UNDATED

DATA EVALUATION RECORD

STUDY 2

CHEM 041402 Molinate §164-1, §164-2
CAS No. 2212-67-1
FORMULATION–12--EMULSIFIABLE CONCENTRATE

STUDY ID 44970002
Curry, K.K. 1987. Molinate and propanil field dissipation study for aquatic food crop uses, Mississippi, 1986. Laboratory Project ID: RRC 87-10. Unpublished study performed by Stauffer Chemical Company, Richmond Research Center, Richmond, CA; and submitted by Zeneca Ag Products, Wilmington, DE.

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ABSTRACT

1. The terrestrial/aquatic/tank mix field dissipation study data requirements are satisfied with the two tank mix studies conducted in Texas and Mississippi (MRID's 44970002 and 44970003) for molinate and propanil, the new information presented in the responses (MRID 44956602) and incorporated under the individual guidelines, and the air monitoring data in California.

2. ARROSOLO® 3-3E Selective Herbicide, an emulsifiable concentrate containing 3 lb ai/gallon of molinate (S-ethyl N,N-hexamethylenethiocarbamate; ORDAM) and 3 lb ai/gallon of propanil (3',4'-dichlororopionanilide), was applied once at a nominal application rate of 1 gallon/acre to plots of silty clay loam soil in Leland, Mississippi, that were planted to rice. The plots were flooded to a depth of 4 inches 14 days after treatment. In Mississippi, molinate and total propanil residues [propanil plus 3,4-dichloroaniline (DCA)] dissipated with reviewer-calculated half-lives of 2.9 and 4.5 days, respectively (molinate, r^2=0.83, F=63, p=2.3e^{-6}; total propanil residues, r^2=0.6, F=6, p=7e^{-2}). In the soil (0- to 3-inch depth), DCA dissipated with a reviewer-calculated half-life of 5.09 days (r^2=0.55). Concentrations of molinate and total propanil residues in the floodwater were a maximum 0.003 and 0.009 ppm, respectively, at 1 day postflooding. Molinate decreased to below detection level (0.001 ppm) in the floodwater at 14 days. Total propanil residues (DCA, except immediately after flooding) in the floodwater dissipated with a reviewer-calculated half-life of 6.9 days. Soil and water samples were analyzed only for molinate, propanil, and DCA. The degradation of both compounds appeared to be biphasic, with over half of the compound (0- to 12-inch depth) dissipating by 1 day posttreatment and the remainder decreasing slowly through 14 days, when the plots were flooded. Concentrations of molinate and total propanil residues in the floodwater were a maximum 0.003 and 0.009 ppm, respectively, at 1 day postflooding. Rice plants were not analyzed for the parent or degradates

MATERIALS AND METHODS

ARROSOLO® 3-3E Selective Herbicide, an emulsifiable concentrate containing 3 lb ai/gallon of molinate (S-ethyl N,N-hexamethylenethiocarbamate; ORDAM) and 3 lb ai/gallon of propanil (3',4'-dichlororopionanilide), was applied once on September 3, 1986, at a nominal application rate of 1 gallon/acre to plots of silty clay loam soil (12.6% sand, 60.4% silt, 27% clay, 0.6% organic matter, pH 5.5, CEC 19.6 meq/100 g; p. 7) in Leland, Mississippi, that had been planted to rice (7-inch row spacing, p. 87) on August 14, 1986. There were two treated and two control plots (each 140 feet x 160 inches), separated by 80-inch buffer strips (pp. 63, 67). The application was made when the rice was in the two-leaf stage using a tractor-mounted boom sprayer calibrated for a delivery of 30 GPA at 39 PSI (p. 63). The application rate was not confirmed. The plots were flooded with well water from near the site to a depth of 4 inches on September 17, 1986, and remained flooded to this depth through November 19, 1986.

In the preceding year (1985), the test site was uncropped and no herbicide was applied (p. 63); additional plot history was not reported. The depth to the water table was >5 feet, and the slope gradient as 0.1% (p. 7). Meteorological data were not provided for each day after treatment (pp. 65-66). The "mean low/high" temperatures of the soil before flooding (9/2-9/17/86) and after drainage (11/19-12/30/86), reported by sampling dates, were 50-69°F and 68-88°F, respectively, and of floodwater (9/17-11/19/86) were 57-

67°F and 78-90°F, respectively. A total of 1.44 inches of rain fell prior to flooding and 13.04 inches fell while the plots were flooded (pp. 65-66).

