

Shaughnessy No: 128974

Date Out of EAB: MAR 18 1988

To: Robert Taylor  
Product Manager 25  
Registration Division (TS-767)

From: Paul Mastradone, Ph.D. *PM*  
Chief (acting), Section 1  
Exposure Assessment Branch/HED (TS-769C)

Thru: Paul F. Schuda, Chief  
Exposure Assessment Branch/HED (TS-769C) *Paul F. Schuda*

Attached, please find the EAB review of:

Reg./File # : 7969-EUP-EL  
Chemical Name : Quinclorac  
Type Product : Herbicide  
Product Name : Facet  
Company Name : BASF Corporation  
Purpose : Experimental Use Permit  
MRID : 40320816-19

Date Received : 10/9/87 Action Code: 700

Date Completed:                      EAB #(s): 80030

Monitoring study requested:        Total Reviewing Time: 3 days

Monitoring study volunteered:       

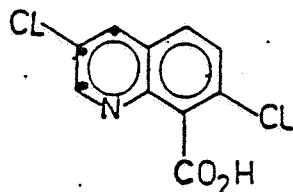
Deferrals to:            Ecological Effects Branch

           Residue Chemistry Branch

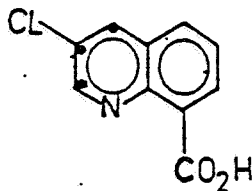
           Toxicology Branch

1. CHEMICAL: Quinclorac, BAS 514 H, Facet (BAS 514 16H), 3,7-dichloro-8-quinolinecarboxylic acid.

THIS EUP APPLICATION SPECIFIES A USE RATE OF 0.5 LB AI/A.



BAS 514 H (quinclorac)



BH 514-1 (degradate)

2. TEST MATERIAL: See individual studies.
3. STUDY /ACTION TYPE: Experimental Use Permit application.
4. STUDY IDENTIFICATION:
  - Eswein, R. P. 1987. Hydrolysis of BAS 514 H in pH 5, 7 and 9 Solutions at 25 C. Report No. 87/5038, BASF Corporation Chemicals Division. June 1987. 403208-16.
  - Clark, J.R. 1987. BAS 514 H - <sup>14</sup>C Laboratory Soil Metabolism Study: Aerobic Aquatic System. Report No. 87/5034, BASF Corporation Chemicals Division. January 1987. 403208-17.
  - Winkler V. 1987. Confined Accumulation Study of <sup>14</sup>C-BAS 514 H Residues in Fall and Spring Rotational Crops. Report No. 87/5037, BASF Corporation Chemicals Division. April 1987. 403208-18.
  - Forbis, A.B., L.T. Schoen and L. Stuermer. 1986. Uptake, Depuration and Bioconcentration of <sup>14</sup>C-BAS 514H by Channel Catfish (*Ictalurus punctatus*). Report No. 87/5002, BASF Corporation Chemicals Division. July 22, 1986. 403208-19.

5. REVIEWED BY:

Stephen Simko, Chemist  
Section 1  
EAB/HED/OPP

S Simko  
3.8.88

6. APPROVED BY:

Paul Mastradone, Ph.D.  
Chief (acting), Section 1  
EAB/HED/OPP

Paul J Mastradone

MAR 18 1988

7. CONCLUSIONS:

Quinclorac was found to be persistent in the environment. It was stable to hydrolysis and persistent in the aerobic aquatic metabolism study (the main metabolite was parent compound minus one chlorine atom). Residues accumulated in rotated crops planted one year after application. The bioconcentration factor in fish was less than 1. Details are as follows:

Quinclorac was found to be stable to hydrolysis at pH 5, 7 and 9.

