UNDATED

DATA EVALUATION RECORD

STUDY 7

CHEM 041402 Molinate §164-2

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC), 04--GRANULAR

STUDY ID 41421803
Curry, K.K., B.D. Riggle, and R.E. Hoag. 1989a. Ordram 8-E aquatic field dissipation study for aquatic use post-flood. Report No. RR 89-025B. Unpublished study performed and submitted by ICI Americas, Inc., Richmond, CA.

STUDY ID 41421804
Curry, K.K., B.D. Riggle, and R.E. Hoag. 1989b. Ordram 15-G aquatic field dissipation study for aquatic use post-flood. Report No. RR 89-055B. Unpublished study performed and submitted by ICI Americas, Inc., Richmond, CA.

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact

1. This aquatic field dissipation (164-2) study provides supplemental information but does not satisfy the 164-2 data requirement at this time. Only 35 % of applied 8E or 15G molinate was confirmed in the California studies. Therefore, no meaningful half-lives could be calculated where the application rate was not confirmed. In general, molinate appeared to volatilize and partition to sediment in

the rice paddies, but no route of dissipation could be confirmed since the recoveries in the field were low.

2. To satisfy the terrestrial and aquatic field dissipation data requirements, EFED is requiring three new studies to cover the use of molinate in dry-seeded and water-seeded rice in California, Arkansas, and southwestern Louisiana. These studies must be representative of rice production practices where they are conducted, and must address all routes of dissipation in the field (e.g. biological degradation, chemical degradation, air sampling over space and time for molinate volatility, the volume and concentrations of water that are released from the rice fields, and the amount of molinate that remains in the field. The registrant should submit protocols for each study. One study must be conducted using Arrosolo, which is formulated product of molinate and propanil. The fate and transport of both pesticides must be studies.

3. Molinate (8 lb/gal EC and 15% G) were applied twice at an interval of 7 days at 5 lb ai/A/application (10 lb ai/A total). Meaningful half-lives in soil and water could not be calculated since the application rate could not be confirmed. The maximum percent recoveries were about 35 %. However, it appeared that molinate was more persistent in soil when applied as 15-G. This is probably because the granules would be likely to sink to the bottom of the water, where they would interact with sediment and reduce the amount of probable volatility loss. Only molinate was detected in the soil; carboxymolinate and molinate sulfoxide were detected in the irrigation water at up to 0.10 and 0.19 ppm, respectively.

Ancillary Study - Freezer Storage Stability

1. Freezer storage stability studies are not specifically required by Subdivision N guidelines.

2. These data are of questionable value and should not be used to predict the environmental behavior of molinate and its degradates.

3. This study is unacceptable for the following reason:

   the data were too variable to accurately assess the freezer storage stability of molinate.

4. Because the data were too variable to accurately evaluate the freezer storage stability, the problems with this portion of the study cannot be resolved with the submission of additional data. A new study is required.

METHODOLOGY:

Field Dissipation - Aquatic and Aquatic Impact

Field plots of clay soil (21% sand, 25% silt, 54% clay, 2.7% organic matter, pH 6.1, CEC 33.7 meq/100 g) located near Durham, California, were flooded (4-inch depth) on July 5, 1988; planted to rice on July 7; and aerially-treated with molinate (Ordram 8-E, 8 lb/gal EC, plot 3.11; or Ordram 15-G, 15% G, plot 2.11; Stauffer Chemical) at 5 lbs ai/A/application (10 lbs ai/A total) on July 15 and 22 (Figure 1). The rice seedlings were 2-5 inches in height at the time of the first application and 3-5 inches in height at the time of the second application. An untreated plot (plot 1.01) near the treated plots was maintained as a control. The plots were not cultivated after treatment; the flood water was maintained at a 4-inch depth until it was drained from the plots on October 11, 1988, 81 days after the second molinate application. The irrigation water was usually drawn from an irrigation canal; occasionally, the water was drawn from an on-site well.

Soil cores were collected from the treated and control plots to a depth of only 3.5 inches while the plots were flooded "to avoid contamination problems in deeper cores, and to avoid puncturing the clay that held the flood" (1, 2, and 7 days after the first application and 1, 3, 8, 15, 29, 57, and 78 after the second). When the plots were not flooded, soil cores were collected to a depth of 15.5 inches (prior to flooding, and days 83, 85, 88, 96, 101, 108, 188, and 279 after the second application), and occasionally to 42 inches. Twenty-one soil cores were collected from the 3.5-inch depth at each sampling interval; 21 cores were collected from the 3.5- to 15.5-inch depth and nine cores were collected from the 15.5- to 42-inch depth when that soil layer was sampled. Soil cores were collected using a zero-contamination corer; sampling procedures were modified so that flood water was collected in the same sample as the soil. Samples were stored at -20 C in the collection tubes for up to 56 days (average 37 days). To separate the irrigation water from the soil, the sample was sawed at the soil:water interface. Cores collected deeper than 3.5 inches were divided into 3.5-inch segments to 15 inches, then into 15.5- to 27.5- and 27.5- to 39.5-inch segments. Soil and water samples were thawed briefly before being transferred into glass containers. The samples were then stored at -20 C for up to 325 days (average 118 days).

