

US EPA ARCHIVE DOCUMENT

In a letter from Barbara Gingher, Chair, Malathion Reregistration Task Force (MRTF) to Joanne Edwards, PM 74, dated October 10, 1991 (attached), it was revealed that the MRTF did not believe that this study would be acceptable because only about 1-2% of the intended rate was applied to the plot.

2. Furthermore, acceptable hydrolysis, anaerobic and aerobic aquatic and aerobic soil metabolism laboratory studies are needed in order to be able to know what degradates to look for in the aquatic field dissipation studies. The soil and water were 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%.

In the partially acceptable hydrolysis study the main degradates formed at pH 7 and 9 were monoethyl-[(dimethoxy phospho-thioyl)thio]-butanedioate (malathion monoester); (e)-2-butenedioic acid, monoethyl ester (monoethyl fumarate); and 2-thiobutanedioic acid, diethyl ester (diethyl thiosuccinate).

In the supplemental anaerobic aquatic (Study 13, MRID 422163-01) and aerobic (Study 14, MRID 422716-01) aquatic studies, besides CO₂, the main degradates formed in water and soil were: mono- and dicarboxylic acids, demethyl monoacid and demethyl diacid.

3. The registrant needs to propose a route of dissipation from the aquatic system. It appears that malathion is stable to unstable to hydrolysis (depending on pH) at environmental pH values and stable to aqueous photolysis at lower pH values; conversely, malathion appears to dissipate rapidly in aquatic field studies. However, at the present time the primary route of dissipation is not clear to EFGWB.
4. The registrant should provide more details related to normal cultural practices for a typical rice crop grown in Madera County, California (these should include, but not be limited to: typical soil series on which the crop is cultivated, typical planting dates, fertilization and cultivation practices, irrigation schedules, irrigation application rates and runoff when irrigating, harvest dates, etc.). This will allow EFGWB to ascertain if the study was conducted under typical conditions for the crop.
5. Since this study shows that malathion appears to degrade rapidly in water, the registrant should consider sampling at shorter intervals in order to be able to determine an accurate half-life in soil and water.

6. This study should be repeated taking into consideration all the reviewer's comments related to this study and the suggestions in Subdivision N Guidelines and in Section No. 164-2. This includes determining the characteristics of the irrigation water (pH, hardness, sediment load, etc.)
7. Further details related to the review of the study are noted below under the section listed as "REVIEWER'S COMMENTS".

METHODOLOGY:

Field

Malathion (9.33 lb a.i./gal, Cythion ULV insecticide, American Cyanamid Company) was applied at a rate of 0.58 lb a.i./A in three weekly applications (initial application on 8/14/89) to a flooded rice paddy (50 x 100 feet) soil (Table 1) located in Madera County, CA using a hand held CO₂-powered sprayer attached to a 27.5 foot spray boom. The Cal Pearl rice (planted 7/21/89) stage of development was at jointing (two-leaf stage) when the initial application was made. An untreated plot at the same location served as the control. The water level of the plots was maintained approximately 6 in. deep by the addition of water as needed weekly (Table 2). There was no overflow from the plots, except on September 14 and 15 when an adjacent untreated pond overflowed causing the treated plot to overflow by about 50%.

Five 10-ml spray solution samples were collected directly from the spray tank immediately before each application in order to have sufficient material to assist in confirming the application rate.

Soil samples were collected (Tables 6 and 7) using a hand-operated zero contamination sampler with acetate liners. The treated plots was sampled immediately before and after the initial application, immediately after each subsequent application and then 1, 3, 7, 10, 14, 21, 28, 56, 84, 182 and 364 days after the last application on 8/28/89. The control plot was sampled at initial and final application and then 1, 7, 14, 28, 56, 84, 182 and 364 days following the final application to the treated plot.

At each sampling interval in the treated rice plot, three 24-inch long soil cores were taken from each of five predesignated subplots and composited into three replicates of five cores each designated either A, B or C. The control plot was sampled at each sampling period by collecting one 24-inch long soil core from each of the five designated subplots.

