

Biochemistry Department  
Ciba-Geigy Corporation  
Ciba Crop Protection  
Greensboro, North Carolina

STORAGE STABILITY OF TOTAL RESIDUES OF METALAXYL IN WEATHERED  
CROPS UNDER FREEZER STORAGE CONDITIONS

AMENDMENT 1

Report No.: ABR-93009 Project No.: 409986  
(MRID No. 42919401) Study No.: 8-90

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This amendment is being issued to report additional freezer storage stability data at longer storage intervals for four substrates. Results from analyses of weathered samples of peppers, potatoes, and spinach (24 months) and cranberries (18 months) were previously reported in ABR-93009 (MRID No. 42919401). Recovery tables have also been updated to include "actual ppm found."

Testing Period: January 31, 1992 - December 22, 1993

European Registration Dossier  
Dossier File N°: 6.3.3 /04A  
Ciba File N°: 48988/3617

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STATEMENT CONCERNING GOOD LABORATORY PRACTICES

This study was conducted in accordance with the applicable EPA Good Laboratory Practice Standards (40 CFR Part 160) with the following exceptions:

1. The biological phase of the study was initiated prior to and completed after the effective date of the applicable GLP regulations (October 16, 1989).
2. In accordance with 40 CFR Part 160, Subpart F, 160.113, tank mix stability was not determined for any of the test substance treatments in any of the projects from which samples were obtained for this storage stability study.

5.1.2.e Woo

5.1.2.e Woo, Ph.D.  
Study Director

9-1-94  
Date

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Ciba-Geigy Corporation  
Ciba Crop Protection  
Quality Assurance Unit

QUALITY ASSURANCE STATEMENT

Final Report Amendment Title: STORAGE STABILITY OF TOTAL  
RESIDUES OF METALAXYL IN WEATHERED CROPS UNDER FREEZER  
STORAGE CONDITIONS

AMENDMENT 1

Study Director:

5.1.2.9 Woo Ciba

Ciba Study No.: Protocol 8-90 with Amendments

Final Report Amendment Number: ABR-93009, Amendment 1

Pursuant to Good Laboratory Practice Standards, this statement verifies that this study was inspected and/or audited and the findings reported to the study director and management by the Ciba Crop Protection Quality Assurance Unit on the dates listed below.

INSPECTION/AUDIT TYPE      INSPECTION/AUDIT DATES      REPORTING DATE

In-Progress Inspection      6/22/93      7/6/93

Final Report Amendment  
Audit (ABR-93009,  
Amendment No. 1)      8/1-2/94      8/2/94

Prepared by:

5.1.2.9 Woo

Date:

8/2/94

GENERAL INFORMATION

Study Participants:

Study Director:

5.1.2.e Woo

(6/26/92 - present)

Technical Personnel:

5.1.2.e Woo

5.1.2.e Woo

5.1.2.e Woo

Test Material:

Ciba-Geigy Code: CGA-48988

Generic Name: Metalaxyl

(See Table I for details.)

Protocol Number:

8-90<sup>1</sup> and Amendments 1-6

Testing Facility:

Biological Phase

Refer to ABR-93009 for details.

Analytical Phase

Residue Chemistry Laboratory

Biochemistry Department

Ciba Crop Protection

Ciba-Geigy Corporation

410 Swing Road

Post Office Box 18300

Greensboro, NC 27419

Study Initiation Date:

January 30, 1990

Testing Period:

January 31, 1992 -

December 22, 1993

Archive Location:

The protocol, raw data, final report, and amendment 1 to the final report are archived at the Biochemistry Group Archives, Ciba-Geigy Corporation, Greensboro, North Carolina. Samples are stored in L-Building, freezer L-0018 or in the Cold Storage Building, Greensboro, North Carolina.

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I. SUMMARY/INTRODUCTION

Introduction

This amendment is being issued to report results of analyses of total residues of metalaxyl in pepper, potato, and spinach samples stored at approximately -20°C at intervals of 24-39 months. Results of analyses of cranberry samples stored for 18-38 months are also presented. Previously, results of analyses of peppers, potatoes, and spinach samples stored for 0-24 months and cranberry samples stored for 0-18 months were reported in ABR-93009<sup>2</sup> (MRID No. 42919401).

Recovery tables which include "actual ppm found" for all recovery samples have also been included in this amendment.

Summary

Weathered samples of peppers, potatoes, spinach, and cranberries were stored for up to 38-39 months under freezer storage conditions (approximately -20°C). These samples were analyzed for total residues of metalaxyl determined as 2,6-dimethyl-aniline (DMA). Results show that total residues of metalaxyl, i.e., combined parent and metabolites containing the DMA moiety and N-[2-(hydroxy-methyl)-6-methylphenyl]-N-(methoxyacetyl) alanine methyl ester, are stable in peppers, potatoes, and spinach for at least 39 months and in cranberries for at least 38 months under freezer storage conditions.