After 360 days of incubation under aerobic aquatic conditions, the extracted residues were essentially undegraded parent compound in both CA and MS soil samples at the 0.5 ppm treatment rate. Unextractable residues accounted for up to 15%,  $^{14}\text{CO}_2$  accounted for up to 9%, and extractable residues up to 80% (about 15% of which was extracted by reflux). At the 5 ppm treatment rate (which was originally conducted for structure elucidation), no significant degradation was detected in the CA sample. After six months in the MS sample, the parent compound degraded almost exclusively to 3-chloro-8-quinolinecarboxylic acid (BH 514-1) and other minor products. The half-life of quinclorac was estimated at 4.7 months; the degradate BH 514-1 (parent compound minus one chlorine atom) had a estimated half-life of 7.4 months. The MS sample's bound residues at 6 months were 12%, 77% were extractable (20% of which was by reflux) and  $\text{CO}_2$  levels were not measured since this part of the study was for qualitative use only.

In the confined rotational crop study (120 and 360 day rotation intervals), quinclorac was applied at 0.75 lb ai/A. Plant residues were found to be undegraded parent compound with the exception of soybean seed and hay residues which were 75% non-extractable (incorporated into the plant). Mature plants contained up to 0.010 ppm for root and bottom

(turnip), 0.015 ppm for leafy vegetables (mustard), 0.025 ppm (winter wheat and soybeans) and 0.013 ppm (sorghum) for the small grain and stalk.

Fish accumulation was studied using channel catfish in a 1 ppm quinclorac flow-through system for 28 days. Residues were below detectable levels at all times except for days 3, 7 and 14 where residues were detected at  $\leq 0.86$  ppm. The level of detection was 0.61 - 0.62 ppm.

8. RECOMMENDATIONS: The studies submitted for this review are acceptable for this EUP. A leaching study was not submitted with this package. A leaching study is needed before EAB can fully evaluate this EUP request.
9. BACKGROUND: This is a crop destruct experimental use permit application for Facet herbicide 50W preemergence and postemergence use in rice. A maximum of 0.5 lb ai/A would be used on 200 acres for a total use of 100 lb ai of quinclorac. A total of 40 acres would be used in each of five states (MS, AR, LA, TX and CA).
10. DISCUSSION OF INDIVIDUAL TESTS AND STUDIES:
  - 10.1 Study Identification

Eswein, R. P. 1987. Hydrolysis of BAS 514 H in pH 5, 7 and 9 Solutions at 25 C. Report No. 87/5038, BASF Corporation Chemicals Division. June 1987. 403208-16.

#### Conclusions

This study demonstrates that quinclorac was found to be stable to hydrolysis at pH 5, 7 and 9.

#### Materials and Methods

Hydrolysis of quinclorac in buffered solutions was studied at pH 5, 7 and 9. Solutions were prepared using a mixture standard and radiolabeled quinclorac to give a final concentration of approximately 50 ppm. Reaction vessels (5 ml serum bottles) were heat sterilized and 5 ml aliquots of sample solution were filtered through 0.22  $\mu$ m filters directly into the serum bottles and the bottles were sealed. The samples were kept in a darkened chamber maintained at 25  $\pm$  1 C for up to 737 hours.

Solutions were analyzed by LSC using 10  $\mu$ L aliquots of solution mixed with 10  $\mu$ L of Aquasol-2 scintillation cocktail. Residues were identified by HPLC using UV and radioactivity monitoring detection systems and confirmed by

GC with a nitrogen detector. Samples for HPLC were extracted 3X with ethyl acetate after making the solutions acidic. Based on LSC, recoveries of product in the organic layer ranged from 98 to 111%. Samples were then concentrated, dissolved in 2 ml of methanol and 10 ml of diethylether and treated by bubbling with diazomethane, and allowed to stand loosely capped for one hour. The samples were concentrated and redissolved in acetone.

#### Reported Results

Quinclorac did not degrade under the test conditions. See tables.

### 10.2 Study Identification

Clark, J.R. 1987. BAS 514 H -  $^{14}\text{C}$  Laboratory Soil Metabolism Study: Aerobic Aquatic System. Report No. 87/5034, BASF Corporation Chemicals Division. January 1987. 403208-17.

