A DEGRADATION STUDY OF DISLODGEABLE ENDOSULFAN (THIODAN) RESIDUES ON ROW CROPS IN FRESNO AND SAN LUIS OBISPO COUNTIES DURING JUNE 1984

By

Keith T. Maddy, Staff Toxicologist
Dorothy A. Shimer, Environmental Hazards Specialist
Karl C. Jacobs, Environmental Hazards Specialist
Clifford R. Smith, Environmental Hazards Specialist III
Steven L. Kilgore, Environmental Hazards Specialist
Vincent Quan, Agricultural Chemist
Sheila Margetich, Agricultural Chemist
Catherine Cooper, Agricultural Chemist II

HS-1263 Revised May 29, 1985

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Unit
1220 N Street, Sacramento, CA 95814

Summary

During June and July 1984, a degradation study of dislodgeable endosulfan residues was conducted in Fresno and San Luis Obispo Counties. Leaf punch samples were taken at time intervals ranging from before application to 13 days after application. The study included aerial application to tomatoes and ground application to bok choy, celery, and napa cabbage. Total endosulfan residues declined with a half-life of 3.85 days. At the current 2 day reentry time, total dislodgeable foliar residues averaged 0.08 and 0.45 ug/cm^2 for ground and air applications, respectively. The current reentry interval appears adequate as few illnesses have been reported. This study has generated data that can be used in setting more restrictive reentry intervals if future additional animal toxicity studies or human poisonings indicate their need.

Introduction

The California Department of Food and Agriculture has established safety intervals for specific crop and pesticide combinations. The safety interval is the time period that must elapse between the application of a pesticide and the entry of an unprotected worker into the treated area. This interval is designed to allow time for the pesticide to environmentally degrade to a level that is sufficiently non-toxic to the worker. The purpose of this study was to measure the foliar decay rate of dislodgeable residues of endosulfan. Forty-eight hours are currently required before entering a field treated with endosulfan.

Endosulfan is an organochlorine insecticide which has been registered for use on various crops since the 1950s. Endosulfan use in California has been on the decline since 1971. In 1983, 330,168 pounds were reported used on 74 different crops. (Since products containing endosulfan are not restricted, growers applying it to their own crops need not report such use.) Its only documented toxic effects are acute effects. They have resulted in its classification as a Toxicity Category I pesticide. Oral LD_{50}s for the most sensitive animal are 6.9 mg/kg for mouse (males) and 18 mg/kg for rat (females). Some LD_{50} values for dermal toxicity include 681 mg/kg for rat (male) in cottonseed oil and 175 mg/kg for rabbit (female) in chloroform. Acute toxicity is associated with interference of the central nervous system and leads to convulsions. Recently, some concern has arisen regarding possible embryotoxic and teratogenic effects of endosulfan. The main problem in assessing the human health impact of endosulfan exposure is the absence of information on chronic toxicity, especially of the oxidative product, endosulfan sulfate.

The formulated product is applied as two isomers, 1 and 2, of the cyclic sulfite compound. They are lost to the environment by volatilization and environmental degradation, the primary routes being hydrolysis and oxidation. The primary degradation intermediate is the oxidation product endosulfan 3, a sulfate, which is persistent in the environment. This study investigated the rates at which endosulfan 1, 2 and 3 were degraded after application of formulated product to various crops.

Methods and Materials

With assistance from the Fresno and San Luis Obispo County Agricultural Commissioner's Offices, cooperation was obtained from growers and licensed Pest Control Operators (PCOs) who would be using endosulfan in formulated products. Two tomato fields in Fresno County were monitored after an aerial application of Thiodan 3. Five fields were monitored after ground application of Thiosulfan 2EC. See Appendix 1 for a thorough description of the fields surveyed and the application rates used.

One-hundred foot sections of three rows were selected in each field for sampling. The rows were selected at 15-row intervals and marked for future sampling. A pre-application sample was taken on the day of application. Samples were then collected at 4 or 9 hours after application, and one, two, three, seven and thirteen days after application. Three replicate samples were taken at each interval; each was analyzed for endosulfan 1, 2 and 3.

Foliar samples were collected with a 2.5 cm diameter leaf punch. Each sample consisted of 45 leaf punches, 15 taken randomly along each of the pre-selected rows. The leaf punch was cleaned with alcohol between successive samples. Sample jars were sealed with alunimun foil, capped and stored on wet ice.

