

DEGRADATION OF DISLODGEABLE
FOLIAR RESIDUES OF ENDOSULFAN
ON CHINESE CABBAGE

By

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SUMMARY

In August 1985, foliage samples were collected from one field of Chinese cabbage that had been treated with endosulfan. Leaf punch samples were collected over a period of four days. Endosulfan (both isomers) degraded quite rapidly. The endosulfan sulfate breakdown product gradually increased through time for about 60 hours. It appears that the 48-hour reentry interval currently required by California regulations should be adequate to protect workers.

INTRODUCTION

Endosulfan (Thiodan) is a mixture of two stereoisomers of 6,7,8,9,10, 10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide. Endosulfan I (α -endosulfan) has the exo-configuration and makes up about 70% of the pure mixture. Endosulfan II (β -endosulfan) has the endo-configuration and constitutes about 30% of the mixture (1). Endosulfan, a moderately toxic chlorinated hydrocarbon is used to control a variety of insect pests, including thrips, beetles, cutworms, and whiteflies on fruit, vegetables, forage crops, grains, forest ornamentals and many other crops. It has an oral LD₅₀ (rat) of 18-43 mg/kg and a dermal LD₅₀ (rat) of 74-130 mg/kg (2). The signs and symptoms of acute illness are similar to most other chlorinated hydrocarbons.

Ely, et. al., (3) reported on nine workers who suffered one or more convulsions following exposure (primarily in the bagging operations) to a 50% wettable-powder. From 1980 through 1983 a total of six cases of illness or injury related to exposure to endosulfan have been reported to the California Department of Food and Agriculture. Of these, three were the result of working in previously treated fields.

This study was conducted in order to evaluate the 48-hour reentry interval currently required by California Food and Agriculture regulations.

MATERIALS AND METHODS

Pending applications of endosulfan were located with the assistance of the staff of the Monterey County Agricultural Commissioner (CAC). Assistance in locating application sites was provided by the staff of SoilServ, Inc. in Salinas. Permission to sample the crop was obtained from the grower. The application was completed with a standard ground rig/boom sprayer. The product used was Simplot Thiosulfan 2E at a rate of 0.5 lbs. active ingredient (A.I.) per acre (maximum rate from an SLN is 1 lb./acre) in 60 gallons of water per acre. Also in the tank mix were mevinphos (0.25 lbs A.I./acre) and Diazinon (0.5 lbs. A.I./acre). The application was completed on August 13, 1984 at approximately 10:00 p.m.

Foliar samples were collected using the methods described by Gunther, et. al. (4) and Iwata, et. al. (5) and adapting them to row crops. Fields to be treated were divided into three areas. One sampling row was marked in each area of the field. Sixteen leaf punches (each 2.54 cm in diameter) were collected from each sampling row. One sample consisted of 48 leaf punches collected in a glass jar (a composite of punches from the three sampling rows); three replicate samples were collected at each sampling interval.

Samples were generally collected twice per day, approximately 7 hours apart. Pre-application samples were collected in the same manner as the post-application samples to determine residue levels present prior to the monitored application. Once collected, the sample jars were sealed with aluminum foil, capped and stored on wet ice. Samples were delivered to a mobile laboratory stationed in Monterey County within one hour of collection. Residue extraction began as soon as samples were delivered to the lab.

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.

RESULTS AND DISCUSSION

Samples were collected from one field of Chinese cabbage following application of endosulfan. The results are recorded on Table 1 and Figure 1.

Table 1: Mean Foliar Residues Following Application to Chinese Cabbage.

<u>Sample Interval</u>	<u>Residue Detected (ug/cm²)</u>		
	<u>E-I</u>	<u>E-II</u>	<u>E-III</u>
Pre-application	ND*	ND	ND
9 hours	0.537	0.427	0.0073
16 hours	0.080	0.157	0.0080
33 hours	0.061	0.137	0.0133
40 hours	0.063	0.101	0.0096
57 hours	0.028	0.047	0.0140
64 hours	0.012	0.020	0.0049
80 hours	0.024	0.026	0.0127

