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To: Robert Taylor,  
Product Manager 25  
Registration Division (H-7505C)

From: Paul Mastradone, Chief  
Environmental Chemistry Review Section #1  
Environmental Fate and Ground Water Branch/EFED

Through: Henry Jacoby, Chief  
Environmental Fate and Ground Water Branch/EFED

Attached, please find the EAB review of . . .

Reg./File # : 7969-OG  
Common Name : Quinclorac.  
Type Product : Herbicide.  
Product Name : Facet.  
Company Name : BASF Corporation.  
Purpose : BASF Response to EFGWB Quinclorac New Chemical  
Science Chapter  
Date Received : 3/7/91 EFGWB #s : 91-0434, 91-0440, 91-0441,  
91-0756  
Action Code : 101

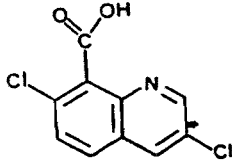
Deferrals to: \_\_\_ Ecological Effects Branch, EFED  
\_\_\_ Science Integration and Policy Staff, EFED  
\_\_\_ Occupational and Residential Exposure Branch, HED  
\_\_\_ Dietary Exposure Branch, HED  
\_\_\_ Toxicology Branch I, HED  
\_\_\_ Toxicology Branch II, HED

1.0 CHEMICAL:

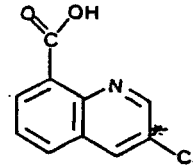
Common Name: Quinclorac, Facet

Chemical Name: 3,7-dichloro-8-quinolinecarboxylic acid

Chemical Structure:



BAS 514 H (quinclorac)



BH 514-1 (degradate)

2.0 TEST MATERIAL:

3.0 STUDY/ACTION TYPE: Review BASF response to the EFGWB science chapter of the Quinclorac new chemical registration standard dated 12/3/90.

4.0 STUDY IDENTIFICATION: BASF response to the quinclorac new chemical registration standard, that consists of 37 submissions that are listed in the attached Appendix A. The submissions include BASF's responses to EFGWB's comments and new data and literature reviews in support of their responses to comments. All submissions were reviewed by EFGWB.

5.0 REVIEWED BY:

Richard J. Mahler  
Hydrologist, Review  
Section 1, EFGWB, EFED

Signature: *Richard J. Mahler*  
Date: NOV 5 1991

6.0 APPROVED BY:

Paul J. Mastradone, Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: NOV 5 1991

7.0 CONCLUSION:

In response to EFGWB's review and subsequent meeting with the Branch, BASF submitted numerous non-guideline studies to support the degradation of quinclorac in the environment. EFGWB's review pointed out discrepancies between laboratory data and field data relating to dissipation. While BASF's submission has provided information that shows dissipation through photodegradation and volatilization from the flood water is the probable routes of dissipation in rice culture, the studies are generally lacking in information related to degradates, material balance and determination of

quinclorac in the soil. Since quinclorac has many of the characteristics of other chemicals that are known leachers which have been detected in ground water, the registrant should have sampled the soil in the field studies to a sufficient depth to demonstrate that quinclorac residues do not leach. Knowledge of this information plus the results of other studies is needed to adequately understand the route of dissipation of quinclorac when use as a rice herbicide.

In the EFGWB Science Chapter for the Quinclorac New Chemical Registration Standard dated December 3, 1990, the registrant submitted 30 environmental fate studies in support of the registration of quinclorac. The acceptable as well as supplemental laboratory data indicated that the compound is stable to hydrolysis, photolysis in sterile water, as well as aerobic and anaerobic metabolism. The leaching data indicated that the compound is mobile. Furthermore, crop rotation restrictions listed on the rice label of 3 months for small grain crops and 10 months for all other crops imply that quinclorac is persistent. Conversely, the submitted field studies indicated that quinclorac dissipates rapidly with little reported mobility in soil. However, because no attempt was made by the registrant to connect the studies together into a coherent description of the environmental fate of quinclorac and to discrepancies between laboratory (which indicate persistence) and field data (which indicate moderately rapid dissipation), EFGWB at that time was not able to assess the environmental fate of quinclorac.

Subsequent to the EFGWB Science Chapter and in conjunction with the registrant's responses, the registrant expressed concern that the laboratory studies performed according to the Subdivision N Guidelines would not adequately represent what would happen during actual field use conditions. Consequently, a meeting with EFGWB and BASF representatives was requested by BASF and held on June 18, 1991 so that BASF could summarize the Environmental Fate Package sent in response to the EFGWB Science Chapter. At this meeting BASF requested and EFGWB agreed to review all the material, including non-guideline studies and other pertinent data, that were submitted to support the registration of quinclorac, in order to reach a conclusion regarding the environmental fate of quinclorac.

In reply to the EFGWB Science Chapter, the registrant presented their responses in the form of 37 new submissions, including 12 new studies and ancillary data to support registration of quinclorac. EFGWB has carefully evaluated all BASF's responses to original

comments and the new studies/data. However, many major questions remain unanswered in regards to their responses and to the new studies that do not satisfy the data requirements.

The registrant maintains that the disparate results between lab and field studies are probably the result of:

1. Changes in microbial population or susceptibility of certain microbes to artificial situations that occur in the laboratory under aerobic conditions. This seems to be an acceptable theory since the laboratory data show that fresh soil, either alone or added to stored soil, increases degradation of quinclorac as compared to stored soil. However, the registrant did not compare the same soils, stored or fresh, in order to conclusively show that there is something in fresh soils that is not in stored soils. They may need to do this before EFGWB is completely satisfied that there is validity to their theory. Furthermore, EFGWB notes the non-guideline studies submitted indicate that even when fresh soil is used and degradation is increased as compared to stored soil, quinclorac can still be considered stable to aerobic metabolism (i.e., half-life >30 days).

2. Photodegradation in the presence of naturally occurring sensitizers, such as, humic acids, tryptophan, tyrosine, riboflavin and  $H_2O_2$ ,  $NO_3$ ,  $NO_2$  and ozone, which can be found in rice paddy or natural waters, but not in sterilized and distilled water.

EFGWB concludes that this is a plausible theory since the registrants have submitted non-guideline data and literature reviews which show quinclorac and other zenobiotics to degrade more rapidly in natural occurring waters and those treated with soil humic materials and other naturally occurring substances than in sterilized waters.

For example, the half-life of quinclorac in sterile water was much greater than 30 days since little degradation occurred during the 30 days of the study. In the non-guideline studies submitted, quinclorac half-lives were 24-65 hours in  $H_2O_2$  solutions, 5-10 days in non-sterilized rice paddy and river waters and activated sludge solutions, and 7 and 22-38 days, respectively, in rice paddy water and buffered solutions containing soil humic acid and humic acid or rose bengal.

In other studies cited in a submitted literature review, the half-life of quinclorac in laboratory photodegradation studies using field water, was always greater than the field half-life. For example, in the laboratory studies, the half-life was 41.1 days; while it was stated that residues in the field studies declined 34-40%, 47-57% or 71-76% during the first day of the studies, indicating rapid dissipation. In two studies carried out in rice paddies in Japan, the soil sediment half-lives were 13 and 30 days; while the residue concentrations in surface water declined 65% within the first 15 days at one location and 83% within 30 days at another.

However, in the non-guideline studies cited above, degradates and/or volatiles were not quantified and/or identified and consequently, material balances could not be determined. Since it appears that volatilization of quinclorac degradation products from aqueous media may be an important route of dissipation, how much is volatilizing and in what form, should be determined.

The aquatic field dissipation studies submitted and/or cited provide supplemental data that show quinclorac dissipates from rice floodwater with half-lives from 7-30 days. However, the studies were not acceptable because sampling was inadequate to assess dissipation of quinclorac from the soil of the test plots, the application rate was not confirmed and insufficient data were presented regarding the storage of water samples containing quinclorac for 30-33 months. One recurring problem with these studies is that insufficient soil/sediment samples were collected for analysis. This information may have assisted in ascertaining the dissipation of quinclorac from aquatic systems. Since quinclorac has many of the characteristics of other chemicals that are known leachers and have been detected in groundwater, the registrant should have sampled the soil in the field studies to a sufficient depth to demonstrate that quinclorac residues do not leach.

Upon review of the submitted responses to the EFGWB New Chemical Science Chapter, it has become increasingly clear that the the majority of non-guideline studies submitted and reviewed for that chapter can only be classed as preliminary. While they provide information that shows dissipation of quinclorac from aquatic systems, the studies are generally lacking in information related to degradates, material balance and determination of quinclorac in the soil. Knowledge of this information

plus the results of other studies is probably needed to adequately understand the route of dissipation of quinclorac in aqueous conditions.

In addition, the registrant repeatedly refers to the Subdivision N Guidelines and uses them as a reason for not providing information or providing only limited information.

It is strongly suggested that:

1. The registrant be reminded to read and understand the purpose of each study as described in the guideline.
2. The registrant be reminded that these are guidelines and not protocols and are intended only as that.
3. The registrant bear in mind the overall purpose of the Subdivision N Guidelines: that is to provide at least a qualitative as well as limited quantitative assessment of the exposure as well as a description of decomposition and dissipation of the compounds in question.

EFGWB notes that the Registrant has stated in a letter to Robert Taylor, dated February 7, 1990 (sic) from Bob Rohde, that "BASF is responding only to those studies supporting the use on rice. At a later date, [REDACTED]

[REDACTED] Accordingly, the data requirements listed below pertain only to aquatic food (rice) use.

As noted below, only 6 of 13 guidelines required for registration are fulfilled. Seven remain as data gaps.

The only studies that have met the requirements of 40 CFR part 158.290 and the guidance of Subdivision N are:

161-1--HYDROLYSIS

161-2--PHOTODEGRADATION IN WATER

161-3--PHOTODEGRADATION ON SOIL

162-1--AEROBIC SOIL METABOLISM

163-1--LEACHING AND ADSORPTION/DESORPTION

165-4--ACCUMULATION IN FISH

The following studies are required for the full registration of quinclorac on aquatic food (rice) use sites:

162-3--ANAEROBIC AQUATIC METABOLISM

162-4--AEROBIC AQUATIC METABOLISM

164-2--AQUATIC FIELD DISSIPATION

165-1--CONFINED ACCUMULATION IN ROTATIONAL CROPS

165-2--ACCUMULATION IN IRRIGATED CROPS

201-1--DROPLET SIZE SPECTRUM

202-1--DRIFT-FIELD EVALUATION

EFGWB comments, BASF response to EFGWB comments and EFGWB rejoinder are listed below under section 10.0, "Discussion of Individual Studies," and are ordered by guideline number.

8.0 RECOMMENDATIONS:

1. Inform the registrants of EFGWB's specific reply to each of their responses to the EFGWB Science Chapter New Chemical Registration Standard for Quinclorac dated 12/3/90 and to the status of the new studies submitted for review.
2. Inform the registrant that only the guidelines noted above as having acceptable data are fulfilled.
3. Inform the registrant that the remaining data gaps be filled and that the data submitted be of solid scientific value and not speculative. These data should provide a solid qualitative and quantitative assessment of the environmental fate, dissipation and transport (if any) of quinclorac.

- 9.0 BACKGROUND: The applicant has responded to the EFGWB Science Chapter for the New Chemical Registration Standard for Quinclorac.



10.0 DISCUSSION OF INDIVIDUAL STUDIES:

10.1 161-2 PHOTOLYSIS IN WATER

10.1.1 BASF responses (MRID 417814-06) to EFGWB review of Study 2: Photolysis of BAS 514 H in aqueous solution, (MRID 41063560).

1. EFGWB Original Comment: The registrant did not explain the disparity between this study and the following two aqueous photolysis studies (Study 3 and 4). Those studies show fairly rapid half-lives (5 and 10 days) of quinclorac in unsterilized non-buffered rice-paddy and river waters and water containing activated sludge when exposed to sunlight. The half-life in this study, using sterilized water buffered at Ph 7 and irradiated with a xenon lamp, showed little degradation after 29 days.

BASF Response: Study 2, conducted under EPA guidelines, only addressed the fate of quinclorac in sterile, pure water and sterile, pure water that had 0.5% acetone added as a possible photosensitizer. Indeed Study 2 demonstrated that in pure water alone with 12 h light and dark periods, quinclorac was relatively stable ( $t_{1/2} = 100$  days), and that the addition of 0.5% acetone accelerated the half life to about 50 days.

Studies 3 and 4, on the other hand, were submitted as supplemental information and addressed whether water obtained from "natural" sources (i.e., rice paddies, ponds, rivers, etc.) could produce additional photosensitization. As Studies 3 and 4 point out, the allowance for natural organic compounds in the test system produces very different results from those obtained using pure water as the test system. Study 3, for instance, showed that the half-life of quinclorac in both rice paddy and river water was about 5 days, while Study 4 showed a half-life of quinclorac to be about 10 days in water containing activated sludge.

An important factor missing from the latter two reports, however, is an identification of the fate of the parent molecule. For this reason, supplementary report BASF M9102 has been attached<sup>1</sup>. Report M9101 (*sic*) demonstrates that when quinclorac is photolyzed in the presence of either pure or pond water to which the oxidant hydrogen peroxide has been added, carbon dioxide originating from the heterocyclic ring of the parent

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<sup>1</sup> For the review of this study, see DER for Study 1.

molecule is found in the atmosphere trapped above the photolyzed solution. Given the same amount of H<sub>2</sub>O<sub>2</sub> added to pond water and HPLC water, both the total amount and rate of degradation of quinclorac was nearly two-fold greater in pond water than in pure water. Although the mechanism by which the photolysis is sensitized by hydrogen peroxide is not known, it very likely involves the presence of superoxide (O<sub>2</sub><sup>-</sup>) ion-radicals. The important conclusion from Studies 3, 4 and the submitted BASF report M9102 is that compounds found in natural waters lead to a very significant increase in the rate of photolysis of the parent molecule compared to photolysis in pure water, and that at least one of the products of this photolysis is CO<sub>2</sub>. Since all natural waters contain various oxidants and other sensitizing compounds, it is postulated that the observed disappearance of quinclorac under field conditions is due to degradation of the parent molecule and not to inability of analytical procedures to isolate and identify the parent.

EFGWB Rejoinder: It is clear from the data, from the above mentioned study (See attached DER for Study 1) that the photodegradation half-life of quinclorac in water photosensitized with hydrogen peroxide solutions is <65 hours and that degradation in nonsensitized water is extremely slow. However, insufficient information was provided in the submitted document to accurately assess the validity of the experiment, since degradates were not identified or quantified, and data were not expressed in units that would allow a material balance to be determined.

2. EFGWB Original Comment: The acetone added as a sensitizer in Study 3 seemed to decrease apparent photodegradation of quinclorac, while acetone added in this study (Study 2) slightly increased photodegradation.

BASF Response: In response to the question of why acetone accelerated the photodecomposition of quinclorac in Study 2, while acetone appeared to impede the photolysis of quinclorac in Study 3:

There is no a *priori* reason that acetone should have similar effects in the two studies because the two studies involved two different test systems. While the test system for Study 2 consisted of water, acetone and quinclorac, the test system for study 3 included water, acetone, quinclorac and natural contaminants. Until the exact mechanisms for photodegradation of quinclorac in natural water and pure water are known, the expected

effect of acetone on these two different systems cannot be assumed to be the same.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

3. EFGWB Original Comment: The study author stated that "...two other samples (one after 8 h of darkness, the other after 24 h) were withdrawn from the sensitized and nonsensitized reaction solutions at the end of the experiment to verify that no dark-dependent changes in reaction components occurred. The HPLC traces...indicate that within experimental limitations, the solutions at the beginning and end of the dark period were identical."

It is uncertain whether these two dark samples are meant to represent the storage stability of the irradiated solution or to demonstrate that the dark periods interspersed with irradiation had no effect on degradation (so that the irradiation could be considered cumulative). Two data points are not considered adequate for the dark control required by Subdivision N guidelines; the study author referred to 40320816 (Study 1) for information about the hydrolytic behavior of quinclorac.

BASF Response: The two dark samples addressed in the reviewers remarks were meant to present information on the storage stability of the irradiated solution. The two samples were not intended to represent the dark controls for the experiment. The hydrolysis study, MRID 40320816, which demonstrated that quinclorac is entirely stable in the dark in an aqueous solution, were referenced as control samples for the photolysis experiment.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

4. EFGWB Original Comment: The study author calculated the half-lives of quinclorac in the nonsensitized and sensitized solutions to be 2416-3240 hours and 1030-1238 hours, respectively. However, the statistical estimations of the photodegradation half-lives of quinclorac reported in these experiments are of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

BASF Response: The author agrees that extrapolation of limited data can be misleading. However, a requirement to report a half-life was addressed by extrapolating the data that were available.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

5. EFGWB Original Comment: EFGWB prefers that [<sup>14</sup>C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R<sub>f</sub> of reference standards.

In this study, the sample extracts were analyzed using one-dimensional TLC with one solvent system and by HPLC with UV and radioactive flow detection. Although analytical reference standards of quinclorac were used in the HPLC-UV analyses, it could not be determined from the "Experimental Section" whether reference standards were used with the TLC and [<sup>14</sup>C]HPLC analyses.

BASF Response: We agree that had there been any compound other than the parent molecule that was reported to be identified, confirmatory data would be required. However, since authentic standards were used with the TLC and HPLC systems in question, there is no reason to believe that the material identified as the parent was anything else less than the parent.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

6. EFGWB Original Comment: The method detection limit was not reported. Recovery efficiencies are not required because the samples were analyzed directly without extraction.

BASF Response: The limit of detection for the method was not reported but is approximately 5 ng/injection using the HPLC method described in Study 2.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

BASF CONCLUSIONS: This study was not accepted to fulfill the data requirements primarily because of unexplained disparities between this study and the two supplementary studies (Study 3, MRID 41063564-A and Study 4, MRID

41063564-B). In addition, it was noted by the reviewer that acetone added as a sensitizer in this study (Study 2, MRID 41063560) increased the rate of photodegradation, while acetone added as sensitizer in Study 3 decreased the rate of photodegradation.

Explanations for the disparities noted above are given. In addition, supplemental studies are provided that demonstrate that in the presence of naturally occurring oxidizing species, the parent molecule can be degraded in a light-dependent manner to CO<sub>2</sub> and other possible organic compounds. Other technical questions are also addressed in this response.

EFGWB CONCLUSIONS: EFGWB concludes, after thoroughly reviewing the studies and responses related to quinclorac photolysis in water, that this study (Study 2, MRID 41063560) is scientifically valid and can be used to fulfill the data requirements.

EFGWB concludes that quinclorac is stable to aqueous photolysis under sterile conditions. The half-life of quinclorac using sterilized water at Ph 7 and irradiated with a xenon lamp is much greater than 29 days based on the data that showed little degradation after 29 days.

- 10.1.2 BASF responses (MRID 417814-07) to EFGWB review of Study 3: Photodegradation study of quinclorac in aqueous solution (MRID 4103564-A).

1. EFGWB Original Comment: The water used was naturally occurring and the photodegradation in water study must be conducted in sterilized distilled or deionized water.

BASF Response: This study was not intended to fulfill the guideline requirement 161-2. This study was a supplementary submission to show that quinclorac undergoes photolysis rapidly in natural rice paddy water, even though it does not undergo photolysis in the sterile distilled water as required in guideline Study 161-2.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

2. EFGWB Original Comment: Although EFGWB concludes that quinclorac degraded in this study, the authors did not attempt to identify the degradates. In addition to not adequately satisfying the requirement of the photodegradation in water study, lack of this information makes it difficult to know what degradates might be found in the aquatic field dissipation studies.

BASF Response: This study was only designed to see if the parent compound degraded with time when exposed to sunlight under the experimental conditions of the study. The study showed that the disappearance of quinclorac obeyed first order kinetics giving a half-life of 5 days. As stated by the reviewer, the degradates of quinclorac were not identified in this study. However, photodegradation products are given in the attached Review Document<sup>2</sup> (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

3. EFGWB Original Comment: The registrant should explain the disparity between this study and the previous aqueous photolysis study (Study 2). This study shows a fairly rapid half-life (5 days) of quinclorac in non-sterilized rice-paddy and river waters when exposed to sunlight, while the half-life in Study 2, using sterilized water buffered at pH 7 and irradiated with a xenon light source, showed little if any degradation after 29 days. Conversely, while the acetone added as a photosensitizer in this study seemed to decrease apparent photodegradation of quinclorac, acetone added in Study 2 slightly increased photodegradation.

BASF Response: The disparity between this study and Study 2 (MRID 41063560) is addressed in detail in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05).

In Study 3, in which the photolysis was carried out in rice paddy water, the water already contained numerous natural photosensitizers. When acetone is added to this system, it competes with other photosensitizers which may be more effective, thus reducing the rate of photolysis. When acetone is added to a distilled water system, as in Study 2, it has no competition and hence raises the rate of photolysis.

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<sup>2</sup> This document is summarized in section 10.1.5. below.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

4. EFGWB Original Comment: The temperature was not controlled at  $25 \pm 1^{\circ}\text{C}$ . Instead the temperature was allowed to vary with the ambient outdoor temperature of 21-28 to 28-40  $^{\circ}\text{C}$  as measured at the start and conclusion of each day's exposure period.

