

METALAXYL

STUDY TITLE

PHOTODEGRADATION OF AQUEOUS SOLUTIONS OF METALAXYL
EXPOSED TO NATURAL SUNLIGHT

DATA REQUIREMENT

Environmental Fate Data Requirement
40 CFR 158
Subdivision N: Series 161-2

AUTHOR

512 e Woo

STUDY COMPLETED ON

July 6, 1988

PERFORMING LABORATORY

Springborn Life Sciences, Inc.
790 Main Street
Wareham, MA 02571

LABORATORY PROJECT ID

SLS Report No. 88-09-2799

AGRICULTURAL DIVISION
CIBA-GEIGY CORPORATION
POST OFFICE BOX 18300
GREENSBORO, NC 27419

TABLE OF CONTENTS

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt op grond van een wettelijke verplichting tot openbaarmaking. Voorts kan dit document verspreid worden en worden gebruikt voor andere doeleinden. Het gebruik van dit document valt onder de rechten van de rechthebbende van dit document, kan derhalve verboden zijn en een inbreuk opleveren van de rechten van de rechthebbende.

This document is not the property of the Ctgb and only provided based on a regulatory data protection regime. Consequently, this document may fall under a regulatory data protection regime. Without the permission of the owner, reproduction and/or publishing of any commercial publication, distribution, reproduction and use of this document may therefore be prohibited and violate the right of its owner.

Title Page.....	1
Statement of No Data Confidentiality Claims.....	2
Sponsor Certification of Good Laboratory Practice.....	3
Table of Contents.....	4
Study Director Good Laboratory Practice Statement.....	6
Quality Assurance Final Report Statement.....	7
1.0 Abstract.....	8
2.0 Introduction.....	10
3.0 Methods and Materials	
3.1 Test Material.....	10
3.2 Test Solutions.....	11
3.3 Test System.....	12
3.4 Natural Sunlight Exposure.....	12
3.5 Test Procedures.....	12
3.6 Analysis.....	13
4.0 Results and Discussion	
4.1 Radiochemical Purity.....	14
4.2 Exposure.....	14
4.3 Material Balance.....	15
4.4 Characterization of ¹⁴ C-metalaxyl and its Degradates.....	15
4.5 Half-life Calculations.....	16
5.0 References.....	16
Protocol Deviations.....	17
Signature Page.....	18

GOOD LABORATORY PRACTICES STATEMENT

The data and report prepared for this study were produced and compiled in accordance with all pertinent EPA Good Laboratory Practice Standards except in the case of characterization and verification of the test substance identity. Maintenance of these records is the responsibility of the test sponsor. This study was conducted based on the procedures described in Springborn Life Sciences, Inc.'s (SLS) protocol entitled "Protocol for Conduct of a Photodegradation Study in Water Following EPA/FIFRA Guidelines," Protocol # 070987/APH.FIF. A copy of this protocol is maintained in SLS's project file.

This study was initiated on June 8, 1988, and the in-life phase of the study was completed on July 6, 1988. Analyses by radiochemical techniques were completed on July 14, 1988.

5.1.2.e Woc

Study Director

9-28-88
Date

QUALITY ASSURANCE FINAL REPORT STATEMENT

The raw data and the final report for this study were inspected by the Springborn Life Sciences, Inc., Quality Assurance Unit (QAU) to assure compliance with the study protocol, laboratory standard operating procedures and the pertinent EPA Good Laboratory Practice Standards (reference 1) on the following date (s):
September 13-15, 23 and 28 1988.

QAU inspection report (s) were issued to the Study Director on September 15, 23 and 28, 1988. A QAU inspection summary report is issued to the laboratory management at the end of each month.

It is the opinion of the QAU that this report accurately reflects the raw data generated during this study.

5.1.26 WOO

Quality Assurance Unit

9-29-88
Date

1.0 ABSTRACT

Agricultural pesticides introduced into aqueous systems in the environment can undergo photolytic transformation by sunlight. Data on the photolytic half-life and transformation process are necessary to determine the fate and persistence of agricultural chemicals. The objective of this study was to determine the photolytic half-life and rate constant of an aqueous solution of metalaxyl exposed to natural sunlight according to EPA Guidelines.

An aqueous solution of metalaxyl was prepared in a pH 7.0 buffer at a concentration of 9.6 mg A.I./L. Aliquots of this solution were placed into 4.0 mL borosilicate glass vials and exposed to natural sunlight irradiation for periods up to 28 days. At periodic intervals triplicate vials (duplicate exposure and one dark control vial) were removed from the exposure system and the solution was analyzed by thin layer chromatography (TLC) and liquid scintillation counting.

The results of this study indicate that metalaxyl is resistant to photolytic degradation at pH 7.0 under the conditions used in this test. A summary of results including the percentages of metalaxyl and a potential degradation product (CGA-62826) recovered from the TLC plates is as follows:

Time Interval Days	Exposed Solution ^a		Dark Control ^b	
	Metalaxyl	CGA-62826	Metalaxyl	CGA-62826
0	92.4 ^b	1.9 ^b	92.4	1.9
1	92.1	2.0	91.8	1.7
3	92.7	1.8	91.2	2.5
5	92.0	2.0	92.1	2.0
7	91.0	3.1	92.0	2.7
14	89.5	5.7	91.0	4.9
21	89.0	5.5	89.3	5.7
28	88.5	5.3	89.9	6.1

^aMean of two replicates.

^bOne replicate, Day 0 values from test solution.

The half-life calculations yielded values of 400 days for irradiated samples and 660 days for dark control samples. However, the half-life data indicates that this difference is due to a lower correlation coefficient for the dark samples. Review of the above data shows essentially no difference between irradiated and control samples.

2.0 INTRODUCTION

The objective of this study was to determine the potential for photolytic degradation of aqueous solutions of metalaxyl exposed to natural sunlight. This study was designed and conducted to satisfy the requirements recommended in the EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry : Environmental Fate, 161-2, Photodegradation Studies in Water (reference 1).

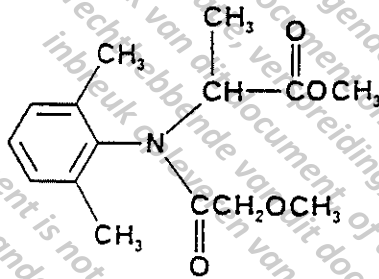
This study was initiated on June 8, 1988 and completed on July 6, 1988. All raw data generated and a copy of the report are stored at Springborn Life Sciences, Inc. (SLS), Wareham, Massachusetts.