Samples were shipped to the Department's Chemistry Laboratory Services in Sacramento for next-day analysis. Dislodgeable residues were removed by mechanically shaking the leaf discs with a water-surfactant solution. The aqueous wash was extracted with methylene chloride, dried with anhydrous sodium sulfate, concentrated, then brought to volume with ethyl acetate. The samples were analyzed by gas chromatography with an electron capture detector. Weather conditions during the study were hot in Fresno County, mild in San Luis Obispo County, with no rainfall in either location. Weather data is reported in Appendix II.

Results and Discussion

Table 1 A through G presents analytical results of each sample taken in each field for endosulfan 1, 2 and 3. Table 2 presents the averages of combined fields for each isomer at each sampling interval. The ground and aerial applications are shown separately. Data from Table 2 is represented in graph form in Figures 1 and 2.

The degradation curve of each isomer can be fitted to a straight line with correlation coefficients ranging from 0.889 to 0.965 (Table 3). The half-lives for each isomer and for the total residue were calculated (Table 3). Half-lives of the air and ground applications are quite similar despite the fact that the aerial applications were located in much hotter Fresno County.

This study is in agreement with the literature in that endosulfan 1 is more volatile than endosulfan 2 with half-lives of 1.75 and 2.15 days, respectively.

Endosulfan 3 is a breakdown product, increasing after the initial sampling period as the parent isomers decline. It then remains relatively stable with a slower degradation represented by a half-life of 3.85 days.

The current reentry interval after an endosulfan application is 2 days. This study indicates that at two days after application total endosulfan residues are 0.08 and 0.45 ug/cm^2 for ground and aerial applications, respectively.

A safe level has not yet been established for foliar residue of endosulfan. It would appear that the two day interval is adequate since there are very few illnesses related to entry into endosulfan treated fields. In 1982 and 1983, there were a total of four reported topical injuries associated with exposure to endosulfan residues in California. In 1983, there were three systemic illnesses associated with exposure of field workers to a combination of endosulfan and methidathion residues. This study has generated data that can be used to determine more protective reentry intervals if additional animal studies or human poisonings indicate a need to further reduce potential exposure of field workers to endosulfan residues.

TABLE 1A

Pesticide Residue (ug/cm^2)
Found After Aerial Application
of Thiodan 3 to Tomatoes
in Study Field 1

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-sample	.0002	.00047	.00065	.0011
9 hours	.1900	.1400	.0009	.2408
	.1300	.1000	.0009	
	.0900	.0700	.0005	
24 hours	.0100	.0700	.0010	.0743
	.0110	.0600	.0005	
	.0100	.0600	.0005	
72 hours	.0020	.0300	.0020	.0307
	.0010	.0200	.0020	
	.0020	.0300	.0030	
5 days	.0008	.0100	.0010	.0117
	.0006	.0100	.0010	
	.0006	.0100	.0010	
13 days	.0003	.0030	ND	.0027
	.0003	.0020	ND	
	.0005	.0020	ND	

ND - None detected, <0.002 ug/cm^2

TABLE 1B

Pesticide Residue (ug/cm^2)
Found After Aerial Application
of Thiodan 3 to Tomatoes
in Study Field 2

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-sample	ND	ND	ND	ND
9 hours	.3700	.2700	.0005	.4671
	.2200	.1700	.0005	
	.2000	.1700	.0004	
24 hours	.0300	.0500	.0003	.1036
	.0400	.0900	.0003	
	.0300	.0700	ND	
72 hours	.0020	.0070	.0040	.0133
	.0020	.0060	.0030	
	.0030	.0100	.0030	
5 days	.0030	.0200	.0060	.0250
	.0030	.0200	.0060	
	.0020	.0100	.0050	
13 days	.0020	.0080	.0050	.0097
	.0010	.0020	.0040	
	.0020	.0030	.0020	

ND - None detected, <0.0001 ug/cm^2

TABLE 1C

Pesticide Residue (ug/cm^2)
Found After Ground Application
of Thiosulfan 2EC to Napa Cabbage
in Study Field 3