BASF Response: Since this study was designed to mimic the natural environment, the temperature of the photolysis solutions were allowed to vary with the outdoor temperature.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

5. EFGWB Original Comment: The study was not performed under sterile conditions to minimize biological degradation. Sterilization may have assisted in determining if the microorganisms present were enhancing degradation or some other factor, such as the present of chemical sensitizers. The waters used in the study were not characterized in relation to physical and chemical properties.

BASF Response: A photodegradation study using sterile water was submitted as Study 2 (EFGWB Study ID 41063560). We agree that chemical sensitizers in the water used in this study did promote the photolysis of quinclorac. For more evidence of this, see the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05). The water used in this study was not characterized.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

6. EFGWB Original Comment: A record of the intensity of incident sunlight was not provided. Furthermore, the length of exposure was only 6 hours per day. Accordingly, had a longer daily sunlight exposure regime been utilized, the half-life, as determined may have differed from that reported and may have been less by at least one-half, based on a typical 12-hour daylight exposure period.

BASF Response: The intensity of the incident sunlight was not recorded in this study. We agree that a longer

exposure per day would have reduced the observed half-life.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

7. EFGWB Original Comment: Mass balance calculations were not determined, primarily because there were no apparent degradation products detected in the study. However, this reviewer concludes that there has to be some type of measurable degradation product for quinclorac and that it does not just disappear without an identifiable route of degradation. Use of radiolabeled quinclorac may have provided for an accountability of material balance as well as identification of degradation products.

BASF Response: The design of this study did not include a mass balance determination. The primary objective of the study was to see if irradiation in rice paddy water would produce a more rapid photolysis than in sterile distilled water.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

8. EFGWB Original Comment: There was no indication of when the samples were analyzed in relation to when they were sampled. From the discussion it appears that the solutions were analyzed the day after sampling; however, if they were not then a storage stability test should be performed on the solutions for as long as they were stored before analysis. This is needed to show that the samples did not degrade in storage.

BASF Response: The report states that the samples were analyzed the following day. Therefore, no storage stability test was necessary. However, a freezer storage stability study of quinclorac in pond water was included in this submission review as Study 29 (MRID 41063571).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

EFGWB CONCLUSION: EFGWB concludes that this study is scientifically valid and provides supplemental data that shows quinclorac to degrade photolytically in non-sterile naturally occurring rice paddy and river waters. The calculated half-lives in both waters was approximately 5 days.



- 10.1.3 BASF response (MRID 417635-08) to EFGWB review of Study 4: The study of biodegradation of quinclorac by microorganisms in activated sludge under sunlight (MRID 41063564-B).

1. EFGWB Original Comment: The water used was naturally occurring and the photodegradation in water study must be conducted in sterilized distilled or deionized water.

BASF Response: This study was not intended to fulfill the guideline requirement 161-2. This study was a supplementary submission designed to show that quinclorac undergoes rapid photolysis in activated sludge under the conditions of the experiment. It was meant to show a contrast to the guide-line study which requires irradiation in sterile distilled water. Further evidence for the degradation of quinclorac in water containing natural products is given in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

2. EFGWB Original Comment: Although EFGWB concludes that quinclorac degraded in this study, the authors did not attempt to identify the degradates. In addition to not adequately satisfying the requirement of the photodegradation in water study, lack of this information makes it difficult to know what degradates might be found in the aquatic field dissipation studies.

BASF Response: This study was only designed to see if quinclorac would undergo photolysis in activated sludge under the conditions of the experiment. Studies presented in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05) identify the photodegradation products.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

3. EFGWB Original Comment: The registrant should explain the disparity between this study and a previous aqueous

photolysis study (Study 2) performed under sterile conditions. This study shows a fairly rapid half-life (10 days) of quinclorac in an activated sludge solution when exposed to sunlight, while the half-life in study 2, using sterilized water buffered at pH 7 and irradiated with a xenon light source, showed little degradation after 29 days.

BASF Response: The disparity between the photodegradation half-life obtained in this experiment and the one obtained in Study 2 (EFGWB Study ID 41063560) is explained in detail in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05). This document explains the photosensitizing effect of natural products.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

4. EFGWB Original Comment: Quinclorac degraded in this study; however, the authors did not attempt to identify the degradates. Use of radiolabelled quinclorac may help in identifying the degradates as well as the route of degradation. This information is needed in determining degradation products that need to be identified in field dissipation studies.

BASF Response: This study was only designed to determine if the photolysis of quinclorac would occur more rapidly in the presence of activated sludge. No attempt was made to identify the degradates. The attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05) gives details of experiments designed to identify the degradates.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

5. EFGWB Original comment: The registrant needs to explain the disparity between this study and a previous aqueous photolysis study (Study 2) performed under sterile conditions. This study shows a fairly rapid half-life (10 days) of quinclorac in an activated sludge solution when exposed to sunlight, while the half-life in study 2, using sterilized water buffered at pH 7 and irradiated with a

xenon light source, showed little degradation after 29 days.

BASF Response: This disparity is addressed in detail in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC.; MRID 417814-05). The photodegradation of quinclorac is dependent on photosensitizers present in waters containing natural products.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

6. EFGWB Original Comment: The temperature that the study was conducted under was not determined or mentioned in the study report.

BASF Response: The temperature of the test solution which was exposed to sunlight was not recorded.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

7. EFGWB Original Comment: EFGWB notes that the data presented appears to support the authors conclusion related to the symbiotic affect of sludge plus sunlight on the degradation of quinclorac. However, the study should be performed with sterilized activated sludge as one treatment to support the conclusion. Although there is still the possibility that other factors may mediate the degradation.

BASF Response: We agree that other factors did act as photosensitizers in this study. The study also showed that biodegradation does occur as seen in the dark control tests but was slow compared to the degradation seen in the tests exposed to light.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

8. EFGWB Original Comment: A record of the intensity of incident sunlight was not provided. Furthermore, the length of exposure was only 6 hours per day. Accordingly, had a longer daily sunlight exposure regime been utilized, the half-life, as determined may have differed from that reported and may have been less by at least one-half, based on a typical 12-hour daylight exposure period.

BASF Response: The intensity of the sunlight was not recorded. We agree that a longer exposure to sunlight per day would have resulted in a shorter half-life of the quinclorac than that observed in the experiment.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

9. EFGWB Original Comment: Mass balance calculations were not determined. Use of radiolabeled quinclorac may have provided for an accountability of material balance as well as identification of degradation products.

BASF Response: The study was not designed to provide the identity of the photoproducts. This information is provided in the attached Review Document (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

10. EFGWB Original comment: The authors did not determine a half-life of quinclorac under the conditions of this study. The reviewers calculated half-life, using the linear regression analysis on the data in Table II-2 was determined to be 10 days ( $Y = -0.038X + 0.86$ ,  $R^2 = 0.9709$ , where  $Y = \text{days}$  and  $X = \text{ppm quinclorac}$ ).

BASF Response: We agree with the calculation of a 10 day half-life.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

11. EFGWB Original comment: There was no indication of when the samples were analyzed in relation to when they were sampled. If the samples were stored before analysis, then a storage stability test for as long as the samples were stored has to be performed. This is needed to show that the samples did not degrade in storage.

BASF Response: From the study data given on the title page of the report, the time periods given in the report, and the data given on the chromatographic scans, the following schedule could be determined:

August 31, 1987 to October 31, 1987 = preparation of solution for test.

October 31, 1987 to November 21, 1987 = sunlight exposure period.

November 21, 1987 to January 9, 1988 = sample analysis period.

A storage stability study for quinclorac in pond water for 6 months was included in this submission and reviewed as Study 29 (EFGWB Study ID No. 41063571).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

EFGWB CONCLUSION: EFGWB concludes that this study is scientifically valid and provides supplemental data that shows quinclorac to degrade photolytically in non-sterile activated sludge solution. The EFGWB calculated half-life using linear regression analysis was approximately 10 days.

10.1.4 New data in support of response to reviewer's comments to photodegradation in Water Study:

1. Ellenson, J. L. January 1991. Photolysis of <sup>14</sup>C-BAS 514 H in water sensitized with hydrogen peroxide. Registration Document No. 91/5003. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplement to: Photolysis of BAS 514 H in pH 7 aqueous solution at 25° C, BASF Report M8806, MRID 41063560. (MRID 417814-02).
2. Huber, R. November 1990. Preliminary investigation of the humic acid sensitized aqueous photolysis of quinclorac. Registration Document No. 90/0487. Unpublished study performed by BASF Akteingesellschaft, Product Safety Crop Protection, Limburgerhof, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-03, supplements MRID 41063560).
3. Goto, S. May 1989. Solar photolysis of quinclorac in aqueous solutions. Registration Document No. 89/0191. Unpublished study performed by The Institute of Environmental Toxicology, Tokyo University of Agriculture and Technology, Tokyo, Japan. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-04, supplements MRID 41063560).

See attached Data Evaluation Records (DERs) for Studies 1, 2 and 3 for the complete review of these studies. These studies provide information which demonstrates that photodegradation of quinclorac is accelerated when quinclorac is added to naturally occurring water or when photosensitizers, such as H<sub>2</sub>O<sub>2</sub>, humic acid or rose bengal, are added to distilled water. Half-lives of quinclorac in H<sub>2</sub>O<sub>2</sub> solutions was estimated to be between 24 and 65 hours; while half-lives in rice paddy water and buffered solutions containing humic acid and humic acid or rose bengal were estimated to be, respectively, 7 and 22-38 days.

10.1.5. Literature review in support of response to reviewer's comments to Photodegradation in Water Study:

Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-05).

10.1.5.1. The registrant submitted a summary of references which indicates (according to the registrant) that photosensitizing agents exist in natural waters which facilitate the photodegradation of compounds with limited UV absorption and that these agents facilitate photodegradation of quinclorac. The abstract was arranged in two sections with a summary:

I. Research supporting the existence of photosensitizing agent in natural waters which affect the photolysis of compounds with limited UV adsorption. This section is a synopsis of 8 journal articles that presents evidence that various naturally occurring substances (H<sub>2</sub>O<sub>2</sub>, humic acid, tryptophan, tyrosine, riboflavin, etc.) can act as photosensitizers and accelerate the rate of photodegradation of many xenobiotics that weakly absorb light above 290 nm. In the majority of these experiments, the addition of these photosensitizers greatly increased photolysis as compared to water without these agents added.

II. Research supporting the photodegradation of quinclorac in rice paddies (natural waters). This section is a synopsis of 5 studies related to the photodegradation of quinclorac in laboratory or field water (unsterilized rice paddy water, humic acid added to distilled water, H<sub>2</sub>O<sub>2</sub> added to distilled water).

Three of these studies were submitted, reviewed and the DERs for Studies 1, 2 and 3 are attached. The three reviewed studies are all considered supplemental data and provide information that demonstrates H<sub>2</sub>O<sub>2</sub>, humic acid and

rose bengal added to rice paddy water and/or aqueous buffered solutions act as photosensitizers and can increase the photodegradation of quinclorac as compared to degradation in pure sterilized water.

The other two studies<sup>3</sup> are summaries of laboratory and field studies that also indicate the photolytic degradation and aerobic metabolism of quinclorac in laboratory or field studies was more rapid than when the studies were performed according to the Subdivision N Guidelines.

In the studies by Wang and Crosby, the half-life of quinclorac in the laboratory photodegradation studies was always greater than the field half-life. For example, the authors stated in laboratory studies the half-life was 41.1 days; however, while no field half-lives were stated in the "Overview", residues declined 34-40%, 47-57% or 71-76% during the first day of the studies.

In the studies by Kotoh, carried out in rice paddies in two locations in Japan, the sediment half-lives were 13 and 30 days. The residue concentration in surface water declined 65% within the first 15 days at one location and 83% within 30 days at the other location.

EFGWB CONCLUSIONS REGARDING WATER PHOTOLYSIS STUDIES:

EFGWB concludes that the registrant has submitted sufficient evidence that shows photosensitizing compounds are present in natural waters which promote the photodegradation of xenobiotics with restricted UV absorption and that these compounds promote the photodegradation of quinclorac.

Based on this information, the original Photolysis in Water Study (MRID 41063560, EFGWB Study 2), is now acceptable and satisfies the data requirements for which it was intended. The data shows that after 29 days of irradiation with a xenon lamp in sterilized water buffered at pH 7, little degradation of parent quinclorac had occurred.

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<sup>3</sup> Wang, Y. and D. G. Crosby. 1990. The environmental fate of quinclorac in California rice fields. Department of Environmental Toxicology, University of California, Davis, California.

Katoh, S. 1988. BAS 514 OOH - Soil residue analysis of free quinclorac (Field test). BASF Reg. Doc. No. 88/0643. Japan Food Research Laboratories. Shibuya-Ku, Japan.

EFGWB concludes that quinclorac degrades more rapidly in natural occurring waters than in sterilized waters. However, more data is needed to conclusively show how the chemical is dissipating from aquatic systems. This information should include material balances, identification of degradates, volatiles, etc.

In the non-guideline submitted studies, volatiles were not quantified and/or identified and consequently, material balances could not be determined. Since it appears that volatilization of quinclorac degradation products from aqueous media may be an important route of dissipation, how much is volatilizing and in what form, should be determined. Knowledge of this information plus the results of other studies should allow EFGWB to understand the route of dissipation of quinclorac in aqueous conditions.

The authors of these studies have proposed, and other research, cited in the literature reviews, supports the following route of quinclorac dissipation in water:

1. In the presence of photosensitizers such as, humic acids, tryptophan, tyrosine, riboflavin and  $H_2O_2$ , which can be found in natural waters, oxygen is reduced to form superoxide anions which can react with hydrogen to form  $H_2O_2$ . The peroxide photochemically decomposes in sunlight to form hydroxyl free radicals ( $HO\cdot$ ) which, with  $NO_3$ ,  $NO_2$  and ozone can oxidize quinclorac to 7-chloroquinoline carboxylic acid, 2-hydroxy-3,7-dichloro quinoline carboxylic acid, 3,7-dichloroquinoline and 2-hydroxy-3,7-dichloroquinoline.

2. The above compounds can undergo further photolytic degradation to 3-chloronicotinic acid and 2-ethyl-5-chloroaniline which can then degrade to  $CO_2$ .

## 10.2 161-3 PHOTODEGRADATION ON SOIL

### 10.2.1 New study submitted:

Goetz, A.J. and V. W. Winkler. February 1991. Photolysis of  $^{14}C$ -BAS H in soil. Registration Document No. 91/5005. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-09).

EFGWB concludes that this study is scientifically valid and can be used to fulfill the data requirements by providing information showing that quinclorac is stable to photodegradation on soil. Quinclorac photodegraded with a half-life of 122-162 days; while little degradation



occurred in the dark controls. After 30 days approximately 78-87% of the applied quinclorac remained. Carbon dioxide was the major degradate that accounted for 1.6% of the applied radioactivity after 30 days; while unidentified degradates in extracts and unextractable radioactivity were  $\leq 8.9\%$  and  $\leq 7.8\%$  of the applied radioactivity, respectively. See attached DER No. 4 for the complete review of this study.

### 10.3 AEROBIC SOIL METABOLISM--162-1

10.3.1 BASF response (MRID 417814-15) to EFGWB review of Study 6: Respiration of live soil treated with  $^{14}\text{C}$ -quinclorac (MRID 41403506).

BASF Overview: This study was considered to be invalid by EFGWB because experimental variation could not be established since the study was not replicated (Data Evaluation Record for Study 6, p 6.3). Other concerns included limited sampling (two times) and test duration (28 days) as well as no explanation to explain discrepancies between studies.

This study was never intended to satisfy the aerobic soil metabolism guideline requirements. Rather, it was conducted to supplement an outdoor  $^{14}\text{C}$ -dissipation study in North Carolina which showed an apparent decrease in total radioactivity. Since there was no indication of leaching, the loss of radioactivity through  $^{14}\text{CO}_2$  production was suspected. Thus, a fresh sample of the same soil was incubated with  $^{14}\text{C}$ -quinclorac in the laboratory to test for any respired  $^{14}\text{CO}_2$ . After 28 days, the production of  $^{14}\text{CO}_2$  was validated and the experiment was terminated.

The need for replication should not be an issue because the objective of the study was to determine if North Carolina sandy loam was capable of metabolizing quinclorac to  $\text{CO}_2$ . This information was expected to be valuable in further defining soil metabolism and field dissipation under field environmental conditions. Moreover, this was essentially a qualitative all or nothing type experiment which makes replication less important.

1. EFGWB Original Comment: The number of samples collected were inadequate to accurately assess the amount of  $\text{CO}_2$  produced other than at the two sampling times. From the data, it can not be determined what the rate of  $\text{CO}_2$  production would be, since insufficient number of samples were collected at various times. Samples should have been collected over a longer period of time.

BASF Response: The objective of this study was simply to determine if the North Carolina sandy loam soil used in the dissipation study was capable of converting quinclorac to CO<sub>2</sub>. Determining the rate of CO<sub>2</sub> production was not an objective and thus should not be considered an issue. Samples were not collected longer than 28 days because the soil's ability to convert quinclorac to CO<sub>2</sub> was confirmed.

EFGWB Rejoinder: EFGWB recognizes that under the conditions of the experiment, the soil microorganisms in the North Carolina sandy loam soil used in this study are capable of converting quinclorac to CO<sub>2</sub>. Therefore, EFGWB accepts this response as resolving the original comment.

2. EFGWB Original Comment: 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 that may occur in soil and analytical procedures.

BASF Response: The value of replicates is debatable. In fact, replicates are not required by the guideline. For example, trend analyses can be more meaningful in the interpretation of systems and/or models. This study was essentially an all or nothing qualitative experiment to determine if the soil was capable of mineralizing quinclorac to CO<sub>2</sub>. Thus, experimental variation is not an issue.

EFGWB Rejoinder: Based on the Registrant's response, EFGWB accepts this response as resolving the original comment. However, there is no way to assess the variation that occurs in soil and analytical procedures without replicates or duplicate determinations.

EFGWB notes that, while the guidelines do not specifically suggest replicates, they do imply the need for them. For example, Subdivision N Guideline Number 162-1 (c)(2)(v) states:

"Sufficient soil samples should be taken at each sampling interval to ensure interpretable results."

EFGWB interprets this to mean at least duplicate samples need to be collected, either by test replication or collecting more than one sample at each sampling period. The samples should not be composited, but reported as the individual results.

Furthermore, extrapolation of this data to a longer time period is not justified without some measurement of

variation and the determination of CO<sub>2</sub> for longer time periods.

3. EFGWB Original Comment: The authors did not explain the discrepancy between this aerobic soil metabolism study and Study 5, also an aerobic soil metabolism study. In this study, the authors concluded that 5.11% of the initial radioactive quinclorac occurred as CO<sub>2</sub> after 28 days. However, in Study 5, <0.10% CO<sub>2</sub> was produced after 365 days of incubation.

BASF Response: Explanations for the disparate behavior of the test systems are based on differences in microflora populations with and without enhancement. These are discussed in detail in the Response to EPA Data Evaluation Records for Study 8, for the aerobic aquatic metabolism report (Clark, BASF Report M8716, MRID No. 40320817) and Study 11, (Winkler and Lewandowski, BASF Report M8905, MRID No. 41432101). Differences in microbial populations is a factor because the primary microbes capable of metabolizing quinclorac appear to be sensitive to environmental conditions such as storage before conducting laboratory studies. These sensitive bacteria are quite likely aerobic nonspore forming types, such as pseudomonas spp which are known to metabolize quinoline. This was the reason this experiment was conducted with freshly collected nonstored soils.

EFGWB Rejoinder: EFGWB accepts this response as one possible explanation in the discrepancy between the two studies. However, to confidently conclude that the observed CO<sub>2</sub> production was due to some component in the fresh soil but not in the stored soil, both a stored and fresh soil should have been studied under identical conditions.

BASF CONCLUSIONS: All of the reviewer's questions have been addressed to show this to be a scientifically valid study. This study should be used as a supplementary study for both soil metabolism and confined field dissipation to show that quinclorac metabolism to CO<sub>2</sub> by soil microorganisms is a viable route of dissipation.

EFGWB CONCLUSIONS: EFGWB concludes that this study, for the purposes for which it was conducted, is scientifically valid and provides supplemental information that shows quinclorac metabolism to CO<sub>2</sub> by soil microorganisms may be a viable, although slow, route of dissipation in the soil tested. In the sandy loam soil from North Carolina, after 28 days of incubation, an accumulated total of 5.11% CO<sub>2</sub> was produced.

10.3.2. New Data in Support of Response to reviewer's Comments to Aerobic Soil Metabolism Study:

1. Schmider, D. R. April 1988. Studies on the behavior of quinclorac in soil. Registration Document No. 88/0642. Unpublished study performed by BASF Aktiengesellschaft, Agricultural Research Station Ludwigshafen, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-10, supplements MRID 412473-01).

EFGWB concludes that this study provide information that demonstrates quinclorac to degrade more rapidly in fresh laboratory and field soils than in stored soils. However, no direct comparison was made between a fresh soil and the same soil stored in the laboratory which probably would have conclusively proven that there was something in the soil influencing degradation.