Two water samples were collected from previously designated quadrants (Figure 4) in the treated and control plot by placing a one-liter plastic container beneath the surface of the pond water and filling it approximately half full. The treated plot was sampled immediately before and after each application and then 1, 7, 14, 21 and 28 days after the last application. The control plot was sampled before and after the initial, and after the second and third application, and then 14 and 28 days after the final application to the treated plots.

Sample Handling

All spray tank, water and soil samples were placed into coolers containing blue ice within 15 to 120 minutes after they were collected. All the samples were returned to the Pan-Agricultural Lab. facilities and kept frozen (-20°C) until shipped in dry ice to ABC Laboratory for further storage at -20°C until analysis. Soil samples were stored from 276 to 365 and water samples were store from 64 to 106 days prior to analysis.

Freezer Stability

Since the treated water samples were stored frozen for up to 106 days, duplicate 100 ml samples of non-treated water was fortified at levels of 0.10 ppm with malathion and malaoxon and assayed after 1, 15, 30, 60, 90 and 180 days of storage at -20°C in order to determine their stability under storage conditions.

Similarly, since treated soil samples were stored frozen for up to 365 days prior to analysis, 20 g samples of control soil were fortified with 0.20 ppm malathion and malaoxon and assayed after 1, 15, 30, 60, 90, 180 and 390 days of storage at -20°C in order to determine their stability under storage conditions.

Laboratory

Soil

The soil cores were divided into 0-4, 4-8, 8-12, 12-18 and 18-24 inch increments and finely ground in a grist mill type grinder and returned to freezer storage prior to analysis. A soil moisture determination was performed on each soil sample analyzed for malathion/malaoxon.

Twenty g of soil was placed in a glass jar and shaken for 30 minutes with 250 ml of acetonitrile and then filtered through a glass fiber filter paper; the jar was rinsed with an additional 50 ml acetonitrile which in turn was poured over the filter paper cake in order to achieve quantitative recovery of the material.

One hundred and fifty ml of the sample extract was shaken by hand for 1 minute with 50 ml of hexane and the mixture was allowed to separate. The acetonitrile phase was then quantitatively filtered through rinsed Na_2SO_4 and evaporated to dryness in a 40°C water bath in a rotary evaporator under partial vacuum. The sample was dissolved in 1 ml acetone, mixed with 9 ml methylene chloride, filtered through a silica gel column (SPE), dried under N gas and diluted with appropriate volumes of 0.02% polyethylene glycol (PEG) in acetone prior to GC analysis for malathion and malaoxon with a H-P 5890 GC equipped with a flame photometric detector.

Water

One hundred ml of water was extracted twice with 75 ml of methylene chloride in a separatory funnel, shaken by hand for 2 minutes, filtered through rinsed

Na₂SO₄, dried on a rotary evaporator under partial vacuum with a water bath at 40°C. The residue was dissolved in acetone, dried under N gas and diluted with appropriate volumes of 0.02% PEG in acetone prior to GC analysis.

Spray Tank Water

The aliquot from the spray tank was quantitatively transferred to a 250 ml volumetric flask and brought to volume with acetone. A 1-ml aliquot was removed from the flask, diluted with appropriate amounts of acetone/PEG and analyzed by GC.

Method Validation and Procedural Recovery

The methods for soil and water samples were validated by fortifying duplicate nontreated control samples at 0.01, 0.5 and 5.0 ppm of malathion and malaoxon and extracting as above; while % procedural recovery was determined by fortifying soil (0.01, 0.05, 0.10, and 0.50 ppm) and water (0.01, 0.10 and 1.0 ppm) samples and extracting and analyzing them at the same time as the treated samples. The % procedural recovery values were used to correct the residues found in the treated samples only if the % recovery was <100%; if ≥100%, 100% was used.

DATA SUMMARY:

Method Validation and Procedural Recovery

The % recovery for the method validation results for malathion and malaoxon in soil and water are given in Table 13 and 14 and ranged from 73 to 140% (average = 96.5%, N = 12) in soil to 89 to 112 % (average = 102.7%, N = 12) in water with the limit of detection (LOD) calculated to be 0.01 ppm in both media.

The recoveries of malathion and malaoxon from fortified soil samples analyzed concurrently with field samples were reported to be 93% ± 12% and 90% ± 11% for malathion and malaoxon, respectively (Table 26).