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-sample	ND	ND	ND	ND
	.5800	.1100	.0026	.8497
	.8300	.0610	.0070	
	.8900	.0630	.0056	
24 hours	.0700	.0900	.0400	.2133
	.0800	.0900	.0400	
	.0800	.1000	.0500	
48 hours	ND	.0013	.0022	.0019
	ND	.0001	.0009	
	ND	.0002	.0010	
72 hours	.0036	.0170	.0076	.0509
	.0074	.0540	.0180	
	.0041	.0290	.0120	
7 days	.0024	.0013	.0073	.0079
	.0007	.0007	.0035	
13 days	.0129	.0086	.0049	.0401
	.0140	.0110	.0060	
	.0330	.0250	.0050	

ND - None detected <0.0005 ug/cm^2

TABLE 1D

Pesticide Residue (ug/cm^2)
Found After Ground Application
of Thiosulfan 2EC to Celery
in Study Field 4

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-sample	ND	ND	ND	ND
4 hours	.0600	.0500	ND	.1123
	.0500	.0760	.0070	
	.0410	.0600	.0011	
24 hours	.0110	.0220	ND	.0322
	.0130	.0320	ND	
	.0045	.0140	ND	
36 hours	.0120	.0440	.0220	.1008
	.0140	.0600	ND	
	.0180	.0870	.0230	
48 hours	.0160	.0730	.0220	.2270
	.1000	.2200	.0230	
7 days	.0030	.0050	.0120	.0193
	.0040	.0040	.0140	
	.0020	.0020	.0120	
13 days	.0026	.0011	.0017	.0056
	.0013	.0017	.0018	
	.0019	.0018	.0028	

ND - None detected <0.0004 ug/cm^2

TABLE 1E

Pesticide Residue (ug/cm^2)
Found After Ground Application
of Thiosulfan 2EC to Bok Choy
in Study Field 5

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-sample	ND	ND	ND	ND
4 hours	.0350	.0660	.0019	.1313
	.0940	.1050	.0029	
	.0310	.0560	.0022	
24 hours	.0140	.0180	.0050	.0403
	.0130	.0160	.0060	
	.0130	.0240	.0120	
48 hours	.0350	.0320	.0110	.0433
	.0150	.0150	.0040	
	.0080	.0060	.0040	
60 hours	.0220	.0210	.0300	.0683
	.0300	.0290	.0250	
	.0140	.0160	.0180	
72 hours	.0100	.0430	.0290	.0677
	.0060	.0430	.0200	
	.0080	.0150	.0290	
8 days	.0006	.0003	.0054	.0207
	.0020	.0030	.0026	
	.0014	.0004	.0230	
14 days	.0002	ND	.0026	.0027
	.0001	ND	.0018	
	.0002	ND	.0025	

ND - None detected <0.0003 ug/cm^2

TABLE 1F

Pesticide Residue (ug/cm^2)
Found After Ground Application
of Thiosulfan 2EC to Bok Choy
in Study Field 6

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-application	NS	NS	NS	
4 hours	.0157	.0156	.0007	.0214
	.0086	.0080	.0004	
	.0079	.0070	.0003	
24 hours	.0028	.0028	.0056	.0076
	.0029	.0027	.0006	
	.0027	.0021	.0006	
48 hours	.0016	.0010	.0008	.0035
	.0016	.0012	.0008	
72 hours	.0012	.0007	.0011	.0033
	.0018	.0010	.0015	
	.0011	.0006	.0009	
7 days	.0002	.0001	.0007	.0012
	.0002	.0001	.0008	
	.0003	.0002	.0010	
14 days	ND	ND	ND	ND

NS- No sample
ND - None detected <0.0018 ug/cm^2

TABLE 1G

Pesticide Residue (ug/cm^2)
Found After Ground Application
of Thiosulfan 2EC to Bok Choy
in Study Field 7

Time After Application	Endosulfan 1	Endosulfan 2	Endosulfan 3	Average Total Residue
Pre-application	ND	ND	ND	
	.0020	.0100	.0070	
5 hours	.1700	.1400	.0040	
	.0070	.0970	.0040	
	.0690	.0910	.0030	.1950
24 hours	.0330	.0730	.0040	
	.0340	.0840	.0060	
	.0480	.0790	.0060	.1220
48 hours	.0330	.0500	.0040	
	.0640	.0900	.0060	
	.0200	.0960	.0090	.1240
72 hours	.0080	.0700	.0080	
	.0160	.0760	.0100	
	.0150	.0800	.0018	.0950
7 days	.0007	.0026	.0016	
	.0008	.0031	.0022	
	.0013	.0040	.0022	.0060
12 days	.0001	.0004	.0009	
	.0001	.0007	.0009	
	.0001	.0005	.0008	.0016