In this study, degradation of quinclorac was assessed using carrots as a biological indicator plant. Although EFGWB does not consider bioassay techniques as acceptable analytical procedures, the study does show that fresh soils lost herbicidal activity for up to 8 months when steam sterilized and incubated with quinclorac. Similarly, when the same soil was air dried, sieved and stored for 4 months at 20°C, the same effect as sterilization with steam occurred. This implies that microbiological activity in the soil may be the predominant factor in the degradation of quinclorac under aerobic conditions.

See attached DER of Study 5 for the complete review of this study.

2. Mittelstaedt, W. and F. Fuhr. September 1988. BASF 514 H - Degradation according to the German Federal Biological Institute of Agricultural and Forestry (modified in accordance with leaflet 36). Registration Document No. 88/0426. Unpublished study performed by Institute for Radio Agronomy, Nuclear Research Facility at Julich, Julich, west germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-11, supplements MRID 41247301).

EFGWB concludes that this study provides information that demonstrates quinclorac to degrade more rapidly in a stored soil supplemented with a fresh field soil than in stored soils with no added fresh field soil. In this study, after 138 days, 42.4% of the applied radioactivity was parent quinclorac, and 9.7% CO<sub>2</sub> was produced, as

compared to 84-98% parent quinclorac and <1% CO<sub>2</sub> produced in the original aerobic soil metabolism study after 365 days. However, insufficient information was provided in the submitted study to accurately assess the scientific validity of the experiment. Rates of degradation varied between soils and the same soil was not used in the original study (MRID 41247301, EFGWB Study 5) and this study, and the experimental setup, including trapping systems, were not identical.

See attached DER of Study 6 for the complete review of this study.

10.3.3. Literature Reviews in Support of Response to Reviewer's Comments to Aerobic Soil Metabolism Study:

1. Bicki, T. J. January 1991. Review of literature relating variability of microbial degradation to environmental variables, soil properties and pesticide concentration. Registration Document No. 91/5131. Unpublished study performed by Roux Associates, Inc. Huntington, NY. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-12, supplements MRID 400001247301).

This is a review of 49 journal articles relating to microbial and environmental effects and how they may impact soil degradation of pesticides. The review demonstrates the complexity of factors which impact pesticide soil metabolism.

Because no new data was presented directly relating to the environmental fate of quinclorac, no DER was prepared for the literature review. However, it was reviewed by EFGWB in order to assist in the understanding of the degradation of quinclorac in soil.

The study author's summary of the review is as follows:

A review of literature revealed that persistence of microbially degraded pesticides was found to be controlled by a number of biotic, environmental, and edaphic variables. The types, amounts, and activities of microorganisms, capable of degrading, vary in soils. Environmental factors such as temperature, moisture, and previous pesticide application history mediate degradation rates by affecting both the dynamics of the microbial population and the rates of chemical reactions. Soil properties such as organic matter content, particle size fractions, pH, and water holding capacity have been correlated with degradation rates in a number of studies. Soil properties influence microbial degradation directly by their effect on the growth and activity of the microorganisms and indirectly by controlling the adsorption and bioavailability of the applied pesticides. The concentration of

applied pesticides has also been shown to influence degradation rates. Degradation of pesticides has been described in several studies by first-order kinetics, where degradation rates are proportional to concentration, but higher-order rate kinetics have also been used successfully.

2. Akkari, K. H. January 1991. Literature review of some biochemical factors affecting the degradation of organic chemicals in soil. Registration Document No. 91/5030. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-13).

Because no new data was presented directly relating to the environmental fate of quinclorac, no DER was prepared for the literature review. However, it was reviewed by EFGWB in order to assist in the understanding of the degradation of quinclorac in soil.

This is a review of 70 journal articles relating to chemical and microbial factors how they may impact degradation and/or transformation of pesticides in soil. The review was ordered into five sections with a discussion of pertinent information gleaned from the journal articles in each section:

BIOCHEMICAL TRANSFORMATIONS IN SOIL  
KINETICS OF BIODEGRADATION IN SOIL  
KINETICS OF BACTERIAL PROCESSES  
EFFECT OF PHYSICAL PROCESSES IN SOIL ON MICROBIAL DEGRADATION  
HYDROLYTIC TRANSFORMATIONS

These above literature reviews do not present any new information not already understood by EFGWB since they are summaries of journal articles already published. Therefore, EFGWB considers this material as supplemental data relating to the aerobic soil metabolism of quinclorac.

EFGWB CONCLUSIONS REGARDING AEROBIC SOIL METABOLISM

STUDIES: EFGWB concludes that the data as presented show that quinclorac is stable under aerobic conditions. In the original acceptable aerobic soil metabolism study (MRID 41247301, EFGWB designated Study Number 5), the half-life of quinclorac was >1 year in the two silt loam soils tested. In the supplemental studies submitted using combinations of stored and fresh soil (both not necessarily the same soil), the half-life of quinclorac was estimated to be approximately 90 days (indicating stability under aerobic conditions) when fresh soil was used. However, more data is needed to conclusively show how the chemical is dissipating from aerobic soils. The

registrant needs to conduct studies under identical conditions where there is a direct comparison between fresh soils and the same soils stored in the laboratory for extended periods of time.

10.4 162-3 ANAEROBIC AQUATIC METABOLISM

- 10.4.1. BASF response (MRID 417814-16) to EFGWB review of Study 7: BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: Anaerobic aquatic system (MRID 41063561).

BASF Overview: This study was not accepted to fulfill the data requirements primarily because of questions regarding complete material balance and potential loss of radioactivity through volatilization. The reviewer misinterpreted material balance values to mean total recovery when, in fact, they were % recovery. However, total recovery results are available in the report that show no loss of material from volatilization. In addition to pointing this out, a response has been made for each comment made by the reviewer.

1. EFGWB Original Comment: Incomplete material balance; up to 27% not accounted for by termination of study.

BASF Response: For all but two samples, the "material balance" values given in Tables V and VI are, in fact, the % TRR recovery value for aliquots of mixed sediment and water samples when subjected to fractionation. Since some samples were aliquots, % material balance was intended to be used to evaluate the precision and accuracy of the fractionation procedure rather than the amount of total radioactivity recovered from the whole sample. In this case, it was quite good with a mean  $\pm$  standard deviation of  $97.8 \pm 10.2$  (n=6) for the 0.5 ppm treated systems given in Table V. However, total radioactivity was measured in two samples, the 180 day, 0.5 ppm California and the 365 day, 5.0 ppm Mississippi samples, with respective material balances of 92.3 and 92.5%.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment, since from the response it is not clear what is transpiring. Are the reported results in Table V "Material Balances" or "% TRR?" Please explain. Moreover, there is still the question of what happened to the 27.3% (114.1-86.8%, Table V) unaccountable radioactivity that occurred in the Mississippi soil treated with 0.5 ppm quinclorac. See EFGWB Rejoinder below.

2. EFGWB Original comment:  $^{14}\text{C}$ -volatiles were not reported.

BASF Response:  $^{14}\text{C}$ -volatiles measured after up to 200 days incubation for the 0.5 ppm samples showed less than 0.1% TRR in Oxyfluor traps. This result was inadvertently omitted from the report. From these results, it is clear that there was no loss of radioactivity through volatilization or fractionation procedures.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The data demonstrate that there was not a significant amount of  $\text{CO}_2$  produced during the first 200 days. However, there is still the question of whether or not volatile parent or degradate was lost, since there were no traps used specifically to capture these components. This may explain what happened to the 27.3% unaccountable radioactivity that occurred in the Mississippi soil as discussed above.

3. EFGWB Original Comment: The experiment was not replicated.

BASF Response: The value of replicates is debatable and, in fact, is not a guideline requirement. For example, trend analyses can be more meaningful than the use of replicates in interpreting systems and/or their models. In this study, it is clear that under the conditions of the experiment, very little metabolism of quinclorac occurred. Also, replication was not needed for the fractionation procedures because the precision and accuracy was quite good at  $97.8\% \pm 10.2$  (n=6).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. EFGWB does not agree with the registrant that "the value of replicates is debatable and, in fact, is not a guideline requirement." There is no way to assess the variation that occurs in soil and analytical procedures without replicates or duplicate determinations.

Furthermore, EFGWB does not agree that "very little metabolism of quinclorac occurred", since it appears that approximately 27% (114.1-86.8%) of the 0.5 ppm quinclorac treatment applied to the Mississippi soil had degraded by 365 days. Although it still can be concluded that quinclorac is stable to anaerobic aquatic metabolism.

4. EFGWB Original Comment: CEC units were not given.

BASF Response: The CEC units were meq/100g.



EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

5. EFGWB Original Comment: Method detection limits and recovery efficiencies from fortified samples were not provided.

BASF Response: Recovery efficiencies ranging from 86.8% to 114.1% were given in Table V of the report. The lower limit of detection was not reported because there were no values below the lower limit of detection. However, based on a specific activity of 89,300 dpm/g for the test substance, the lower limit of detection is ca 0.005 ppm for soil combustions (i.e., 89 dpm/200 mg combustion sample). Also, as discussed in item 1, total radioactive recoveries for the 180 day California 0.5 ppm and 365 day Mississippi 5 ppm samples was ca 92.5%.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The registrant appears to have misunderstood the original comment. EFGWB was referring to recovery of quinclorac from control samples that had been fortified. This is needed to present some data related to the efficiency of the extractants used.

6. EFGWB Original Comment: EFGWB prefers that [<sup>14</sup>C]residues in samples be separated by chromatographic methods (such as TLC or HPLC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R<sub>f</sub> of reference standards.

In this study, the samples extracts were analyzed by one-dimensional TLC with one solvent system with what appears to be a cochromatographed labeled reference standard of quinclorac; however, the study authors did not state this in the discussion of the results.

BASF Response: The review is correct. However, the identity of quinclorac was confirmed by derivatizing it to its methyl ester and matching TLC R<sub>f</sub>'s with authentic standards in a number of aquatic aerobic and anaerobic samples. This data was not included because it was obvious that there was essentially no metabolism of quinclorac in these systems. These results can be made available should the agency still believe it necessary to show that essentially no metabolism of quinclorac occurred.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment; however, EFGWB prefers, for future submissions, the registrant use techniques (i.e., GC/MS) that will confirm the presence of the chemical being studied.

BASF CONCLUSIONS: Results showed that under the test system used in this study, there was very little metabolism of quinclorac under totally anaerobic conditions. To date, quinclorac metabolism has only occurred twice in laboratory studies, both of which were under aerobic conditions. The first time was with a 5 ppm Mississippi silty clay aerobic aquatic system (MRID 4032087). Since there was a long lag time greater than 2 months before metabolic activity was observed, breakdown was probably caused by microbial enhancement. The rate limiting step was dechlorination at the 7 position followed by a rapid breakdown to a number of minor components ultimately mineralized to  $^{14}\text{CO}_2$ .

The second time was with a 28 day respiration study using fresh collected nonstored soil which showed ca 5% conversion to  $\text{CO}_2$  (MRID 41403506). This study was a supplement to an outdoor  $^{14}\text{C}$ -dissipation study which showed quinclorac dissipation to have a half-life of ca 45 days and no buildup of metabolites. On the other hand, the laboratory anaerobic test systems used to date have not shown metabolism of quinclorac with or without enhancement. The most plausible reason for this is anaerobic organisms do not readily degrade quinclorac. However, it is also possible the microbial flora was not specific, either because of the natural population, per se, or because of alterations of the natural population in the test system employed.

EFGWB CONCLUSIONS: EFGWB concludes, after thoroughly reviewing the study and responses related to quinclorac degradation in the anaerobic aquatic system, that the study (Study 7, MRID 41063561) is scientifically valid and provides supplemental information demonstrating that quinclorac is stable to anaerobic aquatic metabolism. The half-life of quinclorac is much greater than 1 year based on the data that showed little degradation after 365 days. However, since the material balance problem has not been adequately responded to and recovery efficiency has not been properly addressed, the data cannot be used to fulfill the data requirements.

Furthermore, this study authors need to explain the disparate behavior of quinclorac in this study and the new submitted study (Mittelstaedt, W. and F. Fuhr. 1988.

BASF 514 H - Degradation according to the German Federal Biological Institute of Agriculture and Forestry (modified in accordance with leaflet 36) Registration Document No. BASF 88/0426. Unpublished study performed by the Institute for Radio Agronomy, Julich, Germany, and submitted by BASF Corporation, Research Triangle Park, NC., MRID 41781411, EFGWB designated Study 6) which shows 5.4% CO<sub>2</sub> produced after 138 days of essentially anaerobic soil metabolism.

#### 10.5 162-4 AEROBIC AQUATIC METABOLISM

- 10.5.1. BASF response (MRID 417814-19) to EFGWB review of Study 8: BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: Aerobic aquatic system (MRID 40320817).

BASF Overview: This study was not accepted to fulfill the data requirements for aerobic aquatic metabolism (162-4) primarily because there was no adequate explanation provided for disparate behavior (only one out of four test systems showed any appreciable metabolism) and three minor metabolites were not identified.

An explanation for the disparate behavior of the test systems given in this response is based on differences in microbial populations and microbial enhancement. Also new data is presented on elucidating the identity of one of the three unknown minor metabolites. In addition, results of supplemental studies on soil metabolism of quinclorac under natural condition are given to confirm that all the metabolites of concern have been adequately identified and to show that degradation occurs with half-lives between 30 and 60 days.

Also responses have been made for each comment made the reviewer to clarify technical questions.

1. EFGWB Original Comment: No adequate explanation was provided for the disparate behavior of quinclorac. In the silty clay loam and silty clay soils treated at 0.5 ug/g and in the silty clay loam soil treated to 5.0 ug/g, "almost all" extractable residues (which comprised approximately 75% of the applied) were undegraded quinclorac at 1 year posttreatment. In contrast, in the silty clay soil treated at 5 ug/g, the study author estimated a half-life for quinclorac of 4.7 months. The study authors stated that the degradation rate was dependent on the origin of the sediments and associated waters, but this does not explain why the differences were observed only at the 5 ug/g treatment rate.

BASF Response: Out of four treatments (MS silty clay and CA silty loam each dosed at 0.5 and 5 ppm) only the 5 ppm dosed MS silty clay resulted in metabolism of quinclorac. There are two good explanations why this occurred.

The first reason for disparate behavior is the major microbes capable of metabolizing quinclorac quite likely are relatively labile and sensitive to environmental conditions. For example, Pseudomonas spp has been shown to be a principle degradative microbe for quinoline. Pseudomonas are nonspore forming aerobic gram negative bacteria, and consequently tend to die off under artificial laboratory conditions. This type of sensitivity was specifically shown in a 1988 study conducted by Schmider (Schmider, D. R. 1988. Studies on the behavior of quinclorac in soil. Registration Document No. BASF 88/0642. Unpublished studies performed by BASF, Ludwigshafen, Germany, and submitted by BASF Corporation, Research Triangle Park, NC. MRID 41781410). In this study, quinclorac had degradative half-lives of 30 to 70 days when added to freshly collected soils. However, when added to soils that had been stored for 3 months in the dark under optimal storage conditions, there was no degradation even after 6 months incubation. (EFGWB notes that the above mentioned study provides information that demonstrates quinclorac to degrade more rapidly in fresh laboratory and field soils than in stored soils. However, no direct comparison was made between a fresh soil and the same soil stored in the laboratory which probably would have conclusively proven that there was something in the soil influencing degradation. See attached DER of Study 5 for the complete review).

The second reason for disparate behavior is microbial enhancement. This is the effect when after a period of exposure to the pesticide, certain microorganisms acquire the complement of enzymes permitting metabolism of the pesticide and then derive a growth advantage so that they proliferate rapidly and consume the pesticide. Clearly, there was little if any degradation of quinclorac within the first 30 days of incubation. Although the guideline incubation trial requirement for aquatic aerobic studies is only 30 days, the study was designed to run for a full year. As a result, extensive metabolism of quinclorac occurred in one system. (EFGWB notes that no data was presented to support this conclusion related to microbial enhancement).

In the EPA review of this study for the 1988 EUP (dated March 18, 1988), the Agency concluded aerobic aquatic degradation seems to be dependent on the origin of the

sediment used. We agree with the reviewer's suggestion that this could be caused by the existence of differing types of microorganisms in different soils. However, we do not agree with the reviewer's opinion that the extreme variation in the metabolism rates in the two soils is so unusual when one considers the enhancement effect and potential dependency on microbes sensitive to the environment, such as pseudomonas for degradation.

Further studies were carried outdoors in order to eliminate artifacts of laboratory systems (MRID No. 41432101, EFGWB Study 11). Specifically, radioactive tracer studies were designed to study both metabolism and leaching under natural conditions. Two sites of diverse soil types and geographical location were selected. One was a North Carolina sandy loam with 0.5% organic matter (OM) and the other an Iowa loam with 3.7% OM. This study was originally submitted to fulfill soil dissipation guideline 164-1 requirements. However, based on the EPA reviews, we recognized that this study is equally suited as a supplementary study for the aerobic soil and aquatic metabolism as well as dissipation guideline studies.

Contrary to the laboratory studies, the field results showed a relatively rapid metabolic breakdown in both soils with half-lives ranging between 30 and 60 days under natural conditions. Concurrent with the breakdown of quinclorac, metabolites were detected in low amounts. Two appeared to be 3-chloro-8-quinolinecarboxylic acid and 2-hydroxy-7-chloro-8-quinolinecarboxylic acid. The important point is there was a relatively rapid decomposition of quinclorac with no significant buildup of any metabolites. From this result it is concluded that soil microbes which readily metabolize quinclorac under natural conditions were altered when tested under artificial laboratory conditions. Under the extended conditions of the aerobic aquatic study which was conducted for 12 months, microbial enhancement quite likely occurred with the high dose 5 ppm treated MS silty clay to utilize quinclorac as a carbon source. It is theorized that the 0.5 ppm quinclorac level was too low in the MS silty clay to effect enhancement and that the microflora of the CA silty loam was different. (EFGWB notes, after reviewing the registrant's responses that Study 11 is still not scientifically valid because of the discrepancy between TRR and parent quinclorac, recovery efficiencies from fortified samples were not provided and there was too much variation in the accountability percentages (material balance). See Section 10.7.1. below for the EFGWB rejoinder to BASF's response).

EFGWB Rejoinder: EFGWB believes that the above explanation is a possible reason for the disparate behavior of quinclorac in the study. It appears that there are four factors (1, 2 and 4 are mentioned above and #3 is mentioned in New Studies 5 and 6) that could influence the behavior of quinclorac in this and other studies:

1. Sensitivity of microorganisms to "artificial" environmental conditions in the laboratory.
2. Microbial enhancement.
3. Sensitivity of microorganisms to storage conditions prior to laboratory use.
4. Lack of specific quinclorac degrading microorganisms.

EFGWB does not accept this response as resolving the original comment. Very little real data was presented to support the Registrant's theory for the disparate behavior.

2. EFGWB Original Comment: From the description of the methodology, it is difficult to determine if the experiments were replicated. Absence of replicates does not allow EFGWB to assess the experimental variation inherent in this type of experiment. 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. Also, if duplicate samples were analyzed, the results should be presented as individual analyses and not just averages.

BASF Response: The value of replicates is debatable and, in fact, not a prescribed guideline requirement. For example, trend analyses can be much more meaningful in interpreting systems and/or models. In this study, it is clear that there was little metabolism in the 0.5 ppm treated sediments and the 5 ppm CA silty loam sediment; whereas, there was extensive degradation in the MS silty clay sediment. In addition to the trend analysis, the precision and accuracy of the analytical procedures were evaluated by determining the material balance or recovery of radioactivity. In this study, the mean % material

balance and standard deviation for the total radioactivity for the 0.5 ppm samples was  $99.1 \pm 5.3$  (n=6).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment since the study showed little degradation of quinclorac. However, EFGWB does not agree with the registrant that "the value of replicates is debatable and, in fact, is not a guideline requirement." There is no way to assess the variation that occurs in soil and analytical procedures without replicates or duplicate determinations.

3. EFGWB Original Comment: Although it was stated that samples were taken immediately posttreatment, no time 0 data were provided and the application rate was not confirmed. The first sampling interval reported for the 0.5 ug/g treatment was 30 days; the first sampling interval reported for the 5.0 ug/g treatment was 4 months.

BASF Response: Referring to MRID No. 40320817 (EFGWB Study 8), analysis of the 0 time sample was not necessary because practically all of the theoretical radioactive dose (99%) was recovered in the subsequent samples taken at later time periods (see Table VI). The application rate was confirmed by direct radioassay of spiked paddy water which was added to the flasks containing sediment. This is stated on page 10 of the report under "Contents of Reaction Flasks" and results are given in Table IV.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. However, EFGWB strongly suggests that in future studies, the registrant collect samples at the start of the study (Time = 0) in order to confirm the application rate.

4. EFGWB Original Comment: Three compounds were isolated from the 5.0 ug/g silty clay soil:water system but were not identified. These compounds reached maximum concentrations of 5% (0.25 ppm), 6.7% (0.33 ppm), and 7.6% (0.38 ppm) of the applied at 12 months posttreatment.

