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DATA EVALUATION RECORD

STUDY 21

CHEM 128974 Quinclorac §165-1

FORMULATION--1% GRANULAR-ACTIVE INGREDIENT

STUDY ID 41063566
Winkler, V., and M. Brown. 1987. Confined accumulation study of ^{14}C-BAS 514H residues in fall and spring rotational crops. Registration Document No. 87/5094. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC/Parsippany, NJ.

DIRECT REVIEW TIME = 38

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CONCLUSIONS:

165-1--Confined Accumulation - Rotational Crops

These studies can not be used towards the fulfillment of data requirements for the following reasons:

1. Application prior to flooding

   a. A significant amount of quinclorac may have leached from the root zone by the time the rotational crops were planted, thus precluding any significant uptake of quinclorac residues by the crops.

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b. Although the soil sample collected immediately after application of quinclorac seemed to confirm the intended application rate, the next sample, collected 28 days after application, indicated that the soil residues had decreased to 0.056 ppm. This suggests that a significant amount of quinclorac had dissipated from the soil by the time the rotational crops were planted.

c. The data were too variable. The study authors did not explain why, from day 28 to 187, the total concentration of quinclorac residues varied from 0.029 to 0.056 ppm, while on day 326 the concentration increased to 0.123 ppm and then decreased again on the remaining sampling days to 0.043 and 0.059 ppm.

2. Application while flooded

The stated application rate of 0.75 lb ai/A was not confirmed, and there was reason to believe that at least half of the initial quinclorac was lost when the flood water failed to remain on the plot during the first 20 days of the study. No soil and water samples were collected immediately posttreatment; the first soil sample was not collected until 103 days posttreatment. Since the application rate for the soil that was treated while flooded was not confirmed, a new study must be conducted.

3. This study should be performed in a closed system that does not allow any of the pesticide residues to leave the system. This is needed because of the known leaching characteristics and persistence of the chemical. Data from an actual confined accumulation in rotational crop study with quinclorac will enable EFGWB to determine the nature and amount of pesticide residue uptake in rotational crops under a "worst case" scenario.

Other problems that were noted by the reviewer are listed under the section below identified as "REVIEWERS COMMENTS".

METHODOLOGY:

Field plots (4 x 8 feet) containing silty clay soil (9.6% sand, 40.4% silt, 50% clay, 2.2% organic matter, pH 6.5, CEC 33.18 meq/100 g) that were located in Greenville, MS, were flooded and seeded to rice at 26 seeds/foot row on May 1, 1984. The plots were allowed to dry, and one plot was treated with [2,3,4-^{14}C]quinclorac (radiochemical purity 95.7%, specific activity 9.74 mCi/mM, BASF) at 0.75 lb ai/A

on June 5. At 7 days posttreatment, all plots were flooded. On June 19, a second plot was treated with quinclorac (1% G, radiochemical purity 95.7%, specific activity 5.028 mCi/mMol, made specifically for this experiment by study authors) at 0.75 lb ai/A. It was reported that the plot that had been treated while flooded did not maintain a permanent flood, and that the water level in this plot did not stabilize until July 10 (21 days posttreatment). Following harvest of the rice seed on September 24 and rice straw on October 1, the field plots were plowed (8-inch depth), raked smooth, and fertilized.

On October 27, 1984 ("fall rotation", 129-147 days posttreatment), subplots of each treated plot were planted with mustard, turnips, and wheat. Immature samples of each crop were harvested on December 6 (169-187 days posttreatment). Also, mustard (tops) was harvested on April 3, 1986 (288-302 days posttreatment); turnips (tops and roots) were harvested on April 3 and April 17 (288-316 days posttreatment); and wheat (tops, and grain, straw, and stems) was harvested on April 3 and May 20 (288-302 and 335-349 days posttreatment, respectively). On April 2, 1985 ("annual rotation", 286-303 days posttreatment), subplots of each treated plot were planted to mustard, turnips, soybeans, and sorghum. Immature samples of sorghum and mustard greens were harvested on April 25 (309-326 days posttreatment), and of turnips and soybeans on May 22 (336-353 days posttreatment). Also, mustard (tops) was harvested on May 13 (327-344 days posttreatment); turnips (tops and roots) on June 6 and June 23 (351-382 days posttreatment); soybeans (plant, and seed, hulls, and stalks) on June 6 and June 23 (351-382 days posttreatment); and sorghum (plant, and seeds, heads, and stalks) on June 6 and September 20 (351-365 and 457-471 days posttreatment, respectively). All crop samples were frozen immediately after collection and stored frozen until analysis.

Soil samples (0- to 12-inch depth, 2.5-cm width) were collected at 0, 28, 88, 139, 187, 326, 385, and 474 days posttreatment from the field plot that had been treated with [^{14}C]quinclorac prior to flooding. In addition, soil samples were collected from all plots at the time of crop planting and harvest. The holes remaining in the fields after soil sampling were filled with wooden dowels. All soil samples were frozen immediately after collection and stored frozen until analysis.

