

12-15-92

DATA EVALUATION RECORD

STUDY 7

CHEM 057701

Malathion

§164-1

FORMULATION--90--FORMULATION NOT IDENTIFIED

STUDY MRID 41727701

Rice, F., B. Jacobson, and C. Lochhaas. 1990. Terrestrial field dissipation for malathion in cotton (California). Laboratory Report No. 38003. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by the Malathion Reregistration Task Force.

DIRECT REVIEW TIME = 8

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DEC 15 1992

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid and provides supplemental information that shows malathion dissipates with a half-life of <2 days in the sandy loam soil used in California. For this study to be acceptable the study authors need to resolve the following issues:

1. The concentration of malathion in the "time 0" soil samples from the cropped and bareground plots failed to confirm the application rate; soil samples collected at "0 days" contained only approximately 7-24% of the theoretical application (0.58 ppm). This low recovery might be expected in the cropped soil, since the cotton leaves probably intercepted a significant portion

of the applied spray. However, plant interception could not be a reason for lack of confirmation in the bareground plots.

EFGWB notes that the low recovery of malathion residues is not unexpected and probably was a result of degradation in the samples prior to collection, or between collection and frozen storage. This explanation is supported by data from the supplemental aerobic soil metabolism study (Study 5) which shows rapid degradation of malathion (<1 day).

2. EFGWB needs more information on the proposed route of dissipation of malathion. The study authors did not offer an explanation of how malathion dissipates from the soil in this field dissipation study.

2. The sampling intervals were inadequate to accurately establish the half-life of the test substance, since 100% of the residues detected at 1 day posttreatment had dissipated by the next sampling interval (3 days). This deficiency is probably not too important given that malathion has a short half-life (<1-2 days) as noted in the supplemental aerobic metabolism study (Study 5).
3. EFGWB notes that the soil was analyzed for malathion and malaoxon only. In the aerobic soil metabolism study (Study 5, MRID 41721701), which was supplemental, malaoxon was a minor degradate, comprising a maximum of 1.8% of the applied radioactivity. More significant degradates in the aerobic metabolism study were the dicarboxylic acid of malathion at a maximum of 18.7-36.7% of the applied, the beta monomethyl ester of the dicarboxylic acid of malathion at 6.0-6.7%, the dimethyl ester of the dicarboxylic acid of malathion at 4.8-4.9%, the beta monocarboxylic acid of malathion at 2.8-7.3%, and the monomethyl ester of the beta monocarboxylic acid of malathion at 5.8-6.1%. If the above cited degradates are of concern in the future, then further information on their environmental fate may be required.
4. Further details of the study noted by the reviewer are listed below under the section "REVIEWER'S COMMENTS".

#### METHODOLOGY:

Malathion (Cythion ULV, 91% ai, formulation not described) was broadcast weekly for 6 weeks at a nominal rate of 1.16 lb ai/A/application (total 6.96 lb ai/A) to three vegetated and three bareground plots (15 X 125 feet, Figure 3) of sandy loam soil (Table 1) located in Madera County, California. The vegetated plots had been planted to cotton (5JC-1) on July 14, 1989; all plots were treated in July and August, 1989. Three untreated plots located approximately 505 feet north of the treated plots served as controls.

The application rate and spray distribution were estimated by placing five filter paper discs (5.9-inch diameter) at staggered intervals across each treated plot. Also, five samples (10 mL each) were collected from the tank solution at the time the plots were treated.

Five soil cores were collected from each plot immediately before the first treatment, immediately after each treatment, and at 1, 3, 7, 14, 28, 60, 90, 120, 150, 180, 210, 270, 330, 390, 450, and 540 days after the last treatment. Soil in the treated bareground plots was collected to a depth of 12 inches, and the cores were divided into 0- to 6- and 6- to 12-inch segments. Soil in the vegetated and control plots was collected to a depth of 48 inches.

At all sampling intervals up to 28 days after the last treatment, the 0- to 6-inch soil depth was excavated using a "can" (6-inch length, 3-inch id), then a zero-contamination hydraulic probe (48-inch length, 1.75-inch id) was inserted into the same hole to collect the 6- to 48-inch soil depth; the cores were divided into 0- to 6-, 6- to 24-, and 24- to 48-inch segments. At sampling intervals later than 28 days following the last treatment, the entire 0- to 48-inch core was collected using the hydraulic corer; the cores were divided into 0- to 24- and 24- to 48-inch segments. The holes left by the removal of the cores were filled with untreated soil and marked to prevent resampling.

The filter paper discs, solution samples, and all soil segments were frozen "as soon as they were returned to the ... Laboratory", were shipped to the analytical laboratory, and were stored frozen (-20° C) until analysis.