BASF Response: One of these, UNK 3 at 7.6% TRR (0.38 ppm) was methylated and identified by GC/MS and TLC profiles to be a 2-hydroxy-3-chloro-8-quinoline-carboxylic acid. The other two, UNK 4 and 2 at 6.7% TRR (0.33 ppm) and 5.0% TRR (0.25 ppm), had TLC profiles consistent with 7-chloro-8-quinoline-carboxylic acid and 8-quinolinecarboxylic acid, respectively. These results were not given in the original report. However, they have been submitted in a separate report (Wood, N. F. and V. W. Winkler. February 1991. Further identification studies on quinclorac

aerobic soil/sediment metabolites. Registration Document No. 91/5009. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC, MRID 417814-17) to supplement this study.

EFGWB Rejoinder: Upon review of the above mentioned study (see attached DER 7 for the complete review), EFGWB does not accept this response as resolving the original comment. The origin of the material analyzed in the above mentioned supplemental was not clear; the study authors did not specify if this study was a reanalysis of the soil extracts from the original study or extracts from an experiment conducted under similar conditions. The study authors implied that the source of the material was the original extracts [if so, the extracts were stored for approximately four years before reanalysis; storage stability data are required for the maximum time the extracts were stored].

5. EFGWB Original Comment: (1) No quantitative data were provided for the concentration of quinclorac in both soil:water systems treated at 0.5 ug/g. (2) No quantitative data of any kind were provided for the silty clay loam soil:water system treated at 5.0 ug/g. (3) Detailed information about the distribution of [<sup>14</sup>C]residues on the TLC plates was reported only for the silty loam soil:water system treated at 5.0 ug/g.

BASF Response: (1) Quantitative data were provided for the concentration of quinclorac on both soil:water systems treated at 0.5 g/g in Table IV. Confirmation of the dose is seen in Table VI with an average material balance (total radioactive recovery) of  $99.1\% \pm 5.3$  (n=6). The terminal samples shown in Table V have about 75 to 80% extractable residues. These residues were shown in Figure 3 to be essentially all unchanged quinclorac.

(2) Quantitative data for the concentration of the California 5.0 ppm soil:water system was also provided in Table IV. TLC analysis of the terminal 365 day sediment showed all residues essentially to be unchanged quinclorac. Since the 5 ppm dose sample was only to be used to identify metabolites, no further work was done.

(3) Detailed information about the distribution of residue on TLC plates was reported only for the Mississippi soil:water system treated at 5.0 ppm because this was the only system that showed any metabolism.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.



6. EFGWB Original Comment: The units for the CECs of the test soils were not provided.

BASF Response: The units were meq/100 g;

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

7. EFGWB Original Comment: Although the study author reported that the flooded soils treated at 0.5 ug/g were sampled at 0, 7, and 14 days and 1, 2, 4, 6, and 12 months posttreatment and the flooded soils treated at 5.0 ug/g were sampled at 2, 4, 6, and 12 months, data were provided only for the:

(1) 30-, 180-, and 360-day samplings for the 0.5 ug/g treatment, and

(2) 4-, 6-, and 12- month samplings for the 5.0 ug/g treatment.

BASF Response: (1) It was not necessary to analyze all the samplings from the 0.5 ppm treatment because the 30, 180, and 360 day samples clearly showed the only metabolism that occurred was ionic and covalent binding under the test conditions.

(2) The same logic holds for the 5.0 ppm treatments. Only the 4, 6 and 12 month MS silty loam samples showed any metabolism of quinclorac in addition to ionic and covalent binding.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

BASF CONCLUSIONS: Results showed that under the test systems used in this study, only one (MS silty loam at 5.0 ppm) out of four (MS silty loam and CA silty clay at 0.5 and 5.0 ppm, each) resulted in extensive metabolism other than ionic and covalent bonding of parent quinclorac to the sediment.

In the aerobic aquatic study, the major metabolite was shown to be 3-chloro-8-quinolinecarboxylic acid (BH 514-1), the des 7-chloro analog of quinclorac. In addition to BH 514-1, there were three minor metabolites. Although not given in the original report, GC/MS analysis showed one to be a mono-chloro analog of 2-hydroxy-8-quinolinecarboxylic acid. Based on TLC  $R_f$  and GC  $R_t$  values, this metabolite is 2-hydroxy-3-chloro-8-quinolinecarboxylic acid. The other two metabolites had

chromatographic profiles which are consistent with 7-chloro-8-quinolinecarboxylic acid. These results are given in Report M9101 and provide the basis for the initial degradation pathway for quinclorac as shown below in Figure 1.

These results are supplemented by those recently reported in a Ph.D. Thesis which describes the microbial degradation of the major metabolite, 3-chloro-8-quinolinecarboxylic acid (BH 514-1). In this work, pseudomonas spp were isolated which grew on BH 514-1 and led to the degradative pathway given in Figure 2.

In the same work, another bacteria (mycobacterium spp) was isolated from soil which grew on 5-chloro-2-hydroxynicotinic acid and resulted in the isolation of 5-chloro-2,6-dihydroxynicotinic acid. No further degradation products were isolated except mineralization to CO<sub>2</sub> and Cl which was assumed to have gone through the malemate pathway. Based on these results, the Figure 3 presents the proposed degradation scheme for quinclorac.

The methyl ester, A, was not found in this study but probably exists in equilibrium as a minor metabolite. The identified metabolites, B and C show dechlorination and hydroxylation. Progression of degradation to the intermediate D can occur from B or C as well as a number of other similar metabolites from parent quinclorac. The transitory compound, D, will easily "meta cleave" to E which is probably more rapidly degraded to F or G with the cleaving of pyruvic acid in the process. Metabolite G, a hydroxynicotinic acid derivative, proceeds to the maleic (L) and fumaric (M) analogs which are ultimately mineralized to CO<sub>2</sub> and Cl.

EFGWB CONCLUSIONS: EFGWB concludes that the study is still not acceptable for the reasons listed above and does not fulfill the data requirements for an aerobic aquatic metabolism study. The authors should provide supporting information such as the history of soil storage, soil respiration data, quinclorac degradation in fresh soil and in stored soil, microflora characterization, etc., to support the hypothesis presented that the Mississippi soil contained "bacteria which is [sic] very sensitive to environmental conditions" and the California soil did not contain this species. This hypothesis does not, by itself, sufficiently explain the differences in the rates of quinclorac degradation between the soils.

In addition, for such studies, every effort should be made to store and treat the soils in as similar a manner as

possible so as to avoid introducing factors which could result in such disparities resulting from storage conditions. Based on this hypothesis, the argument could be made that this fragile organism may not occur in California soil and therefore was never in the California soil sample in the first place.

EFGWB concludes that this study provides supplemental data that shows quinclorac to be stable in an aerobic aquatic soil environment. Since the registrant has presented evidence that there are important differences between a stored and fresh soil, EFGWB strongly advises that fresh soil be used in any new studies submitted for review. Unless it can be justified to do so, combining soils that originate from stored and fresh soils should be avoided since this will only confuse the issue related to degradation.

10.5.2. New data in support of response to Reviewer's comment to Aerobic Aquatic Metabolism Study (Study 8, MRID 40320817):

1. Wood, N. F. and V. W. Winkler. February 1991. Further identification studies on quinclorac aerobic soil/sediment metabolites. Registration Document No. 91/5009. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplement to: Clark, J. R., BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: aerobic aquatic metabolism, MRID 40320817, BASF registration document No. 87/5034, Report No. M8716. (MRID 417814-17).

This study purports to identify the three degradates from the Mississippi samples of the original Study 8. Because the origin of the material analyzed to identify the three degradates was not clear, EFGWB does not consider the study scientifically valid. The registrant needs to provide more information on the origin of the material used.

See attached DER 7 for the complete review of this study.

2. Brode, S. January 1991. The determination of the electronic properties of quinclorac and its important metabolite BH 514-1 and intermediate E by quantum mechanical Ab initio calculations. Registration Document No. 91/5132. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-18, supplements 40320817).

Because no new data was presented directly relating to the environmental fate of quinclorac, a DER was not prepared

for this study. However, it was reviewed by EFGWB in order to assist in the understanding of the degradation of quinclorac in soil.

This document is a theoretical calculation of bond strengths and partial charges for quinclorac and degradates at the carbon atoms and was presented to show the theoretical basis for considering which degradates would occur in the degradative pathway for quinclorac in soil.

Based on the analysis of the calculated partial charges, replacement of a chlorine by a hydrogen atom would most likely occur at Carbon 7 instead of Carbon 3. This replacement results in the formation of the quinclorac metabolite BAS 514-1. Ring opening of BAS 514-1 between Carbons 8 and 9 is supported by the calculation, which shows this to be the weakest bond in the molecule. The calculation also supports the assumption that the first step of the formation of the intermediate E from BAS 514-1 is an electrophilic attack on the C8-atom, since the calculations show this bond to be the weakest bond.

EFGWB concludes that this report provides supplemental information demonstrating that formation of BH 514-1 and an intermediate E structure from BH 514-1 is theoretically possible by use of quantum mechanical AB initio calculations.

10.5.3. Abstract of Ph.D. thesis and complete translation of Ph.D. thesis in support of Aerobic Aquatic Metabolism Study (MRID 40320817):

Huber, R. November 1988. Microbial degradation of the quinclorac metabolite 3-chloroquinoline-8-carboxylic acid: An abstraction of a Ph.D. Thesis by P. Tibble. University of Hohenheim. Registration Document No. 91/5135. Unpublished study performed by The Institute of Microbiology, University of Hohenheim, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-14, supplements MRID 40320817).

The above abstract was reviewed by EFGWB but not included in this action because the original Ph.D. thesis was reviewed and is included below.

Tibbles, P. 1988. The microbial degradation of 3-chloroquinoline-8-carboxylic acid and 5-chloro-2-hydroxynicotinic acid. BASF Registration Document No. 88/0647. Unpublished Ph.D. dissertation performed at the Institute of Microbiology of Hohenheim University,

Germany. Submitted by BASF Corporation, Research Triangle Park, NC. (MRID 41919601)

EFGWB concludes that this study is scientifically valid and provides supplemental information that indicates BH 514-1 and 5-chloro-2-hydroxynicotinic acid, respectively, are capable of being degraded by isolated strains of Psuedomonas spp. and Mycobacterium spp.

However, EFGWB concludes the registrant has not conclusively shown that this study presents evidence that quinclorac can be expected to degrade in soil to CO<sub>2</sub> as suggested in BASF Registration Document No. 91/5134 (Nelsen, T. R. January 1991. An overview of the environmental fate of quinclorac, page 14). The data as presented show that a bacterial strain, Psuedomonas spp., not from any of the soils studied, but from a starter culture for effluent treatment plants, was able to utilize 3-chloroquinoline-8-carboxylic acid (BH 514-1) as the sole source of C and transform it to 5-chloro-2-hydroxynicotinic acid. Although another bacterial strain, Mycobacterium spp., was isolated from one soil (Greenville, MS) that was able to use 5-chloro-2-hydroxynicotinic acid as the sole source of C, no bacterial strain was isolated from any of the soils studied that was capable of degrading quinclorac or BH 514-1.

See attached DER No. 8 for the complete review of this Ph.D. Thesis.

#### 10.6. 164-1 TERRESTRIAL FIELD DISSIPATION

- 10.6.1. BASF response (MRID 417814-20) to EFGWB review of Study 11: Confined field <sup>14</sup>C-quinclorac (BAS 514 H) dissipation study (MRID 41432101).

BASF Overview: This study was not designed to fulfill the field dissipation guideline requirements but rather to provide additional information regarding the metabolism and leaching of quinclorac under normal field environmental conditions.

Because this study is a confined field study conducted with radiolabelled material, technically, it is neither a guideline field dissipation study nor a guideline soil metabolism study. However, it is an important bridge between both, and provides information useful to the understanding and interpreting of both guideline studies. The study was designed in light of the knowledge that laboratory studies had shown limited and variable

metabolism in soil; while other tests, including biological efficacy trials, indicated dissipation. The data gathered from this study should not be viewed as a "stand-alone" field dissipation study but rather should be viewed in concert with both laboratory soil metabolism and typical field dissipation studies.

1. EFGWB Original Comment: 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.

BASF Response: In reviewing the raw data, an error was found in the calculations used to obtain the TRR values given in Table XIII. The TRR values reported were for 0-6 inch sample depths and the GC/MS values for parent were for 0-9 inch sample depths. Thus, since all the residues were on the surface at  $t = 0$ , the GC/MS values are biased low by about 33% (i.e., 0-9" ppm = 6/9" ppm). A corrected Table XIII with a new % difference column is given below. The column showing % difference between TRR and quinclorac emphasizes the conversion of  $^{14}\text{C}$ -quinclorac into radiolabeled humic material which was the whole point of Table XIII. This will be discussed further after addressing the verification of the application issue.

NORTH CAROLINA 0.5% OM SANDY LOAM

DAT <sup>a</sup>	TRR <sup>b</sup>	PARENT <sup>c</sup>	%ACC <sup>d</sup>	%DIFF <sup>e</sup>
0	0.20	0.131	66	+34
33	0.07	0.112	160	-60
61	0.08	0.029	36	+64
113	0.05	0.065	130	-30
140	0.11	0.012	11	+89
IOWA 3.7% LOAM				
DAT	TRR	PARENT	%ACC	%DIFF
0	0.18	0.193	107	-7
30	0.22	0.195	87	+13
60	0.22	0.086	39	+61
93	0.13	0.071	55	+45
124	0.14	0.025	18	+82

- a) Days after treatment at 0.5 lb ai/A
- b) Total radioactive residues
- c) Determined by GC/MS
- d) % Accountability = (ppm parent/ppm TRR) x 100
- e) % Difference = 100% TRR - % GC/MS Accountability

It can be seen from this table that the application rates were verified by both total radioactive residues and GC/MS analysis of parent. The theoretical 0-9 inch TRR value for 0.5 lb ai/A rates is ca 0.17 ppm versus 0.18 and 0.20 ppm found for Iowa and North Carolina, respectively. The theoretical value is based on the rule of thumb that 1 acre of soil 0 to 3 inches deep weighs  $1 \times 10^6$  lbs. Thus 0.5 lb/0-9 inch acre equals  $0.5 \text{ lb} / 3 \times 10^6 \text{ lb} = .17 \text{ ppm}$ . GC/MS accountability values were 106 and 66%, respectively for Iowa and North Carolina. It is recognized that analytical variances were inherently high because these were only single analyses. Thus, high variance is probably the reason for parent values being higher than TRR for the North Carolina 33 and 113 DAT samples. However, when analyzed by linear regression, the effect of the variances in the GC/MS analytical results are greatly minimized to the point of essentially not being significant.

Test solution volumes and concentrations were also confirmed by analytical measurement immediately prior to treatment (Table I). Therefore, there is no doubt as to

the verification of the application rates. The error in calculating the % accountability is regrettable, but the data given in Table XIII was not intended to be used for verification of application rates. Rather it was intended to show that <sup>14</sup>C-quinclorac dissipated by decomposition relatively rapidly to nondescriptive polar degradative or humic material rather than by leaching. This was addressed in the report on page 18 under the GC/MS section of the Residue Characterization discussion.

"Although there was variation, ranging from 42% to 102%, the overall accountability was good for 0 and ca 30 DAT samples with an average value of 70%." [This statement was intended to show that not much decomposition had occurred within 30 DAT and that most of the TRR was in fact parent]. The accountabilities decreased to about 10% for the last sampling period for both soil sites presumably because of metabolism to humic material. [This process can be seen by the % difference (TRR less quinclorac) increasing trend over time shown in Table XIII above]. "Since there was no accumulation of metabolites greater than 7% of the initial amount of applied quinclorac, metabolite breakdown rate must be faster than that for quinclorac."

The review focused on the verification of application and the 58 and 29% TRR that was not accounted for in the initial sample rather than the fact that the point was to show degradation to humic materials. Nevertheless, in response to this concern, there is clear evidence for verification of application rates. The concentration and volumes of the test solutions were measured before treatment; the soil radioactivity levels corresponded to both the 0.5 and 1.0 lb ai/A rates with 0-3" TRR values at ca 0.5 and 1.0 ppm, respectively; and the 0.5 ppm application was confirmed by GC/MS. Therefore, there is no doubt that meaningful conclusions can be reached regarding the dissipation of quinclorac from these soils or any other parameter of interest, for that matter.

EFGWB Rejoinder: EFGWB cannot accept this response as satisfying the original comment. The theoretical application rate was calculated to be 0.17 ppm, and the determined rate, based on TRR and after correction for error, averaged 0.19 ppm in the two soils.

Since the TRR analysis verified the application rate, it is difficult to understand why the analysis of parent by GC/MS did not verify it also. Only 66% of the TRR added to the North Carolina soil was parent quinclorac. The question still remains of what happened to the other 34%.



Sampling variation may explain variability from one sampling date to the next. However, it is difficult to believe that this variability would occur within each sample collected for analysis, especially if the soil was ground to a fine powder in a blender prior to analysis of TRR by combustion and parent quinclorac by GC-MS. Were separate samples collected for TRR and GC/MS analysis?

There is also the possibility that the extraction technique used for GC/MS evaluation is quite variable.

2. EFGWB Original Comment: 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<sub>2</sub>. They stated that "laboratory studies (Study 6) showing approximately 5% metabolized to CO<sub>2</sub> in 30 days gives strong support to this contention." The authors did not explain why there was no metabolism to CO<sub>2</sub> 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 degradation 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<sub>2</sub> production for longer than 28 days.

BASF Response: The variation in the material balance was a concern but not discussed because it seemed obviously to be a function of the limited number of sample cores taken at each time period. Also the variation did not significantly affect the dissipation analysis since this was a radiotracer study. Clearly it would have been better to take more samples but the plot size of ca 21 sq ft made this impossible.

Differences in the dissipation between the two sites could be attributed to leaching or metabolism. Since there was no evidence to show mass leaching to account for 40% loss of material balance, a possible route of dissipation was thought to be mineralization to CO<sub>2</sub>.

Thus, the laboratory respiration study (study 6) was conducted to confirm if the North Carolina soil was capable of mineralizing quinclorac to CO<sub>2</sub>. A respiration study was not conducted with the Iowa soil because there was no apparent loss of mass balance. Reasons for differences in metabolism between these sites could be attributed to a number of factors such as temperature, binding capacity, and pH, all of which can affect microbial populations involved in metabolism. This was, in fact, recognized by Dr. Paul Mastradone (EFGWB) in his environmental fate review for the quinclorac EUP and has been discussed in detail in the response to the EPA Data Evaluation Record for the aquatic aerobic metabolism studies (Guideline 162-3).

The validity of the laboratory respiration study on the North Carolina soil (Study 6) has been discussed separately. The rationale for conducting this study for 28 days will be discussed below in item 3.

EFGWB Rejoinder: EFGWB can accept the rationale that the variable material balance data might be due to the limited number of samples taken at each date. However, since the registrant probably was aware that limited number of samples would impact the variation, larger plots should have been utilized so sufficient samples could have been collected to take care of this contingency. The fact remains that the data is too variable to accurately assess the dissipation of quinclorac residues.

3. EFGWB Original Comment: The CO<sub>2</sub> 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.

BASF Response: The sole purpose of the laboratory respiration study was to demonstrate that the North Carolina sandy loam was capable of relatively rapid mineralization of quinclorac to CO<sub>2</sub>. However, we certainly agree that such data are often incapable of predicting trends outside their range for a variety of reasons. In fact, with quinclorac it is clear that the laboratory results showing little soil degradation have no predictive value for what actually happens in the environment. The major explanation for this discrepancy is that natural conditions cannot be maintained in an artificial environment. This was the main reason

nonstored fresh soils were used in the respiration study. The 5% conversion to CO<sub>2</sub> after 28 days was believed to be a good indicator for a route of material balance loss in the North Carolina test site. Extending the time to 8 months under natural conditions to account for 30 to 40% of the material balance was used as a possibility and not a fact. Unfortunately, clearly showing mineralization to CO<sub>2</sub> is not possible under field conditions.

EFGWB Rejoinder: EFGWB recognizes that under the conditions of the experiment, microorganisms in the North Carolina sandy loam soil used in this study are capable of converting quinclorac to CO<sub>2</sub> and therefore, accepts this response as resolving the original comment. However, EFGWB does not believe as stated in the registrant's response above that "the North Carolina sandy loam was capable of relatively rapid mineralization of quinclorac to CO<sub>2</sub>." EFGWB does not consider 5% conversion of quinclorac to CO<sub>2</sub> in 30 days to be relatively rapid, in fact, it is slow. Furthermore, there is no way to assess the variation that occurs in soil and analytical procedures without replicates or duplicate determinations. Therefore, extrapolation of this data to a longer time period is not justified without some measurement of variation and the determination of CO<sub>2</sub> for longer time periods.

4. EFGWB Original Comment: 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 then increased to 69% on later sampling days. Similarly, no explanation was given for the disparate behavior of TRR in soil samples collected from Iowa.

