January 20, 1977

# A STUDY OF THE DECAY OF LANNATE (METHOMYL) ON GRAPE FOLIAGE IN FRESNO COUNTY, CALIFORNIA AUGUST 1974

By

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## INTRODUCTION

Methomyl, a carbamate insecticide, is registered for use on a wide variety of vegetable, field and fruit crops and certain ornamentals. Its major use is on lettuce; in 1975 21,120 pounds of methomyl were reported as applied to nearly 30,000 acres of grapes.

This pesticide has an acute oral $LD_{50}$ (rat) of 17 mg/kg. Its acute dermal $LD_{50}$ is reported as being greater than 5000 mg/kg.

Methomyl is marketed under the trade names of Lannate and Nudrin as a 90% water-soluble powder or a liquid concentrate containing 1.8 pounds of methomyl per gallon. For grapes, the Lannate L (liquid concentrate) label recommends using 2-4 pts/acre with a one-day preharvest interval for fresh grapes and raisins and a 14-day preharvest interval for wine grapes. This study was an early range-finding study to determine the presence of dislodgeable residues on foliage to set a schedule for more detailed sampling later.

## APPLICATION

Lannate L was applied to 3 grape vineyards at the maximum rate allowable. Each field was treated with 4 pints (0.9 lbs actual methomyl) of Lannate per acre.

Samples were taken before application and 3, 7 and 14 days post-application. Samples consisted of leaf punches taken randomly throughout the vineyard. The leaves sampled were the older leaves near the clusters of grapes. Each sample was analyzed for surface and penetrated residues.

## 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. It has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites, that our Worker Safety Unit has been concerned with.



ACF 59-352

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

## Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of organic solvent are added.

3. The sample is blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a teflon-capped bottle and stored in the freezer piror to clean up and analysis.

## Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) are added to the sample containers. The containers are capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 min. This is added to the first extraction.

3. The sample is then hand-shaken for approximately 10 secs with 30 mls of water. The container is drained into the separatory funnel with the first two extractions.

4. The aqueous solution is extracted three times with 50 ml of organic solvent. The solvent is filtered through sodium sulfate into a glass stoppered mixing cylinder and the volume is recorded. The solvent is mixed in the cylinder. An aliquot is 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 is drained for the dislodgeable residue, the punches are transferred to a blender jar. The empty sample container is weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of solvent are added.

3. The sample is 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 squeous solution. The aqueous solution was extracted a total of three times with 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 with 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 place 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 $N_2$ | - | 80 ml/min |
| Injector temp. | - | 220°C | $H_2$ | - | 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

Daily temperatures were recorded on Table 1. The average maximum and minimum temperatures for the study period were 95.3 and 60.3 °F, respectively. Results of the analysis were recorded on Table 2 and Figure 1. Most residue levels were below 1 ppm by day 10. All residues showed a fairly steady rate of decline.