3.0 MATERIALS AND METHODS

3.1 Test Material

A 40.0 mg sample of radiolabeled metalaxyl (reference CL-XII-29; ϕ - ^{14}C -CGA-48988; purity 95.5 %, a yellow liquid) with a total activity of 0.972 mCi was received at SLS on November 11, 1987 from the CIBA-GEIGY Corporation. The ampule containing radioactive metalaxyl was stored under freezer conditions. Approximately 100 mg of metalaxyl analytical grade standard (lot # 57869, purity of 99.2 %, a brown powder) was received at SLS on December 15, 1987 and stored at room temperature. Approximately 50.0 mg of CGA-62826 (lot # 585-0650, purity 98.1 %, a tan crystal) was received at SLS on January 18, 1988 and stored at room temperature. The purity of

^{14}C -metalaxyl by TLC at SLS was determined to be 95.4 %. The solubility of metalaxyl is 7000 mg/L in water. The molecular structure of metalaxyl appears below. A copy of the autoradiograph produced from the purity determination appears as Figure 1.



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

3.2 Test Solutions

A stock solution of 3.82 mg A.I./mL in acetonitrile was prepared by dissolving the entire contents of the ampule containing the radiolabeled material (40.0 mg) in 10.0 mL of reagent grade acetonitrile. A test solution of metalaxyl was prepared by diluting 0.500 mL of the stock solution to 200.0 mL with aerated pH 7.0 buffer solution to provide a concentration of 9.6 mg A.I./L. The pH 7.0 buffer solution for dilution of the stock was prepared with deionized water and consisted of 250 mL of 0.100 M potassium dihydrogen phosphate; 145 mL of 0.100 M sodium hydroxide; and adjusted to 500 mL with deionized water. The pH was adjusted to 7.0 with dilute sodium hydroxide or hydrochloric acid as necessary.

During the aeration process a microbial filter was placed in-line to minimize biodegradation. All glassware and buffer solution was sterilized in an autoclave prior to study initiation.

3.3 Test System

The test system for this study consisted of each 4.0 mL borosilicate glass, screw capped (teflon lined) vial, buffer solution and metalaxyl. Individual test systems were identified by project number, interval and replicate.

3.4 Natural Sunlight Exposure

Test systems were placed on a black, nonreflective background, inclined at approximately 30° from the vertical, with the upper end of the vial pointing due north. The area selected for the natural exposure was free of shade and sunlight reflections. All test systems were placed outdoors at 10:30 AM on Day 0 and remained outdoors for the appropriate period until sampled to ensure maximum exposure to natural sunlight. All testing was conducted at SLS at 41° 46' N Latitude and 70° 45' W Longitude.

3.5 Test Procedures

The borosilicate glass vials were completely filled with the radioactive metalaxyl buffer solution to limit the potential for volatility. Triplicate test systems (consisting of 2 exposure and

1 control replicates) were established for seven sampling intervals giving a total of 21 vials. Control vials (7) were wrapped in aluminum foil to exclude light. Daily measurements of the solution temperature and light intensity and weather conditions were recorded. Temperature was measured using a Brooklyn alcohol thermometer. Natural sunlight intensity was measured using a Black-Ray Ultraviolet Meter, Ultra-Violet Products, Inc., San Gabriel, California, a General Electric Light Meter Type 214, General Electric, Cleveland, Ohio, and a National Bureau of Standards calibrated International Light Radiometer/Photometer Model IL 1350, International Light, Newburyport, Massachusetts.

3.6 Analysis

Sampling of the aqueous solution was performed at test initiation (0 hour) and after 1, 3, 5, 7, 14, 21 and 28 days of natural sunlight exposure. At each sampling interval three vials (2 exposure replicates and the dark control) were removed from the exposure unit and analyzed for material balance by liquid scintillation counting and for photochemical degradation by TLC. A 100.0 μL aliquot of each exposure replicate and the dark control was placed on the origin of individual TLC plates. Analytical grade metalaxyl and CGA-62826 were dissolved in methanol at a concentration of approximately 10 mg/mL and spotted on the origin of each plate to assist in the characterization of ^{14}C -material present. Each plate was developed using an ethyl acetate:acetic acid (9:1) solvent system. Each plate was placed on X-ray film

after drying to produce an autoradiograph. After developing the autoradiograph, each TLC plate was divided into zones, each zone was scraped into a scintillation vial, 15 mL of Monophase scintillation cocktail added, and radioactivity was quantitated by liquid scintillation counting. All radioactivity analyses were performed using a Beckman LS-1801 Liquid Scintillation Counter calibrated with factory prepared standards. All samples were counted until a 2 sigma error of 5 % was attained, or for five minutes (whichever period was shorter).

4.0 RESULTS AND DISCUSSION

4.1 Radiochemical Purity

The radiochemical purity of ^{14}C -metalaxyl was determined to be 95.4 % by TLC. The autoradiograph is shown in Figure 1.

4.2 Exposure

All test solutions were placed in direct sunlight for 28 days. Temperature, light intensity measurements and weather conditions during the exposure are presented in Table 1. The temperature ranged from 14 to 45 °C with a mean of 31 ± 7.9 °C. Light intensity ranged from 200 to 7500 $\mu\text{W}/\text{cm}^2$ (1,000 to >10,000 footcandles). Climatological data compiled by the National Oceanic and Atmospheric administration (NOAA) for Boston, MA (Latitude 42° 22' N and 71° 02' W Longitude) for June 1988 has been included for reference in Appendix II.

4.3 Material Balance

Total recovery of radiocarbon for all exposed samples ranged from 93 to 100 % with a mean material balance of 97.1 % (Table 2). In addition, the dark control samples showed a similar mean material balance (97.1 %) indicating that no binding occurred to the surface of the test container.

4.4 Characterization of ¹⁴C-metalaxyl and its Degradates

After 28 days of exposure, the total radiocarbon remaining as metalaxyl was 88.5 % for the irradiated samples and 89.9 % for the dark controls (Table 2). The major degradation product identified was CGA-62826 (5.7 and 6.1 %), respectively, in Day 14 irradiated and Day 28 dark control samples. There were no unknown products detected greater than 5 %; however, the low Rf zone between the origin and CGA-62826 (Rf = approx. 0.49) showed a maximum radiocarbon of 4.2 % (Day 28, Rep. 2 irradiated). Copies of autoradiographs produced at 0 hour and after 28 days of natural sunlight exposure are presented as Figures 2 and 3, respectively.