BASF Response: This comment is a repeated concern stated in Item 2. The basic reason for the variation is attributed to the small number of sampling cores (1 to 3) taken at each time period, and inherent distribution variances of applied test material under field conditions. However, the effect of such variation is greatly minimized with radioactive studies because the relative amount of degradation and metabolites can be determined based on the sample TRR.

EFGWB Rejoinder: EFGWB does not accept this response as satisfying the original comment. Although the variation can be attributed to small number of sampling cores taken at each time period, it is also possible that the original

material was not applied evenly to the plots; therefore, making the data too variable to accurately assess the dissipation of quinclorac residues.

Also, EFGWB does not agree with the rationale that the variation is greatly minimized by the use of radioactive materials, since the sampling variation would also affect the amount of TRR in the sample and consequently the quantity determined at each sampling time.

The technique used to determine TRR could also be variable in extracting capability.

5. EFGWB Original Comment: 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 that 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.

BASF Response: As discussed, TRR variances are not an issue in evaluating quinclorac dissipation with respect to metabolism and mobility, primarily because the relative ratio of parent to total nonvolatile residues are easily measured. Also the leaching profiles of parent and all metabolic degradative products are measured at very low levels. The mass balance changes in the North Carolina and Iowa sites simply reflect the distribution variances of radioactive test substance which are seen with the small number of samples taken per sampling interval. The variation is greater in North Carolina than Iowa because only one sample was taken compared to three. The important point, however, is this is a supplementary study conducted for discovery purposes in the natural environment. Furthermore, the experiment was replicated at two sites with two rates at each site and in all cases showed good correlation between dissipation routes and no buildup of metabolites.

EFGWB Rejoinder: EFGWB cannot accept this response as satisfying the original comment. Although the variation can be attributed to small number of sampling cores taken at each time period, it is also possible that the material was not applied evenly to the plots; therefore, making the data too variable to accurately assess the dissipation of quinclorac residues.

Also, as mentioned above, EFGWB does not agree with the rationale that the variation is greatly minimized by the use of radioactive materials, since the sampling variation would also affect the amount of TRR in the sample and consequently the quantity determined at each sampling time. Also at issue is the possibility that the extraction procedure is variable resulting in the discrepancy between TRR and residues.

6. EFGWB Original Comment: 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 not 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.

BASF Response: A description of how many soil samples were taken per test is given in Tables IX and X under footnote C. The small plot size (21 sq ft) limited the number of cores taken per time period.

EFGWB Rejoinder: Although EFGWB accepts this response in resolving the original comment, this does not relieve the registrant from collecting sufficient number of samples to minimize variation.

7. EFGWB Original Comment: 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.

BASF Response: The test plots were known not to have previously received any radioactive treatments. Also, results clearly show there were no radioactive residues in treated plots other than quinclorac immediately after application. For these reasons, it did not seem necessary

to report that control samples taken immediately adjacent to the test plot were found to contain no radioactive residues.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

8. EFGWB Original Comment: 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.

BASF Response: When working with a radioactive test substance, this information is obtained with the initial t=0 samples. The extraction recoveries for the North Carolina and Iowa t=0 samples were quantitative. For North Carolina, 89% TRR was extracted as free residues and 6% as ionically bound residues. These values can be calculated from Table XI. TLC analysis showed the residues to be exclusively parent quinclorac. The TLC results were not reported because they were not considered to be necessary since quinclorac was also analyzed by GC/MS. The t=0 Iowa soils were not fractionated into free, ionically bound, covalently bound and nonextractable residues because such data did not seem relevant. However, there can be little doubt that the extraction recovery was good because the GC/MS results agreed with the TRR value with an accountability of 107%.

The overall GC/MS recovery for the t=0 and 30 DAT samples was stated to be ca 70% TRR in the report. However, after correcting for the calculation error this value becomes 105% (see corrected Table XIII given in the Item 1 response).

EFGWB Rejoinder: EFGWB does not accept this response in resolving the original comment. It appears that the registrant has misunderstood the original comment. EFGWB was referring to recovery of quinclorac from control samples that had been fortified. This is needed to present some data related to the efficiency of the extractants used.

Furthermore, in answer to the above response, even after correcting for the calculation error there is still too much variation in the accountability percentages (average = 107%, range = 66-160%).

BASF CONCLUSIONS: Scientifically, all questions have been addressed to show this to be a valid study. Because this is a special study, it should be considered supplementary

to both soil metabolism and field dissipation guideline studies. Results obtained in this study are very meaningful in assessing the environmental fate of quinclorac.

First and foremost, contrary to laboratory studies, this study showed under normal field environmental conditions quinclorac was metabolized with half-lives ranging from ca 30 to 60 days. Furthermore, there were metabolites in trace amounts which did not accumulate, thus supporting a microbial degradative pathway to humic materials and/or CO<sub>2</sub> as the terminal metabolic products. Equally important is the fact that there was no evidence to indicate leaching of parent or degradates beyond 12 inches in low organic matter sandy loam and 9 inches in high organic matter loam. The sensitivity limit of 0.005 ppm is 5 to 10 times lower than otherwise obtainable using conventional analytical methods. The predictive value of this study is demonstrated by the fact that the mobility and dissipation profiles were confirmed by five conventional turf dissipation studies (MRID Nos. 641403505-A-E). Therefore, this study explains more about what happens to quinclorac in the environment than the guideline laboratory soil metabolism, absorption, and photolysis studies which showed no degradation of quinclorac.

EFGWB CONCLUSIONS: EFGWB concludes, after reviewing the registrant's responses that this study is not scientifically valid. The following deficiencies in the study and responses are still noted:

1. The discrepancy between TRR and parent quinclorac: The TRR verified the initial application; however, only 66% of the TRR was parent quinclorac. Recovery efficiencies from fortified samples were not provided. This information may have helped in explaining the difference in TRR and parent quinclorac.
2. There was too much variation in the accountability percentages (material balance). This variation could be caused by insufficient sampling and/or the extraction technique used for GC/MS evaluation is quite variable.

Since the registrant believes that this study is an important bridge between soil metabolism and field dissipation studies, it probably should be repeated taking into account the above mentioned criticisms of the study and the suggestions contained in the Standard Evaluation Procedure for Terrestrial Field Dissipation Studies. The

registrant should also consider using larger plots so that sufficient samples can be collected to reduce variation, and that the extraction technique used is adequate.

10.7. 164-2 AQUATIC FIELD DISSIPATION

10.7.1. BASF response (MRID 417814-21) to EFGWB review of Study 17:  $^{14}\text{C}$ -quinclorac confined field aquatic dissipation study in rice paddy water (MRID 41063565).

1. EFGWB Original Comment: (a) The application rate was not confirmed by collecting soil samples as suggested by Subdivision N Guidelines §164-2 (d)(4). Although quinclorac was applied to soil in the plot under nonflooded conditions, an immediate posttreatment soil sample was not taken. Therefore, the dissipation of quinclorac from the test site could not be adequately evaluated.

(b) This was further confounded by the periodic removal of 10-20% of the water for use on other plots, and replenishing the plots with a like quantity of water.

BASF Response: (a) The soil data for this study was included in the confined rotation crop report (Study 21; MRID 41063566). It can be seen in context with the water data in this reply, Table 2.

(b) It is true that this study was complicated by the periodic removal of a portion of the flood water. However, the impact on residue dissipation was slight. It can be seen from Table 1 of the report (Table 2 in this reply) that the residues declined even during the period when no water was removed for irrigation; that is, from June 13 to July 3, residues declined from 0.013 ppm to 0.004 ppm. Altogether, not more than about 20% of the original water residue was removed in these aliquots, even while residues remaining in the plot declined by >90% (see calculation following):

Calculation of  $^{14}\text{C}$  residues removed for irrigation:

Volume of water layer = 151 to 302 liters; i.e.  $4 \times 8 \times (2-4 \text{ in. deep}) \times (2.54 \text{ cm/in})^3 10 \text{ cm /L}$

Total dose in water June 13 = 2.0 to 4.0 mg; i.e.,  $[0.013 \text{ ppm} \times \text{mg/kg} \times 1 \text{ kg/L} \times (384 \text{ to } 767)\text{L}]$

Total dose removed for irrigation = 0.41 mg; i.e.,  $[24\text{L} \times (0.013 + 0.002 + 0.002 + <0.001 \text{ ppm})]$



$$\% \text{ Removed} = \frac{0.41 \text{ mg}}{2 \text{ to } 4 \text{ mg}} \times 100\% = 10 \text{ to } 20\%$$

EFGWB Rejoinder: (a) EFGWB accepts this response in confirming the application rate. EFGWB notes that the rate determined in the time = 0 sample (0.424 ppm) was 75% of the target application rate.

(b) EFGWB concludes that the periodic sampling of the flood water probably had minimal impact on the residues in the water. However, of greater concern is the variation in quinclorac concentration in the sampled water. For example, on DAT 8-15, 22, 28, 36, 59 and 77, the concentration of quinclorac were 0.013, 0.005, 0.007, 0.009, 0.013, 0.008, 0.009, 0.011, 0.011, 0.004, 0.002, 0.001 and <0.001, respectively.

2. EFGWB Original Comment: The experiment was not replicated in regards to treatments.

BASF Response: Replicate plots were not prepared; the guidelines do not require this. However, replicate soil core measurements were made during the rotation crop phase of the study. These are presented in Tables II, VI and VII of the study, and are combined here in Table 2 of this reply.

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment. However, there is no way to assess the variation that occurs in soil and analytical procedures without replicates or duplicate determinations.

3. EFGWB Original Comment: No pretreatment samples were taken to confirm that the site had not been contaminated with the test substance prior to the initiation of the study.

BASF Response: Pretreatment samples, per se, are not usually taken for radioactive studies. The history of radioactive plots on the BASF test farm was known, precluding the possibility that this <sup>14</sup>C test material had been previously applied to this plot. Control samples were taken from adjacent, untreated plots; the analyses of these samples would not be reported as they are used only in the raw data to correct for background radioactivity.

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment.

4. EFGWB Original Comment: The study author stated that quinclorac residues in the water were determined to be exclusively parent quinclorac, based on TLC analysis of the

water samples. However, the TLC radioscan do not support this conclusion (Figures 5-8); the TLC radioscan show that quinclorac decreased with time from 96.15% of the recovered radioactivity at 7 days posttreatment (immediately after flooding) to 67.92% of the recovered at 98 days posttreatment (91 days after flooding). The question still remains as to what was the disposition of the other 32.08%.

BASF Response: Quinclorac residues were the only measurable, discrete residues found in all the water samples. There were no measurable levels of any degradation product. In the case cited, that of the 98 day sample, note that the water concentration was <1 ppb (<0.001 ppm). There may have been quinclorac degradation products in this sample, but the amounts were much too low for analysis. Visual inspection of the TLC scan does not show a single discrete peak which could represent 32% of TRR. Thus, there may possibly be several products present, at <0.2 ppb each (<0.001 ppm x 22% in the "hottest" TLC region #1). If so, they could not be identified at those levels. By the same logic, the maximum degradation product concentration could not be more than 0.2 ppb at 28 days (0.004 ppm x 6%) or 0.1 ppb at 63 days (0.001 ppm x 10%).

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment.

5. EFGWB Original Comment: It was stated that the water samples were frozen prior to analysis; however, the length of storage and the storage temperature were not reported. In a freezer storage stability study (STUDY ID 41063571 and 41063570, Study 28), it was determined that quinclorac residues were stable for up to 6 months in pond water that was stored frozen at <-5° C.

BASF Response: Water was sampled June through September, 1984. They were analyzed in February, 1987. Thus, they were stored for 30-33 months. Data was previously submitted showing quinclorac stability for 6 months of storage in water (Study 29; MRID 41063570) and 36 months in a soil:sediment mixture (Study 28; MRID 41063572). Elsewhere in this reply is new data (MRID 417814-33) showing stability in water up to 17 months [Eswein, R. January 1991. Freezer storage stability of quinclorac (BAS 514 H) in water - 15-17 month analysis. BASF Registration Document No. 91/5015]. This stability study is ongoing.

In the results of this particular study, storage stability could play only a minor role. The relative amounts of quinclorac in the samples would not change. Since the samples were all analyzed at the same time, there would be

only a 3 month difference in storage time, and in Study 29 (MRID 41063571) it was demonstrated that there was no degradation for at least 6 months. Thus, there would be no significant difference in the amount of degradation, if any, between 30 and 33 months. If anything, since the 0-day samples were stored for the longest time period, the only effect could have been to slightly depress the apparent dissipation rate by lowering the initial concentration measurement.

EFGWB Rejoinder: EFGWB does not accept this response in resolving the original comment. In the above referenced freezer storage stability of quinclorac in water, EFGWB concludes that quinclorac is stable for up to 17 months in the particular water used in the stability study (For a complete review of the study see the DER for Study 9). However, since the samples in this study were stored for up to 33 months prior to analysis, it will have to be demonstrated that quinclorac is stable up to 33 months.

Furthermore, it should be mentioned that the value of the data from the water stability data is limited to those particular pond water samples since the water was not characterized. See comments below.

6. EFGWB Original Comment: Characteristics of the test water, including pH and dissolved oxygen content, were not reported.

BASF Response: The test water was not analyzed for pH or dissolved oxygen content. There is no requirement for this data in either the aquatic metabolism or aquatic dissipation guidelines, nor in the anaerobic aquatic metabolism SEP.

EFGWB Rejoinder: These characteristics are needed to demonstrate that the physical, chemical and biological parameters of the pond water are within normal ranges.

EFGWB notes that Subdivision N Guidelines Section 160-5 (c)(9)(ii) state: "In cases of aquatic field tests, characteristics of water obtained from a use site must be reported (e.g., pH, temperature, oxygen content, flow rate, and percent suspended solids)."

7. EFGWB Original Comment: Meteorological data were incomplete. The only temperature and precipitation data provided for the study period were monthly averages (Figures 3 and 4); minimum and maximum daily temperatures and total daily precipitation data for the duration of the study period were not provided. However, the study author stated

that daily temperature and precipitation records were available.

BASF Response: Daily weather data for the test site in the period May 1 through October 31, 1984, is included here as Table 3.

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment.

8. EFGWB Original Comment: Sampling procedures used to collect the water samples were not described; the sampling technique, the number of samples collected at each sampling interval, and the depth at which the water samples were taken were not reported.

BASF Response: Water was dipped from the paddy with a glass beaker, then poured into a plastic bottle, which was frozen. Since the water in rice paddies is only about 4" deep, it is not possible to take samples at different depths. Only one sample was taken at each interval.

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment. Perhaps the lack of sufficient samples was the reason for the variation in quinclorac concentration in the sampled water as mentioned in #1 above.

9. EFGWB Original Comment: EFGWB prefers that [<sup>14</sup>C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R<sub>f</sub> of reference standards.

In this study, the sample extracts were analyzed using one-dimensional TLC with one solvent system. Radioactive areas on the TLC plate were identified only by comparison to the location of known reference standards. It is unclear if reference standards were cochromatographed on the same plate or were chromatographed separately.

BASF Response: Standard practice was to chromatograph standards on each TLC plate, adjacent to the sample extracts.

EFGWB Rejoinder: Upon consideration of the response and further review of the original study, EFGWB does not accept this response in resolving the original comment. EFGWB needs to know if any confirmatory techniques such as GC/MS were used to identify the quinclorac residues. With out

confirmation, it is difficult to conclusively identify the residue solely based on comparison to unlabeled reference standards. It is strongly suggested that the registrant use confirmatory methods, such as GC/MS, for identifying residues of concern in future studies submitted to EFGWB for review.

10. EFGWB Original Comment: In a description of the analytical methodology, it was stated that aliquots of the water samples were "adjusted to 0.1 N hydrochloric acid" prior to extraction. Apparently, this is a typographical error, and the pH that the water was adjusted to using 0.1 N hydrochloric acid was inadvertently omitted.

BASF Response: A review of the raw data shows that 1 mL of 1N HCl was added per 100 mL of water sample, bringing the sample to 0.01N HCl. (The "0.1N" is a typographical error in the report.) The standard practice was to check for acidic conditions with pH paper.

EFGWB Rejoinder: EFGWB accepts this response in resolving the original comment.

11. EFGWB Original Comment: Recovery efficiencies for quinclorac were not provided.

BASF Response: Total radioactivity recoveries were used as a measure of accountability, not quinclorac per se, since there may have also been other (degradation) products present to be measured.

EFGWB Rejoinder: EFGWB does not accept this response in resolving the original comment. It appears that the registrant did not understand the original comment. What is needed is analytical method recovery of quinclorac in soil and water to verify that the method of extraction, separation, etc. was removing substantially all the material from the matrix. This can be accomplished using fortified control samples.

12. EFGWB Original Comment: It was stated that the recoveries of total radioactivity in ethyl acetate extracts of water samples taken at 7, 35, 70, and 98 days posttreatment averaged 80%, and ranged from 70 to 90%. Since recoveries at each sampling interval were not provided, data for the amount of parent quinclorac recovered from the extracts could not be converted to percent of the applied radioactivity.

BASF Response: Total radioactivity recoveries for the ethyl acetate extractions were as follows:

<u>Days After Treatment</u>	<u>Sample</u>	<u>% TRR</u>	<u>PPB TRR</u>
7	84-6	81	0.013
35	84-88	84	0.002
70	84-118	90	0.001
98	84-131	ca.66	<0.001

Total counts for the 98 day sample were too low to quantify accurately.

Accountability as quinclorac for each sample, then, was:

<u>Days After Treatment</u>	<u>% TRR Extracted</u>	<u>TLC</u>	<u>Minimum Quinclorac % TRR</u>	<u>PPB</u>
7	81	96	78	10
35	84	92	77	1.5
70	90	85	77	0.8
98	ca.66	68	ca.45	<0.5

Note that in no case, even that of the 7 days posttreatment sample, is there sufficient radioactivity (>10 ppb) present as unknowns to require identification.

The quinclorac accountability for the samples from 7-70 days after treatment are comparable. Only in the 98 day sample, when the levels were extremely low (<1 ppb) is there a problem with the accountability.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

13. EFGWB Original Comment: This study was not conducted using a typical end-use product; instead, the radiolabelled active ingredient that was used was dissolved in acetone.

BASF Response: As previously stated, this study was not intended to completely fulfill the 164-2 guideline requirement. Radio labelled studies are not typically performed with a formulated test substance, since the formulation would have no impact on the nature of the degradation products.

The typical end use product is a wettable powder formulation which is applied as a dilute aqueous suspension. In a study like this, the carrier (whether water or acetone) would have little influence once the solution dries on the soil surface. Either one would give a uniform dispersion.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

14. EFGWB Original Comment: The conditions in this study were not typical of actual use conditions. The plot was (4 x 8 feet, 1 foot depth) was enclosed on the bottom and sides, with the walls extending 1 foot above the plot, so that water could not flow either vertically below the 1-foot soil depth or horizontally outside of the plot. However, it is not clear what impeded the movement of water past the 1-foot soil depth.

BASF Response: The test plot was constructed of heavy clay soil from a commercial rice paddy, filled to a depth of 4 feet below the surface. The plot was prepared 6 months before application of the test material, to allow for compaction, resembling normal rice fields. Surrounding the plot, below soil level, was 1 foot of the plastic-covered aluminum frame, plus an additional 2 feet of plastic sheeting. These were designed to prevent horizontal water movement down to 3 feet below the surface. Nothing prevented downward water movement except the natural tendency of these soils to swell and form a clay seal when wet. As far as was possible, then, this was a natural, miniature rice paddy. The fact that it was capable of holding a flood shows that the soil formed a seal, as expected, preventing leaching.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

15. EFGWB Original Comment: The study author stated that the probable causes for dissipation of the test substance were dilution of residues by replacement of water removed from the plot, and a reduction of residues by plant uptake and absorption and/or diffusion into the soil. This reviewer notes that these causes of dissipation may be correct. However, until positive proof is presented in the form of acceptable data, the conclusions as to route of dissipation remain highly speculative. The question that still remains is how quinclorac dissipates from the aquatic system.

BASF Response: The author also states that "dissipation could also result from photolytic and microbial actions". As addressed elsewhere, in replies to Studies 2-4 (MRID's 41063560, 41063564A/B), photolysis is a very significant contributor to dissipation in natural waters, and may well be the primary mechanism of loss (Reference 6).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. However, EFGWB agrees,

based on reviews of other studies, that photolytic and microbial action, plant uptake, and adsorption and/or diffusion into the soil may all be modes of dissipation of quinclorac from aquatic systems. At the present time, EFGWB can not determine, with any degree of confidence, what relative portion, the above modes of dissipation have in the degradation of quinclorac.

EFGWB CONCLUSIONS: After thoroughly reviewing the original study and the responses to original comments, EFGWB concludes that this study still does not meet the data requirements for an Aquatic Field Dissipation Study. Because of the variation in the data, no definitive conclusion can be reached regarding a half-life of quinclorac in the rice paddy water. Moreover, no conclusion can be reached regarding the half-life in the soil, since insufficient number of samples were collected during the study, and only 13% of the original amount applied remained when the second sample was collected.