ND - None detected <0.006 ug/cm^2

Table 2

Combined Field Average of Dislodgeable Endosulfan Residue
(Data Reported in ug/cm^2)

- Ground Applications -

	4 hours	24 hours	48 hours	72 hours	7 days	13 days
Endosulfan 1	.2119	.0281	.0240	.0099	.0013	.0028
Endosulfan 2	.0853	.0433	.0489	.0330	.0021	.0041
Endosulfan 3	.0023	.0121	.0075	.0141	.0084	.0023
Total Residue	.2300	.0835	.0804	.0570	.0119	.0092

- Aerial Application -

	9 hours	24 hours	72 hours	5 days	13 days
Endosulfan 1	.2000	.0218	.0020	.0017	.0011
Endosulfan 2	.1533	.0667	.0172	.0133	.0033
Endosulfan 3	.0006	.0005	.0028	.0034	.0029
Total Residue	.3540	.0890	.0220	.0184	.0073

Table 3

Calculations Based on Degradation Profile Line of Best Fit

Aerial Application (Fresno County)

	Correlation Co-Efficient	Half Life (Days)
Endosulfan I	.933	1.9
Endosulfan II	.950	2.2
Endosulfan III	.889	4.3
Total Residue	.945	2.0

Ground Application (San Luis Obispo County)

Endosulfan I	.955	1.6
Endosulfan II	.965	2.1
Endosulfan III	.934	3.4
Total Residue	.964	4.5