4.5 Half-life Calculations

No photolytic degradation of metalaxyl occurred during this study (Table 3). The calculated half-life values were 400 days for irradiated samples and 660 days for dark control samples. The difference between the irradiated and control values is most likely

due to the lower correlation coefficient of the dark controls since the metalaxyl concentration from Day 0 to Day 28 was essentially the same between irradiated and control samples.

The photolytic rate constant of the test material is calculated from the following equation which assumes first order reaction kinetics:

$$\ln C = -kt + \ln C_1 \quad (y = mx + b)$$

Where k = rate constant
C = Chemical concentration as percent
t = time
C₁ = Initial chemical concentration as percent

The half-life of the test material is calculated from the following equation:

$$T_{1/2} = \frac{\ln 2}{k}$$

5.0 REFERENCES

- 1). "Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate", U. S. Environmental Protection Agency, Office of Pesticide and Toxic Substances, Washington, D.C., 20460: EPA 540/9-82-021, October 18, 1982. NTIS PB83-153973.

Protocol Deviations

1. The pH of the test solution was not analyzed at each sampling interval. A pooled sample at the conclusion of testing was determined to have a pH of 7.1.
2. Dark control samples were not maintained at 25.0 ± 1 °C as stated in the protocol. Dark control samples were maintained with the exposure samples.
3. Borosilicate vials (4.0 mL) were used for the exposure not 13 X 100 mm culture tubes.

It is our opinion these deviations did not alter the conduct of the study, interpretation of the results, or the conclusions drawn from this study.

5.1.2.e Woo

9-28-88

Study Director
SPRINGBORN LIFE SCIENCES, INC.

SUBMITTED BY:

Springborn Life Sciences, Inc.
790 Main Street
Wareham, Massachusetts

STUDY DIRECTOR:

5.1.2.e Woo

5.1.2.e Woo - 9-28-88
Fate

PRINCIPLE INVESTIGATOR:

5.1.2.e Woo

5.1.2.e Woo - 9-28-88
Chemistry Technician II

ANALYTICAL SUPERVISOR:

5.1.2.e Woo

5.1.2.e Woo - 9/28/88
Environmental Chemistry

AUDITED BY:

5.1.2.e Woo

5.1.2.e Woo - 9/29/88
Quality Assurance Unit

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt op grond van een wettelijke verplichting tot openbaarmaking. Op dit document kunnen rechten van derden rusten, waaronder intellectuele eigendomsrechten en/of auteursrechten. Voorts kan dit document verspreiding, vermenigvuldiging, commerciële exploitatie vallen. Publicatie, verspreiding, vermenigvuldiging, commerciële exploitatie en gebruik van dit document, of de inhoud daarvan zonder de toestemming van de rechthebbende van dit document, kan derhalve verboden zijn en een inbreuk opleveren van de rechten van deze rechthebbende.

This document is not the property of the Ctgb and is only provided based on a mandatory freedom of information requirements. The document may be subject to rights of third parties. Furthermore, this document may be subject to rights of third parties. Consequently, any publication, distribution, reproduction and use of this document and/or publishing and any commercial exploitation, distribution and use of this document may therefore be prohibited and violate the right of its owner.

Table 1. Outdoor temperature and natural light intensity measurements during the period from June 8 to July 6, 1988.

Date	Time	Light Intensity ^a		Temperature ^b	Weather Conditions ^c
		$\mu\text{W}/\text{cm}^2$	Footcandles	$^{\circ}\text{C}$	
6-8-88	10:30 AM	5,500	9,000	Not Recorded	Clear, Sunny
	12:00 PM	7,500	>10,000	35	
	3:00 PM	3,000	>10,000	33	
6-9-88	8:30 AM	500	1,000	14	Cloudy, Rainy
	10:30 AM	500	1,000	15	
	3:00 PM	500	1,000	15	
6-10-88	8:00 AM	1,250	5,000	14	Clear, Sunny
	10:30 AM	6,500	>10,000	31	
	12:00 PM	6,500	>10,000	33	
	3:00 PM	2,000	>10,000	34	
6-11-88	10:30 AM	4,500	>10,000	34	Sunny, Partly Cloudy
	12:00 PM	2,250	>10,000	34	
	3:30 PM	3,500	>10,000	32	
6-12-88	9:00 AM	1,900	6,000	32	Sunny, Hazy
	10:30 AM	4,550	8,160	39	
	3:30 PM	3,500	5,000	36	
6-13-88	8:30 AM	1,600	5,000	33	Sunny, Hazy Hazy, Humid
	10:30 AM	4,900	9,000	42	
	3:00 PM	5,000	>10,000	40	
6-14-88	8:30 AM	1,400	4,000	33	Sunny, Hazy
	10:30 AM	4,000	8,000	42	
	3:00 PM	2,000	6,000	45	
6-15-88	8:30 AM	1,600	5,000	33	Sunny, Hazy
	10:30 AM	4,100	8,000	40	
	3:30 PM	3,000	7,000	42	
6-16-88	8:30 AM	1,200	4,000	28	Sunny, Hazy
	10:30 AM	4,000	9,000	41	
	3:30 PM	2,100	5,000	34	
6-17-88	8:00 AM	750	1,300	18	Cloudy
	10:30 AM	1,000	3,000	22	
	3:30 PM	1,500	3,000	30	
6-18-88	10:30 AM	4,200	9,000	31	Partly Cloudy, Hazy & Sunny
	3:30 PM	3,000	5,000	42	
6-19-88	10:30 AM	2,000	7,000	40	Sunny
	3:30 PM	3,000	7,000	42	
6-20-88	8:30 AM	1,600	5,000	26	Partly Sunny, Hazy
	10:30 AM	3,300	8,000	34	
	3:30 PM	2,100	6,000	32	
6-21-88	8:30 AM	1,600	5,000	29	Partly Sunny, Hazy Sunny, Hazy Sunny, Clear
	10:30 AM	3,900	8,200	41	
	3:30 PM	2,800	8,000	44	

^aFootcandles measured with a General Electric Light Meter Type 214.

^bTemperature measured with a Brooklyn alcohol thermometer.

^cWeather Conditions apply for entire day unless otherwise indicated.

Table 1 (cont.). Outdoor temperature and natural light intensity measurements during the period from June 8 to July 6, 1988.