Furthermore, insufficient data was presented to determine if quinclorac is stable in stored frozen water. Water samples were stored frozen for 30-33 months before analysis; however, storage stability results are only presented for 17 months.

Also, there were no data on recovery from fortified samples that would support the belief that the extraction techniques used, i.e., combustion and chemical, were adequate.

10.7.2. BASF response (MRID 417814-22) to EFGWB review of Study 18: Quinclorac aquatic field dissipation study in Chico, CA (MRID 41063564-A-C, -F, -I, 41063568, -69, -70).

1. EFGWB Original Comment: In this study, sampling was inadequate to accurately assess the dissipation of quinclorac from the soil of the test plot. Although more than 50% of the quinclorac dissipated from the floodwater between 0 and 14 days posttreatment, soil was sampled only at one interval during this time period (7 days posttreatment). Therefore, it cannot be determined if losses of quinclorac from the water were due to movement of quinclorac into the soil, to the degradation of quinclorac in the water, or to the loss of water from the system.

BASF Response: The study was designed based on the information available to us at the time from laboratory studies. Thus, moderately slow water solution and slow sediment degradation rates were expected. For these reasons, water sampling was scheduled mainly for the first



portion of the study, and soil sampling was evenly distributed throughout the study.

The manager of the facility where the field portion of the study was done has confirmed that no water was drained from the field until September 13 (90 DAT). The water level was allowed to drop on June 30 (15 DAT) to expose the broadleaf weeds for the Basagran herbicide treatment (This drop was accomplished by not pumping any water into the plot and allowing the water in the plot to evaporate). The water depth was brought back up after 24 hours. Thus, the loss of quinclorac should not be due to the loss of water from the system, but is due to degradation in the soil and/or water phases.

EFGWB Rejoinder: EFGWB does not accept the response as resolving the original comment. EFGWB still maintains that soil sampling was inadequate to assess the dissipation of quinclorac from the test plot. Although this alone does not invalidate the study scientifically, the lack of this information makes it difficult to determine rate of dissipation from the soil. Furthermore, as discussed below under No. 8, only 40% of the amount applied was recovered in the water. Sampling the soil nearer the time of application could have helped in confirming the application rate.

2. EFGWB Original Comment: Freezer storage stability data were inadequate for quinclorac in water samples and for 3-chloro-8-quinolinecarboxylic acid in soil samples. Water samples from this study were stored frozen for up to 14 months before analysis; however, freezer storage stability of quinclorac in water was only studied for 6 months (Study 28, MRIDs 41063571 and 41063570). It was reported that a freezer storage stability study of quinclorac in natural water for the entire period the samples were stored is currently in progress. The soil samples in this study were stored frozen for up to 20 months before analysis; however, adequate data for the storage stability of 3-chloro-8-quinolinecarboxylic acid were not available (Study 27, MRID 41063572). Freezer storage stability data were adequate for quinclorac in soil; quinclorac was stable in soil frozen for up to 36 months (Study 27, MRID 41063572).

BASF Response: Additional storage stability data have been obtained which demonstrate that quinclorac is stable in frozen water for at least 17 months (BASF Registration Document No. 91/5015) and that 3-chloro-8-quinolinecarboxylic acid is stable in frozen soil for at least 21 months (BASF Registration Document No. 91/5016).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. See DERs for the complete review of Studies 9 (storage stability in water) and 10 (storage stability in soil).

3. EFGWB Original Comment: The water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. The registrant concluded that it was not necessary to analyze water samples for 3-chloro-8-quinolinecarboxylic acid based on analysis of water samples taken from an aquatic field dissipation study (Study 17, MRID 41063565) at 7, 35, 70, and 98 days posttreatment (0, 28, 63, and 91 days after flooding). Although 3-chloro-8-quinolinecarboxylic acid was not detected in these water samples, most of the quinclorac had degraded by the second sampling interval; total quinclorac residues declined from 13 ppb at 7 days posttreatment to 2 ppb at 35 days posttreatment. It is possible that 3-chloro-8-quinolinecarboxylic acid may have been present at 7 and 35 days posttreatment.

BASF Response: As stated by the reviewer, the registrant concluded analysis of water samples for 3-chloro-8-quinolinecarboxylic acid was not necessary based on the results of Study 17 (MRID 41063565). In that study, the metabolite would have been detected if it had been present. The TLC method of analysis used in study 17 could detect 3-chloro-8-quinolinecarboxylic acid and was calibrated using both quinclorac and 3-chloro-8-quinolinecarboxylic acid standards. The detection limit for 3-chloro-8-quinolinecarboxylic acid is about 0.2 ppb in the water with the procedure used (see response to question 4, study 17, BASF Registration Document No. 91/5011). Thus, we believe our original conclusion is still correct.

EFGWB Rejoinder: EFGWB still maintains that the water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. It has been demonstrated that dissipation of quinclorac varies between locations. Therefore, it can not be assumed that degradation products of quinclorac would be the same at different locations, since Study 17 (MRID 41063565) was performed in MS, while this study was conducted in CA.

4. EFGWB Original Comment: The study authors stated that batch equilibrium data (Study 10) explain why 3-chloro-8-quinolinecarboxylic acid was not detected in the water. They concluded that since  $K_d$  values for 3-chloro-8-quinolinecarboxylic acid were 11-30 for three soils, 3-chloro-8-quinolinecarboxylic acid will strongly adsorb to soil. However,  $K_d$  values of 11-30 indicate that 3-chloro-8-quinolinecarboxylic acid is not tightly bound to soil;

therefore, 3-chloro-8-quinolinecarboxylic acid would be expected to be in the water if it is present in the field plots under flooded conditions. Thus, the arguments presented by the registrant do not support the conclusion that it was not necessary to analyze the water samples for 3-chloro-8-quinolinecarboxylic acid.

BASF Response: The batch equilibrium data based argument was poorly stated. The intended conclusion is that since 3-chloro-8-quinolinecarboxylic acid is more strongly bound to soil (ca 40 X) than quinclorac, for equal soil concentrations of the two compounds, the water concentration of quinclorac will be ca 40 times greater than the water concentration of 3-chloro-8-quinolinecarboxylic acid. We were not trying to imply that  $K_d$  values of 11-30 meant strong binding to soil.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. EFGWB notes that  $K_d$  values between 11-30 probably indicate moderate binding to soil.

5. EFGWB Original Comment: Soil samples taken below the 0- to 6-inch depth were not analyzed; therefore, the extent of leaching could not be determined. Prior to September 13, soil cores collected from the plots were 24 inches long; after September 13, soil cores were collected from the plots were 36 inches long.

BASF Response: The guideline for 164-2 requires only 15 cm soil core sample and only 5 cm sediment core samples. The greater than 6-inch depth sediment samples were collected for possible future analysis if significant residues were present in the sediment. We are not certain how valid any of the deeper core samples taken during the flood are due to the effects of compression during sampling under the saturated conditions (That is, the depth of deeper core samples cannot be accurately determined). For these reasons it was decided not to analyze these samples.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. As has been previously mentioned, the guidelines are not protocols and are to be used by the registrant as guidance in performing studies. Because this chemical appears to have the characteristics of a chemical that leaches, it would be prudent to analyze the samples to determine if any had moved below the 6 inch depth. This information would assist EFGWB in determining the environmental fate of quinclorac.

6. EFGWB Original Comment: Quinclorac was applied as a tank mix with BAS 090 02 S (1 qt/A) instead of as a single active

ingredient formulation. Data requirements for combination products and tank mix uses are currently not being imposed; therefore, this study was reviewed for the aquatic dissipation data requirement. If this study had been acceptable, the registrant would have had to demonstrate that the presence of BAS 090 02 S does not affect the dissipation of quinclorac.

BASF Response: BAS 090 025 is not a pesticide, it is a proprietary spray tank adjuvant developed by BASF. It is similar to Crop Oil Concentrate in its use and effects. For postemergent applications, the use of spray tank adjuvants is recommended by BASF.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The effect of the adjuvant on the dissipation of quinclorac will have to be demonstrated.

7. EFGWB Original Comment: A half-life of 54 days was calculated by the study authors for the dissipation of quinclorac from soil; however, since soil samples were not taken until 7 days posttreatment, and this was the only sampling interval at which quinclorac was detected, a dissipation half-life for quinclorac in soil cannot be accurately calculated. Therefore, the dissipation half-life calculated by the study authors was not reported in this review.

BASF Response: The sediment sampling schedule was based on the expected (from laboratory studies) slow degradation rate (see 1). Based on the available data a half-life was calculated. We agree that an accurate dissipation half-life for quinclorac in sediment cannot be calculated based on the limited data available.

What is important is that the quinclorac has dissipated from both the sediment and water phases prior to harvest.

EFGWB Rejoinder: EFGWB agrees that quinclorac has dissipated from the water phase prior to harvest, since sufficient water samples were collected and analyzed that showed this. However, since quinclorac was only detected in the soil samples collected at 7 days posttreatment, it is difficult to suggest anything about soil dissipation without collecting and analyzing soil samples collected earlier in the study. EFGWB is especially concerned about quinclorac residues in soil since it has the characteristics of a chemical that can leach.

8. EFGWB Original Comment: Water and soil samples taken immediately posttreatment from the treated plot showed that approximately 40% of the applied was recovered (Table IX). The registrant attributed the loss of applied quinclorac to interception of quinclorac by rice plants.

BASF Response: This explanation of a ca 40% recovery of applied material is reasonable based on results from our confined field study. (See Study 17 responses, BASF Registration Document No. 91/5011.)

In this study <sup>14</sup>C-labeled quinclorac was applied at the rate 0.75 pounds/acre to a drained 4 x 8 foot plot planted with six rows of 3-5 leaf rice. The rice plants contained 35 ppm of residues 3 days after application (rice metabolism study, Table V, MRID 41063534). The initial concentration of soil residues in the 0- to 4-inch profile is only 0.424 ppm, rather than the expected 0.6-0.7 ppm (study 21, MRID 41063566). Thus, the possibility of significant plant interception of spray is confirmed.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The data in Table IX also demonstrates that the application material balances for the other rice dissipation studies (Studies 19 and 20). In those studies, application material balances for the flooded part of the experiments were 105 and 117%, respectively, for the experiments in TX and MS. This seems to imply that very little of the material was intercepted by the rice plants in these studies.

9. EFGWB Original Comment: Although the majority of soil samples were analyzed using the analytical method A8903, fortified soil samples were analyzed only using the analytical method A8901. In the study conducted in Mississippi (Study 19) using clay soil that was analyzed by method A8903, recoveries from soil samples fortified at 0.05-0.5 ppm ranged from 66 to 103% for quinclorac, and from 56 to 98% for 3-chloro-8-quinolinecarboxylic acid.

BASF Response: The soil fortification recovery results are given in Table IV of report A8915 (MRID 41063564-F). Since the majority of the samples containing residues were analyzed by Method A8903, the majority of the fortification recovery results were obtained by Method A8903.

Early time period (0 through 60 days) soil samples were analyzed by the HPLC Method A8903 (MRID 41063569). Since residues were detected in most of these samples, recoveries at several fortification levels were done. Recoveries by Method A8903 from soil samples fortified by 0.05-0.5 ppm

ranged from 78-91% for quinclorac (5 examples) and from 63-87% for 3-chloro-8-quinolinecarboxylic acid (5 examples).

Later time period samples (60 through 316 days) were analyzed by the GC/MS Method A8901 (MRID 41063568). Since these samples contained low or non-detectable residues only, single fortification recoveries by Method A8901 were done at 0.05 ppm. These recoveries are 90% for quinclorac and 64% for 3-chloro-8-quinolinecarboxylic acid.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. However, EFGWB notes that 64% recovery for 3-chloro-8-quinolinecarboxylic acid indicates that the method is not sensitive to the degradate.

10. EFGWB Original Comment: The question that still remains is what is the route of quinclorac dissipation from aquatic systems.

BASF Response: The field studies reported here (studies 17, 18, 19, 20, and 21) and those cited in the new aqueous photolysis overview paper (Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Report No. ER91004. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC., MRID 417814-05) all have a common outcome; rapid dissipation of the quinclorac. Significant water losses from all these paddies does not seem to be the explanation. Uptake by the rice plants, sediment metabolism, and/or degradation in the water layer seem to be reasonable dissipation routes.

Laboratory aquatic sediment metabolism and sterile, deionized water photolysis studies do not predict the rapid dissipation seen in the field studies.

One explanation for this disparity lies in the fact that although quinclorac has limited UV absorption, the compound rapidly undergoes photolysis in water containing photosensitizing agents such as humic acids, tryptophan, tyrosine, riboflavin and hydrogen peroxide. This facilitated photooxidation reaction is not unique to quinclorac but has been demonstrated for a large variety of xenobiotics.

Some examples of this photosensitized decomposition were included as study 3 (MRID 41063564-A) and study 4 (MRID 41063564-8). Additional examples and further details are given in the previously cited aqueous photolysis overview paper.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. Although it appears that photodegradation is the main route of degradation in aquatic systems, EFGWB still can not determine conclusively how it dissipates and what the degradates are.

EFGWB CONCLUSIONS: EFGWB concludes that this study is scientifically valid and provides supplemental information related to the dissipation of quinclorac from rice floodwater. This study does not satisfy the data requirements for an aquatic field dissipation study because:

1. Sampling was inadequate to assess the dissipation of quinclorac from the soil of the test plot.
2. The application rate was not confirmed.
3. Furthermore, insufficient data was presented in relation to storage of quinclorac in water. Water samples were stored for 30-33 months before analysis; however, storage stability results are only presented for 17 months.

EFGWB concludes that quinclorac in the rice floodwater study dissipated with a half-life of approximately 9 days.

10.7.3. BASF response (MRID 417814-01) to EFGWB review of Study 19: Quinclorac aquatic field dissipation study in Leland, MS (MRID 41063565-A-C, -E, -H, 41063569, 41063570).

1. EFGWB Original Comment: In this study, sampling was inadequate to accurately assess the dissipation of quinclorac from the soil of the test plots.

(a) In the plot treated while under flooded conditions, quinclorac in the water declined from 805-922 ug/kg immediately posttreatment to 12-106 ug/kg at 1 day posttreatment; however, no soil samples were taken at 1 day posttreatment. Therefore, it cannot be determined if losses of quinclorac from the water are due to movement of quinclorac into the soil or due to the degradation of quinclorac in the water.

(b) In the plot treated before flooded conditions, the soil was sampled too infrequently. Quinclorac declined from a maximum concentration of 0.143-0.241 mg/kg at 1 day posttreatment to 0.041-0.52 mg/kg at the next sampling interval of 31 days posttreatment. Although the plot was flooded at 15 days posttreatment, no soil samples were taken immediately prior to and after flooding, and water was not

sampled until two days after flooding. Therefore, the effect of flooding on the dissipation of quinclorac from the soil could not be assessed.

BASF Response: The reviewer made a typographical error in paragraph two. The determined concentration range for quinclorac is 0.041-0.052 mg/kg at 31 days posttreatment, not 0.041-0.52 mg/kg. Also, the first water sample was taken one day postflooding, not two.

The study was designed based on the information available to us at the time from laboratory studies. Thus, moderately slow water solution and slow sediment degradation rates were expected. For these reasons, water sampling was scheduled mainly for the first portion of the study, and soil sampling was evenly distributed throughout the study.

(a) In the flooded conditions study, we acknowledge that by taking no sediment samples in the first week, we cannot establish the quinclorac did not move into the sediment in this field study. However, the measured  $K_d$  values for quinclorac do not predict that this compound will move into the soil. And the results obtained in the laboratory aerobic aquatic metabolism study (Study 8, MRID 40320817) indicate that the quinclorac preferentially remains in the aqueous phase (after 30 days 68-78 percent of the applied quinclorac is in the aqueous phase). Thus, the loss of quinclorac is probably due to degradation in the water.

(b) In the plot treated before flooded conditions, the soil sampling schedule was based on the results obtained from the laboratory terrestrial aerobic soil metabolism study (study 5, MRID 41247302). The monthly soil sampling schedule seems appropriate when compared to the lab results.

The director of the facility where the field portion of this study was done has confirmed that once flood was established, it was not removed until just prior to harvest. Thus, the losses of quinclorac should not be due to the loss of water from either test plot, but are due to degradation in the soil and/or water phases.

EFGWB Rejoinder: (a) EFGWB does not accept this response as resolving the original comment. EFGWB notes that analysis of the floodwater on the day of treatment resulted in an application material balance of approximately 117%. This seems to indicate that all of the quinclorac applied was in the floodwater and little, if any, in the soil at the time of sampling. However, at one day posttreatment, the quinclorac concentration declined to approximately 7% of that applied. Therefore, without adequate soil sampling, it cannot be



determined if losses of quinclorac from the water are due to movement of quinclorac into the soil and subsequent degradation or due to the degradation of quinclorac in the water.

(b) EFGWB does not accept this response as resolving the original comment. Insufficient soil samples were collected and analyzed that would yield any indication of the dissipation of quinclorac from the soil. Without this information an assessment of the half-life in soil would not be accurate.

2. EFGWB Original Comment: Freezer storage stability data were inadequate for quinclorac in water samples and for 3-chloro-8-quinolinecarboxylic acid in soil samples. Water samples from this study were stored frozen for up to 14 months before analysis; however, freezer storage stability of quinclorac in water was only studied for 6 months (Study 28, MRIDs 41063571 and 41063570). It was reported that a freezer storage stability study of quinclorac in natural water for the entire period the samples were stored is currently in progress. The soil samples in this study were stored frozen for up to 21 months before analysis, however, adequate data for the storage stability of 3-chloro-8-quinolinecarboxylic acid were not available (Study 27, MAID 41063572). Freezer storage data were adequate for quinclorac in soil; quinclorac was stable in soil frozen for up to 36 months (Study 27, MAID 41063572).

BASF Response: Additional storage stability data have been obtained which demonstrate that quinclorac is stable in frozen water for at least 17 months (BASF Registration Document No. 91/5015) and that 3-chloro-8-quinolinecarboxylic acid is stable in frozen soil for at least 21 months (BASF Registration Document No. 91/5016).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

3. EFGWB Original Comment: The water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. The registrant concluded that it was not necessary to analyze water samples for 3-chloro-8-quinolinecarboxylic acid based on analysis of water samples taken from an aquatic field dissipation study (Study 17, MRID 41063565) at 7, 35, 70, and 98 days posttreatment (0, 28, 63, and 91 days after flooding). Although 3-chloro-8-quinolinecarboxylic acid was not detected in these water samples, most of the quinclorac had degraded by the second sampling interval; total quinclorac residues declined from 13 ppb at 7 days posttreatment to 2 ppb at 35 days posttreatment. It is

possible that 3-chloro-8-quinolinecarboxylic acid may have been present at 7 and 35 days posttreatment.

The study authors also stated that batch equilibrium data (Study 10) explain why 3-chloro-8-quinolinecarboxylic acid was not detected in the water. They concluded that since  $K_d$  values for 3-chloro-8-quinolinecarboxylic acid were 11-30 for three soils, 3-chloro-8-quinolinecarboxylic acid will strongly adsorb to soil. However,  $K_d$  values of 11-30 indicate that 3-chloro-8-quinolinecarboxylic acid is not tightly bound to soil; therefore, 3-chloro-8-quinolinecarboxylic acid would be expected to be in the water if it is present in the field plots under flooded conditions. Thus, the arguments presented by the registrant do not support the conclusion that it was not necessary to analyze the water samples for 3-chloro-8-quinolinecarboxylic acid.

BASF Response: As stated by the reviewer, the registrant concluded analysis of water samples for 3-chloro-8-quinolinecarboxylic acid was not necessary based on the results of study 17 (MRID 41063565). The TLC method of analysis used in study 17 could detect 3-chloro-8-quinolinecarboxylic acid and was calibrated using both quinclorac and 3-chloro-8-quinolinecarboxylic acid standards. The detection limit for 3-chloro-8-quinolinecarboxylic acid is about 0.2 ppb in the water with the procedure used (see response to question 4, study 17). Thus, we believe our original conclusion is still correct.

The batch equilibrium data based argument was poorly stated. The intended conclusion is that since 3-chloro-8-quinolinecarboxylic acid is more strongly bound to soil (ca 40 X) than quinclorac, for equal soil concentrations of the two compounds, the water concentration of quinclorac will be ca 40 times greater than the water concentration of 3-chloro-8-quinolinecarboxylic acid. We were not trying to imply that  $K_d$  values of 11-30 meant strong binding to soil.

EFGWB Rejoinder: EFGWB still maintains that the water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. Because quinclorac declined to less than 7% of the applied 1 day after treatment, it is possible that 3-chloro-8-quinolinecarboxylic acid was present in this and subsequent samples.

EFGWB accepts the explanation related to the batch equilibrium data.

4. EFGWB Original Comment: Soil samples taken below the 0- to 6-inch depth were not analyzed; therefore, the extent of leaching could not be determined. The soil cores collected

from the plots treated under flooded conditions were 16-18 inches long; the soil cores collected from the plots treated under nonflooded conditions were 42-48 inches long.