The soil samples were analyzed for molinate, S-methyl molinate, and molinate sulfoxide. Portions of the soil samples were shaken with water:toluene (1:1:1, w:v:v) for 2 hours, then allowed to settle. An aliquot of the toluene layer was analyzed for molinate and S-methyl molinate using GC with nitrogen-phosphorus thermionic detection; the detection limit was 0.01 ppm. Additional portions of soil were shaken with water:methylene chloride (1:1:1, w:v:v) for 2 hours, then allowed to settle. An aliquot of the methylene chloride layer was analyzed for molinate sulfoxide using GC as described above; the detection limit was 0.05 ppm. Recovery from fortified soil samples ranged from 70 to 123% for molinate, 94 to 129% for molinate sulfoxide, and 72 to 113% for S-methyl molinate.

Irrigation water samples were analyzed for molinate, S-methyl molinate, molinate sulfoxide, carboxymolinate, and hexamethyleneimine. To analyze for molinate and S-methyl molinate, aliquots of the water were shaken with toluene (1:1, w:v) for 2 hours, then allowed to settle. An aliquot of the toluene layer was analyzed using GC as described above; the detection limit was 0.01 ppm. To analyze for molinate sulfoxide, aliquots of the water were saturated with sodium chloride and partitioned three times with methylene chloride. The methylene chloride fractions were combined and mixed with toluene, and the methylene chloride was removed by vacuum evaporation. The resulting toluene solution was analyzed using GC; the detection limit was 0.01 ppm. To analyze for carboxymolinate, aliquots of the water were acidified, then mixed with sodium chloride. The solution was partitioned three times with methylene chloride; the methylene chloride fractions were combined and concentrated using vacuum evaporation. Trifluoroacetic anhydride and trifluoroethanol were added to the concentrated solution, the mixture was refluxed for 10 minutes, then vortexed with toluene. The solution was vortexed with sodium bicarbonate, then centrifuged. The toluene layer was dried over anhydrous sodium sulfate and analyzed using GC; the detection limit was 0.01 ppm. To analyze for hexamethyleneimine, aliquots of the water were saturated with sodium chloride, adjusted to a pH >13, and shaken with toluene for 10 minutes. The toluene extract was dried over sodium sulfoxide, treated with acetic anhydride to form the amide derivative of the imine, and analyzed using GC; the detection limit was 0.01 ppm. Recovery from fortified water samples ranged from 80 to 110% for molinate, 51 to 161% for molinate sulfoxide, 108 to 134% for hexamethyleneimine, and 79 to 122% for carboxymolinate.

Ancillary Study - Freezer Storage Stability

In a separate study (details not provided to review), subsamples of the soil collected from the control plots were fortified with "a known amount" of molinate or S-methyl molinate, and subsamples of the water were fortified with molinate, molinate sulfoxide, or hexamethyleneimine. The samples were stored frozen at -20 C in either the zero contamination tubes or in the glass containers for 6 months (molinate-treated soil was stored in the glass containers for up to 12 months). The soil and water samples were analyzed as previously described.

DATA SUMMARY:

Field Dissipation - Aquatic and Aquatic Impact

8-E Formulation: Molinate (8 lb/gal EC), applied twice at 5 lb ai/A/application at a 7-day interval (10 lb ai/A total), dissipated from an irrigated rice plot with calculated half-lives of 25 days in the clay soil and 18 days in the irrigation water. However, these half-lives were questionable due to the low material balance. In the surface 3.5 inches of soil, molinate was 0.11 and 0.32 ppm

immediately following the first and second applications, increased to 0.52 ppm at 3 days, was 0.28 ppm at 15 days and 0.17 ppm at 29 days, and was 0.17-0.39 ppm between 89 and 279 days with no discernable pattern (Table 1). Deeper soil layers were sampled only after the plot was drained at 81 days following the second application; in these deeper samples, molinate was ≤0.01 ppm at all intervals. Neither molinate sulfoxide nor S-methyl molinate were detected (detection limit 0.05 ppm) in the soil at any sampling interval (Tables 2 and 3). In the untreated control, molinate was <0.010-0.028 ppm.

