12-3-90

DATA EVALUATION RECORD

STUDY 11

CHEM 128974 Quinclorac §164-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41432101
Winkler, V. W. and M. Lewandowski. October 9, 1989. Confined field ^{14}C-Quinclorac (BAS-514 H) dissipation study. Registration Document No. 89/5200. Unpublished study performed by Agricultural Custom Research Experimental Services, Cedar Falls, IA, and Bowman Gray School of Medicine, Biochemistry Department, Winston-Salem, NC for BASF Corporation Chemicals Division, Research Triangle Park, NC/Parsippany, NJ.

DIRECT REVIEW TIME = 8

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DATE: DEC - 3 1990

CONCLUSIONS:

Field Dissipation - Terrestrial Crops

1. This study cannot be used to fulfill data requirements.

2. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of quinclorac and its degradates.

3. This study is unacceptable for the following reasons:

a. The application rate of parent quinclorac was not verified from the GC/MS analysis of the soil samples collected immediately after application. At 0 DAT, only 42 and 71% of the total radioactive residues were identified as parent quinclorac at both sites. Without verification of the application rates, no meaningful conclusions can be reached regarding the dissipation of quinclorac from these soils.

b. The material balance for total radioactive residues which ranged from 26 to 164% were too variable.

c. Recovery efficiencies from fortified samples were not provided.

d. The study as submitted does not follow the requirements of Subdivision N Guidelines Section 164-1 in relation to a field dissipation study. The test substance should be a typical end-use product and should be applied under actual use conditions. Also, there is no requirement to sample and/or analyze the crop that is grown on the test plots.

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

4. Since the application rate of parent quinclorac was not confirmed, the problems with this study cannot be resolved with the submission of additional data. A new study must be conducted.

METHODOLOGY:

Aliquots of radiolabeled quinclorac (^{14}C-3,7-dichloro-8-quinolinecarboxylic acid, specific activity = 9.78 Ci/mol, radiopurity = >99%) was mixed with unlabelled stock solutions diluted to 3 liters with water and applied to the test plots so that the resultant application rates were 0.5 and 1.0 lb a.i./A. The studies were conducted in Holly Springs, NC and Waterloo, IA during the corn growing season of 1988. Soil characteristics are presented in Table III.

Prior to applying the treatments, the plots were tilled to a depth of about 4 to 6 inches and raked smooth and Pioneer 3965 corn was planted in two rows 30-36 inches wide in each plot. Preemergence applications of quinclorac were applied to the North Carolina plots on June 29, 1988 and on July 11, 1988 to the plots

in Iowa. The plots were irrigated bimonthly to make up 125% of the normal rainfall for each area.

Sampling:

Soil Samples: Soil samples were collected immediately after treatment and at approximately 15, 30, 60, 90, 120 and 240 days after treatment (DAT). The soil samples in Iowa were collected using an 1 inch diameter hydraulic probe fitted with a plastic tube. Either a 1 inch diameter probe fitted with a plastic tube manually hammered into the soil, or a 3 inch diameter auger fitted with a 12 inch plastic liner was used in North Carolina. Because of the difficulty in preventing contamination of the lower core samples using the auger technique, the upper inch of each lower depth was removed and analyzed separately. Prior to storage, soil samples were divided into 3- or 6-inch sections, air dried and ground to a fine powder using a Waring blender and stored in plastic bags at <-5 °C prior to analysis.

Plant Samples: Plant samples were collected at various growth stages, cut into 1 to 3 cm sections and then ground to a fine powder in the presence of dry ice using a Waring blender and stored in plastic bags at <-5 °C prior to analysis.

Analysis of Plant and Soil Samples:

In order to determine total radioactivity, soil (300-400 mg) and plant (200-300 mg) samples were combusted using Harvey Biological Oxidizers. The radioactivity was trapped in Harvey scintillation cocktail and analyzed using a Beckman 5800 Liquid Scintillation Spectrometer.

Quinclorac residues of the 60 and 90 day soil samples from the 1.0 lb a.i./A treatment were fractionated into free, ionically and covalently bound components by sequential extraction with, respectively, water, dilute alkali or refluxing alkali with heat as shown in Figure 4. Aliquots were taken for LSC quantitation and TLC analysis.

Soil samples at the 0-6 inch depth taken at various times from the 0.5 lb a.i./A treatment were also assayed for parent chemical and metabolites by GC/MS by the procedure as shown in Figure 5.

DATA SUMMARY:

Radioactive Mobility

North Carolina Sandy Loam

Total radioactive residues (TRR) expressed as ppm are shown in Table IX. The concentration of TRR immediately after treatment

in the 0-3 inch soil sample were 0.61 and 1.36 ppm, respectively, for the 0.5 and 1.0 lb a.i./A treatment. The authors stated that it could be seen from the data in Table IX that residues penetrated to 12 inches by the DAT 15 with an average material balance of 101%. The authors noted that residues generally remained confined in the 0-12 inch soil sampling zones for the length of the study.

There was approximately a 40% mass balance loss between 16 and 205 DAT. The authors attributed this to mineralization to $^{14}CO_2$, rather than leaching since there was not indication of penetration beyond 12 inches. The authors noted that a laboratory study (Study 6) showing about 5% metabolism of quinclorac to CO_2 in 30 days supports this contention. Extrapolating the time to 8 months under the conditions of the test results in approximately 30-40% conversion to $^{14}CO_2$. The authors also stated that plant uptake also accounted for the dissipation of TRR.

Iowa Loam

Total radioactive residues determined in the Iowa soil plots are shown in Table X. The concentration of TRR immediately after treatment in the 0-3 inch soil sample were 0.52 and 0.99 ppm, respectively, for the 0.5 and 1.0 lb a.i./A treatment. The authors stated that it could be deduced from the data that there was no leaching of residues below 9 inches even 245 DAT. In contrast to the North Carolina plots, the mass balance throughout the length of the study averaged 95%.