Date	Time	Light Intensity ^a		Temperature ^b	Weather Conditions ^c
		$\mu\text{W}/\text{cm}^2$	Footcandles	$^{\circ}\text{C}$	
6-22-88	8:30 AM	1,400	5,000	30	Sunny
	10:30 AM	2,200	5,800	40	Sunny, Hazy
	3:30 PM	1,000	3,000	34	Cloudy
6-23-88	10:30 AM	200	3,000	18	Rainy, Cloudy
	3:30 PM	2,400	7,200	33	Sunny, Clear
6-24-88	8:30 AM	1,600	6,000	23	Sunny, Partly Cloudy
	10:30 AM	5,900	>10,000	30	Sunny
	3:30 PM	2,900	7,000	27	Sunny
6-25-88	10:30 AM	4,000	6,000	28	Sunny, Partly Cloudy
6-26-88	8:30 AM	200	3,000	23	Rainy, Cloudy
6-27-88	8:30 AM	1,000	4,000	16	Partly Sunny
	10:30 AM	4,400	10,000	25	Sunny
	3:30 PM	3,200	8,200	30	Sunny
6-28-88	8:30 AM	1,600	6,200	28	Sunny, Clear
	10:30 AM	4,400	9,600	36	Sunny
6-29-88	10:30 AM	2,000	5,200	25	Sunny, Cloudy
	3:45 PM	2,100	3,080	30	Sunny, Partly Cloudy
6-30-88	8:30 AM	700	1,320	18	Cloudy
	11:00 AM	5,200	8,860	32	Sunny, Clear
	4:00 PM	1,000	1,750	26	Sunny, Partly Cloudy
7-1-88	8:30 AM	2,500	6,400	24	Sunny, Clear
	10:30 AM	5,100	9,900	27	Sunny, Partly Cloudy
	3:30 PM	1,000	1,360	25	Sunny
7-2-88	10:45 AM	5,200	10,000	23	Sunny, Partly Cloudy
7-3-88	10:45 AM	5,000	8,940	36	Sunny, Clear
	3:30 PM	2,100	8,610	38	Sunny
7-4-88	10:30 AM	2,000	9,850	35	Sunny, Clear
	3:30 PM	3,000	10,160	37	Sunny
7-5-88	8:30 AM	900	1,070	17	Cloudy, Humid
	10:30 AM	1,200	8,070	28	Cloudy, Hazy
	3:30 PM	2,000	9,500	34	Sunny, Clear
7-6-88	8:30 AM	1,500	3,770	27	Sunny, Hazy
	10:30 AM	4,100	7,780	37	Sunny

^aFootcandles measured with a General Electric Light Meter Type 214 from June 22-29, 1988 and with an International Light Radiometer/Photometer Model IL 1350 from June 30-July 6, 1988.

^bTemperature measured with a Brooklyn alcohol thermometer.

^cWeather Conditions apply for entire day unless otherwise indicated.

Table 2. Percentages^a of metalaxyl and the degradation product (CGA-62826) recovered from the TLC plates and material balance after exposure to natural sunlight.

	Sampling Interval (Days)											
	Day 0*		Day 1		Day 2		Day 3		Day 4		Day 5	
	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark
Origin	NA	NA ¹	0.5	0.9	0.8	0.7	0.9	1.0	0.8	0.8	0.8	0.8
Low Rf ^b	NA	NA	1.7	1.9	2.7	2.5	1.3	1.2	2.0	2.6	1.9	1.5
CGA-62826	NA	NA	1.9	2.1	1.8	1.7	1.7	1.8	2.5	1.8	2.2	2.0
Mid Rf ^c	NA	NA	NA	0.0	NA	0.8	0.9	1.0	NA	0.9	0.9	1.6
Metaxyl	NA	NA	92.4	91.0	92.3	91.8	92.7	92.6	91.2	91.5	92.5	92.1
High Rf ^d	NA	NA	3.5	2.4	2.4	2.5	2.4	2.5	3.5	2.5	2.3	2.1
Total DPH Recovered	NA	NA	734.70	60312	61422	59768	57629	57497	61918	60064	59480	59249
Total DPH Applied	NA	NA	624.60	60597	60674	61100	60555	60198	60135	61268	61625	61708
Percent Recovered	NA	NA	120	100	100	98	95	96	100	98	97	96
Material Balance ^e	NA	NA	100	97	97	98	97	96	98	98	99	99

*Serves as Initial Dark Control and for exposed Day 0.

¹NA = Not Applicable.

^bDPH per zone(s) X 100

Total DPH recovered

^bLow Rf-refers to zone(s) between origin and CGA-62826.

^cMid Rf-refers to zones(s) between CGA-62826 and metalaxyl.

^dHigh Rf-refers to zone(s) above metalaxyl.

^eMaterial balance as a percent of Day 0 Total DPH Applied (62460).

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt voortdurend op grond van een wettelijke verplichting tot openbaarmaking van de voortzetting van de rechten van de rechthebbende. Op dit document kunnen auteursrechten, intellectuele eigendomsrechten en/of andere rechten van derden rusten, waaronder intellectuele eigendomsrechten, vermenigvuldiging, commerciële exploitatie en/of gebruik van dit document, of de inhoud hiervan zonder de toestemming van de rechthebbende. Dit document is niet de eigendom van het Ctgb en wordt beschikbaar gemaakt voortdurend op grond van een wettelijke verplichting tot openbaarmaking van de voortzetting van de rechten van de rechthebbende. Op dit document kunnen auteursrechten, intellectuele eigendomsrechten en/of andere rechten van derden rusten, waaronder intellectuele eigendomsrechten, vermenigvuldiging, commerciële exploitatie en/of gebruik van dit document, of de inhoud hiervan zonder de toestemming van de rechthebbende.

Table 2. (cont.) Percentages^a of metalaxyl and the degradation product (CGA-62826) recovered from the TLC plates and material balance after exposure to natural sunlight.

	Sampling Interval (Hours)											
	Day 1			Day 2			Day 3			Day 4		
	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark	Rep. 1	Rep. 2	Dark
Origin	0.7	1.1	0.7	1.0	1.5	0.8	1.2	1.4	1.2	1.4	1.6	1.2
Low Rf ^b	2.3	2.4	2.2	2.0	2.3	1.8	2.6	2.3	1.7	2.5	4.2	2.1
CGA-62826	3.0	3.2	2.7	5.3	6.1	4.9	5.7	5.3	5.7	5.6	5.0	6.1
Mid Rf ^c	0.6	0.5	0.8	0.5	NA	NA	0.7	1.0	0.8	NA	NA	NA
Metalaxyl	91.0	91.0	92.0	89.8	89.2	91.0	88.8	89.1	89.3	88.9	88.0	89.9
High Rf ^d	2.3	2.6	1.5	1.5	1.1	1.4	0.9	0.9	1.3	1.4	1.2	0.6
Total DPH Recovered	59122	60000	60477	54648	55367	53790	60071	64168	59921	55433	56338	58414
Total DPH Applied	62261	63424	60625	58014	59302	59318	61655	65434	60004	58417	59601	59572
Percent Recovered	95	95	100	94	93	91	97	98	99	95	95	98
Material Balance ^e	100	100	97	93	95	95	99	100	97	95	95	95

^aNA = Not Applicable.
^bDPH per zone(s) X 100
 Total DPH recovered
^bLow Rf-refers to zone(s) between origin and CGA-62826.
^cMid Rf-refers to zone(s) between CGA-62826 and metalaxyl.
^dHigh Rf-refers to zone(s) above metalaxyl.
^eMaterial balance as a percent of Day 0 Total DPH Applied (62460).