Before analysis, the soil samples were divided into 6-inch segments. The five segments collected from the same soil depth, sampling interval, and plot were composited, and the composited samples were ground with dry ice. Subsamples of the soil were extracted with acetonitrile and the extracts were filtered through a glass fiber filter. The container and filter cake were rinsed with acetonitrile. An aliquot of the filtrate was partitioned with hexane. The acetonitrile phase was dried over sodium sulfate, which had been rinsed with "methyl chloride/hexane/acetone". The acetonitrile extract was then dried (rotary vacuum evaporation) at 40 C, and the resulting residues were redissolved in acetone and diluted with methylene chloride. The solution was chromatographed on a silica gel column which had been pre-washed with acetone and methylene chloride. The eluate was concentrated to dryness under nitrogen; the residues were redissolved in 0.02% polyethylene glycol in acetone and analyzed by GC with flame photometric detection.

#### DATA SUMMARY:

Malathion (Cythion ULV, 91% ai, formulation not described), applied at a nominal rate of 1.6 lbs ai/A/application, dissipated with an observed half-life of <2 days from bareground and vegetated (cotton) field plots of sandy loam. The plots, located in California, were treated with six weekly applications of malathion during July and August 1989, for a total application of 6.96 lb ai/A. The tank application solution contained 46-127% of the theoretical application (Table 7, average = 90%, std dev = 19%, N = 29), application measurement samples (filter paper discs) contained 20-250% of the theoretical application (Table 8

and 9, average =  $55 \pm 19\%$  and  $66 \pm 29\%$ , cropped and bareground, respectively), and soil samples collected immediately posttreatment contained approximately 10-20% (Tables 7, 8, 11, and 12). Malathion did not accumulate in the soil as a result of repeated applications, and did not appear to leach below the 12-inch soil depth (Summary Tables).

In the 0- to 6-inch soil depth of the three vegetated plots immediately after each application, malathion averaged 0.055 ppm after the first application, 0.072 ppm after the second, 0.11-0.13 ppm after the third through fifth, and 0.082 ppm after the sixth application (Summary Tables). Malathion averaged 0.14 ppm at 1 day after the sixth application, and decreased to  $<0.01$  ppm (detection limit) at 3 days posttreatment. In the 6- to 12-inch soil depth, the average concentration of malathion ranged from 0.047 to 0.14 ppm immediately after each application; malathion averaged 0.13 ppm 1 day after the sixth application and  $<0.01$  ppm at all other sampling intervals. The average malathion concentration was  $<0.01$  ppm in the 12- to 18-inch depth at all sampling intervals and was detected only once in the 18- to 24- inch soil depth, at an average of 0.023 ppm immediately after the second application. Malaoxon was not detected at any soil depth at any sampling interval (Summary Tables).

In the 0- to 6-inch soil depth in the three bareground plots immediately after each application, malathion averaged 0.037-0.088 ppm with no discernible pattern (maximum following the first application; Summary Tables). Malathion averaged 0.067 ppm immediately after the sixth treatment, 0.11 ppm at 1 day after the sixth application, and  $<0.01$  ppm at all other sampling intervals. In the 6- to 12-inch soil depth, malathion was detected only once, at an average of 0.004 ppm immediately after the fourth application; no soil samples were collected deeper than 12 inches. Malaoxon was not detected at any soil depth at any sampling interval (Summary Tables).

During the study, air temperatures ranged from 50 to  $101^{\circ}$  F. Soil temperatures (8-inch depth) ranged from 69 to  $95^{\circ}$  F. Rainfall and irrigation at the site between July 25 and September 26 totaled 9.65 inches. The slope of the study site was zero, and there was no subsurface drainage.

#### REVIEWER'S COMMENTS:

1. The study authors stated that the 45 soil cores (9 plots x 5 cores/plot), collected immediately after treatment of the plots, were frozen upon return to the laboratory, but no information was provided on how the soil samples were handled prior to their return to the laboratory. This may have helped explain the non-confirmation of the application rate in the soil samples collected immediately after application of malathion.
2. The formulation of the test substance was described only as Cythion, 91% ai and a ULV.

3. Freezer storage stability data were provided for malathion and malaoxon in soil. After 90 days of freezer storage ( $-20^{\circ}\text{C}$ ), the average recoveries were 98% for malathion and 102% for malaoxon. After 180 days of freezer storage, average recoveries had decreased to 84% for malathion and 89% for malaoxon. The majority of field samples were stored for 120-135 days before extraction.
5. During the study, the bareground plots were treated five times with glyphosate at 0.94-2 quarts/A and the vegetated plots were treated four times with glyphosate at various concentrations.
6. The pesticide use history of the site prior to the initiation of the experiment was not reported. However, the study authors stated that "No previous studies had been conducted on the site."
7. The sampling interval designation used by the study authors, "0 days", is imprecise; it is improbable that all soil cores were collected immediately after treatment of the plots. When dealing with a pesticide with a half-life of <1 or 2 days, a sampling difference of several hours can be critical in obtaining an accurate estimate of the pattern of dissipation of that pesticide in the soil.

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MALATHION

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