Soil samples were collected from the treated and control plots 1 day prior to treatment and 0, 3, 5, 7, and 14 days posttreatment. The soil was flooded at 14 days, and water samples were collected at 14, 15, 17, 19, 21, 28, and 35 days posttreatment (p. 5). No soil samples were collected while the plots were flooded. Although it was stated that soil samples were collected after the plots were drained (p. 63), no data from these intervals is presented. At each sampling interval, five soil samples (1-inch diameter; 0- to 3-, 3- to 6-, and 6- to 12-inch depths) were randomly collected from each treated and control plot using an Oakfield soil probe (p. 64) and placed in aluminum containers. Water samples (number not specified) were collected in glass bottles sealed with aluminum foil-lined caps. No additional information about the sampling procedures were provided. The samples were chilled in the field and transported to a temporary storage location. The soil samples were composited, but it is not clear if this occurred in the field or the temporary storage location; composited samples were transferred to glass jars sealed with aluminum foil-lined caps. Samples were frozen, shipped to the analytical laboratory on dry ice, and stored frozen (-20°C) until analysis. Samples were stored frozen for up to 10 weeks prior to analysis (p. 35). Rice plants were not collected for analysis.

Samples were analyzed for molinate using Methods RRC 85-25 (water) and RRC 85-26 (soil), and for propanil and 3,4-dichloroaniline (DCA, 3.4-dichlorobenzenamine), its primary degradate, using Propanil (Update) by Adler and Zogorski (Analytical Methods of Pesticides and Plant Growth Regulators, 1984)(p. 35).

To analyze for molinate in soil, portions (50 g) of thoroughly mixed soil samples were weighed into 8-oz wide mouth bottles. The subsamples were slurried with distilled water (100 mL) by shaking on a reciprocating shaker for 30 minutes (p. 85). Toluene (50 mL) wa added, and the slurries were shaken for an additional 60 minutes. The slurries were centrifuged for 5 minutes to separate the toluene and aqueous phases. The organic layer was transferred into a 1-oz Poly-sealed bottle and a layer (0.5 cm) of sodium sulfate was added. Aliquots of the organic phase were analyzed by capillary GC with nitrogen-phosphorous detection. The detection limit for molinate in soil was 0.01 ppm (p. 8). The results of the soil sample analyses were not adjusted for soil moisture content. Instrument operating conditions were as follows:

Analytical Column: Fused silica construction, crosslinked methyl silicone, 12 m x 0.20 mm i.d.
Injection Port: 220°C isothermal
Nitrogen-Phosphorous Detector: 300°C isothermal
Column Oven Temperature Program: 90°C for 1 minute, then 160°C at 25°C per minute
Flow Rate: Helium - 2 mL/minute
Retention time: 4.4 minutes

To analyze for molinate in water, aliquots (50 mL) of the water samples were transferred into a Poly-seal capped 2-oz bottle and extracted with toluene (5 mL) by shaking for 30 minutes (p. 76). The toluene extracts were sonicated for 1 minute. The organic phase was transferred into a clean Poly-seal capped vial, a layer (0.5 cm) of sodium sulfate was added (p. 82). Aliquots of the organic extracts were analyzed by GC as described for the soil samples. The detection limit for molinate in water was 0.001 ppm (p. 8).

To analyze for propanil and DCA in soil, portions of the soil samples were slurried with water, shaken with toluene, and the mixture was centrifuged to separate the toluene and aqueous phases. An aliquot of the toluene extract was analyzed by capillary GC with nitrogen-phosphorous detection as described for the molinate analyses of soil and water samples. The detection limits for propanil and DCA in soil were 0.01 ppm (p. 8).

To analyze for propanil and DCA in water, aliquots of the water samples were extracted with toluene as described for the molinate analysis of water samples. Aliquots of the organic extracts were analyzed by GC as described for the molinate analyses of soil and water samples. The limit of detection limits for propanil and DCA in water were 0.001 ppm (p. 8).

