DATA EVALUATION RECORD

STUDY 3

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

STUDY ID 44970003
Curry, K.K. 1987. Molinate and propanil field dissipation study for aquatic food crop uses, Texas, 1986. Laboratory Project ID RRC 87-11. Unpublished study performed by Stauffer Chemical Company, Richmond Research Center, Richmond, CA; and submitted by Zeneca Ag Products, Wilmington, DE.

DIRECT REVIEW TIME =

REVIEWED BY: Joan Harlin
TITLE: Senior Staff Scientist
SIGNATURE:
DATE:

EDITED BY: Dan Hunt
TITLE: Staff Scientist
SIGNATURE:
DATE:

EDITED BY: Kathi Ferguson
TITLE: Senior Staff Scientist
SIGNATURE:
DATE:

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERB2/EFED/OPP
TEL: 703-305-5925

SIGNATURE:

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; ORDRAM) and 3 lb ai/gallon of propanil (3,4-dichloropionanilide), was applied once at a nominal application rate of 1 gallon/acre to a field of sandy loam soil near Brookshire, Texas, that was planted to rice. The field was flooded 6 days after treatment. In the soil (0- to 3-inch depth), molinate and total propanil residues [propanil plus 3,4-dichloroaniline (DCA)] each dissipated with registrant-calculated half-lives of 0.85 and 0.67day, respectively (molinate, r^2=0.95, F=86, p=7.5e^{-4}; total propanil residues, r^2=0.90, F=52, p=3.5e^{-4}). The observed half-lives were <2 days for molinate and <1 day for total propanil, propanil, and DCA residues. In the floodwater, molinate was a maximum 0.240 ppm at 2 days postflooding and decreased to 0.025 ppm by 4 days, and propanil residues (DCA) were a maximum 0.012 ppm immediately after flooding, and were not detected at later sampling intervals. Soil and water samples were analyzed only for molinate, propanil, and DCA. Rice plant samples were not analyzed.

MATERIALS AND METHODS

ARROSOLO® 3-3E Selective Herbicide, An emulsifiable concentrate containing 3 lb ai/gallon of molinate [S-ethyl N,N-hexamethylenethiocarbamate; ORDRAM) and 3 lb ai/gallon of propanil (3,4-dichloropionanilide), was applied once on September 15, 1986, at a nominal application rate of 1 gallon/acre to a plot (1 acre, not replicated, p. 38) of sandy loam soil (55% sand, 40% silt, 5% clay, 0.5% organic matter, pH 6.0, CEC 3.7 meq/100 g, p. 7) near Brookshire, Texas, that had been planted to rice (*var.* Skybonnet; row spacing not reported) on August 11, 1986. The rice was in the 2-4 leaf stage at the time of treatment (p. 33). The application was made using a tractor-mounted sprayer calibrated for a delivery of 26 GPA at 30 PSI (p.38). The application rate was not confirmed. The field was flooded (depth unspecified) with well water from near the site on September 21, 1986, and remained flooded until November 1, 1986 when it was drained.

A plot history (years unspecified) indicated that the field was uncropped and no herbicides were applied prior to the study (p. 45). The depth to the water table was > 5 feet, and the slope gradient was 0.02% (p. 7). On the day of application day, the air temperature was 92°F and the soil temperature was 80°F at the 2-3 inch soil depth. Meteorological data were not provided for the period following treatment.

Soil samples were collected from the treated field at 0, 1, 2, 4, 49, 50, 51, 53, 56, 58, 66, 71, 77, and 91 days posttreatment. No soil samples were collected while the field was flooded (See Comment #3). To confirm that the field was not contaminated prior to treatment, soil samples were collected from the field 38 days prior to treatment. At each sampling interval, five soil cores (1-inch diameter; 0- to 3-, 3- to 6-, 6- to 12-, and 12- to 24-inch depths) were randomly collected from the field using a soil probe. At each sampling interval, the soil cores were composited into a single soil sample, and the soil

samples were placed into clean glass jars that were then sealed with aluminum-foil-lined caps. Water samples (number not specified) were collected at 7, 8, 9, 11, 14, 21, 28, 32, 39, and 46 days posttreatment, and were placed in glass bottles that were then sealed with Teflon-lined caps. The soil and water samples were chilled in the field, then transported to a temporarily storage location where they were stored frozen. Afterwards, the frozen samples were shipped on dry ice to the analytical laboratory where they were stored frozen (-20°C) until analysis. Soil samples were stored frozen for up to103 days prior to analysis. Water samples were stored frozen for up to 51 days prior to analysis. 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-dichlorobenzeneamine), its primary degradate, using "Propanil (Update)" by Adler and Zogorski (Analytical Methods for Pesticides and Plant Growth Regulators, 1984) with modifications.