#### Conclusions

After 360 days of incubation under aerobic aquatic conditions, the extracted residues were essentially undegraded parent compound in both CA and MS soil samples at the 0.5 ppm treatment rate. Unextractable residues accounted for up to 15%,  $^{14}\text{CO}_2$  accounted for up to 9%, and extractable residues up to 80% (about 15% of which was extracted by reflux). At the 5 ppm treatment rate (which was originally conducted for structure elucidation), no significant degradation was detected in the CA sample. After six months in the MS sample, the parent compound degraded almost exclusively to 3-chloro-8-quinolinecarboxylic acid (BH 514-1) and other minor products. The half-life of quinclorac was estimated at 4.7 months; the degradate BH 514-1 (parent compound minus one chlorine atom) had a estimated half-life of 7.4 months. The MS sample's bound residues at 6 months were 12%, 77% were extractable (20% of which was by reflux) and  $\text{CO}_2$  levels were not measured since this part of the study was for qualitative use only.

#### Materials and Methods

Aerobic aquatic metabolism was studied using sediment and water from the intended use sites for this EUP: Davis, CA and Greenville, MS. Approximately 100 g of sediment and 100 ml of water were placed in 250 ml Erlenmeyer flasks and treated to ~0.5 or ~5 ppm of [2,3,4- $^{14}\text{C}$ ] quinclorac. The flasks were then fitted with a stopper containing a glass inlet tube to allow a stream of  $\text{CO}_2$ -free air to be supplied. Exit gas was passed through a trap containing OXIFLUOR- $\text{CO}_2$

scintillation cocktail. The flasks were kept in a growth chamber in the dark at 23°C.

Samples were subjected to successive water, cold alkali and hot alkali extractions to determine free, ionically and covalently bound residues (see attached diagrams). Residues extracted with NaOH were assumed to be ionically bound to the soil and residues extracted by refluxing with NaOH were assumed to be covalently bound. Residues were identified using 2-dimensional TLC; ethyl acetate:methanol:acetic acid - 80:15:5 and toluene:methanol - 70:30. TLC residues were located by autoradiography and quantitated by LSC using 10 ml of Aquasol. Radioassay for total  $^{14}\text{C}$  content was by combustion followed by LSC. Confirmation was by HPLC (using UV detection) and GC/MS.

### Reported Results

After 360 days, the extracted residues were essentially undegraded parent compound in both the CA and MS soil samples at the 0.5 ppm treatment rate. Unextractable residues accounted for up to 15%,  $^{14}\text{CO}_2$  accounted for up to 9%, and extractable residues up to 80% (about 15% of which was extracted by reflux). At the 5 ppm treatment rate (which was originally conducted for structure elucidation), no significant degradation was detected in the CA sample. After six months in the MS sample, the parent compound degraded almost exclusively to 3-chloro-8-quinolinecarboxylic acid (BH 514-1) and other minor products. The half-life of quinclorac was estimated at 4.7 months; the degradate BH 514-1 had a estimated half-life of 7.4 months (see tables). The MS sample's bound residues at 6 months were 12%, 77% were extractable (20% of which was by reflux) and  $\text{CO}_2$  levels were not measured since this part of the study was for qualitative use only.

Recoveries ranged from 89 to 105%. See tables.

### Discussion

Aerobic aquatic degradation seems to be dependent on the origin of the sediment that is used. This may be explained by the existence of differing types of microorganisms in different soils. However, the extreme variation in metabolism rates in the two soils used in this study is unusual. It should be noted that the degradate BH 514-1 is parent compound minus one chlorine atom. Future studies by the registrant should attempt to further clarify this issue.

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### 10.3 Study Identification

Winkler V. 1987. Confined Accumulation Study of  $^{14}\text{C}$ -BAS 514 H Residues in Fall and Spring Rotational Crops. Report No. 87/5037, BASF Corporation Chemicals Division. April 1987. 403208-18.

#### Conclusions

In the confined rotational crop study (120 and 360 day rotation intervals), quinclorac was applied at 0.75 lb ai/A. Plant residues were found to be undegraded parent compound with the exception of soybean seed and hay residues which were 75% non-extractable (incorporated into the plant). Mature plants contained up to 0.010 ppm for root and bottom (turnip), 0.015 ppm for leafy vegetables (mustard), 0.025 ppm (winter wheat and soybeans) and 0.013 ppm (sorghum) for the small grain and stalk.