Residue Characterization

Fractionation

For North Carolina, 97% of the TRR was extracted as free residues from the sample at 0 DAT (Table XI). The 61 DAT free residues decreased to 5% TRR with ionically and covalently bound residue values at 36 and 28%, respectively. The 113 DAT residues were similar to the 61 DAT except the nonextractable residues increased from 9 to 17% TRR, with a corresponding decrease in the covalently bound residues from 28 to 13%.

The separation of residues for the Iowa soil (Table XI) resembled that of the North Carolina soil. The primary difference between the two soils was that the Iowa soil had a higher percentage of free residues (19%) than the North Carolina soil (4%). EFGWB notes that the authors did not report the fractionation for the Iowa soil samples at 0 DAT.

The material balances for these fractionations ranged from 75 to 109% (average = 85.8).

TLC and GC/MS

The nature of the residues as determine by TLC and GC/MS is such that quinclorac (Table XII) is the only significant component for measuring the residue dissipation to 0.05 ppm levels. There were trace amounts of two metabolites, BH 514-1 (the des-7 chloro analog of parent BAS 514) and BH514-X (the structure was not fully elucidated due to insufficient material). There was no accumulation of either metabolite with maximum levels in the 0.05 ppm range for the 0-3 inch soil sample. Since there was no apparent build up of metabolite residues it is likely they are intermediates for the mineralization of quinclorac to CO_2, non-distinctive components and/or humic material. These metabolites, including parent, can be immobilized as ionically and covalently bound residues. A flow diagram for the proposed metabolic pathway is given in Figure 12.

Dissipation

Dissipation profiles of quinclorac for the two sites are shown in Figure A. The study authors reported that the dissipation profiles fit first order kinetics with correlation coefficients of -0.79 and -0.95 and half-lives of 50 and 42 days, respectively, for the North Carolina and Iowa sites.

Crop Residues

The TRR residues were high for the North Carolina forage, fodder and grain roots, ranging from 0.236 to 0.297 ppm for the 0.5 lb a.i./A treatment (Table XIV). The study authors concluded from this that plant uptake was a route of residue dissipation (EFGWB notes that the authors did not identify the nature of the residues, only the TRR), and was a contributor to the the lack of material balance in this treatment in North Carolina.

The TRR in crops for the Iowa soil were low in all plant parts analyzed, ranging from 0.007 to 0.51 ppm. The study authors concluded that the difference in the residue profiles is explained by stratification of residues in the root zones. The residues in the North Carolina soil were distributed in the upper 9 inches of soil and available for plant uptake. Conversely, the residues in the Iowa soil were confined to the upper 3 inches of soil and were not available for plant uptake except in the early stages of growth.

REVIEWERS COMMENTS:

1. The application rate was not supported by the data (Table XIII). Although at 0 DAT the recovery of the TRR at both locations and application rates was 100%, there was no explanation why on 0 DAT, only 42 and 71% of the TRR, respectively, at North Carolina and Iowa, was determined to

be parent quinclorac. Also, the authors did not identify the 58 and 29% of the TRR that was not parent quinclorac. Without verification of the application rates, no meaningful conclusions can be reached regarding the dissipation of quinclorac from these soils.

2. The study authors did not attempt to explain the reason for the material balance differences between soil samples from North Carolina (Average 64%, range 26-108%, N = 20) and Iowa (Average 95%, range 35-164%, N = 17). In these studies, the 40% mass balance loss in North Carolina was thought to result from mineralization to CO_2. They stated that "laboratory studies (Study 6) showing approximately 5% metabolized to CO_2 in 30 days gives strong support to this contention." The authors did not explain why there was no metabolism to CO_2 in the Iowa soil. It is very difficult for this reviewer to believe that there is such a discrepancy in metabolism between the two soils. This difference would also imply a difference in the microorganism composition of the two soils that is responsible, in part for metabolism of pesticides.

   Furthermore, EFGWB concludes that Study 6 is not scientifically valid because experimental variation could not be established since the study was not replicated. Also, samples were not collected for a sufficient length of time to establish a rate of CO_2 production for longer than 28 days.

3. The CO_2 data (From Study 6), based on 28 days of incubation and estimated to 8 months for this study, are of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

4. The study authors did not attempt to explain the wide variation in mass balance for TRR in the soil samples. For example, no explanation was given why from sampling day 0 (samples taken immediately after application) to 113 DAT in North Carolina, the mass balance for TRR decreased from 100 to 26% and them increased to 69% on later sampling days. Similarly, no explanation was given for the disparate behavior of TRR in soil samples collected from Iowa.

5. Without replication, variations of the magnitude listed above cannot be explained or tolerated. The experiments should have been replicated in regards to treatments and soil 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 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. Adequate replication plus a sufficient number of soil samples collected per plot, as described below, should adequately describe the variation of pesticide concentration in the study.

6. There was no description of how many soil samples were taken per plot. For a field plot as typically used in field dissipation studies, EFGWB prefers that 15 soil cores per sampling interval are collected in order to adequately characterize the pesticide residues in the field. These 15 cores may be composited to a smaller subset of samples for analysis. For example, 3 composite samples consisting of 5 cores each is acceptable. EFGWB would like to emphasize that all cores should <u>not</u> be composited to 1 sample for analysis. More than 1 sample is necessary for analysis so that variation in the residue concentration in the field may be determined.

7. No soil samples were obtained from the application sites immediately prior to the application to check for any background residues of pesticide in the soil.

8. Recovery efficiencies from fortified samples were not provided. This information is needed to ensure that the extraction techniques used were removing all of the pesticide of concern.