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. 91). Toluene (50 mL) was 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 limit of detection 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. 82). 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 limit of detection 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 limit of detection for propanil and for DCA was 0.001 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 for propanil and for DCA was 0.001 ppm (p. 8).

To determine concurrent recoveries, nine soil samples were fortified with molinate at 0.0106, 0.3180, and 0.4240 ppm and four water samples were fortified with molinate at 0.00106 or 0.106 ppm (pp. 24 and 27). Mean recovery (across all fortifications) of the parent from soil was 102 ± 10% (range of 85 to 113%) and from water was 106 ± 6% (range of 99 to 113%). Additional recoveries for method validation provided in the residue method for fortified soil and water samples were provided; raw data were not provided.

To determine concurrent recoveries, five soil samples were fortified with propanil at 0.00999, 0.2997, and 0.3996 ppm and four water samples were fortified with propanil at 0.00106 and 0.106 ppm (pp. 25 and 28). Mean recovery (across all fortifications) of the parent from soil was 98 ± 17% (range of 77 to 115%) and from water was 96 ± 12% (range 89 to 112%).

To determine concurrent recoveries, five soil samples were fortified with DCA at 0.0101, 0.303, and 0.404 ppm and four water samples were fortified with DCA at 0.00101 and 0.101 ppm (pp. 26 and 29). Mean recovery (across all fortifications) of DCA from soil was 89% (reviewer-calculated; range of 80 to 96%) and from water was 103 ± 2% (range of 100 to 103%) (pp.26 and 29).

DATA SUMMARY

ARROSOLO® 3-3E Selective Herbicide, an emulsifiable concentrate containing 3 lb ai/gallon of molinate (S-ethyl N,N-hexamethylenethiocarbamate; ORDRAM) and 3 lb ai/gallon of propanil (3,4-dichloropionanilide), was applied once at a nominal application rate of 1 gallon/acre to a plot of sandy loam soil near Brookshire, Texas, that was planted to rice. The field was flooded 6 days after treatment. In the soil (0- to 3-inch depth), molinate and total propanil residues [propanil plus 3,4-dichloroaniline (DCA)] dissipated with registrant-calculated half-lives of <1 and 1 day, respectively (molinate, r^2=0.946; propanil residues, r^2=0.815) (Tables 1-2; pp.19-22). The reviewer-calculated half-lives were 0.73 days for molinate and 0.84 days for total propanil residues (r^2=0.9556 and 0.823, respectively; Attachment 2). In the floodwater, concentrations of molinate residues were a maximum 0.240 ppm at 2 days postflooding and decreased to 0.025 ppm at 4 days, and concentrations of propanil residues, detected only once, were 0.012 ppm immediately

after flooding (Table 3, p. 23). Molinate, propanil, and DCA were not detected in the soil (<0.01 ppm) prior to treatment; floodwater samples were not collected prior to application to the field. Soil and water samples were analyzed only for molinate, propanil, and DCA. Rice plants were not analyzed for parent or degradates.

In the 0- to 3-inch soil depth, molinate was 3.90 ppm immediately posttreatment, 0.82-0.86 ppm at 1 day, 0.38 ppm at 2 days, 0.11 ppm at 4 days, and varied from 0.03 to 0.12 ppm at 49 through 91 days posttreatment, with no discernible pattern of decline (Table 1, p. 19). In the 3- to 6-inch depth, molinate was 0.01 ppm immediately posttreatment, was not detected (<0.01 ppm) at 1 through 4 days, was 0.09-0.24 ppm at 49 through 53 days with no discernible pattern, and was 0.05 and 0.09 ppm at 58 and 91 days, respectively. Molinate was not detected (<0.01 ppm) in soil depths below 6 inches, except once at 0.02 ppm in the 12- to 24-inch depth at 49 days posttreatment. In the floodwater, molinate was not detected (<0.001 ppm) immediately after flooding, increased to a maximum of 0.240 ppm at 2 days, decreased to 0.025 ppm at 4 days, and was 0.018 ppm at 7 days, 0.006 ppm at 14 days, and <0.001 ppm by 21 days (Table 3, p. 23).

