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DATA EVALUATION RECORD

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Merricks, D.L. 1989b. Metolachlor field dissipation study in California-Site C. Agrisearch Project No. 1265-C. Unpublished study performed by Agrisearch Incorporated, Frederick, MD, and submitted by Ciba-Geigy Corporation, Greensboro, NC.

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is considered supplemental at present.

2. This study will be reevaluated upon receipt of an explanation of the following:

The results from the laboratory fortified control samples, fortified at 0.05 to 5.0 ppm (all degradates) or to 10.0 ppm (metolachlor), carried through the procedure with the test samples indicate a wide variation in the recovery efficiencies. These recovery efficiencies ranged from 49 to 175% of the applied for metolachlor, 47 to 153% for CGA-51202, 44 to 155% for CGA-40172, 62 to 223% for CGA-40919, and 43 to 150% for CGA-50720 (Table 7).

The degradates CGA-40172 and CGA-40919 were included in this field dissipation study. In the aerobic and anaerobic soil metabolism study (MRID # 41309801-B), under aerobic conditions these two degradates were only detected but were not quantifiable. However, other degradates (CGA-41638 was 2.06% of applied at 90 days, CGA-37735 was 1.27% at 30 days, and CGA-13656 was 1.02% immediately posttreatment) were not also included or used in place of degradates that occurred at such a minimal level that they could only be detected but not quantitated (See Comment # 3).

3. Metolachlor dissipated with a registrant-calculated half-life of 292 days from the upper 6 inches of a bareground field plot of loamy sand that was treated with metolachlor (25% G) at 6 lb ai/A. In an adjacent plot that was treated with metolachlor at 4.0 lb ai/A and then immediately planted to corn, metolachlor dissipated with a registrant calculated half-life of 193 days from the 0-to 6-inch soil layer.

METHODOLOGY:

Metolachlor (Dual 25G, 25% G, Ciba-Geigy) was surface-applied by hand, using a broadcast spreader, at 4 and 6 lb ai/A to two field plots (50 x 50 feet) of loamy sand soil (0- to 6-inch layer; 78.0% sand, 15.6% silt, 6.4% clay, 0.8% organic matter, pH 6.8, CEC 4.9 meq/100 g) located in Kerman, California, on June 18, 1987. The test plots were located at the corner of a larger field; untreated bareground and corn plots (sizes unspecified) located 150 feet south of the test plots were maintained as controls (Figure 3). Immediately following treatment, the test substance was incorporated by disking to a 6-inch depth. The plot treated at 4 lb ai/A was planted to corn immediately posttreatment; the plot treated at 6 lb ai/A were left bare. Four cores per subplot from three randomly-selected subplots were taken prior to treatment and at each sampling interval between 0 and 505 days posttreatment. Samples from the 0- to 6-inch soil layer were taken with a soil corer (1-inch diameter); for depths below 6 inches in each subplot, an Arts Machine Shop bucket auger was used to obtain two 12- x 12- x 6-inch soil samples from which two 1- x 6-inch cores were taken (Figure 7). Cores for each subplot were composited in the field, and the samples were frozen with dry ice, and stored frozen for up to 767 days prior to extraction (Appendix D).

Frozen soil samples were homogenized in the bag, and a subsample (50 g) was refluxed with methanol:water (1:1) for 1 hour. Water: saturated sodium chloride solution (100:10) was added to an aliquot (60 mL) of the extract and the pH was adjusted to 1-1.5 with 1 N sulfuric acid; the solution was then partitioned three times with hexane:ethyl acetate (1:1, v:v). The organic phases were combined and dried with anhydrous sodium sulfate; the solution was then methylated with diazomethane. After 30 minutes, the solution was evaporated to dryness, redissolved in hexane, and analyzed for metolachlor and its degradates CGA-51202, CGA-40172, CGA-40919, and CGA-50720 by GC using an OV-17 capillary column and a flame-thermionic detector. The detection limits were 0.05 ppm for metolachlor, CGA-51202, and CGA-40172; 0.06 ppm for CGA-40919; and 0.07 ppm for CGA-50720. Recovery efficiencies from soil samples fortified at 0.05 to 5.0 ppm (all degradates) or to 10.0 ppm (metolachlor) ranged from 49 to 175% of the applied for metolachlor, 47 to 153% for CGA-51202, 44 to 155% for CGA-40172, 62 to 223% for CGA-40919, and 43 to 150% for CGA-50720 (Table 7). The concentrations of metolachlor and its degradates detected in the field soil samples were corrected for recoveries that were <100%.