Plant samples containing sufficient radioactivity were analyzed according to Figures 6 and 7. The samples were ground with dry ice, and subsamples were analyzed for total radioactivity by LSC following combustion. Mustard tops and soybean hay were homogenized twice with acetone:water (7:3,

v:v); the homogenates were filtered after each extraction. The extracts were combined, concentrated, and acidified. The extracted plant tissues were refluxed with 1 N HCl and filtered. The acidified acetone:water extract and the acid refluxes were combined and partitioned three times with ethyl ether. Aliquots of the resulting aqueous and ether phases were analyzed using LSC. The ether fraction was dried, and the resulting residues were methylated with diazomethane and analyzed for specific compounds by TLC on silica gel plates developed in ethyl acetate:hexane (80:20). The extracted plant solids were dried and analyzed for total radioactivity by LSC following combustion.
Wheat and soybean seed samples were homogenized twice with hexane; the hexane filtrates were combined and analyzed using LSC. The defatted seed samples were then refluxed with 1 N HCl, and the acidic filtrate and residual material were analyzed as previously described.

Soybean seeds and hay were fractionated according to Figure 7 into proteins, carbohydrates, polysaccharides, lignins, and hemicellulose to determine the distribution of radioactivity within the plant tissues. The soybean seeds were homogenized twice with hexane. The hexane was discarded, and the defatted seeds were homogenized with 0.1% N sodium sulfate. The supernatant was adjusted to pH 4.6; the resulting precipitate was characterized as protein and radioactivity remaining in solution was characterized as carbohydrate. The mixture was centrifuged, and the liquid and solid fractions were analyzed using LSC and LSC following combustion, respectively. The soybean hay was refluxed twice in 1% sodium chloride; the extract was characterized as soluble polysaccharides. The extracted plant material was then refluxed twice with a 0.5% solution of the disodium salt of EDTA; the extract was characterized as soluble pectic polysaccharides. The extracted plant material was extracted twice with 5% sodium hydroxide at room temperature, twice with 1% sodium chloride at 80 °C, and twice with 24% sodium hydroxide at room temperature. The 5% sodium hydroxide extract was characterized as soluble hemicellulose I, the 1% sodium chloride extract as soluble lignin, and the 24% sodium hydroxide extract as soluble hemicellulose II.

The soil samples were sectioned into 4-inch segments, air-dried for two days, ground, and sieved. Subsamples of each segment were analyzed for total radioactivity using LSC following combustion. The surface segments were also analyzed for free, complexed (ionic and covalent bound), and unextractable [^{14}C]residues (Figure 5). The soils were extracted with water by sonication, then centrifuged. The soil pellet was resuspended in 0.1 N NaOH, refluxed for 1 hour, and centrifuged. The soil pellet was dried and

analyzed for unextractable radioactivity by LSC following combustion. The aqueous and alkali extracts were combined, acidified with HCl, and partitioned three times with methylene chloride. The water fraction was discarded; the methylene chloride extracts were combined, concentrated, and analyzed for specific compounds by TLC on silica gel plates developed in ethyl acetate:methanol:acetic acid (80:15:5). The extracts were cochromatographed with [^{14}C]quinclorac reference standards. Radioactive zones on the TLC plates were located using autoradiography and quantified using linear scanning.

DATA SUMMARY:

[^{14}C]Quinclorac residues were ≤0.025 ppm in mature wheat, turnips, and mustard planted 147 days posttreatment in silty clay loam soil that was treated with 2,3,4-[^{14}C]quinclorac (active ingredient, radiochemical purity 95.7%) at a nominal rate of 0.75 lb ai/A and maintained under permanent flood conditions between 7 and 111 days posttreatment (Table VI). [^{14}C]Quinclorac residues were ≤0.025 ppm in mature sorghum, mustard, turnips, and soybeans planted 303 days post-treatment in similar plots (Table VII). In immature plants, [^{14}C]residues were 0.012-0.028 ppm in crops planted at 147 days and <0.002-0.042 ppm in crops planted at 303 days (Tables VI and VII). Fractionation of [^{14}C]residues in soybean seeds characterized 35% of the recovered as soluble carbohydrates, 34% as protein, and 37% as insoluble debris (Table IX). Fractionation of [^{14}C]residues in soybean hay characterized 11.7% as water soluble polysaccharides, 21.8% as pectic polysaccharides, 36.8% as hemicellulose I, 11.8% as lignin, and 10.7% as hemicellulose II (Table X). In the surface 4 inches of the soil that was treated prior to flooding, total [^{14}C]residues were 0.42 ppm immediately posttreatment and ranged from 0.029 to 0.123 ppm with no discernable pattern between 28 and 474 days posttreatment (Table II). During the study, "free" (water-extractable) residues in the surface soil decreased from 75% of the recovered immediately posttreatment to 5-20% during the remainder of the study; ionic plus covalent (alkali-extractable) residues fluctuated with no definitive pattern (Table II, Figure 9). The extractable soil residues were "mainly" quinclorac, with "trace" amounts of

3-chloro-8-quinolinecarboxylic acid (BH 514-1)

(individual compounds in the soil were not quantified). Total quinclorac [^{14}C]residues in the 4- to 8- and 8- to 12-inch soil depths ranged from 0.021 to 0.107 and <0.002 to 0.058 ppm, respectively, between 121 and 474 days posttreatment (Tables VI and VII).