In the 0- to 3-inch soil depth, total propanil residues were 11.9 ppm immediately posttreatment, 3.53 ppm at 1 day, 1.64 ppm at 2 days, 1.20-1.27 ppm at 4 days, and were ≤0.03 ppm at 49 through 58 days posttreatment (Table 2, p. 21). Of this, propanil was 11.30 ppm immediately posttreatment, 1.50 ppm at 1 day, 0.51 ppm at 2 days, 0.17-0.19 ppm at 4 days, and was not detected (<0.01 ppm) at 49 through 58 days posttreatment. DCA was 0.46 ppm immediately posttreatment, increased to 1.50 ppm at 1 day, decreased to 0.76-0.84 ppm at 2-4 days, and was ≤0.02 ppm at 49 through 58 days. In the 3- to 6-inch soil depth, total propanil residues were 0.02 ppm immediately posttreatment, 0.01-0.04 ppm at 2-4 days, and were not detected (<0.02 ppm) at 49 through 58 days; all of the detected residues were propanil. In the 6- to 12-inch soil depth, total propanil residues were 0.02 ppm immediately posttreatment, all of which was propanil, and were not detected (<0.02 ppm) at all other sampling intervals. Propanil residues were not detected in the 12- to -24 inch soil depth. In the floodwater, total propanil residues were a maximum 0.012 ppm immediately postflooding, all of which were DCA, and were not detected (<0.002 ppm) at 1 through 39 days postflooding (Table 3, p. 23).

DEFICIENCIES/DEVIATIONS

1. No data on field spikes were provided to confirm that sample handling procedures between sampling and arrival at the laboratory were adequate. The soil samples were stored for up to 103 days (3.4 months), and water samples were stored for up to 51 days (1.7 months) prior to analysis (pp. 38, 47, 55, 62, 70). Storage stability data were not provided.

2. The application rates were not confirmed. No inert surfaces were placed in the field to intercept residues at any treatment interval. The concentrations of molinate and total propanil residues (propanil and DCA) in the soil immediately following treatment were higher than 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 concentrations of molinate and total propanil residues in composited soil samples from the 0- to 3-inch depth of the treated field were 3.90 and 11.9 ppm, respectively.

3. 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.

4. 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. 9). However, two methods for propanil/DCA analyses were provided in the Propanil (Update)" report (pp. 97). 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. 9 and 100). The second method (Gordon *et al.*, 1964) is a method for measuring propanil residues based on an alkaline hydrolysis to DCA (p. 102). 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.

5. Field test data were incomplete. Meteorological data, including air and soil temperatures, rainfall, and precipitation data, for the entire study period were not reported. Total water output (rainfall plus irrigation) during the entire study period was not reported. The only meteorological data provided were air and soil temperatures recorded on the day of application, and precipitation data recorded for the sampling days of November 25 and December 15, 1986 when flooding occurred due to heavy rain. Also, the depth to which the field was flooded was not reported.

6. Molinate residues were 0.01 ppm in the 12- to 24-inch soil depth at 49 days posttreatment. However, molinate residues were not detected in the 6- to 12-inch soil depth or in any other 12- to 24-inch soil depth sample at any sampling interval. Therefore, it is likely that the molinate residues in the 12- to 24-inch soil depth are not related to treatment.

7. The rice plants were not analyzed for molinate, propanil or DCA. It is necessary that total residues in the crops be monitored so that the routes of dissipation of the test compound can be adequately determined.

8. 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.

9. Molinate and propanil are normally applied during May, and were applied in this study in the fall.

ATTACHMENT 1
Tables cited in DER

THE FOLLOWING ATTACHMENT IS NOT AVAILABLE ELECTRONICALLY
SEE THE FILE COPY

ATTACHMENT 2
Excel Workbook