In the irrigation water, molinate was 0.11 and 0.454 ppm immediately following the first and second applications, respectively; and was 0.581 ppm at 1 day after the second application, 0.198 ppm at 3 days, and ≤0.012 ppm at 15 through 78 days (Table 4). In the irrigation water,

carboxymolinate was ≤0.029 ppm at 2 days after the first application, and

molinate sulfoxide was ≤0.053 ppm at 3 days after the second application (Table 4).

Hexamethyleneimine was ≤0.010 ppm (detection limit) at all sampling intervals.

During the study, air temperatures ranged from 16 to 110 F, soil temperatures (2-inch depth) ranged from 26 to 86 F, and rainfall totaled 20.38 inches. The slope of the field was 0-2%. The depth to the water table was estimated to be 45-50 feet; there was no subsurface drainage.

15-G Formulation: Molinate (15% G), applied twice at 5 lb ai/A/application at a 7-day interval (10 lb ai/A total), dissipated from irrigated rice plots with calculated half-lives of 44 days in the clay soil and 5 days in the irrigation water. In the surface 3.5 inches of soil, molinate was 0.72 and 1.34 ppm immediately following the first and second applications, was 0.66 ppm at 29 days, and was 0.14-0.24 ppm between 96 and 279 days with no discernable pattern (Table 5). Deeper soil layers were sampled only after the plot was drained at 81 days following the second application; in these deeper samples, molinate was a maximum 0.079 ppm (108 days) in the 3.5- to 7-inch depth; a maximum 0.015 ppm (96 days) in the 7- to 10.5-inch depth; and ≤0.011 ppm in the 10.5- to 15.5-, 15.5- to 27.5-, and 27.5- to 39.5-inch depths. Neither molinate sulfoxide nor S-methyl molinate was detected (detection limit 0.05 ppm) in the soil at any sampling interval (Tables 6 and 7). In the untreated control, molinate was measured at <0.010-0.028 ppm.

In the irrigation water, molinate was 0.56 and 0.85 ppm immediately following the first and second applications, and was 0.69 ppm at 1 day after the second application, 0.19 ppm at 3 days, and ≤0.012 ppm at 29 through 78 days (Table 8). In the irrigation water,

carboxymolinate was ≤0.104 ppm (maximum 2 days after the first application) and

molinate sulfoxide was ≤0.19 ppm (maximum 1 day after the second application);

hexamethyleneimine was ≤0.011 ppm at all sampling intervals (Table 8).

During the study, air temperatures ranged from 16 to 110 F, soil temperatures (2-inch depth) ranged from 26 to 86 F, and rainfall totaled 20.38 inches. The slope of the field was 0-2%. The depth to the water table was estimated to be 45-50 feet; there was no subsurface drainage.

Ancillary Study - Freezer Storage Stability

Molinate was stable in soil and water stored frozen in glass containers for 12 and 6 months, respectively (Table 9). Molinate was not stable in soil and was variable in water stored frozen in zero-contamination tubes for 6 months. The concentration of molinate in the soil stored in the tubes decreased from 99 to 70% of the applied during the 6-month storage (Table 9); the concentration of molinate in the water ranged from 56 to 92% during the same period.

S-methyl molinate was stable in soil stored frozen in glass containers for 6 months (Table 9). S-methyl molinate was variable in soil stored frozen in zero-contamination tubes for 6 months, ranging from 68 to 100% of the applied with no discernable pattern.

Molinate sulfoxide was variable in water stored frozen in glass containers for 6 months, ranging from 71 to 110% of the applied (Table 9). Molinate sulfoxide was stable in water stored frozen in zero contamination tubes for 6 months.

Hexamethyleneimine was variable in water stored frozen in glass containers for 6 months, ranging from 69 to 95% of the applied (Table 9). Hexamethyleneimine was variable in water stored frozen in zero contamination tubes for 6 months, ranging from 67 to 85% of the applied.

COMMENTS:

1. Freezer storage stability data provided with the experiments was inadequate. The data were erratic, the majority of the study was terminated after 6 months (in the actual study, samples were stored for up to 1 year), and the stabilities of two degradates (molinate sulfoxide in soil and carboxymolinate in water) during storage were not addressed.

2. The soil was not sampled deeper than 3.5 inches until after the plots were drained. The study author stated that deep samples were not collected so as to avoid contamination of the lower layers and out of fear of "puncturing the clay that held the flood".

3. Although the two field plots were ostensibly treated at the same application rate, immediately after treatment the field treated with the 8-E formulation contained less than 25% of the molinate contained in the plot treated with the 15-G formulation.

4. The study author stated that the maximum application rate for molinate is 9 lbs a.i./A in two applications, each not to exceed 5 lbs a.i./A per application.

5. No pesticides were applied to these plots for 2 years prior to this study, molinate 10-G (4 lb a.i./A) had been applied in 1984 and 1985.