To determine concurrent recoveries, soil samples were fortified with molinate at 0.0106 and 0.424 ppm and water samples were fortified at 0.00106 and 0.1060 ppm (three samples at each concentration; pp. 21, 24). Mean recovery (across all fortifications) of the parent from soil was 106 ± 13% (range of 79 to 117%) and from water was 106 ± 6% (range of 99 to 113%).

To determine concurrent recoveries, soil samples were fortified with propanil at 0.00999 and 0.3996 ppm and water samples were fortified at 0.000999 and 0.0999 ppm (three samples at each concentration; p. 22, 25). Mean recovery (across all fortifications) of the parent from soil was 104 ± 11% (range of 87 to 116%) and from water was 96 ± 12% (range of 89 to 112%).

To determine concurrent recoveries, soil samples were fortified with DCA at 0.0101 and 0.404 ppm and water samples were fortified at 0.00101 and 0.1010 ppm (three samples at each concentration; p. 23, 26). Mean recovery (across all fortifications) of the parent was 94 ± 14% (range of 69 to 106%) and from water was 103 ± 2% (range of 100 to 105%).

RESULTS/DISCUSSION

ARROSOLO® 3-3E Selective Herbicide, an emulsifiable concentrate containing 3 lb ai/gallon of molinate (S-ethyl N,N-hexamethylenethiocarbamate; ORDAM) and 3 lb ai/gallon of propanil (3',4'-dichlororopionanilide), was applied once at a nominal application rate of 1 gallon/acre to plots of silty clay loam soil in Leland, Mississippi, that were planted to rice. The plots were flooded to a depth of 4 inches 14 days after treatment. In Mississippi, molinate and total propanil residues [propanil plus 3,4-dichloroaniline (DCA)] dissipated with reviewer-calculated half-lives of 2.9 and 4.5 days, respectively (molinate, r^2=0.83, F=63, p=2.3e^{-6}; total propanil residues, r^2=0.6, F=6, p=7e^{-2}). In the soil (0- to 3-inch depth), DCA dissipated with a reviewer-calculated half-life of 5.09 days (r^2=0.55). Concentrations of molinate and total propanil residues in the floodwater were a maximum 0.003 and 0.009 ppm, respectively, at 1 day postflooding. Molinate decreased to below detection level (0.001 ppm) in the floodwater at 14 days. Total propanil residues (DCA, except immediately after flooding) in the floodwater dissipated with a reviewer-calculated half-life of 6.9 days. Soil and water samples were analyzed only for molinate, propanil, and DCA. The degradation of both compounds appeared to be biphasic, with over half of the compound (0- to 12-inch depth) dissipating by 1 day posttreatment and the remainder decreasing slowly through 14 days, when the plots were flooded. Concentrations of molinate and total propanil residues in the floodwater were a maximum 0.003 and 0.009 ppm, respectively, at 1 day postflooding. Rice plants were not analyzed for the parent or degradates

In the 0- to 3-inch soil depth, molinate was 0.86 ppm immediately posttreatment, 0.40 ppm at 1 day, 0.67 ppm at 3 days, 0.26 ppm at 5 days, 0.13 ppm at 7 days, and 0.10 ppm at 14 days (Table 1, p. 18). In the 3- to 6-inch soil depth, molinate was 0.21 ppm immediately posttreatment, 0.02 ppm at 7 days, and ≤0.02 ppm at other intervals. In the 6- to 12-inch depth, molinate was 0.15 ppm immediately posttreatment and ≤0.02 ppm at other intervals. In the floodwater, molinate was 0.001 ppm immediately after flooding, 0.003 ppm at 1 day, 0.002 ppm at 3 through 7 days, and was not detected (<0.001 ppm) at 14 and 21 days (Table 3, p. 20).