#### Materials and Methods

Accumulation in rotational crops was studied using a treated rice crop which was planted on May 1, 1984 in silty clay soil in Greenville, Mississippi. Sixteen plots each measuring 2 x 4 x 8 ft were enclosed by an aluminum frame. Radiolabeled [2,3,4- $^{14}\text{C}$ ]-Quinclorac mixed with an equal amount of nonlabeled quinclorac was applied at a rate of 0.75 lb ai/A to the rice plants under both dry and flooded conditions. The sites treated under dry conditions were flooded 7 days later. The rice seeds were collected on September 24 and the straw on October 1. Rotational crops (Mustard, turnips, wheat, sorghum and soybeans) were planted at 129 or 286 days after treatment.

Plant and soil samples were taken at three intervals. Plant samples were extracted with aqueous acetone, concentrated, acidified and extracted with ethyl ether. Soybean and wheat seeds were defatted with hexane, hydrolyzed with 1 N HCL, and extracted with ethyl ether. The ether residues were subjected to diazomethane derivatization and then analyzed by TLC. Soil samples were extracted with water and then with 0.1 N NaOH. The extracts were partitioned between dichloromethane and 0.1 N aqueous HCL and the non-polar fraction analyzed by TLC. Total radiocarbon was determined by combustion followed by LSC. See attached figures.

#### Reported Results

Total radioactivity in the soil was shown to be essentially all parent compound and decreased from time of application level of about 0.4 ppm to approximately 0.05 ppm 30 days later. This level then remained relatively constant through



474 days. Small levels of the degradate BH 514-1 (3-chloro-8-quinolinecarboxylic acid) were detected.

Plant residues were found to be undegraded parent compound with the exception of soybean seed and hay residues which were 75% non-extractable (incorporated into the plant). Mature plants contained up to 0.010 ppm for root and bottom (turnip), 0.015 ppm for leafy vegetables (mustard), 0.025 ppm (winter wheat and soybeans) and 0.013 ppm (sorghum) for the small grain and stalk. See tables.

#### Discussion

Based on the persistence quinclorac in soil and the accumulation in crops planted 360 days after treatment, a tolerance may be required for rotated crops.

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#### 10.4 Study Identification

Forbis, A.B., L.T. Schoen and L. Stuermer. 1986. Uptake, Depuration and Bioconcentration of  $^{14}\text{C}$ -BAS 514H by Channel Catfish (Ictalurus punctatus). Report No. 87/5002, BASF Corporation Chemicals Division. July 22, 1986. 403208-19.

#### Conclusions

Fish accumulation was studied using channel catfish in a 1 ppm quinclorac flow-through system for 28 days. Residues were below detectable levels at all times except for days 3, 7 and 14 where residues were detected at  $\leq 0.86$  ppm. The level of detection was 0.61 - 0.62 ppm.

#### Materials and Methods

Accumulation in fish was studied using channel catfish in a flow-through aquarium system.  $^{14}\text{C}$ -quinclorac was added to a 70 liter glass aquarium using proportional diluter system to give a constant concentration of 1.0 mg/l. The water temperature was maintained at 22°C. The study was started by adding 120 fish (Ictalurus punctatus) to both control and test chambers.

After 28 days of exposure, the treatment of the water with quinclorac was terminated and the aquarium was filled with untreated water for a depuration period of 14 days. Water and fish samples were taken throughout the experiment.

Three fish were pooled for each analysis. They were dissected in fillet/edible (body, muscle, skin and skeleton) and viscera/non-edible (fins, head, internal organs). Samples were homogenized and combusted for analysis by LSC. Water samples were also analyzed by LSC. See tables.

#### Reported Results

Water concentration was confirmed to be 1.0 ( $\pm 0.036$ ) mg/l during the 28 days. Residues were below detectable levels at all times except for days 3, 7 and 14 where residues were detected at  $\leq 0.86$  ppm. The level of detection was 0.61 - 0.62 ppm.

#### Discussion

This study demonstrates that quinclorac will not become concentrated in fish exposed at a level of 1 ppm.

11. COMPLETION OF ONE-LINER:

12. CBI APPENDIX: None.

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