107
Soil (12-18") (2)	2.00	2.00	83	96
	Average		79 ± 11	109 ± 11
Soil (0-6") Control	- CGA-48988: < 0.025 ppm		CGA-62826: < 0.025 ppm	
Soil (12-18") Control	- CGA-48988: < 0.025 ppm		CGA-62826: < 0.025 ppm	

Figure 2. Flow Diagram of the Analytical Procedure for the Determination of CGA-48988 and CGA-62826 in Soil



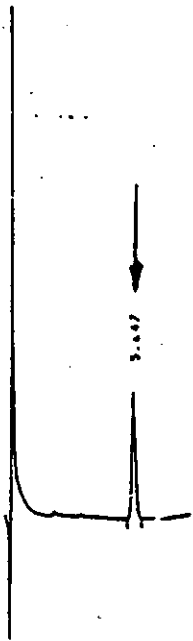
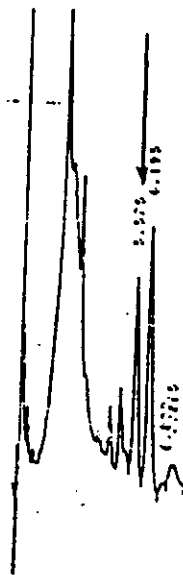
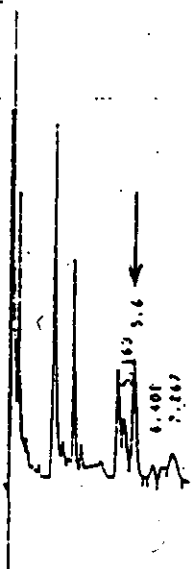


Figure 5. OGA-48988 Fortified Soil,  
0.10 ppm, 83% Recovery  
20 mg injected



Figure 6. Treated Soil (0-6", 122  
0.373 ppm, 8 mg injected





2 ng injected

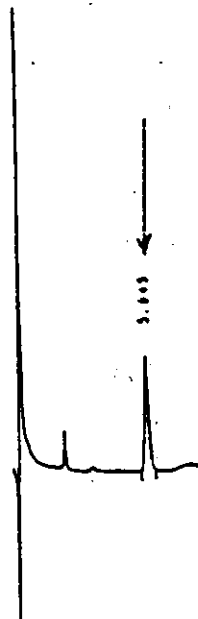


Figure 9. OGA-62826 Fortified Soil,  
0.1 ppm, 82% Recovery,  
20 ng injected

40 ng injected

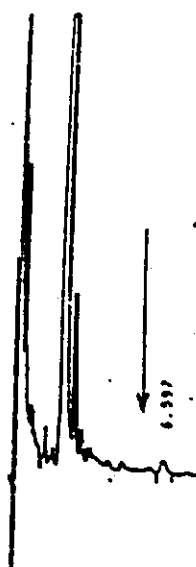


Figure 10. Treated Soil (0-6", 12  
0.098 ppm, 40 ng injected