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[^{14}C]Quinclorac residues were ≤0.016 ppm in mature mustard, turnips, and wheat planted 129 days posttreatment in silty clay loam soil that was treated with 2,3,4-[^{14}C]quinclorac (1% G, radiochemical purity 95.7%) at a nominal rate of 0.75 lb ai/A while flooded, and maintained under permanent flood conditions until 100 days posttreatment (Table IV). [^{14}C]Quinclorac residues were ≤0.028 ppm in mature sorghum, mustard, turnips, and soybeans planted 286 days post-treatment in similar plots (Table V). In immature plants, [^{14}C]residues were 0.002-0.029 ppm in crops planted at 129 days and 0.003-0.006 ppm in crops planted at 286 days (Tables IV and V). In the surface 4 inches of the soil that was treated while flooded, total [^{14}C]residues were 0.004 ppm at 103 days posttreatment (first sampling interval) and ranged from 0.008 to 0.036 ppm with no discernable pattern during the remainder of the study. Total [^{14}C]residues in the 4- to 8- and 8- to 12-inch soil depths ranged from 0.005 to 0.028 and <0.002 to 0.070 ppm, respectively.

REVIEWERS COMMENTS:

General

1. This study should be performed in a closed system that does not allow any of the pesticide residues to leave the system. This is needed because of the known leaching characteristic of the chemical. Data from a confined accumulation rotational crop study with quinclorac will enable EFGWB to determine the nature and amount of pesticide residue uptake in rotational crops. The confined study will present a "worst case" scenario and will result in data that can be used to establish crop rotations or to provide information for determining if tolerances are needed in rotational crops.

2. The studies were not replicated in regards to treatments, soil and water samples collected. Absence of replicates does not allow EFGWB to assess the experimental variation thay may occur in soil and analytical procedures.

   Replication means that each treatment is replicated 2 or 3-fold. In the future, EFGWB suggests that the registrant establish at least two replicated (EFGWB prefers a minimum of 3-fold replication) experimental units for each treatment. The results should be given for each individual sample within a replicate and not as a composite. This is good laboratory practice and good science and gives an idea of the range and variability of possible results.

3. The study author stated that rotation intervals shorter than 129 days were not studied because "emergency replanting is not applicable to rice agricultural practices".

4. A 300 lb ai/A application of 13-13-13 (N-P-K) fertilizer was incorporated into the test soil before both the planting of the target rice crop and the planting of the annual rotation crops. No chemicals were used to control weed and insect populations. The plots were surrounded by an aluminum frame to a 1-foot depth and an outer plastic frame to a 2-foot depth; the field did not contain a subsurface drainage system.

Application prior to flooding

1. A significant amount of quinclorac may have leached from the root zone by the time the rotational crops were planted, thus precluding any significant uptake of quinclorac residues by the crops.

   Although the soil sample collected immediately after application of quinclorac seemed to confirm the intended application rate, the next sample, collected 28 days after application, indicated that the soil residues had decreased to 0.056 ppm. This suggests that a significant amount of quinclorac had dissipated from the soil by the time the rotational crops were planted.

2. The data were too variable. The study authors did not explain why, from day 28 to 187, the total concentration of quinclorac residues varied from 0.029 to 0.056 ppm, while on day 326 the concentration increased to 0.123 ppm and then decreased again on the remaining sampling days to 0.043 and 0.059 ppm.

3. The initial concentration of [^{14}C]quinclorac in the 0- to 4-inch soil depth, 0.424 ppm, was equivalent to approximately 0.56 lb ai/A. The target application was 0.75 lb ai/A; therefore, the actual application was approximately 24% lower than expected.

4. The methodology section stated that the soil extracts were separated by TLC using ethyl acetate:methanol:acetic acid (80:15:5); however, the flow diagram for this extraction (Figure 5) states that the solvent system was methanol:ethyl acetate:acetic acid (80:15:5).

Application while flooded

1. The study authors failed to confirm the initial application of quinclorac.

2. Furthermore, the study authors believed that at least half of the initial quinclorac was lost when the flood water failed to remain on the plot during the first 20 days of the study. The soil in the treated plot was not sampled until

103 days posttreatment, at which time the concentration of [^{14}C]quinclorac residues in the surface 4 inches of soil was 0.004 ppm. The flood water was not sampled at any interval. This reviewer finds it hard to comprehend why the study was continued when half of the initial treatment was lost.

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