### TABLE 1: DAILY TEMPERATURE AND PRECIPITATION

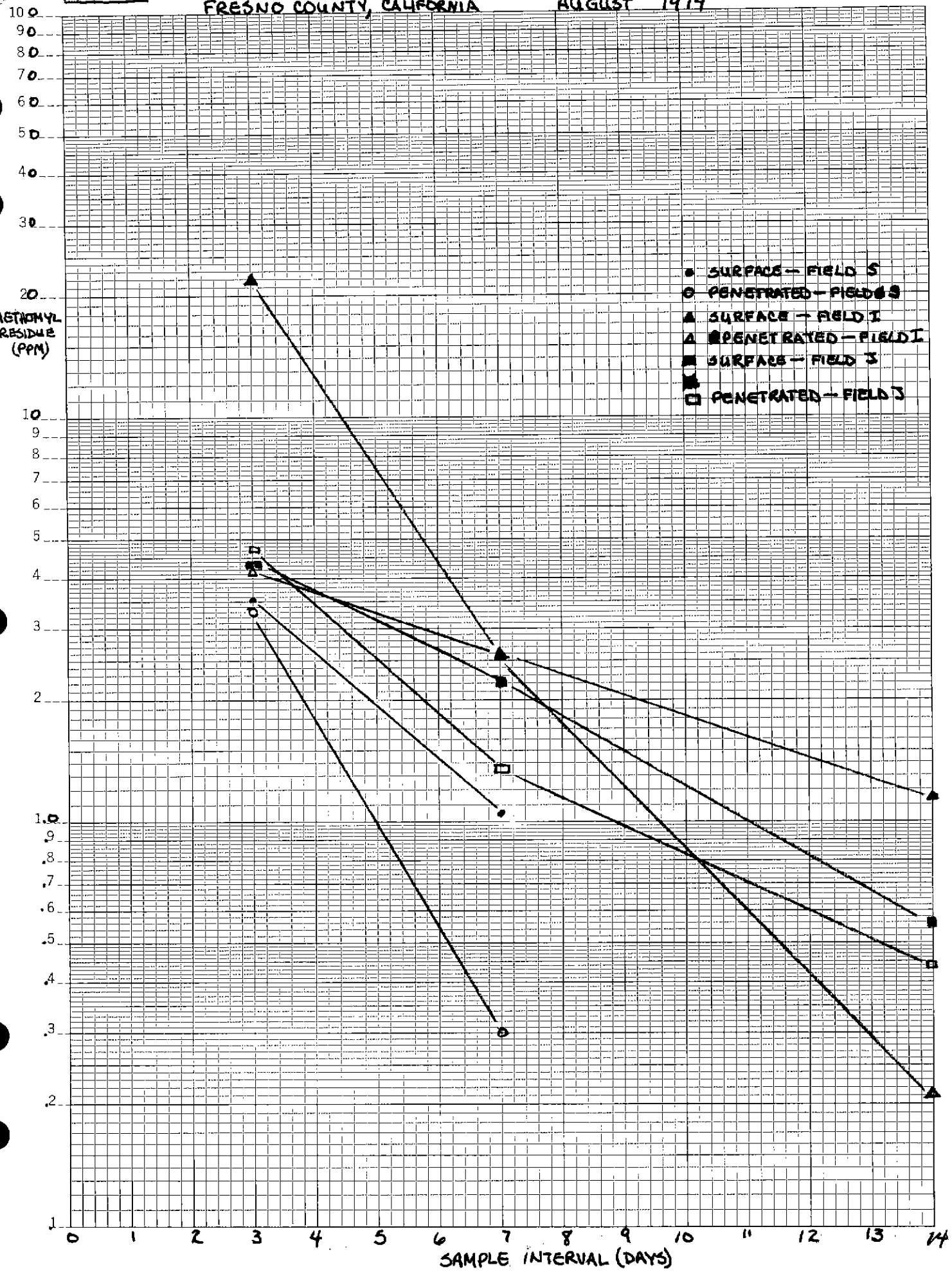
Weather observations taken at Fresno, California, by the National Weather Service.

| | Date (1974) | Temperature °F Maximum | Minimum | Precipitation (inches) |
|---|---|---|---|---|
| | 8/10 | 97 | 65 | |
| | 11 | 97 | 65 | |
| | 12 | 94 | 63 | |
| | 13 | 91 | 59 | |
| | 14 | 91 | 57 | |
| | 15 | 94 | 59 | |
| | 16 | 94 | 57 | |
| | 17 | 94 | 57 | |
| | 18 | 94 | 60 | |
| | 19 | 88 | 55 | |
| | 20 | 90 | 54 | |
| | 21 | 95 | 59 | |
| | 22 | 99 | 61 | |
| | 23 | 101 | 63 | |
| | 24 | 102 | 65 | |
| | 25 | 99 | 65 | |
| | 26 | 99 | 61 | |
| Average | | 95.3 | 60.3 | Total 0.00 |

TABLE 2: METHOMYL RESIDUE ON GRAPE FOLIAGE

| Field Identification | Sample Interval | Methomyl Residue (PPM) Surface | Penetrated |
|---|---|---|---|
| S | Presample | < 0.05 | < 0.05 |
| S | 3 days | 3.54 | 3.27 |
| S | 7 days | 1.06 | 0.30 |
| S | 14 days | < 0.05 | < 0.05 |
| I | Presample | < 0.05 | < 0.05 |
| I | 3 days | 22.0 | 4.21 |
| I | 7 days | 2.59 | 2.57 |
| I | 14 days | 1.15 | 0.21 |
| J | Presample | < 0.05 | < 0.05 |
| J | 3 days | 4.28 | 4.74 |
| J | 7 days | 2.33 | 1.35 |
| J | 14 days | 0.56 | 0.44 |

FIGURE 1: METHOMYL RESIDUE ON GRAPE FOLIAGE
FRESNO COUNTY, CALIFORNIA AUGUST 1974

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