II. MATERIALS

Test Substances

Analytical standards of 2,6-dimethylaniline and metalaxyl were obtained from the Production Technical Analytical Services (PTAS) Department, Ciba Plant Protection, Greensboro, North Carolina. Additional information concerning these standards can be found in Table I.

Test Commodities

Weathered samples of cranberries, peppers, potatoes, and spinach were employed in the study. Refer to ABR-93009 for details.

III. METHODS

Experimental Design

The experimental design is described in detail in Residue Chemistry Department Protocol 8-90 and ABR-93009.

Analytical Method

Analytical method AG-395 (P.A.M. enforcement method) was employed for the analysis of total residues of metalaxyl in weathered crop samples. Modifications to AG-395 are described in ABR-93009. Residue results are reported as ppm metalaxyl equivalents.

IV. RESULTS/DISCUSSION

Residue Results

Fortification, extraction, and analysis dates are presented in Table II. Results of analyses to determine total residues of metalaxyl in weathered samples of cranberries (31 and 38 months) and peppers, potatoes, and spinach (39 months) are presented in Table III.

Results of analyses reported in this ABR amendment are consistent with results previously reported in ABR-93009. Total residues of metalaxyl determined as DMA are stable in peppers, potatoes, and spinach for up to 39 months and in cranberries for up to 38 months when these crops are stored under freezer conditions (-20°C).

Method Recovery Validation Data

Results of procedural recoveries of metalaxyl from control samples of cranberries, peppers, potatoes, and spinach fortified prior to extraction are presented in Tables IV, V, VI, and VII, respectively. Recovery tables include data reported in ABR-93009 as well as results from the longer storage intervals. The tables have been updated to include "actual ppm found."

Circumstances Affecting Study

Refer to ABR-93009.



V. CONCLUSION

Total residues of metalaxyl determined as 2,6-dimethylaniline are stable in peppers, potatoes, and spinach stored for up to 39 months and in cranberries stored for up to 38 months at -20°C.

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VI. TABLES

TABLE I: ANALYTICAL STANDARDS

Metalaxyl

N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine  
methyl ester

Ciba Code Number: CGA-48988

CAS Registry Number: 57837-19-1

Storage Conditions: Room Temperature

2,6-Dimethylaniline (DMA)

Ciba Code Number: CGA-72649

CAS Registry Number: 87-62-7

Storage Conditions: Freezer

<u>Compound</u>	<u>Code Number</u>	<u>Purity %</u>	<u>Dept. ID #</u>	<u>Reassay Date</u>
Metalaxyl	S87-1208	95.8	N/A	5/94
Metalaxyl	S84-0577	99.6	N/A	11/98
DMA	39254	99.0	N/A	4/97

Cranberries: 31 and 38 month intervals

Peppers: 39 month interval

Potatoes: 39 month interval

Spinach: 39 month interval

TABLE II. FORTIFICATION, EXTRACTION, AND ANALYSIS DATES FOR CRANBERRY, PEPPER, POTATO, AND SPINACH SAMPLES

<u>Storage Interval (Days)</u>	<u>Storage Date</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
<u>Cranberries</u>			
950	10/12/90	05/19/93	05/27/93
1166	10/12/90	12/21/93	12/22/93
<u>Peppers</u>			
1196	02/09/90	05/20/93	05/26/93
<u>Potatoes</u>			
1180	03/29/90	06/21/93	06/22/93
<u>Spinach</u>			
1203	01/31/90	05/18/93	05/19/93

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TABLE III. RESULTS FROM THE ANALYSIS OF WEATHERED CRANBERRY, PEPPER, POTATO, AND SPINACH SAMPLES

<u>Storage Interval (Days)</u>	<u>Sample Code</u>	<u>Total Residues of Metalaxyl (PPM) *</u>
	<u>Cranberries</u>	
950	31-C-C	<0.05
	31-W-1-C	0.56
	31-W-2-C	0.77
1166	38-C-C	<0.05
	38-W-1-C	0.38
	38-W-2-C	0.58
	<u>Peppers</u>	
1196	39-C-Pr	<0.05
	39-W-1-Pr	0.44
	39-W-2-Pr	0.54
	<u>Potatoes</u>	
1180	39-C-Po	<0.05
	39-W-1-Po	0.14
	39-W-2-Po	0.20
	<u>Spinach</u>	
1203	39-C-S	0.06
	39-W-1-S	2.1
	39-W-2-S	2.0

\* Detected as 2,6-dimethylaniline and reported as metalaxyl equivalents using the conversion factor 2.308.

Note: Residue results are not corrected for control values. Residue results are corrected for average procedural recoveries <100%. Procedural recoveries are corrected for control values.