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt op grond van de wet op de openbaarheid van de informatie. Het is niet toegestaan dit document te kopiëren, te verspreiden, te verspreiden of anderszins openbaar te maken. Het gebruik van dit document is uitsluitend toegestaan tenzij er schriftelijk toestemming is gegeven door het Ctgb. Het Ctgb aanvaardt geen aansprakelijkheid voor schade van welke aard ook voortvloeiende uit het gebruik van de inhoud van dit document.

Table 3. Aqueous Photolysis Half-life Calculations of metalaxyl.

Sampling Day	Irradiated		Dark Control	
	Average ¹ % Dose	ln % Dose	% Dose	ln % Dose
0	92.4	4.526	92.4	4.526
1	92.1	4.523	91.8	4.520
3	92.7	4.529	91.2	4.513
5	92.0	4.522	92.1	4.523
7	91.0	4.511	92.0	4.522
14	89.5	4.494	91.0	4.511
21	89.0	4.489	89.3	4.492
28	88.5	4.483	89.9	4.499
Correlation:	-0.960		Correlation:	-0.876
Intercept:	4.527		Intercept:	4.524
Slope (-k):	-0.00173		Slope (-k):	-0.00105
T _{1/2} (half-life):	400 days		T _{1/2} (half-life):	660 days

¹Average of Replicates 1 and 2.

Figure 1. Copy of Autoradiograph produced from the radioactive metalaxyl stock solution.

REVERSE OF THIS DOCUMENT IS A COPY OF THE ORIGINAL DOCUMENT. IT IS NOT TO BE REPRODUCED OR TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC OR MECHANICAL, INCLUDING PHOTOCOPYING, RECORDING, OR BY ANY INFORMATION STORAGE AND RETRIEVAL SYSTEM.

This document is the property of the FBI. It is loaned to you for your information only. It is not to be distributed outside your agency. This document is not to be published, reproduced, or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or by any information storage and retrieval system, without the prior written permission of the FBI.

1781-6154
6/6/88 MCS
CGA-48988

Stock 12C CGA-48988
40.0 mg / 10ml acetonitrile
5.5 Ethyl Acetate : Acetic Acid 9:1
12C MIX CGA-62826

RF=0.62

RF=0.49

11	
10	
9	
8	
7	
6	
5	
4	
3	
2	
1	

5.1.2.e Wob

Figure 2. Copy of Autoradiograph produced from the Day 0 sample.

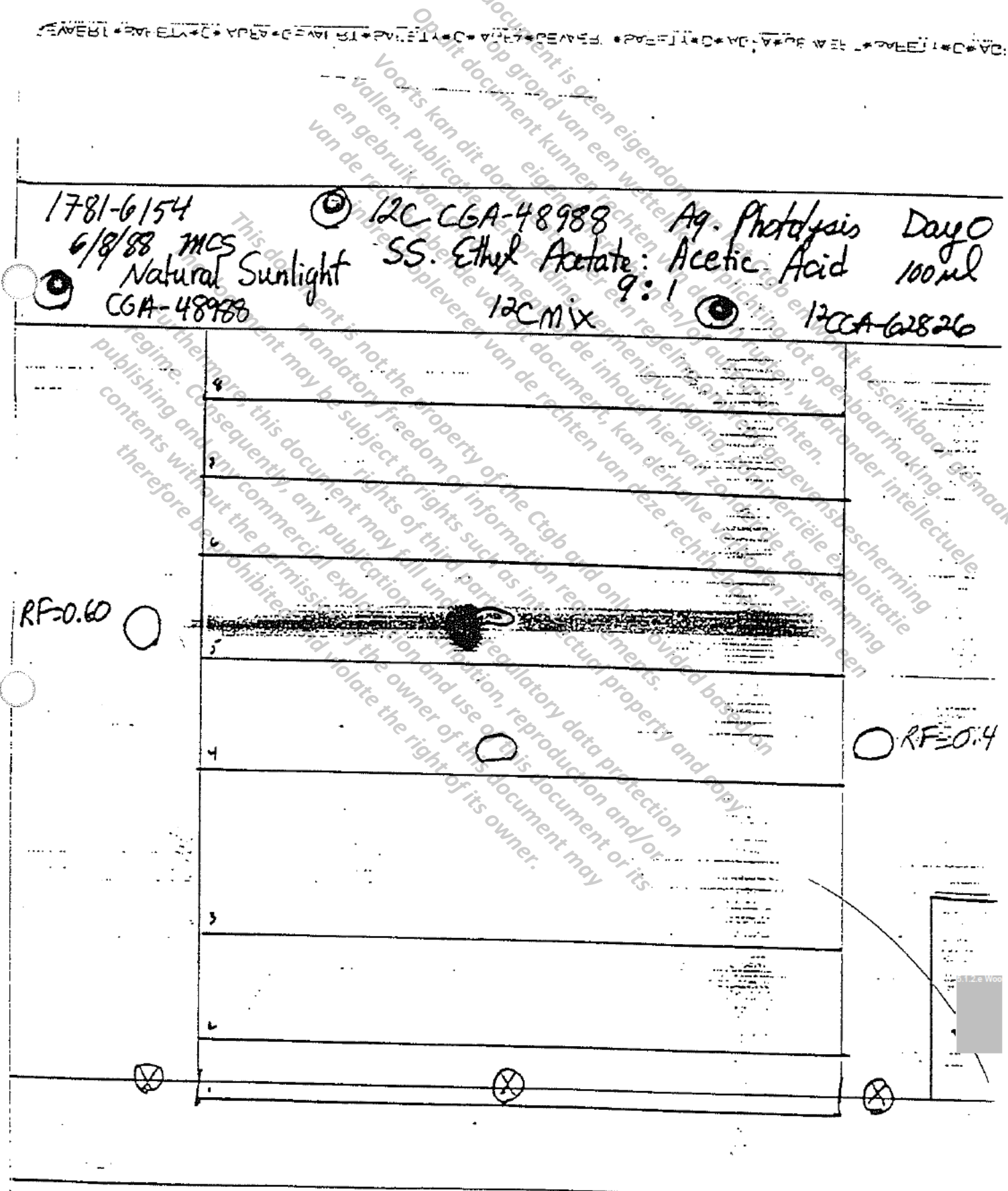


Figure 3. Copy of Autoradiograph produced from the Day 28 exposure
Replicate 1 sample.