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Selected soil samples were also analyzed for metolachlor and its degradates by GC/MS using single ion monitoring; the detection limit was 0.1 ng/uL.

DATA SUMMARY:

Metolachlor dissipated with a registrant-calculated half-life of 292 days (R^2 = 0.397) from the upper 6 inches of a bareground field plot (50 x 50 feet) of loamy sand soil in Kerman, California, that was treated with metolachlor (25% G) at 6 lb ai/A on June 18, 1987. In the 0-to 6-inch soil depth, average metolachlor concentrations ranged from 0.42 to 6.18 ppm between 0 and 361 days posttreatment (maximum 29.49 ppm at 28 days) and was 0.39 ppm at 505 days (final sampling interval) (Table 12).

In an adjacent plot that was treated with metolachlor at 4.0 lb ai/A and then immediately planted to corn, metolachlor dissipated with a registrant-calculated half-life of 193 days (R^2 = 0.553) from the 0- to 6-inch soil layer. In the 0- to 6-inch soil depth, average metolachlor concentrations ranged from 0.44 to 4.81 ppm between 0 and 361 days posttreatment (maximum 14.03 ppm at 5 days) and was 0.11 ppm at 505 days (Table 11).

Concentrations of metolachlor degradates detected in the soil were similar for the bareground and corn plots. In the 0- to 6-inch soil layer, maximum concentrations of the degradates occurred at 83 days posttreatment;

CGA-51202,

CGA-40172, and

CGA-40919

were present at 1.10 ppm, 0.50 ppm, and 0.59 ppm, respectively (Tables 11 and 12).

Downward movement of metolachlor resulted in maximum concentrations of 1.51 ppm in the 6- to 12-inch depth, 0.20 ppm in the 12- to 18-inch depth, and $\leq$0.07 ppm below 18 inches (up to 36 inches). CGA-51202 was detected at maximums of 1.18 ppm in the 6-to 12-inch depth, 0.37 ppm in the 12- to 18-inch depth, 0.11 ppm in the 18- to 24- and 24- to 30-inch depths, and was not detected (<0.05 ppm) in the 30- to 36-inch depth. CGA-40172 ranged from <0.05 to 0.30 ppm from 6 to 30 inches (6-inch increments) and was not detected (<0.05 ppm) in the 30- to 36-inch soil layer. CGA-40919 was not detected (<0.06 ppm) at any depth below 6 inches (up to 36 inches). CGA-50720 was not detected (<0.07 ppm) in any soil sample at any interval.

During the study, rainfall plus irrigation totaled 16.97 inches and air temperatures ranged from 24 to 109^0 F.

COMMENTS:

1. It appears that the analytical method was unreliable, especially when approaching the limit of detection; recovery from fortified samples was unusually low and variable. Recovery efficiencies from spiked samples for metolachlor at 0.05 ppm ranged from 81 to 162% of the applied and at 0.1-10.0 ppm ranged from 49 to 175%; for CGA-51202 at 0.05 ppm, recovery efficiencies ranged from 58 to 153% and at 0.1-5.0

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ppm ranged from 47 to 145%; for CGA-40172 at 0.05 ppm, recovery efficiencies ranged from 50 to 155% and at 0.1-5.0 ppm ranged from 44 to 154%; for CGA-40919 at 0.05 ppm, recovery efficiencies ranged from 70 to 180% and at 0.1-5.0 ppm ranged from 62 to 223%; for CGA-50720 at 0.05 ppm, recovery efficiencies ranged from 60 to 150% and at 0.1-5.0 ppm ranged from 43 to 144% (Table 7).

2. The data were extremely variable making it difficult to accurately assess the dissipation of metolachlor and its degradates in the soil. In addition to the variability of average concentrations of metolachlor in the soil between sampling intervals, metolachlor residues were also highly variable from sample to sample at the same interval. For example, in samples from the 0- to 6-inch soil layer taken at day 0, metolachlor ranged from <0.05 to 10.86 ppm in the crop plot and <0.05 to 8.83 ppm in the bareground plot (Tables 11 and 12). The variability in the field data may have been due to the inability of the method to accurately determine metolachlor residues.