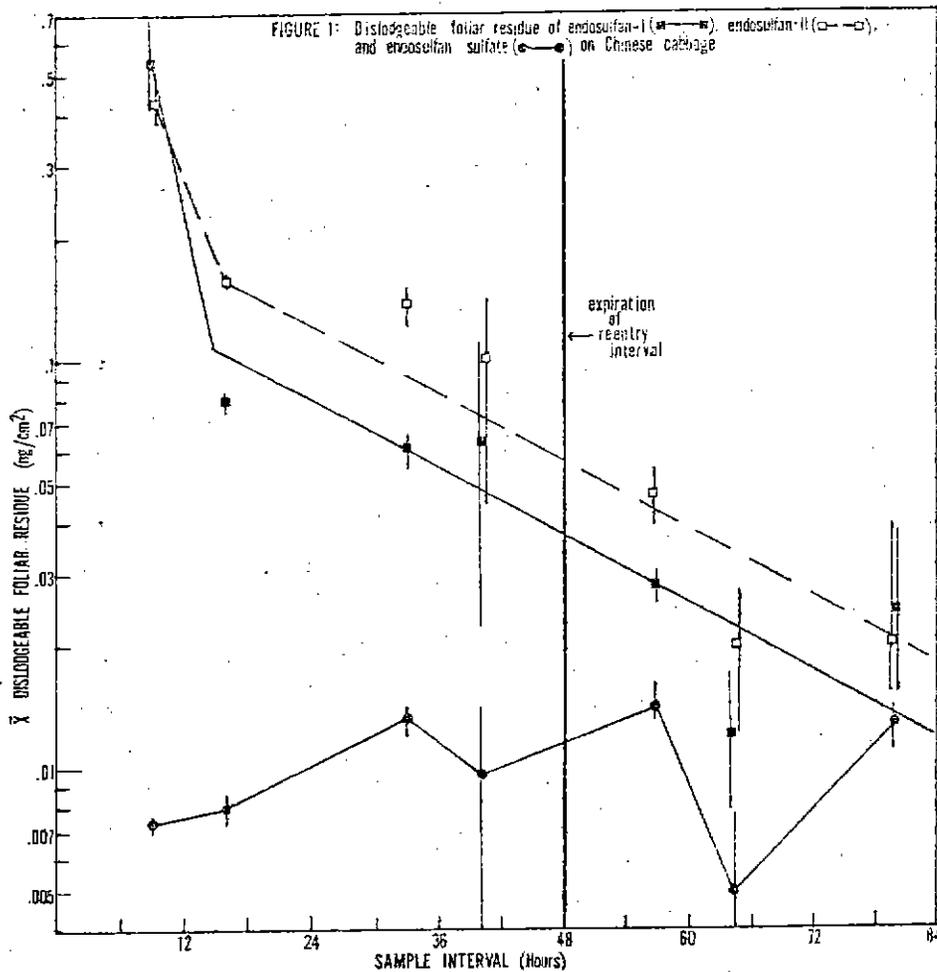
*ND - None Detected

Endosulfan I (E-I) and endosulfan II (E-II) are the two stereoisomers previously mentioned. E-III (endosulfan sulfate) is a breakdown product of both E-I and E-II.

As can be seen the initial decrease in E-I is more rapid than E-II. The E-III residues increase with time for approximately 2 1/2 days after application. These results seem to agree with those of previous studies (6, 7, 8). The weather conditions are given in Table 2.

Table 2: Temperatures and Rainfall During Study Period

<u>Rate</u>	<u>TEMPERATURE (°F)</u>		<u>RAINFALL (Inches)</u>
	<u>Maximum</u>	<u>Minimum</u>	
8-13	70	58	T
8-14	71	53	None
8-15	70	59	None
8-16	81	55	None
8-17	<u>77</u>	<u>57</u>	None
AVERAGE	73.8	56.4	



A safe level of foliar residue has not been established for endosulfan. However, from the data gathered in this study, it appears that the 48-hour reentry should be adequate to protect workers who may come into contact with the foliage.

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REFERENCES

1. Hayes, W.J.: Pesticides Studied in Man, 1st Edition, p. 252. Baltimore, Maryland: Williams & Wilkens (1982).
2. Gaines, T.B.: Acute Toxicity of Pesticides. Toxicol. Appl. Pharmacol. 14, 515 (1969).
3. Ely, T.D., J.W. MacFarlane, W.P. Galen, and C.H. Hine: Convulsions in Thiodan Workers - A Preliminary Report. J. Occup. Med. 9, 35 (1967).
4. Gunther, F.A., W.E. Westlake, J.H. Barkley, W. Winterlin, and L. Langbehn: Establishing Dislodgeable Pesticide Residues on Leaf Surfaces. Bull. Environ. Contam. Toxicol. 9, 243 (1973).
5. Iwata, Y., J. B. Knaak, R.C. Spear, and R.J. Foster: Worker Reentry into Pesticide-Treated Crops. I. Procedure for the Determination of Dislodgeable Pesticide Residues on Foliage. Bull. Environ. Contam. Toxicol. 18, 649 (1977).
6. Cassil, C.C. and P.E. Drummond: A Plant Surface Oxidation Product of Endosulfan. J. Econ. Entomol. 58, 356 (1965).
7. MacNeil, J.D. and M. Hikichi: Degradation of Endosulfan and Ethion on Pears and Pear and Grape Foliage. J. Agri. Food Chem. 24, 608 (1976).
8. Maddy, K.T., D.A. Shimer, K.C. Jacobs, C.R. Smith, S.L. Kilgore, V. Quan, S. Margetich, and Catherine Cooper: A Degradation Study of Dislodgeable Endosulfan (Thiodan) Residues on Row Crops in Fresno and San Luis Obispo Counties During June 1984. Unpublished report, California Department of Food and Agriculture, HS-1263 (1985).