1781-6154 Ag. Photolysis DAY 28 7/6/88 MCS
RIGNAT Natural Sunlight
S.S. Ethyl Acetate: Acetic Acid 9:1
CGA-48948 12C MIX CGA-62628

RF=0.67

RF=0.5

9	
8	
7	
6	
5	
4	
3	
2	
1	
0	

PK6

Dit document is geen eigendomsdocument en kan vertrouwelijk of anderszins wettelijk beschermd zijn. Voorts kan dit document kunnen worden gebruikt voor de afwikkeling van de rechten van derden. Het gebruik van dit document is niet toegestaan zonder de schriftelijke toestemming van de afzender. Het gebruik van dit document kan derhalve tot aansprakelijkheid aan de afzender leiden. Het gebruik van dit document is niet toegestaan voor de afwikkeling van de rechten van derden. Het gebruik van dit document kan derhalve tot aansprakelijkheid aan de afzender leiden.

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt op grond van een wettelijke verplichting tot openbaarmaking. Op dit document kunnen rechten van derden rusten, waaronder intellectuele eigendomsrechten en/of auteursrechten. Voorts kan dit document, verspreiding, vermenigvuldiging, commerciële exploitatie vallen. Publicatie, verspreiding, of de inhoud hiervan zonder de toestemming en gebruik van dit document, kan derhalve verboden zijn en een inbreuk opleveren van de rechten van deze rechthebbende.

APPENDIX I

This document is not the property of the Ctgb and only provided based on mandatory freedom of information requirements. The document may be subject to rights of third parties. Furthermore, this document may fall under a regulatory data protection regime. Consequently, any publication, distribution, reproduction and/or publishing and any commercial exploitation and use of this document may contents without the permission of the owner of this document may therefore be prohibited and violate the right of its owner.

Springborn Life Sciences, Inc.

Environmental Toxicology & Chemistry Division

790 Main Street • Warcham, Massachusetts 02571 • (617) 295-2550 • Telex 4436041 • Facsimile (203) 749-7533

STUDY PLAN AND TEST PROTOCOL

PROTOCOL TITLE: Protocol for Conduct of a Photodegradation Study in Water Following EPA/FIFRA Guidelines

TO BE COMPLETED BY THE STUDY SPONSOR:

Study Sponsor: Ciba-Geigy Corporation

Address: Agricultural Division - Greensboro, NC 27419

Telephone: _____

Sponsor Protocol/Project No.: _____

Test Substance: Metalaxyl

Purity: _____ CAS# or LOT#: _____

Additional Comments and/or Modifications: _____

5.1.2.e Woo

9/28/88
Date

TO BE COMPLETED BY SLS BEFORE TEST INITIATION:

Testing Facility: Springborn Life Sciences, Inc.

Study Director: _____

SLS Project No.: _____

Test Concentrations: _____

Solvent: _____ CAS# or LOT#: _____

Proposed Start Date of Study: _____

Proposed Completion Date of Study: _____

Additional Comments and/or Modifications: _____

5.1.2.e Woo
Study Director

9-28-88
Date

CONDUCT OF A PHOTODEGRADATION STUDY IN WATER
FOLLOWING EPA/FIFRA GUIDELINES

INTRODUCTION

A ^{14}C -radiolabeled test material, dissolved in water, is exposed to artificial and natural sunlight for periods up to 30 days. At each sampling interval aliquots for analysis are taken to determine the rate of photolysis of the test material by thin layer chromatography (TLC) techniques. Photodegradation products are identified by comparison to analytical standards. The photolytic rate constant and half-life of the test material are calculated by correlating the natural logarithm of the observed concentration vs time by linear regression analysis.

METHODS AND MATERIALS

PROCEDURE

A. Test Material Solution- The test material is dissolved in pure water (ASTM Type II A, or equivalent grade) at a pH that minimizes hydrolytic breakdown. Water is saturated with bacteria-free air prior to the preparation of the test material solution to simulate environmental conditions. The proposed buffering solutions for testing at pH 5, 7, or 9 are prepared as follows:

- pH 5 - 200 mL of 0.100M potassium hydrogen phthalate; 113 mL of 0.100M sodium hydroxide; and adjust volume to 500 mL with water.
- pH 7 - 250 mL of 0.100M potassium dihydrogen phosphate; 145 mL of 0.100M sodium hydroxide; and adjust volume to 500 mL with water.
- pH 9 - 250 mL of 0.0250M borax ($\text{Na}_2\text{B}_4\text{O}_7$); 23 mL of 0.100M hydrochloric acid; and adjust volume to 500 mL with water.

One concentration is prepared at a level which will define the kinetics of the reaction and permit the isolation and identification of photoproducts formed. A test material with low water solubility will be dissolved in reagent grade acetonitrile not to exceed one percent by volume.

B. Reaction Vessels- Thin walled borosilicate glass culture tubes (13 X 100 mm) with teflon lined screw caps are used as reaction vessels. The reaction vessels are filled to avoid volatilization of the test material solution. All glassware is sterilized in an autoclave to minimize biodegradation, and aseptic technique is followed during preparation, transfer, and sampling of the test material solution.

C. Artificial Sunlight Source- Artificial sunlight is provided by a Heraeus Suntest Accelerated Exposure Unit utilizing Xenon radiation and appropriate filters to limit the radiation spectrum from 300 - 800 nm. The temperature of the test chamber is maintained at $25 \pm 2^\circ \text{C}$.

D. Photolysis- Aliquots of the test material solution are placed into replicate reaction vessels for each sampling interval to provide for duplicate analysis at each sampling interval. The prepared solution is exposed to the following conditions; 1) artificial sunlight (12 hours/day) at $25 \pm 1^\circ \text{C}$, 2) natural sunlight, and 3) total darkness at $25 \pm 1^\circ \text{C}$. The artificial and natural sunlight intensities are monitored daily using a UV intensity meter ($\mu\text{Watts/cm}^2$) and a standard light meter (footcandles/cm²). Suggested sampling intervals are on Days 0, 1, 2, 3, 4, 7, 14, and 30. The sampling schedule is adjusted based upon the observed photodegradation of the test material to provide an adequate number of data points to determine the rate constant. Natural sunlight exposures can only be conducted during May, June, July, August, and September.