FIGURE 1

DEGRADATION PROFILE OF DISLODGEABLE ENDOSULFAN RESIDUE FOR AERIAL APPLICATIONS

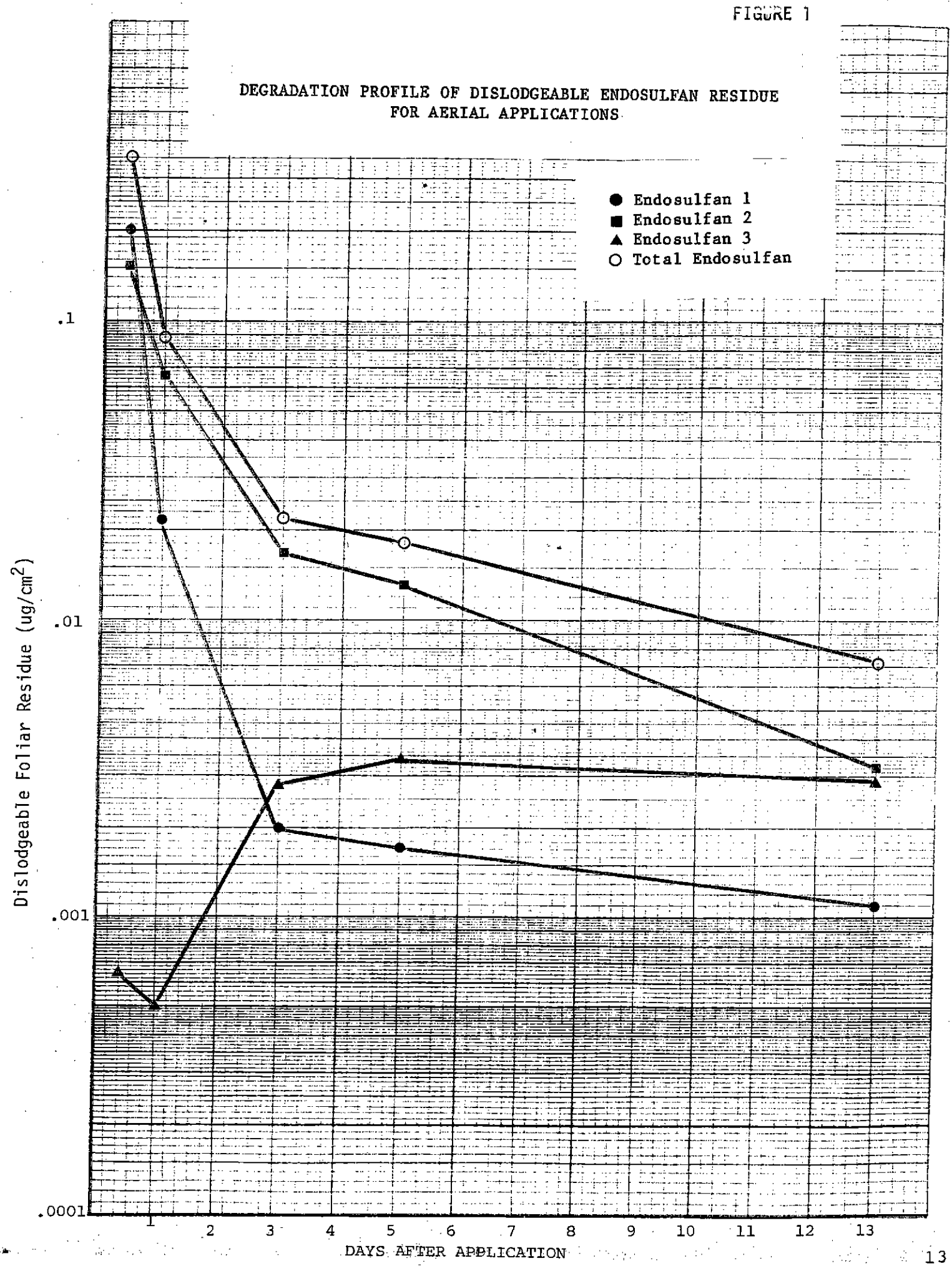
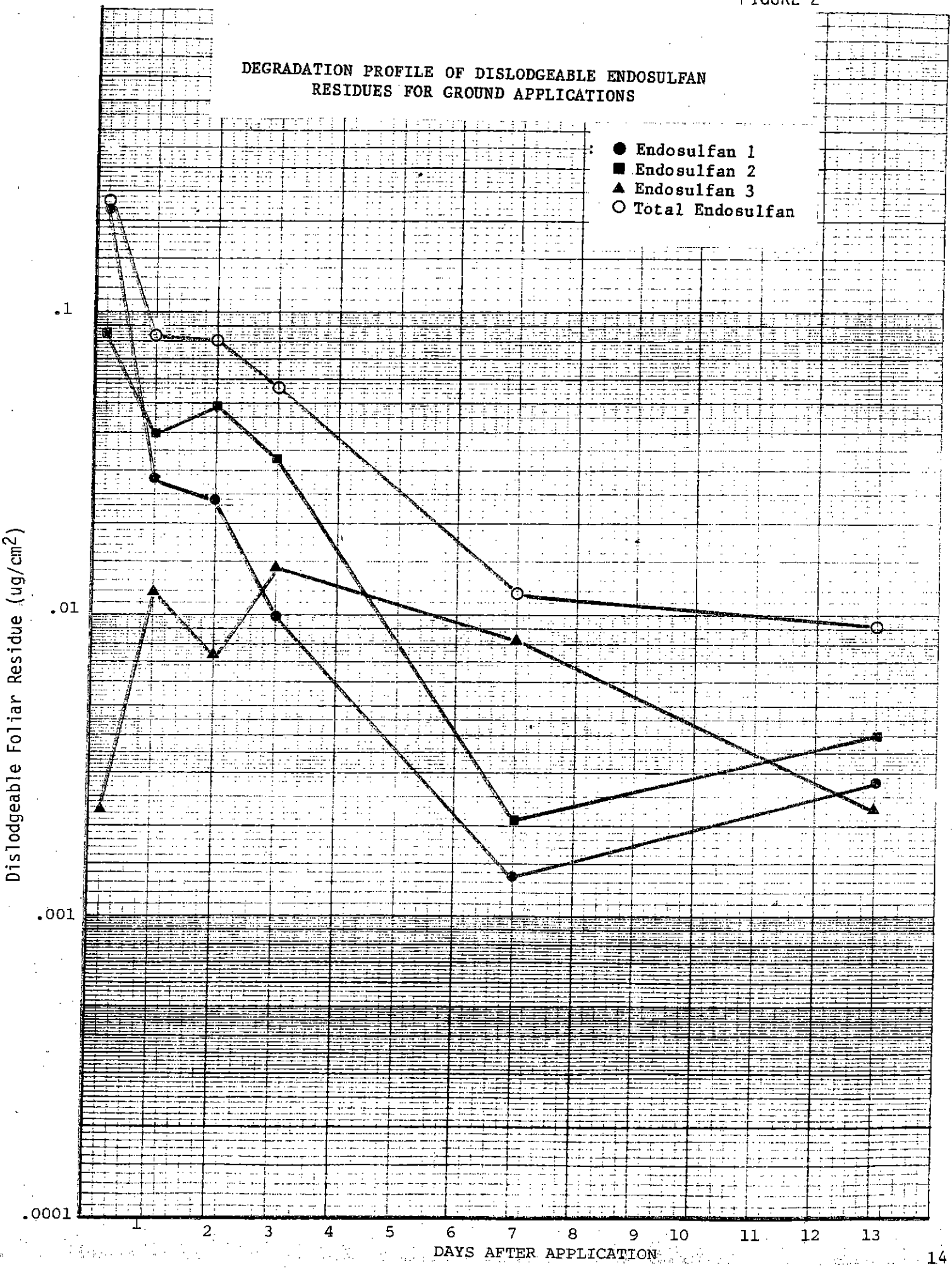