In the 0- to 3-inch soil depth, total propanil residues were 1.24-1.36 ppm immediately posttreatment, 0.13-0.39 ppm at 1 through 7 days with no discernable pattern of decline, and 0.07 ppm at 14 days (Table 2, p. 19). Of this, propanil was 0.58-0.68 ppm immediately posttreatment, 0.05 ppm at 3 days, and <0.01 ppm at 5 through 14 days. DCA was 0.49-0.50 ppm at 0 days, 0.06-0.29 ppm at 1 through 7 days with no discernable pattern of decline, and 0.05 ppm at 14 days. In the floodwater, total propanil residues were a maximum of 0.009 ppm at 1 day, and declined to 0.003-0.004 ppm at 3 through 7 days and <0.002 ppm at 14 and 21 days (Table 3, p. 20). The majority of the residues in the floodwater were DCA; propanil was detected only once in the floodwater, at 0.004 ppm immediately after flooding.

DEFICIENCIES/DEVIATIONS

3. It was not clear if the soil was not sampled deeply enough to establish the depth of leaching. Soil was sampled to a depth of only 12 inches. Molinate, propanil, and DCA were detected in the deepest soil sampled immediately following treatment, and at 1 and 5 days posttreatment. Only one soil depth was shown to be free of these compounds at most other intervals. To establish the depth of leaching, two soil segments below the deepest detection must be shown to have no detectable levels of molinate residues from each sampling interval.

4. The sampling procedures did not appear to be adequate. Molinate and propanil were detected in the 6- to 12-inch soil depth immediately after treatment. It is highly probable that the presence of these compounds at depth resulted from treated surface soil being transported to the deeper soil during sampling.

5. No data on field spikes were provided to confirm that sample handling procedures between sampling and arrival at the laboratory were adequate. Storage stability data were not provided. Based on the information presented in Appendix B (p. 35), the soil and water samples were extracted on November 11 and analyzed on November 12, 1986. The first soil samples were collected on September 2, 1 day prior to treatment. Therefore, samples were stored for up to 10 weeks prior to analysis. No storage stability data were provided.

6. The application rates were not confirmed. No inert surfaces were placed in the field to intercept residues at any treatment interval. The concentrations of residues in the soil immediately following treatment were less than what would be expected. Applications of 3 lb ai/A would be expected to produce a soil concentration of 3 ppm in the 0- to 3-inch depth. The concentration of molinate and total propanil residues (propanil and DCA) in composited soil samples from the 0- to 3-inch depth of the two treated plots were 0.89 and 1.24-1.36, respectively.

7. No soil samples were collected from the plot while it was flooded. Subdivision N guidelines specify that flooded soil samples be collected in aquatic field dissipation studies.

8. No sediment samples were collected. Subdivision N guidelines specify that sediment samples be collected in aquatic field dissipation studies.

9. The analytical methods used to analyze total propanil residues, propanil, and DCA residues in water and soil were not clearly described. In the methods section of the report, it was stated that the soil and water samples were analyzed using "Propanil (Update)" with modifications (p. 8). However, two methods for propanil/DCA analyses were provided in the Propanil (Update)" report (pp. 91). One method (Kearney *et al.*, 1970; Deuel, *et al.* 1977) is a method for analyzing parent compound and includes steps that differ

significantly from the residue analysis summary presented for propanil and DCA determination in the methods section of the report (pp. 8 and 94). The second method (Gordon *et al.*, 1964) is a method for measuring propanil residues based on an alkaline hydrolysis to DCA (p. 96). It was unclear which method was used to analyze the soil and water samples in the present study, and what modifications were made to the methods.

10. Meteorological data were incomplete. Air temperatures were not reported. Soil temperatures were provided only for sampling dates.

11. The rice plants were not analyzed for the parent or degradates. It is necessary that total residues in the crop be monitored in order to accurately determine the routes of dissipation of the test compound.

12. It was stated that the study was not conducted in accordance with 40 CGR Part 160 (Good Laboratory Practices) because the laboratory work was not subject to these requirements, but that the study was carried out using accepted laboratory methods and standard management procedures.

13. The maximum proposed application rate for ARROSOLO 3-3E is 1 gallon/acre. This is the rate used in this study.

14. The concentration of molinate, propanil, and DCA in the total system (soil plus water) could not be determined because soil samples were not collected during flooding.

ATTACHMENT 1
Tables cited in DER

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ATTACHMENT 2
Excel Workbook