E. Analysis- At each sampling interval duplicate reaction vessels for each exposure condition are removed and the test solution is analyzed for test material concentration, photoproducts, pH, and material balance. Analyses for the decline of the test material and the formation of photoproducts are performed by standard TLC techniques. An aliquot of the solution, or extract, is spotted onto the origin of a TLC plate and developed in a suitable solvent system. Authentic standards of the test material and potential photoproducts are co-chromatographed to provide positive identification. Developed plates are allowed to dry, visualized under UV light, and placed on X-ray film to produce an autoradiograph. Quantification of radioactive zones scraped from the TLC plate, and material balance is performed by direct counting for radioactivity in a suitable cocktail utilizing a Beckman LS-1801 Liquid Scintillation Counter calibrated with factory prepared standards.

Photolytic products which exceed 10 percent of the original concentration are identified by comparison to Sponsor supplied standards. Photolytic products formed which do not match Sponsor supplied standards may be identified under separate contract.

CALCULATIONS

The photolytic rate constant of the test material is calculated from the following equation which assumes first order reaction kinetics:

$$\ln C = -kt + \ln C_1 \quad (y = mx + b)$$

Where k = rate constant

C = Chemical concentration

t = time

C₁ = Initial chemical concentration

The half-life of the test material is calculated from the following equation:

$$T_{1/2} = \frac{\ln 2}{k}$$

REPORTING

The report will be a typed document, submitted in triplicate, describing the results of the study, and will be signed by the Study Director and Quality Assurance Unit. It will include, but not be limited to, the following:

- 1) Dates on which the study began and ended.
- 2) Name and address of the testing laboratory.
- 3) Location where the test was performed.
- 4) Name(s) of principle investigator(s).
- 5) Signatures of the senior scientific personnel responsible for the study.
- 6) A full description of the experimental design and procedures followed and a description of the test equipment used.
- 7) Identification of the test substance including chemical name and percentage of active ingredient, molecular structure indicating radiolabel location, and qualitative and quantitative descriptions of the chemical composition (Sponsor supplied).

- 8) Manufacturer and lot and sample numbers of the test substance.
- 9) Properties of the test substance including physical state, pH, and stability (Sponsor supplied).
- 10) The principle mathematical equations used in generating and analyzing the data as well as calculations using these equations. Tabular and graphical representations of the data.
- 11) Ingredients of the pH buffer solution.
- 12) A record of the intensity of incident sunlight, times of exposure, latitude, time of year, atmospheric cover, and other variables affecting incident light.
- 13) The nature of the artificial sunlight source, intensity, wavelength, distribution of spectral energy, and time of exposure.
- 14) Material balance.
- 15) Half-life estimates.
- 16) Identity of each photoproduct produced in greater than 10 percent yield at any point during the course of the study.
- 17) Data evaluation and conclusions.
- 18) Dates of Quality Assurance audits, data inspections, and certification of report approval.
- 19) Location of raw data and report.
- 20) A complete description of any protocol deviations and the impact expected.

REFERENCES

- U. S. EPA. 1982. Pesticide Assessment Guidelines. Subdivision N. Chemistry: Environmental Fate. EPA 540/9-82-021.
- U. S. EPA. 1982. Photolysis in Aqueous Solution in Sunlight CG-6000. Chemical Fate Test Guidelines. EPA 560/6-82-003
- 5.1.2.e Woo and 5.1.2.e Woo 1977. Rates of Direct Photolysis in Aquatic Environment. Environ. Sci. and Technol. 11: 359-366.

SPECIAL PROVISIONS

GOOD LABORATORY PRACTICES (GLP): All test procedures, documentation, records, and reports will comply with the U. S. Environmental Protection Agency's Good Laboratory Practices as promulgated under the Federal Insecticide, Fungicide, and Rodenticide Act (FEDERAL REGISTER, Part IV, 29 November 1983) as appropriate.

TEST MATERIAL DISPOSAL: After 60 days of the issuance of the final report, the test material will be returned to the Sponsor's project officer, at Sponsor expense, unless different arrangements are made.

Dit document is geen eigendom van het Ctgb en wordt beschikbaar gemaakt op grond van een wettelijke verplichting tot openbaarmaking. Op dit document kunnen rechten van derden rusten, waaronder intellectuele eigendomsrechten en/of auteursrechten. Voorts kan dit document, verspreiding, vermenigvuldiging, commerciële exploitatie vallen. Publicatie, verspreiding, of de inhoud hiervan zonder de toestemming en gebruik van dit document, kan derhalve verboden zijn en een inbreuk opleveren van de rechten van deze rechthebbende.

APPENDIX II

This document is not the property of the Ctgb and only provided based on mandatory freedom of information requirements. The document may be subject to rights of third parties. Furthermore, this document, distribution, reproduction and/or publishing and any commercial exploitation and use of this document or its contents without the permission of the owner of this document may therefore be prohibited and violate the right of its owner.

JUN 1988
BOSTON, MA
NAT'L WEA SERVICE
SUITE 102H MASS.TECH.CTR.