3. In the aerobic and anaerobic metabolism study (MRID No. 41309801-B) the major degradates of metolachlor under aerobic conditions were:
CGA-51202, reaching a maximum of 28.09% of the applied at 90 days posttreatment;
CGA-50720, at a maximum of 14.85% of applied at 272 days;
CGA-41638, at a maximum of 2.06% at 90 days;
CGA-37735, at a maximum of 1.27% at 30 days;
CGA-13656, at a maximum of 1.02% immediately posttreatment. Other degradates that were detected but not quantifiable were CGA-40172, CGA-41507, CGA-40919, and CGA-37913.

In the anaerobic metabolism portion of the same study the major degradate in the soil and flood water was CGA-51202 at a maximum of 23.33% of the applied at 29 days after anaerobic conditions were established. Other degradates isolated from the soil and water were:
CGA-41638, at a maximum of 8.30% of the applied at 60 days;
CGA-50720, at a maximum of 7.34% at 60 days;
CGA-13656, at a maximum of 1.46% at 29 days; and
CGA-37735, at a maximum of 1.25% at 29 days.

However, in this field dissipation study metolachlor and its major degradates (CGA-51202 and CGA-50720) were analyzed for as well as the degradates CGA-40172 and CGA-40919, which were only detectable but not quantifiable in the above referenced aerobic metabolism study. No explanation was provided by the registrant as to why the other degradates listed above that were isolated in the aerobic metabolism study and occurred in much greater concentrations were not also included as standards to determine their environmental fate in the field dissipation study.

4. Field soil samples were stored frozen for up to 767 days prior to extraction; however, the stability of metolachlor and its degradates in the soil samples could not be confirmed because the available storage stability data were too variable. In a storage stability experiment conducted with soil taken from the control plot at the test site, soil samples (6-inch increments from depths of 6 inches to 60 inches) were fortified with metolachlor and the degradates CGA-51202, CGA-40172, and CGA-40919 at 1.0 and 5.0 ppm, then stored frozen (temperature not specified) for up to 901 days. After 70 days of storage, recoveries ranged from 60.4 to 170.6% of the applied; after 538/539 days, recoveries ranged from 30.8 to 166.4%; and after 901 days, recoveries ranged from 44.9 to 149.7% (Table 8). The variability in the storage stability data may have been due to the

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inability of the method to accurately determine metolachlor residues.

In addition, the storage stability of the degradate CGA-50720 in soil samples fortified at 1.0 ppm was investigated at only one interval; after 127 days of storage, 60.8-80.4% of the applied was recovered. The 127-day sampling interval is inadequate since the analytical method was not modified to isolate CGA-50720 until the 361-day field soil samples were analyzed (see Comment 6).

5. Prior to analysis of the 361-day soil samples, the analytical method was modified to recover a fourth degradate (CGA-50720). The method description for the soil extraction was not included in the report proper, but was included in the Protocol (Appendix A). The method summarized in this report is the final modified method.

   In addition, although not specifically stated, it appears from the extraction dates (Table 7) that all relevant soil samples were reanalyzed using the modified method.

6. The 6- to 12-inch soil samples taken at 10 and 14 days posttreatment were not analyzed for the degradates CGA-40172 and CGA-40919, and no explanation was provided by the study author.

7. Soil samples were taken to a depth of 5 feet, but were only analyzed to a depth of 3 feet. The study author reported that samples taken below 3 feet were not analyzed because of the lack of metolachlor residues detected below 6 inches during the initial 14 days of the study. The data indicate that residues were not detected below 30 inches during the study.

8. Soil temperature data were not provided. Rainfall and air temperature data were collected at the test site from June 18, 1987 to July 24, 1988; thereafter, the meteorological data were obtained from a NOAA weather station at Fresno, California. The distance from the weather station to the test site was not reported. It is preferable that meteorological data be taken at the test site.

9. The depth to the water table was 70 feet; there was no subsurface drainage. The test plots were described as level. Other than dates of irrigation, field maintenance practices of the treated plots during the study were not reported.

10. Two soil samples from each sampling depth were spiked in the field at 1.0 ppm; samples were placed in glass jars sealed with Teflon-lined caps, frozen with dry ice, and stored frozen (temperature not specified) for 43 days before analysis. Recoveries ranged from 52.8 to 238.9% (Table 9).

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