BASF Response: The guideline for 164-2 requires only 15 cm soil core samples and only 5 cm sediment core samples. The greater than 6-inch depth sediment samples were collected for possible future analysis if significant residues were present in the sediment. We are not certain how valid any of the deeper core samples taken during the flood are due to the effects of compression during sampling under the saturated conditions. (That is, the depth of deeper core samples cannot be accurately determined.) For these reasons it was decided not to analyze the deeper core samples.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. As has been previously mentioned, the guidelines are not protocols and are to be used by the registrant as guidance in performing studies. Because this chemical appears to have the characteristics of a chemical that leaches, it would be prudent to analyze the samples to determine if any had moved below the 6 inch depth. This information would assist EFGWB in determining the environmental fate of quinclorac.

5. EFGWB Original Comment: The depth to the water table in the plots was not reported.

BASF Response: The depth to ground water in Sharkey clay soil is about forty feet during the growing season in the MS delta region.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

6. EFGWB Original Comment: Quinclorac was applied as a tank mix with BAS 090 02 5 (1 qt/A) instead of as a single active ingredient formulation. Data requirements for combination products and tank mix uses are currently not being imposed; therefore, this study was reviewed for the aquatic dissipation data requirement. If this study had been acceptable, the registrant would have had to demonstrate that the presence of BAS 090 02 5 does not affect the dissipation of quinclorac.

BASF Response: BAS 090 025 is not a pesticide, it is a proprietary spray tank adjuvant developed by BASF. It is similar to Crop Oil Concentrate in its use and effects. For postemergent applications the use of spray tank adjuvants is recommended by BASF.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The effect of the adjuvant on the dissipation of quinclorac will have to be demonstrated.

7. EFGWB Original Comment: Soil samples taken immediately posttreatment for the plot treated under nonflooded conditions showed that approximately 51% of the applied was recovered in the soil (Table IX). The registrant attributed the loss of applied quinclorac to interception of quinclorac by rice plants.

BASF Response: This explanation of a ca 50% recovery of applied material is reasonable based on results from our confined field study. (See Study 17 responses, BASF Registration Document No. 91/5011.)

In this study 14C-labeled quinclorac was applied at the rate of 0.75 pounds/acre to a drained 4 x 8 foot plot planted with six rows of 3-5 leaf rice. The rice plants contained 35 ppm of residues 3 days after application (rice metabolism study, Table V, MRID 41063534). The initial concentration of soil residues in the 0- to 4-inch profile is only 0.424 ppm, rather than the expected 0.6-0.7 ppm (study 21, MRID 41063566). Thus, the possibility of significant plant interception of spray is confirmed.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The data in Table IX also demonstrates that the application material balances for the other rice dissipation studies (Studies 18 and 20). In those studies, application material balances for the flooded part of the experiments were approximately 105 and 40%, respectively, for the experiments in TX and CA. Based on those results, it is difficult to conclude whether or not there was plant interception of the material.

The registrant needs to explain the disparate results.

8. EFGWB Original Comment: Half-lives of 14 and 18 days were calculated by the study authors for the dissipation of quinclorac from water in the plot treated under nonflooded conditions. However, since water samples were not taken until 2 days after flooding (17 days posttreatment), and concentrations of quinclorac in water did not steadily decrease with time, a dissipation half-life for quinclorac cannot be accurately calculated. Therefore, the dissipation half-lives calculated by the study authors were not reported in this review.

BASF Response: Water samples were taken 1, 3, 5, 7, 14, 31, and 62 days after establishing flood (17, 19, 21, 23, 30, 47, and 78 days posttreatment). One way to view the results is that a quinclorac water concentration plateau is established at ca 15 ppb for the first 14 days of the flood. By the thirty-first day after flooding, the quinclorac water concentration has dropped to ca 6 ppb. And by the sixty-second day after flooding, the quinclorac water concentration has dropped to ca 1 ppb.

Since quinclorac residues are apparently being transferred between the sediment and water phases during the first days after flooding, a simple dependence between time and quinclorac concentration in the water does not exist. Thus, we agree with the reviewer that an accurate dissipation half-life for quinclorac in the water phase cannot be calculated using the data. However, when only the data from 14 days after flooding and later are considered, a half-life for quinclorac in the water of ca two weeks can be estimated. The important point is that the quinclorac rapidly dissipates in the water phase.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. EFGWB agrees that quinclorac has dissipated from the water phase prior to harvest, since sufficient water samples were collected and analyzed that demonstrate this. However, since only one soil sample was collected and analyzed prior to flooding, and no soil samples were collected until approximately 2 weeks after flooding, it is difficult to suggest anything about migration of quinclorac to the water phase and subsequent dissipation.

9. EFGWB Original Comment: The concentration of quinclorac in individual water samples taken at 1 day posttreatment from the plot treated under flooded conditions was variable, ranging from 12 to 106 ug/kg (Table VI).

BASF Response: Since water is added to rice paddies on a daily basis to make up for evaporation and plant transpiration losses, these water samples are probably taken too soon after water addition. Thus, a quinclorac concentration gradient across the rice paddy was measured (lowest concentrations are nearest the addition point of the make-up water). This gradient did not have a major impact on the calculated half-life since all the data points were used in the calculations.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment related to the reason for the variation in quinclorac concentration in the water samples. However, EFGWB believes that the data is still too variable.

EFGWB CONCLUSIONS: EFGWB concludes that this study is scientifically valid and provides supplemental information related to the dissipation of quinclorac from rice floodwater. This study does not satisfy the data requirements for an aquatic field dissipation study because:

1. Sampling was inadequate to assess the dissipation of quinclorac from the soil of the test plots.
2. The application rate was not confirmed in the plots treated prior to flooding.
3. Furthermore, insufficient data was presented in relation to storage of quinclorac in water. Water samples were stored for 30-33 months before analysis; however, storage stability results are only presented for 17 months.

EFGWB concludes that quinclorac in the rice floodwater dissipated with an apparent half-life of approximately 10 days. Since insufficient soil samples were collected from the plots, a half-life of quinclorac in the soil can not be estimated.

10.7.4. BASF response (MRID 417814-23) to EFGWB review of Study 20: Quinclorac aquatic field dissipation study in East Bernard, TX (MRID 41063565A-D, -G, 41063568, 41063570).

1. EFGWB Original Comment: In this study, sampling was inadequate to accurately assess the dissipation of quinclorac from the soil of the test plots.

(a) In the plot treated under flooded conditions, quinclorac in water declined from 756 ug/kg immediately posttreatment to 191 ug/kg at 1 day posttreatment; however, no soil samples were taken at 1 day posttreatment. Therefore, it cannot be determined if losses of quinclorac from the water are due to movement of quinclorac into the soil or due to the degradation of quinclorac in the water.

(b) In the plot-treated under nonflooded conditions, the soil was sampled too infrequently. Sixty-one percent of the quinclorac dissipated from the soil between the second and third sampling intervals (1 and 41 days posttreatment); quinclorac in the soil declined from 0.146 mg/kg at 1 day posttreatment to 0.057 mg/kg at 41 days posttreatment. In addition, although the plot was flooded at 8 days posttreatment, no soil samples were taken immediately prior to and after flooding; therefore, the effect of flooding on the dissipation of quinclorac from the soil could not be assessed.

BASF Response: The study was designed based on the information available to us at the time from laboratory studies. Thus, moderately slow water solution and slow sediment degradation rates were expected. For these reasons, water sampling was scheduled mainly for the first portion of the study, and soil sampling was evenly distributed throughout the study.

(a) In the flooded conditions study, we acknowledge that by not taking more sediment samples in the first week, we cannot establish the quinclorac did not move into the sediment in this field study. However, the measured  $K_d$  values for quinclorac do not predict that this compound will move into the soil. And the results obtained in the laboratory aerobic aquatic metabolism study (Study 8, MRID 40320817) indicate that the quinclorac preferentially remains in the aqueous phase (after 30 days 68-78 percent of the applied quinclorac is in the aqueous phase). Thus, the loss of quinclorac is probably due to degradation in the water.

(b) In the plot treated before flooded conditions, the soil sampling schedule was based on the results obtained from the laboratory terrestrial aerobic soil metabolism study (Study 5, MRID 41247302). The approximately monthly soil sampling schedule seems appropriate when compared to the lab results.

The director of the facility where the field portion of this study was done has confirmed that once flood was established, it was not removed until just prior to harvest. This water removal was done by just allowing the water to evaporate. Thus, the losses of quinclorac should not be due to the loss of water from either test plot, but are due to degradation in the soil and/or water phases.

EFGWB Rejoinder: EFGWB does not accept the response as resolving the original comment. EFGWB still maintains that soil sampling was inadequate to assess the dissipation of quinclorac from the test plots. Although this alone does not invalidate the study scientifically, the lack of this information makes it difficult to determine the dissipation half-life in the soil.

(a) It appears that the application rate to the flooded plot was confirmed by analysis of quinclorac in the floodwater on the day of application (105% application material balance). However, one day after application, the amount in the floodwater had decreased from 756 ug/kg to 191 ug/kg. More frequent soil samples may have helped to verify whether or not quinclorac was moving into soil.

2. EFGWB Original Comment: Freezer storage stability data were inadequate to assess the stability of quinclorac in water samples and 3-chloro-8-quinolinecarboxylic acid in soil samples. The water samples in this study were stored frozen for up to 27 months before analysis; however, freezer storage stability of quinclorac in water was only studied for 6 months (Study 28, MRIDs 41063571 and 41063570). It was reported that a freezer storage stability study of quinclorac in natural water for the entire period that samples were stored is currently in progress. The soil samples in this study were stored frozen for up to 33 months before analysis; however, adequate data for the storage stability of 3-chloro-8-quinolinecarboxylic acid were not available (Study 27, MRID 41063572). Freezer storage stability data were adequate for quinclorac in soil; quinclorac was stable in soil frozen for up to 36 months (Study 27, MRID 41063572).

BASF Response: Additional storage stability data have been obtained which demonstrate that quinclorac is stable in frozen water for at least 17 months (BASF Registration Document No. 91/5015) and that 3-chloro-8-quinolinecarboxylic acid is stable in frozen soil for at least 21 months (BASF Registration Document No. 91/5016). These studies are continuing.

Since no degradation is observed for 17 to 21 months, it is reasonable to project that no significant degradation will occur within 27 to 33 months. The registrant will inform EPA of further results from these storage stability studies as they become available.

EFGWB Rejoinder: Until EFGWB reviews acceptable data that shows no significant degradation under storage conditions, EFGWB does not accept this rationale as resolving the original comment.

3. EFGWB Original Comment: The water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. The registrant concluded that it was not necessary to analyze water samples for 3-chloro-8-quinolinecarboxylic acid based on analysis of water samples taken from an aquatic field dissipation study (Study 17, MRID 41063565) at 7, 35, 70, and 98 days posttreatment (0, 28, 63, and 91 days after flooding). Although 3-chloro-8-quinolinecarboxylic acid was not detected in these water samples, most of the quinclorac had degraded by the second sampling interval; total quinclorac residues declined from 13 ppb at 7 days posttreatment to 2 ppb at 35 days posttreatment. It is possible that 3-chloro-8-quinolinecarboxylic acid may have been present at 7 and 35 days posttreatment.



The study authors also stated that batch equilibrium (Study 10) data explain why 3-chloro-8-quinolinecarboxylic acid was not detected in the water. They concluded that since  $K_d$  values for 3-chloro-8-quinolinecarboxylic acid were 11-30 for three soils, 3-chloro-8-quinolinecarboxylic acid will strongly adsorb to soil. However,  $K_d$  values of 11-30 indicate that 3-chloro-8-quinolinecarboxylic acid is not tightly bound to soil; therefore, 3-chloro-8-quinolinecarboxylic acid would be expected to be in the water if it is present in the field plots under flooded conditions. Thus, the arguments presented by the registrant do not support the conclusion that it was not necessary to analyze the water samples for 3-chloro-8-quinolinecarboxylic acid.

BASF Response: As stated by the reviewer, the registrant concluded analysis of water samples for 3-chloro-8-quinolinecarboxylic acid was not necessary based on the results of study 17 (MRID 41063565). In that study, the metabolite would have been detected if it had been present. The TLC method of analysis used in study 17 could detect 3-chloro-8-quinolinecarboxylic acid and was calibrated using both quinclorac and 3-chloro-8-quinolinecarboxylic acid standards. The detection limit for 3-chloro-8-quinolinecarboxylic acid is about 0.2 ppb in the water with the procedure used (see response to question 4, study 17, BASF Registration Document No. 91/5011). Thus, we believe our original conclusion is still correct.

The batch equilibrium data based argument was poorly stated. The intended conclusion is that since 3-chloro-8-quinolinecarboxylic acid is more strongly bound to soil (ca 40 X) than quinclorac, for equal soil concentrations of the two compounds, the water concentration of quinclorac will be ca 40 times greater than the water concentration of 3-chloro-8-quinolinecarboxylic acid. We were not trying to imply that values of 11-30 meant strong binding to soil.

EFGWB Rejoinder: EFGWB still maintains that the water samples should have been analyzed for 3-chloro-8-quinolinecarboxylic acid. Because quinclorac declined to less than 25% of the applied 1 day after treatment, it is possible that 3-chloro-8-quinolinecarboxylic acid was present in this and subsequent samples.

EFGWB accepts the explanation related to the batch equilibrium data and notes that  $K_d$  values of 11-30 indicate moderate binding to soil.

4. EFGWB Original Comment: Soil samples taken below the 0- to 6-inch depth were not analyzed; therefore, the extent of leaching could not be determined. Prior to June 21, soil

cores were collected with a 12-inch hand probe; after June 21, 36-inch long cores were collected from each plot.

BASF Response: The guideline for 164-2 requires only 15 cm soil core samples and only 5 cm sediment core samples. The greater than 6-inch depth sediment samples were collected for possible future analysis if significant residues were present in the sediment. We are not certain how valid any of the deeper core samples taken during the flood are due to the effects of compression during sampling under the saturated conditions. (That is, the depth of deeper core samples cannot be accurately determined.) For these reasons it was decided not to analyze the deeper core samples.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. As has been previously mentioned, the guidelines are not protocols and are to be used by the registrant as guidance in performing studies. Because this chemical appears to have the characteristics of a chemical that leaches, it would be prudent to analyze the samples to determine if any had moved below the 6 inch depth. This information would assist EFGWB in determining the environmental fate of quinclorac.

5. EFGWB Original Comment: Quinclorac was applied as a tank mix with Basagran (3.0 lbs ai/A) instead of as a single active ingredient formulation. Data requirements for combination products and tank mix uses are currently not being imposed; therefore, this study was reviewed for the aquatic field dissipation data requirement. If this study had been acceptable, the registrant would have had to demonstrate that the presence of Basagran does not affect the dissipation of quinclorac.

BASF Response: Table I in Report No. E8919 (MRID 41063564-8) is in error when it states the Basagran herbicide and quinclorac were applied as a tank mix. Both products were applied on the same day in both tests, but they were applied at separate times. The quinclorac containing product was applied just after dawn in both cases, and the Basagran herbicide was then applied at about eleven o'clock.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment, since it is not known if the adjuvant BAS 090 02 5 was used in this particular study. If it was used then the effect of the adjuvant on the dissipation of quinclorac will have to be demonstrated.

6. EFGWB Original Comment: Soil samples taken immediately posttreatment for the plot treated under nonflooded conditions showed that approximately 57% of the applied was

recovered in the soil (Table IX). The registrant attributed the loss of applied quinclorac to interception of quinclorac by rice plants.

BASF Response: This explanation of a ca 57% recovery of applied material is reasonable based on results from our confined field study. (See responses to Study 17, BASF Registration Document No. 91/5011.)

In this study 14C-labeled quinclorac was applied at the rate of 0.75 pounds/acre to a drained 4 x 8 foot plot planted with six rows of 3-5 leaf rice. The rice plants contained 35 ppm of residues 3 days after application (rice metabolism study, Table V, MRID 41063534). The initial concentration of soil residues in the 0- to 4-inch profile is only 0.424 ppm, rather than the expected 0.6-0.7 ppm (study 21, MRID 41063566). Thus, the possibility of significant plant interception of spray is confirmed.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The data in Table IX also demonstrates that the application material balances for the other rice dissipation studies (Studies 18 and 20). In those studies, application material balances for the flooded part of the experiments were approximately 105 and 40%, respectively, for the experiments in TX and CA. Based on those results, it is difficult to conclude whether or not there was plant interception of the material.

7. EFGWB Original Comment: There is a discrepancy in the reported half-lives of quinclorac in the soil. In one original report (MRID 41063564-D), it was stated that the half-lives of quinclorac were 53 and 54 days in the plots treated under nonflooded and flooded conditions, respectively. However, in the summary report (MRID 41063564-8), it was stated that the half-lives of quinclorac were 70 and 105 days in the plots treated under nonflooded and flooded conditions, respectively; since these half-lives more accurately reflect the actual data, these values were reported in this review.

BASF Response: The registrant agrees with the reviewer that the quinclorac soil half-lives of 70 and 105 days are more accurate.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

8. EFGWB Original Comment: A half-life of 10.3 days was calculated by the study authors for the dissipation of quinclorac from water in the plot treated under nonflooded conditions. However, since water samples were not taken

until 11 days after flooding (19 days posttreatment), and concentrations of quinclorac in water did not steadily decrease with time, a dissipation half-life for quinclorac cannot be accurately calculated. Therefore, the dissipation half-life calculated by the study authors was not reported in this review.

BASF Response: Water samples were taken 11, 14, 33, and 54 days after establishing flood (19, 22, 41, and 62 days posttreatment). Similarly to what occurred in non-flood application of Study 19, a quinclorac water concentration plateau is established at ca 20 ppb for, in this case, the first approximately 30 days. The quinclorac residues in the water drop to less than 1 ppb by 54 days after flooding.

The registrant agrees with the reviewer that an accurate dissipation half-life for quinclorac in water cannot be calculated using this data. However, the data do indicate that quinclorac rapidly dissipates in the water.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. EFGWB agrees that quinclorac has dissipated from the water phase prior to harvest, since sufficient water samples were collected and analyzed that demonstrate this. However, since no soil samples were collected and analyzed immediately prior to flooding, and no soil samples were collected until approximately 4 weeks after flooding, it is difficult to suggest anything about migration of quinclorac to the water phase and subsequent dissipation.

EFGWB CONCLUSIONS: EFGWB concludes that this study is scientifically valid and provides supplemental information related to the dissipation of quinclorac from rice floodwater. This study does not satisfy the data requirements for an aquatic field dissipation study because:

1. Sampling was inadequate to assess the dissipation of quinclorac from the soil of the test plots.
2. The application rate was not confirmed in the plots treated prior to flooding.
3. Furthermore, insufficient data was presented in relation to storage of quinclorac in water. Samples were stored for 30-33 months before analysis; however, storage stability results are only presented for 17 months.

EFGWB concludes that quinclorac in the rice floodwater dissipated with an apparent half-life of approximately 7 days. Since insufficient soil samples were collected from

the plots, a half-life of quinclorac in the soil can not be estimated.

EFGWB CONCLUSIONS RELATED TO AQUATIC FIELD DISSIPATION

STUDIES: The aquatic field dissipation studies submitted all provide supplemental data that show quinclorac dissipates from rice floodwater with half-lives from 7-21 days. The studies were not acceptable because sampling was inadequate to assess dissipation of quinclorac from the soil of the test plots, the application rate was not confirmed and insufficient data was presented regarding the storage of water samples containing quinclorac for 30-33 months. One recurring problem with these studies is the fact that insufficient soil samples were collected for analysis. This information may have assisted in ascertaining the dissipation of quinclorac from aquatic systems.

10.7.5. Supplementary report in support of studies related to Subdivision N Guideline No. 164-2--Aquatic Field Dissipation. Blasland & Bouck Engineers. 1991. Assessment of quinclorac potential to leach to ground-water from labelled uses on rice in the southern United States. BASF Registration Document No. 91/5133. Unpublished study performed by Blasland & Bouck Engineers, Syosset, NY and submitted by BASF Corporation, Research Triangle Park, NC. (MRID 41781425)

This report does not contain any original data, therefore no DER was prepared. This document was submitted by the registrant to supplement previously submitted aquatic field dissipation studies in response to EPA concerns about ground water contamination by quinclorac. This document is a compilation of information regarding the soil characteristics and hydrogeology of the rice-growing areas in the southern United States in relation to the potential for quinclorac to leach to ground water in those areas. As such, the document does not contain experimental data, but rather presents a descriptive overview of production practices, hydrogeological conditions, and soils of two distinct regions, the Mississippi Alluvial Plain and the Gulf Coastal Plain. As such, this document provides useful information regarding the potential for leaching of quinclorac in these regions and the possibility for ground water contamination following labelled uses of quinclorac on rice.

In summary, the study authors concluded that use of quinclorac in rice culture in these areas is not expected to be problematic from a ground water contamination standpoint. In general, soils in Louisiana, Mississippi, Missouri, and Texas that are used for rice culture are of extremely limited permeability. Viable aquifers are separated from the soil

surface by significant distances and materials separating the surface soils from the aquifers are of limited permeability.