ISSN 0198-2427

LOCAL CLIMATOLOGICAL DATA

Monthly Summary



GEN LOGAN INTERNATIONAL AP

LATITUDE 42° 22' N LONGITUDE 71° 02' W ELEVATION (GROUND) 15 FEET TIME ZONE EASTERN 14739

DATE	TEMPERATURE °F					DEGREE DAYS BASE 65°F		WEATHER TYPES 1 FOG 2 HEAVY FOG 3 THUNDERSTORM 4 ICE PELLETS 5 HAIL 6 GLAZE 7 DUSTSTORM 8 SNOW, HAZE 9 BLOWING SNOW	SNOW ICE PELLETS OR ICE ON GROUND AT 0700 INCHES	PRECIPITATION		AVERAGE STATION PRESSURE IN INCHES	ELEV. FEET ABOVE M.S.L.	WIND IN P.H. 1			SUNSHINE		SEA COVER (TENTHS)				
	MAXIMUM	MINIMUM	AVERAGE	DEPARTURE FROM NORMAL	AVERAGE DEW POINT	HEATING SEASON BEGINS WITH JUL 2A	Cooling Season BEGINS WITH JAN 7B			WATER EQUIVALENT INCHES	SNOW, ICE PELLETS INCHES			RESULTANT DIR.	RESULTANT SPEED	AVERAGE SPEED	PEAK GUST	DIRECTION	HOURS	PERCENT OF TOTAL POSSIBLE	SUNRISE TO SUNSET	MIDNIGHT TO MIDNIGHT	
01	70	58	64	0	50	1	0	0	0	0.01	0.0	29.630	31	9.8	14.0	36	N	23	03	83	9	10	7
02	58	47*	53*	-11	42	12	0	0	0	0.0	0.0	29.880	06	7.0	15.4	33	NE	23	03	606	67	6	6
03	60	48	54	-10	48	11	0	0	0	0.0	0.0	29.930	08	3.1	11.6	21	SW	17	08	624	69	10	7
04	59	52	56	-9	47	9	0	0	0	0.0	0.0	29.850	08	0.2	10.8	20	SW	18	08	206	23	10	7
05	81	54	68	3	49	0	0	0	0	0.0	0.0	29.470	28	18.1	19.7	51	N	36	35	648	71	5	6
06	76	54	65	0	44	0	0	0	0	0.0	0.0	29.520	31	19.2	19.8	45	NW	25	29	767	84	6	5
07	76	58	67	1	39	0	0	0	0	0.00	0.0	29.510	32	15.9	17.3	35	NW	24	30	869	95	4	4
08	76	55	66	0	40	0	0	0	0	0.00	0.0	29.650	31	7.8	12.1	28	N	16	35	754	83	3	4
09	60	50	55	-11	45	10	0	0	0	0.00	0.0	29.650	31	11.9	12.9	24	NE	17	05	0	0	10	10
10	72	49	61	-6	44	4	0	0	0	0.04	0.0	29.920	32	7.2	11.9	28	NW	18	34	703	77	4	4
11	74	55	65	-2	47	0	0	0	0	0.00	0.0	29.940	20	3.1	10.3	22	NE	15	19	805	88	1	2
12	89	61	75	8	55	0	0	0	0	0.00	0.0	29.860	27	11.8	12.7	24	N	16	27	782	86	7	6
13	94	73	84	17	60	0	0	0	0	0.00	0.0	30.020	28	2.8	10.7	22	E	15	28	826	90	7	7
14	94	74	84	16	58	0	0	0	0	0.00	0.0	30.120	26	11.4	12.2	25	SW	17	27	915	100	8	6
15	98*	75	87*	19	61	0	0	0	0	0.00	0.0	30.030	26	12.6	13.2	26	N	17	27	916	100	1	1
16	92	68	80	12	65	0	0	0	0	0.00	0.0	29.940	21	12.1	13.8	26	SW	20	20	704	77	3	5
17	75	64	70	1	62	0	0	0	0	0.21	0.0	29.960	27	2.3	11.5	23	E	17	22	31	3	10	10
18	76	61	69	0	62	0	0	0	0	0.31	0.0	30.080	16	4.8	10.6	30	E	23	02	617	67	7	7
19	88	60	74	5	61	0	0	0	0	0.00	0.0	30.120	20	8.1	12.5	25	SW	17	20	879	96	4	4
20	88	67	78	9	64	0	0	0	0	0.00	0.0	30.040	22	16.9	17.7	30	SW	22	19	782	85	6	5
21	93	71	82	12	63	0	0	0	0	0.00	0.0	29.800	28	9.0	13.8	30	N	18	30	831	91	8	8
22	91	65	78	8	63	0	0	0	0	0.22	0.0	29.740	22	9.9	11.8	68	N	45	28	512	56	9	9
23	86	60	73	3	59	0	0	0	0	0.13	0.0	29.755	30	11.7	16.4	37	N	26	34	556	61	7	7
24	65	56	61	-9	43	4	0	0	0	0.00	0.0	30.175	12	1.6	13.6	23	NW	17	31	819	89	8	6
25	73	57	65	-6	48	0	0	0	0	0.00	0.0	30.020	20	14.1	15.4	31	S	23	19	450	49	10	9
26	84	61	73	2	58	0	0	0	0	0.09	0.0	29.615	26	12.9	17.5	30	N	22	29	524	57	8	9
27	66	58	62	-3	51	3	0	0	0	0.00	0.0	29.790	08	3.9	15.1	26	NW	18	12	729	80	6	7
28	83	57	70	-1	54	0	0	0	0	0.00	0.0	29.810	19	8.8	12.3	29	S	21	19	750	82	2	3
29	69	57	63	-8	52	2	0	0	0	0.24	0.0	29.795	06	1.2	11.7	36	SW	21	22	405	44	8	8
30	68	52	60	-12	49	5	0	0	0	0.04	0.0	29.675	07	1.7	10.8	28	SE	21	12	599	65	6	4

* EXTREME FOR THE MONTH - LAST OCCURRENCE IF MORE THAN ONE.
† TRACE AMOUNT.
+ ALSO ON EARLIER DATE(S).
HEAVY FOG: VISIBILITY 1/4 MILE OR LESS.
BLANK ENTRIES DENOTE MISSING OR UNREPORTED DATA.

DATA IN COLS 6 AND 12-15 ARE BASED ON 21 OR MORE OBSERVATIONS AT HOURLY INTERVALS. RESULTANT WIND IS THE VECTOR SUM OF WIND SPEEDS AND DIRECTIONS DIVIDED BY THE NUMBER OF OBSERVATIONS. COLS 16 & 17: PEAK GUST - HIGHEST INSTANTANEOUS WIND SPEED. ONE OF TWO WIND SPEEDS IS GIVEN UNDER COLS 16 & 19: FASTEST MILE - HIGHEST RECORDED SPEED FOR WHICH A MILE OF WIND PASSES STATION (DIRECTION IN COMPASS POINTS). FASTEST OBSERVED ONE MINUTE WIND - HIGHEST ONE MINUTE SPEED (DIRECTION IN TENS OF DEGREES). ERRORS WILL BE CORRECTED IN SUBSEQUENT PUBLICATIONS.

I CERTIFY THAT THIS IS AN OFFICIAL PUBLICATION OF THE NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION, AND IS COMPILED FROM RECORDS ON FILE AT THE NATIONAL CLIMATIC DATA CENTER

noaa

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NATIONAL ENVIRONMENTAL SATELLITE, DATA AND INFORMATION SERVICE
NATIONAL CLIMATIC DATA CENTER
ASHEVILLE NORTH CAROLINA

5.1.2.e Woo
NATIONAL CLIMATIC DATA CENTER