FIGURE 2


DEGRADATION PROFILE OF DISLODGEABLE ENDOSULFAN RESIDUES FOR GROUND APPLICATIONS
Endosulfan 1
Endosulfan 2
Endosulfan 3
Total Endosulfan
.1
.01
.001
.0001
Dislodgeable Foliar Residue (ug/cm2)
1
2
3
4
5
6
7
8
9
10
11
12
13
DAYS AFTER APPLICATION

Appendix I

Application Parameters of Fields Treated With Endosulfan

Parameter	Field 1	Field 2	Field 3	Field 4	Field 5	Field 6	Field 7
Product Name	Thiosulfan 2EC	Thiosulfan 2EC	Thiosulfan 2EC	Thiosulfan 2EC	Thiosulfan 2EC	Thiodan 3	Thiodan 3
Type of Application	ground	ground	ground	ground	ground	air	air
Application rate (lbs ai/acre)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dilution (gal/acre)	65	65	65	65	65	10	15
Date of application	6/13/84	6/19/84	6/5/84	6/6/84	6/14/84	7/12/84	7/12/84
Average Plant Height at application	10"-12"	4"-6"	mature 15"	mature 24"	4"-6"	mature 24"	mature 24"
Irrigation method	furrow	sprinkler	sprinkler	furrow	sprinkler	furrow	furrow
Irrigation during study period	before day 7	day 3 and day 5	day 2	day 2	day 5	?	?
Precipitation	none	none	none	none	none	none	none
Field Location (county)	San Luis Obispo	San Luis Obispo	San Luis Obispo	San Luis Obispo	San Luis Obispo	Fresno	Fresno
Crop	Bok Choy	Bok Choy	Bok Choy	Celery	Napa Cabbage	Tomato	Tomato

Appendix II

Weather Data Temperature and Precipitation Observations Made at Five Points in Fresno County, California

Date	Temperature (°F)		0.0 inches rain
(1984)	Max.	Min.	
7/11	102	64	
7/12	100	66	
7/13	104	70	
7/14	104	77	
7/15	102	72	
7/16	103	73	
7/17	105	77	
7/18	102	71	
7/19	99	69	
7/20	98	67	
7/21	94	66	
7/22	82	58	
7/23	87	61	
7/24	88	58	
7/25	88	57	
7/26	93	58	
Average	97.0	66.5	

Appendix II

Weather Data Temperature and Precipitation Observations Made at Santa Maria in San Luis Obispo County, California

Date	Temperature (°F)		Date	Temperature (°F)	
(1984)	Max	Min	(1984)	Max	Min
6/1	74	50	6/16	74	56
6/2	68	54	6/17	71	54
6/3	68	54	6/18	70	54
6/4	69	53	6/19	67	54
6/5	67	50	6/20	69	49
6/6	72	48	6/21	69	48
6/7	68	50	6/22	73	44
6/8	68	50	6/23	71	54
6/9	78	46	6/24	76	54
6/10	80	48	6/25	75	53
6/11	70	45	6/26	74	53
6/12	66	46	6/27	77	53
6/13	67	53	6/28	72	56
6/14	70	53	6/29	73	54
6/15	70	53	6/30	72	49
7/1	77	52			
7/2	77	54			
7/3	78	57			
7/4	77	56			
7/5	75	58			
Average	72	52			