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STUDY OF THE DEGRADATION OF LANNATE (METHOMYL)
ON OUTER LEAVES OF HEAD LETTUCE IN IMPERIAL COUNTY, CALIFORNIA
FEBRUARY 1975

By

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INTRODUCTION

Methomyl is an n-methyl carbamate insecticide registered for use on a wide variety of fruit, vegetable and field crops, including head lettuce. During the year 1975, it was reported that more than 206,056 pounds of methomyl were applied to 348,050 acres of head lettuce.

Methomyl has an acute oral LD₅₀ (rat) of 17 mg/kg. The dermal LD₅₀ has been reported as greater than 5000 mg/kg. Methomyl is marketed under the trade names Lannate and Nudrin as a 90% water-soluble powder and a liquid formulation containing 1.8 pounds of methomyl per gallon.

The Lannate L label directions permit the application of up to 2 pints per acre with a 7-day preharvest interval and up to 4 pints per acre with a 10-day preharvest interval. Workers were not permitted to handle treated crops within 24 hours after application according to the label at the time this study was done. The residue tolerance for methomyl in head lettuce is 2 ppm.

APPLICATION

In order to evaluate the need for longer worker reentry safety intervals for the protection of workers, residues on the outer leaves of two fields of head lettuce treated with Lannate L were studied.

Field 1 - Application date 2/19/75
Methomyl/acre 0.68 lbs.
Volume/acre 10 gallons
Method of application Air

Field 2 - Application date 2/24/75
Methomyl/acre 0.45 lbs.
Volume/acre 7 gallons
Method of application Air

SAMPLING

Triplicate samples were taken at intervals beginning 1 hour after application. Each sample consisted of approximately 100 leaf discs, 2.5 cm in

diameter from the outer leaves of separate heads of lettuce. Duplicate samples were analyzed for surface and penetrated residue while the third sample was used for total residue analysis.

ANALYTICAL METHODS (Extraction)

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Gunther in "The Bulletin of Environmental Contamination and Toxicology", 9, 243-249, 1973. The procedure has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites, that the Worker Safety Unit has been concerned with.

The sample container and leaf punches were weighed and the gross weight recorded.

Total Residues

1. The leaf punches were transferred to a blending jar. The empty sample container was again weighed and the net weight of the punches recorded.
2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate were added.
3. The sample was blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup was removed and the sample allowed to settle.
4. An aliquot was decanted into a teflon-capped bottle and stored in the freezer prior to clean up and hydrolysis.

Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) were added to the sample containers. The containers were capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution was decanted through a glass wool plug into a 500 ml separatory funnel.
2. The punches were rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 min. This was added to the first extraction.
3. The sample was then hand-shaken for approximately 10 seconds with 30 mls of water. The container was drained into the separatory funnel with the first two extractions.
4. The aqueous solution was acidified with 1-N H_2SO_4 , and extracted three times with 50 ml of ethyl acetate. The extract was filtered through sodium sulfate into a glass-stoppered mixing cylinder and the volume was recorded. The extract was mixed in the cylinder. An aliquot was decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Penetrated Residue

1. After the last water rinse was drained for the dislodgeable residue, the punches were transferred to a blender jar. The empty sample container was weighed and the net weight of the punches recorded.
2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate were added.
3. The sample was blended and handled the same as the total residue sample.

ANALYTICAL METHODS (Clean-up and Hydrolysis)

The sample was brought to room temperature and a 50 ml aliquot was added to 50 ml of water in a 125 ml 24/40 S.T. erlenmeyer flask. The flask was fitted with a triple ball Snyder column, placed on a hot plate, and heated until the ethyl acetate had evaporated.

Dislodgeable Residues

The cooled aqueous solution was acidified with 1-N H_2SO_4 and transferred to a 125 ml separatory funnel with water washes. The flask was rinsed with 50 ml of chloroform which was used to extract the aqueous solution. The aqueous solution was extracted a total of three times, using 50 ml of chloroform for each extraction.

Total and Penetrated Residues

The cooled aqueous solution was acidified with 1-N H_2SO_4 and transferred to a 125 ml separatory funnel with water washes. The flask was rinsed with 30 ml of hexane which was used to extract the aqueous solution. The hexane layer was discarded and the aqueous solution was extracted once more with 30 mls of hexane. The aqueous solution was then extracted three times, using 50 ml of chloroform for each extraction.