Sample Code:

Interval - Sample Type - Replicate - Substrate

C = Control	C = Cranberries
R = Recovery	Pr = Peppers
W = Weathered	Po = Potatoes
S = Spinach	

TABLE IV. PROCEDURAL RECOVERIES OF METALAXYL DETERMINED AS  
DMA FROM FORTIFIED CONTROLS OF CRANBERRIES

<u>Storage Interval (Days)</u>	<u>Sample Code</u>	<u>PPM Added</u>	<u>PPM Found</u>	<u>Percent Recovery</u>
0	0-R-1-C	0.05	0.040	71
	0-R-2-C	1.0	0.834	83
35	1-R-1-C	0.05	0.055	87
	1-R-2-C	1.0	1.308	130
186	6-R-1-C	0.05	0.053	87
	6-R-2-C	1.0	0.813	80
409	12-R-1-C	0.05	0.046	92
	12-R-2-C	1.0	0.724	72
522	18-R-1-C	0.05	0.023	45
	18-R-2-C	1.0	0.773	77
950	31-R-1-C	0.05	0.043	79
	31-R-2-C	1.0	0.662	66
1166	38-R-1-C	0.05	0.048	96
	38-R-2-C	1.0	0.767	77
		mean		81.6
		std. dev.		18.7
		n		14
		range		45-130

Note: Procedural recoveries are corrected for control values.

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TABLE V. PROCEDURAL RECOVERIES OF METALAXYL DETERMINED AS DMA FROM FORTIFIED CONTROLS OF PEPPERS

<u>Storage Interval (Days)</u>	<u>Sample Code</u>	<u>PPM Added</u>	<u>PPM Found</u>	<u>Percent Recovery</u>
0	0-R-1-Pr	0.05	0.058	91
	0-R-2-Pr	4.0	3.578	89
59	2-R-1-Pr	0.05	0.051	50
	2-R-2-Pr	1.0	0.791	76
201	6-R-1-Pr	0.05	0.077	-154
	6-R-2-Pr	1.0	0.865	87
278	9-R-1-Pr	0.05	0.046	60
	9-R-2-Pr	1.0	0.756	74
376	12-R-1-Pr	0.05	0.101	96
	12-R-2-Pr	1.0	0.998	94
566	18-R-1-Pr	0.05	0.079	60
	18-R-2-Pr	1.0	0.995	95
767	24-R-1-Pr	0.05	0.056	62
	24-R-2-Pr	1.0	0.840	82
1196	39-R-1-Pr	0.05	0.063	83
	39-R-2-Pr	1.0	0.671	65
		mean		82.4
		std. dev		24.0
		n		16
		range		50-154

Note: Procedural recoveries are corrected for control values.

TABLE VI. PROCEDURAL RECOVERIES OF METALAXYL DETERMINED AS DMA FROM FORTIFIED CONTROLS OF POTATOES

<u>Storage Interval (Days)</u>	<u>Sample Code</u>	<u>PPM Added</u>	<u>PPM Found</u>	<u>Percent Recovery</u>
0	0-R-1-Po	0.05	0.049	98
	0-R-2-Po	1.0	0.861	86
196	6-R-1-Po	0.05	0.057	85
	6-R-2-Po	0.50	0.408	79
377	12-R-1-Po	0.05	0.040	80
	12-R-2-Po	0.50	0.356	71
605	18-R-1-Po	0.05	0.045	80
	18-R-2-Po	0.50	0.400	79
718	24-R-1-Po	0.05	0.046	65
	24-R-2-Po	0.50	0.414	80
1180	39-R-1-Po	0.05	0.051	93
	39-R-2-Po	0.50	0.398	79
mean				81.3
std. dev				8.8
n				12
range				65-98

Note: Procedural recoveries are corrected for control values.

TABLE VII. PROCEDURAL RECOVERIES OF METALAXYL DETERMINED AS  
 DMA FROM FORTIFIED CONTROLS OF SPINACH

Storage Interval (Days)	Sample Code	PPM Added	PPM Found	Percent Recovery
0	0-R-1-S	0.05	0.121	122
	0-R-2-S	2.0	1.777	86
51	2-R-1-S*	0.05	0.102	77
253	8-R-1-S	0.05	0.128	58
	8-R-2-S	2.0	1.777	84
384	12-R-1-S	0.05	0.136	64
568	18-R-1-S	0.05	0.098	65
	18-R-2-S	3.0	2.799	91
729	24-R-1-S	0.05	0.052	67
	24-R-2-S	3.0	2.324	77
1203	39-R-1-S	0.05	0.090	82
	39-R-2-S	3.0	2.629	86
		mean		79.9
		std. dev.		16.9
		n		12
		range		58-122

Note: Procedural recoveries are corrected for control values.

\* The control sample (1-1-A) from Field Trial 02-FR-003-89 was used for analysis.



VII. REFERENCES

1. 5.1.2.e Woo, Protocol 8-90, "Storage Stability of Total Residues of Metalaxyl in Weathered Crops under Freezer Storage Conditions."
2. 5.1.2.e Woo and 5.1.2.e Woo, ABR-93009, "Storage Stability of Total Residues of Metalaxyl in Weathered Crops under Freezer Storage Conditions." (MRID No. 42919401)

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