Recoveries in control water samples fortified with malathion and malaoxon and analyzed concurrently with water samples collected from the treated plot were, respectively, 102% ± 5% and 100% ± 5% for malathion and malaoxon (Table 21).

Freezer Stability

Recovery of malathion and malaoxon from the fortified water samples averaged, respectively, from 110 and 112% after one day of storage to 80 and 75% after 180 days of storage (Table 39).

Recovery of malathion and malaoxon from fortified soil samples averaged, respectively, 106% and 95% regardless of length of storage (Table 40).

Application Verification

The average percent of the theoretical concentration for the three spray tank solutions ranged from 0.91 to 2.4% (theoretical concentration = 0.049 lbs a.i./gal), indicating a non-verification of the application rate (Table 20). The study authors speculated, in the report, that the reason for the low recoveries in the spray solutions may have been due to the rapid separation or settling of the test material when the agitation of the sprayer was stopped to collect the samples.

The average concentration of malathion in water samples taken from the treated rice plot immediately after each application averaged 0.019 ppm; this is approximately 6% of the theoretical concentration of 0.32 ppm expected in the water. Again the study authors speculated that the low recoveries may have been due to the rapid dissipation of malathion in water; and to interception of the spray solution by the rice crop. They estimated the percent rice plant cover at each application to be 30, 40 and 50%, respectively.

Water Samples

Table 22 show the results from the analysis for malathion and malaoxon in water samples taken from the treated rice plots. Water samples were analyzed for malathion and malaoxon through Day 21 following the initial application and only for malathion after that day since no malaoxon residues were detected at or above 0.01 ppm in any of the water samples collected in the plots.

Malathion residues averaged 0.019 ppm in water samples taken after each application (Figure 1). Residues were <0.01 ppm in samples collected before the 2nd and 3rd application and one day after the last application. After the 15th day after the initial application samples, and in the control plot all malathion and malaoxon residues were <0.01 ppm.

Soil Samples

No malathion or malaoxon residues were detected in any of the soil samples from the treated or control plots (Table 28 and 30).

REVIEWER'S COMMENTS:

1. Based on the information provided by the MRTF that indicted only 1-2% of the intended amount of malathion was applied to the treated plot plus EFGWB's review of the study, it is concluded that the study can not be used to satisfy the data requirements for which it is intended because less than the maximum application rate was applied.
2. The registrant should provide details related to normal cultural practices for the rice crop grown in Madera County, California (these should include, but not be limited to: typical soil series on which the crop is cultivated, typical planting dates, fertilization and cultivation practices, irrigation schedules, sprinkler application rates and runoff when irrigating, harvest dates, etc.). This will allow EFGWB

to ascertain if the study was conducted under typical growth conditions for the crop.

EFGWB is particularly concerned with the large amount of water that was applied weekly to the rice crop. Typically in California about 5-6 acre-feet of water is required for a mature rice crop. From Table 2, it appears that the amount of water applied greatly exceeded the amount needed. The study authors need to explain this apparent discrepancy.

Also, rice is usually planted in California between April 15 and June 5. In this study the crop was planted on July 21 and no date of harvest was indicated. There was no explanation given as to why the late planting occurred.

3. As mentioned by the study authors, an event occurred approximately 15 days after the final application (September 14 and 15, 1989), when an adjacent untreated rice paddy pond overflowed into the treated plot causing it to overflow by about 50%. The study director believes that since malathion residues had dissipated to <0.01 ppm by Day 1 following the final application that no adverse impact occurred to the study.
4. Characteristics of the test water, including pH and dissolved oxygen content, were not reported. These characteristics are needed to demonstrate that the physical, chemical and biological parameters of the pond water are within normal ranges. Furthermore EFGWB notes that Subdivision N Guidelines Section 160-5 (c)(9)(ii) state: "In cases of aquatic field tests, characteristics of water obtained from a use site must be reported (e.g., pH, temperature, oxygen content, flow rate, and percent suspended solids)."
5. The tank samples taken for verification of application rate probably should have been collected as the solution was spraying out of the nozzles. This may have overcome the problem related to settling of the material.

MALATHION

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Pages 8 through 58 are not included.

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