Dislodgeable, Penetrated and Total Residues

The combined chloroform extracts were added to 50 ml of 0.1-N NaOH in a 250 ml 24/40 S.T. erlenmeyer flask. The flask was fitted with a triple ball Snyder column placed on a hot plate and heated until the chloroform had evaporated. The sample was heated an additional 15 minutes to insure complete hydrolysis.

The sample was cooled, acidified with 1-N H_2SO_4 transferred to 125 ml separatory funnels with water washes and extracted three times with 30 ml of ethyl acetate. The ethyl acetate extracts were filtered through sodium sulfate into a 125 ml 24/40 S.T. erlenmeyer flask. A 0.1 ml portion of triethylamine was added, the flask was fitted with a Snyder column, placed on a hot plate and carefully evaporated to approximately 5 mls. The sample was cooled and quantitatively transferred, to a 15 ml conical tube, to a volume of 10 mls.

Fifty microgram quantities of standard were periodically subjected to the clean-up and hydrolysis and used to quantitate the samples.

ANALYTICAL METHODS (Chromatography)

The samples were analyzed by gas chromatography using a Tracor model 550 equipped with a flame photometric detector in its sulfur mode and the following conditions:

Column - 3% FFAP, 100/120 Chrom W (HP); 6 ft. x 1/4 in. x 2 mm I.D.
Column temp. - 160°C Flow rates N₂ - 80 ml/min
Injector temp. - 220°C H₂ - 100 ml/min
Detector temp. - 220°C Air - 80 ml/min
Retention time - 1.8 min

Due to nonlinearity, the square root of peak height was used to plot linear standard curves. Each sample was quantitated from the average of several injections of standard and sample.

RESULTS

Weather conditions observed during the study period are recorded on Table 1. The average maximum and minimum temperatures were 77.1 and 33.0 °F, respectively.

Results of the analysis are recorded on Table 2 and Figures 1 and 2. On both fields, Lannate showed a fairly steady rate of decay. Field 2 had less Lannate applied to it and showed a faster rate of decay.

TABLE 1: DAILY WEATHER AND PRECIPITATION

Weather observations taken at El Centro, Imperial County, California.

<u>Date</u> <u>(1975)</u>	<u>Temperature (°F)</u>		<u>Precipitation</u> <u>(inches)</u>
	<u>Maximum</u>	<u>Minimum</u>	
2/19	76	29	
20	76	30	
21	76	30	
22	74	30	
23	74	30	
24	78	35	
25	81	40	
26	82	40	
Average	77.1	33.0	Total 0.00

TABLE 2

METHOMYL RESIDUES ON OUTER LEAVES OF HEAD LETTUCE
IN IMPERIAL COUNTY, CALIFORNIA, FOLLOWING APPLICATION
IN FEBRUARY 1975

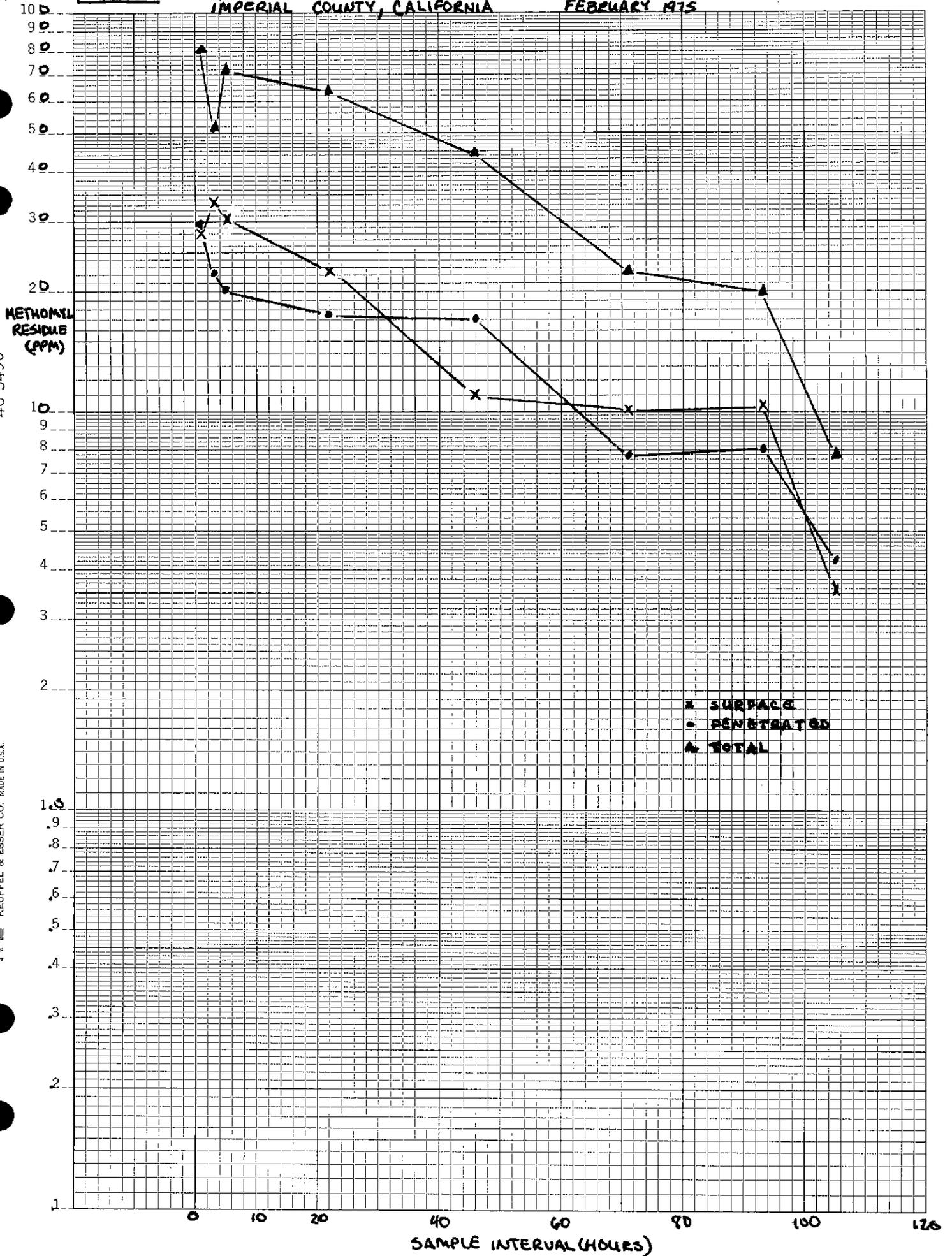
FIELD 1

Sample Interval	Methomyl Residue (PPM)		Total
	Surface	Penetrated	
1 hr	30.6	31.5	
1 hr	24.9	27.6	
1 hr			81.1
3 hrs	38.5	20.4	
3 hrs	28.5	24.2	
3 hrs			51.7
5 hrs	31.5	20.7	
5 hrs	29.8	19.6	
5 hrs			72.5
22 hrs	24.2	17.3	
22 hrs	20.9	17.9	
22 hrs			63.9
46 hrs	11.2	15.0	
46 hrs	10.9	19.2	
46 hrs			44.3
71 hrs	10.9	6.1	
71 hrs	9.3	7.4	
71 hrs			22.5
93 hrs	8.6	7.4	
93 hrs	12.3	8.8	
93 hrs			19.9
115 hrs	3.4	4.8	
115 hrs	3.8	3.7	
115 hrs			7.8

FIELD 2

1 hr	24.9	19.5	
1 hr	18.5	13.3	
1 hr			54.5
13 hrs	17.3	4.6	
13 hrs	14.2	3.4	
13 hrs			28.8
38 hrs	6.4	4.9	
38 hrs	6.5	5.9	
38 hrs			16.3
62 hrs	2.6	2.5	
62 hrs	3.3	4.7	
62 hrs			11.3

FIGURE 1: METHOMYL RESIDUES ON HEAD LETTUCE IN FIELD 1
 IMPERIAL COUNTY, CALIFORNIA FEBRUARY 1975



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SEMI-LOGARITHMIC, 3 CYCLES X 70 DIVISIONS
 KEUFFEL & ESSER CO. MADE IN U.S.A.

FIGURE 1: METHOMYL RESIDUES ON HEAD LETTUCE IN FIELD 2
 IMPERIAL COUNTY, CALIFORNIA. FEBRUARY 1975