Five soil series out of 125 were identified as "vulnerable" to pesticide leaching, and are considered marginal for rice production due to potential problems with flood maintenance. The study authors stated that these marginal soils, located only in Arkansas, present little danger to viable aquifers, since the aquifers are separated by some distance from the surface soils and contain restrictive layers that prevent the surface waters from reaching the aquifer. These "marginal" soils are estimated by the Soil Conservation Service as moderately permeable, but do not exhibit the textures of problematic leaching soils (sand content >75% and organic matter content <2%).

With regard to potential ground water contamination, the authors stated that leakage from confining units to shallow aquifers is restricted by hydrologic conditions of flow and storage. Secondly, in areas where long-term, heavy withdrawals of ground water have induced upward water movement from deeper aquifers, the downward movement of rice pesticides (such as quinclorac) from the surface is inhibited. The authors also noted that rice production on these soils is limited and occurs mainly when market conditions are favorable.

EFGWB CONCLUSIONS: EFGWB concludes that this report provides supplemental information demonstrating that the use of quinclorac in rice culture according to label directions should not result in ground water contamination. However, this is based on the region as a whole and does not take into account specific soils where leaching might occur if quinclorac is used on soils marginally suited for rice production.

- 10.7.6. BASF response (MRID 417814-24) to EFGWB review of Study 28: Freezer storage stability of quinclorac residues (BAS 514 H) and its metabolite (BH 514-1) in aquatic sediment (MRID 41063572).

Overview: The objective of this study was to show the stability of quinclorac and its 7-deschloro metabolite, BH 514-1 in soil sediment under frozen storage conditions. A California aerobic aquatic sample which showed no metabolism of quinclorac after 7 days incubation and 40 months frozen storage was analyzed and showed no loss of quinclorac. The reviewer accepted this validity of this result.

A Mississippi 4 month aerobic aquatic sample which had been stored frozen for 19 months before analysis was used to show

minimum storage stability of BH 514-1. This sample consisted of 55.8% quinclorac, 31.7% BH 514-#, 9.5% unidentified nonvolatiles and 3% unaccounted residues. The unaccounted residues were presumed to be evolved CO<sub>2</sub> since the 6 month incubated samples had produced 6% CO<sub>2</sub>. Quinclorac was assumed to be stable since there was no loss in the California sample. Quinclorac is also hydrolytically stable.

A worse case scenario for a minimum 19 month frozen storage stability of 76.9% was calculated for BH 514-1. However, the reviewer stated the Mississippi results were unacceptable because it could not be determined if degradation occurred during the incubation or during the frozen storage period. Our response to this is since the results were reported for the minimum storage stability profile, it makes no difference at which point the degradation occurred. Therefore, both the California and Mississippi results should be used to help predict the behavior of quinclorac and BH 514-1 when stored under frozen conditions.

1. EFGWB Original Comment: Soil:water samples from California and Mississippi were not analyzed prior to storage. In the portion of this study conducted using the soil from Mississippi, it cannot be determined if degradation of quinclorac and 3-chloro-8-quinolinecarboxylic acid occurred prior to or during freezer storage; therefore, the freezer storage stability of quinclorac and 3-chloro-8-quinolinecarboxylic acid in this experiment cannot be accurately assessed.

However, in the portion of the study conducted using soil from California, since 96% of the applied radioactivity was quinclorac at the end of the experiment, the lack of a soil sample analyzed prior to storage is not critical for the interpretation of the data. Therefore, conclusions concerning the stability of quinclorac can be drawn using data from this experiment; however, the conclusions only apply to the soil from California.

BASF Response: The Mississippi sediment was a 4 month incubated sample taken from the only test system that showed any soil metabolism of quinclorac. It was chosen because it was the longest stored sample that had the des-7-chloro-quinclorac metabolite, BH 514-1.

The primary test system was dosed at the maximum use rate of 0.5 ppm. This test system was at an exaggerated rate of 5 ppm and was only intended to be used to isolate metabolites for identification which might be observed to occur further in the primary system. The problem was essentially no metabolism occurred in the primary system after 12 months.

Thus, analyses of this sample did not begin until it was stored frozen for 19 months after collection. Analysis after 19 months frozen storage showed 55.8% for quinclorac and 31.7% BH 514-1, leaving a total of 12.5% as unidentified material. Since this was the only system out of 16 that showed any metabolism to BAS 514-1, it was highly unlikely BAS 514 H degraded to BH 514-1 under frozen storage conditions.

However, it was recognized that it was not possible to conclusively show if the 12.5% unidentified material resulted from metabolism during the 4 month incubation or decomposition during 19 months frozen storage. Based on the hydrolytic stability of quinclorac, it was highly unlikely that decomposition occurred for quinclorac or for that matter for BH 514-1 during frozen storage.

Nevertheless, we took the worst case scenario and assumed that this was BH 514-1 breakdown during storage. We did take the liberty of subtracting an estimated  $^{14}\text{CO}_2$  loss of 3% from the initial TRR value based on the fact that a 6% loss of  $^{14}\text{CO}_2$  was measured in the 6 month incubated sample. With these assumptions, the recovery of BH 514-1 was at least 76.9%. On the other hand, if one assumes that BH 514-1 did not decompose and all the unidentified material came from quinclorac, then the recovery of quinclorac is at least 84.2% at 19 months storage (i.e. % recovery = [% TRR quinclorac x 100% / 100% TRR -  $\text{CO}_2$  TRR - BH 514-1 % TRR] = [55.8 x 100%] / [100 - 3 - 31.2] = 84.2%).

In summary, it is not likely the 12.5% nonidentified material came from any breakdown during frozen storage. Rather these most likely are products resulting from metabolism of quinclorac and BH 514-1 after four months incubation. However, this can't be shown since the analysis was made after 19 months frozen storage. Nevertheless, the results do conclusively prove that after 19 months storage, at least 76.9% of the BH 514-1 or 84.2% of the quinclorac was recovered.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The study is invalid because the concentration before storage was not determined.

- EFGWB Original Comment: EFGWB prefers that [ $^{14}\text{C}$ ] residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the  $R_f$  of reference standards.



In this study, the sample extracts were analyzed using one-dimensional TLC with one solvent system. Radioactive areas on the TLC plates were identified only by comparison to the location of known reference standards chromatographed on the same plates.

BASF Response: Quinclorac and BH 514-1 were conclusively identified by TLC and GC/MS for the 6 month Mississippi aerobic aquatic sample (MRID 40320817). Once metabolites have been identified, residue methods are developed only using a single detection system. Therefore, using a one-dimension TLC for confirmation and quantitative analysis is sufficient rather than repeating the identification work for the storage stability sample.

EFGWB Rejoinder: Upon consideration of the response, EFGWB does not accept this response in resolving the original comment. EFGWB needs to review confirmatory techniques such as GC/MS to identify the quinclorac residues in this particular study. With out confirmation, it is difficult to conclusively identify the residue solely based on comparison to unlabeled reference standards. It is strongly suggested that the registrant use confirmatory methods, for identifying residues of concern in future studies submitted to EFGWB for review.

3. EFGWB Original Comment: The study author calculated that the minimum recovery of 3 chloro-8-quinolinecarboxylic acid would be 76.9% following freezer storage at  $-5^{\circ}$  C for 19 months; however, this calculation was based upon incorrect reasoning. The results for the California soil showed that parent quinclorac was stable and did not degrade during storage, since no degradate was detected in the soil. Since all parent chemical was recovered and no degradate, it is difficult to assume that BH 514-1 degraded to  $\text{CO}_2$  in the soil from Mississippi during storage as the authors contend.

BASF Response: The calculation of at least 76.9% recovery for BH 514-1 is not based on incorrect reasoning. Likewise, there was never any contention that BH 514-1 degraded to  $\text{CO}_2$  during storage. The reviewer's comment on this matter is either a misquote or misunderstanding of the reported results. The 76.9% calculation simply gives the worst case stability scenario for BH 514-1 after 19 months frozen storage. One can then infer from this result that field samples stored under the same conditions would not lose more than 23% of the BH 514-1 residues which were present at the time of frozen storage after collection. This information is important in determining the lower limit of quantification for a residue analytical method.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. As mentioned above, since quinclorac residues were not measured at Time = 0, the study is invalid because the concentration before storage was not determined.

EFGWB CONCLUSIONS: EFGWB concludes that this study provides ancillary information for the California soil only that indicates quinclorac is stable under frozen storage for up to 40 months. However, because the concentration at the beginning of storage of the Mississippi soil was not determined, the stability of quinclorac in the soil can not be determined.

- 10.7:7. Supplementary report in support of studies related to Subdivision N Guideline No. 164-2--Aquatic field dissipation. Mc Avoy, W. J. January, 1991. FACET herbicide and rice water management. BASF Reg. Doc. No. 91/5140. Unpublished compilation of public literature data submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-26)

This report does not contain any original data, therefore no DER was prepared. It documents (based on discussions with knowledgeable people in each of the below mentioned states) the disposition of tailwater from rice fields in four major rice producing states. In general, tailwater is minimized due to supply side economics and scarcity of water. Permanent floods are held on rice fields from 80 days in Texas to as many as 121 days in Arkansas. Once established, floodwaters are only lowered to prevent straighthead or to expose broadleaf weeds to a postemergence herbicide application. In some situations tailwater is retained for future use.

In Arkansas, tailwater recovery systems are used to capture some tailwater for future use. In other situations, just before harvest, some growers will break their levees and drain the water off. This tailwater remains in ditches until evaporation eliminates the surplus.

In Mississippi, growers are aware of fuel costs needed to pump water and do not purposely pump extra water to have it run out the end of the rice field. If flushing of the rice field needs to occur, some of the flushed water can run out the end of the field into drainage ditches that are also fed by catfish farms, other irrigated crops and excess rainfall.

In Louisiana, rice irrigation water is not deliberately released as tailwater. Essentially no water is used out of the drainage ditches for any other irrigation purpose.

In Texas, because of the cost of water use, very little tailwater is allowed to run off the rice fields.

EFGWB CONCLUSIONS: This document provides supplemental data that demonstrates a minimization of release of rice floodwater containing quinclorac under normal rice cultivation practices in AR, MS, LA and TX. However, EFGWB notes that under abnormal rice culture conditions there is the possibility that substantial quinclorac residues may runoff in tailwater.

#### 10.8 165-1 CONFINED ROTATIONAL CROPS

10.8.1. BASF response (MRID 417814-27) to EFGWB review of Study 21: <sup>14</sup>C-quinclorac confined accumulation study in fall and spring rotation crops (MRID 41063566).

1. EFGWB Original Comment: The study should be conducted in 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.

BASF Response: Presumably this means that there should have been a means of collecting water that might have percolated through the confined plot, not that <sup>14</sup>CO<sub>2</sub> should have been collected. This study was designed to mimic the results on rotation crop residues of normal quinclorac application to rice in the field. The plots were formed in a Mississippi Delta rice-growing soil, flooded to form a seal. The plot history is contained in Table 1. One plot leaked after the first soil cores were taken, and could justifiably be said not to represent a maximum-exposure situation for rotation crops, although it may still be representative of the results from an application to flood.

However, the second plot, where the plot was drained and quinclorac applied to rice and soil, had no problems of leakage, and thus represents a realistic maximum-exposure situation for rotation crops. Whatever the route of loss of the applied test material, this study design still represents normal use conditions, and is adequate for fulfilling this guideline for confined rotation crops. The <sup>14</sup>C residues were measurable in both soil (0.02-0.08 ppm) and crops (0.01-0.02 ppm). Parent quinclorac was the major residue where levels

were high enough for characterization. There was no accumulation, since plant residues were lower than soil. Thus, this study is a valid indicator of what will happen under actual field conditions.

Additional nonradioactive field accumulation studies were conducted in three locations to determine the magnitude of residues in rotation crops (MRIDs 41063567-A/41063569, 41063567-B/41063569, 41063570 and 41063567-C/41063568; referred to as Studies 22, 23, and 24 in the EFGWB review). These studies were conducted under normal use and field environmental conditions. As in the radiolabelled study, no residues were found in any of these rotational crops (<0.05 ppm).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The purpose of a confined accumulation study is to determine the amount and nature of pesticide uptake in rotational crops that would occur in a "worse case" scenario. EFGWB interprets this to mean that the study should be performed in a closed system that does not allow any of the pesticide residues to leave the system, especially due to leaching. EFGWB concludes that this study is more typical of a field accumulation in rotational crops study, since there was no specific barrier to downward movement of quinclorac residues.

2. EFGWB Original Comment: 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 that may occur in soil and analytical procedures.

BASF Response: Replicate plots were not prepared; the guidelines do not require this. However, replicate soil core measurements were made during the rotation crop phase of the study. These are presented in Tables II, VI and VII of the study, and are combined here in Table 2 of this reply.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. EFGWB notes that, while the guidelines do not specifically suggest replicates, they do imply the need for them. For example, Subdivision N Guideline Number 165-1 (d) (2) states:

"Analyses, including a description of data variability, for residues of parent compound and degradates in soil for each sampling interval."

EFGWB interprets this to mean at least duplicate samples need to be collected, either by plot replication or collecting

more than one sample from single plots. The samples should not be composited, but reported as the individual results.

EFGWB suggests, that when performing future studies, the registrant follow the suggestions for analyses in Confined Rotational Crop Accumulation studies. As has been previously mentioned, presentation of the data for individual and not as average values, will allow EFGWB to assess the variation in soil and analytical procedures.

#### Application Prior to Flooding

1. EFGWB Original Comment: 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.

BASF Response: There was no evidence of significant water losses in this plot, due to leaching. Standard agricultural practices were used to simulate the results in actual field tests. Results obtained here were comparable to those in the field studies submitted for dissipation and rotation crop uptake when Facet was applied to soil prior to flooding (MRID's 41063567 and 41063564, respectively; referred to as Studies 19, 20, 22 and 24 in the EFGWB reviews). At about 100 days after application, quinclorac soil residues were 0.05 ppm (TX, Study 20), <0.028 ppm (MS, Study 19), <0.027 ppm (MS, Study 22 and LA, Study 24). In this confined study, total residues were 0.03-0.04 ppm at the same time period, indicating that the rate of loss was typical. Thus, the confined rotation crops were exposed to typical soil residue levels, regardless of the route of loss before rotation planting.

Common routes of loss include degradation in soil or water, or plant uptake. A detailed discussion of rapid aquatic photolysis in natural waters is presented elsewhere, in response to Studies 2-4 (MRID's 41063560 and 41063564-A/B). Aerobic soil and aquatic metabolism studies 5, 6, 8 and 11 (MRIDs 41247301, 41403506, 403209817 and 41432101) show the potential for soil degradation, even though the rates in laboratory studies may be slower than in the field. Uptake through plant roots can also occur, as seen in Study 11 (MRID 41432101) where corn in the pre-emergence treated soil plot contained 0.2 - 0.3 ppm of <sup>14</sup>C in the NC soil where significant soil dissipation occurred, but only 0.01 - 0.05 ppm in the LA study where dissipation was less.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. In a confined study, the crops are not supposed to be exposed to typical soil residue

levels before planting; in fact, the opposite is supposed to occur so that the crops are exposed to the maximum amount of residue possible. It is the field accumulation study that exposes the crops to typical soil residue concentrations, not the confined accumulation study.

Furthermore, since no soil samples were taken with depth until 121 days after treatment, it is not possible to determine if any quinclorac residues had leached into the lower soil profile as the data in Table 2 implies.

2. EFGWB Original Comment: 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.

BASF Response: The replicate soil data compiled in Table 2 of this reply show that when the average value is used for each sampling interval, the 0-4" soil residue varied from 0.03 to 0.08 ppm throughout the period after 28 days from application. Only the single core at 326 days had higher residues. These are not unusual results from a small plot like this, where only limited numbers of cores can be taken. The soil core data are adequate to confirm that application was made, and that measurable residues were present at rotation crop planting and harvest, and that the soil residues were characterized. These data in Table 2 are compiled from Tables II, VI and VII of the original report.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

3. EFGWB Original Comment: The initial concentration of <sup>14</sup>C-quinclorac in the 0- to 4-inch soil depth, 0.424 ppm, was equivalent to approximately 0.56 lb. a.i./A. The target application was 0.75 lb. a.i./A.; therefore, the actual application was approximately 24% lower than expected.

BASF Response: The difference was primarily due to plant intercept of the spray. This plot contained 3-5 leaf rice at the time of application, planted in six rows of 26 plants/foot, in a 4 x 8 ft. plot. The rice plants contained 35 ppm of residues at 3 days after application (Ref. 1, MRID 41063534, Table V), confirming plant intercept of the spray.

In any event, since the application rate was slightly exaggerated, the soil residues were the same as would have resulted from a normal 0.5 lb ai/A application (0.75 lb ai/A x 76%), without plants to intercept the spray.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

4. EFGWB Original Comment: 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).

BASF Response: The statement in Figure 5 is a typographical error.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

#### Application While Flooded

1. EFGWB Original Comment: The study authors failed to confirm the initial application of quinclorac.

BASF Response: This is true. Since the material was applied directly to water as a granule with an unknown rate of release, residues in water immediately after application would have been difficult to correlate to the application rate, anyway. The objective was to determine if this route of application would lead to measurable soil residues after rice harvest, and thus potentially to rotation crop uptake.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. Since the material was applied in granular form, soil and water samples should have been collected in an attempt to confirm the initial application. Furthermore, if the granule rate of release is unknown, how is it possible to determine whether or not residues in water could not be determined. Therefore, EFGWB still maintains that the application rate should have been confirmed.

2. EFGWB Original Comment: 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 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.

BASF Response: It's true that this study did not give the rotation crops a maximum soil residue exposure. This study

can only be considered supplementary to the main study ("application prior to flooding"), to see if application to flood resulted in major differences from application to soil. The data are useful to draw a correlation between low soil residues at planting and low uptake levels in the rotation crops. The results from "application prior to flooding" should suffice to cover the "application while flooded" use pattern, since application to water could hardly result in higher soil residues than direct application to soil at the same rate.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. Since the application rate of quinclorac was not verified, nor any indication of how much was lost, EFGWB does not agree that significant useful relationship between soil residues and plant uptake is possible.

EFGWB CONCLUSIONS: After reviewing the original study and the above responses, EFGWB concludes that this study still does not satisfy the data requirements for a confined accumulation in rotational crops because:

1. There may have been an appreciable amount of quinclorac residues lost from the soil prior to the initiation of the crop rotational part of the study, since it was not conducted as a typical confined accumulation study.
2. The part of the study where quinclorac was applied to the flooded plot is not acceptable because of the previously discussed problems of non-verification of application rate and loss of quinclorac when floodwater was not maintained.

What is of particular concern to EFGWB, after reviewing the data in Table 2 (attached), is the fact that quinclorac residues appear to have leached in the soil down to at least the 12 inch depth. Furthermore, one year after application, there is still approximately 25% of the original amount applied present in the 0-12 inch depth. This data implies that quinclorac is persistent in the soil and has leached at least down to the 12" soil depth. Soil samples should have been collected below the 12" depth to conclusively demonstrate whether or not quinclorac residues had leached.

10.9. 165-2 FIELD ROTATIONAL CROPS

- 10.9.1. BASF response (MRID 417814-29) to EFGWB review of Study 22: Fall and annual rotational crop study for quinclorac following aquatic use (MRID 41063567)

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1. EFGWB Original Comment: The study authors failed to confirm the application of quinclorac to the flooded field plot. Quinclorac was not detected in the soil from this plot at any sampling interval, and no floodwater analyses were provided.

BASF Response: Validation of the application was obtained by the analysis of rice from this plot. As shown in this report, the rice had a residue level of 0.05 ppm which is the expected residue from a 0.5 lb a.i./A application (see Report A8902, MRID 41063542).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. EFGWB does not use crop uptake data as a means of confirming application of chemicals to soils, since there are too many variables that influence plant uptake.

2. EFGWB Original Comment: Soil samples were taken from the 0- to 6- and 6- to 12-inch depths and composited prior to analysis. However, Subdivision N guidelines specify that soil samples should be taken in increments no greater than 6 inches. The study authors stated that this was done because it "better modeled the rotational crop zone". This logic is incorrect because plants are capable of obtaining material only from the soil microsites directly adjacent to the root, not from the bulk of the soil. The most accurate assessment of potential plant exposure would be obtained by decreasing the volume of soil analyzed; for example, plant uptake can be interpreted more accurately if it is reported that the surface 1-inch of soil contains a concentration of 1 ppm and the 1- to 12-inch segments contain no pesticide than to state that the concentration of the pesticide in the 0- to 12-inch depth was 0.08 ppm.

BASF Response: Subdivision N guidelines regarding rotational crops, series 165-2, Field Accumulation Studies on Rotational Crops, EPA 540/9-82-021, October 1982 or EPA 540/9-86-149, Addendum 1 on the Data Reporting, November 1986, do not specify any soil core or soil core section size. The first mention of the 6-inch (15 cm) soil core section was printed in the Environmental Fate and Effects Division Standard Evaluation Procedure-Terrestrial Field Dissipation, EPA 540-09:90-073, December 1989, which was made available 8 months after this study was completed and reported (March 1989).

Knowing the disposition of the residue in small sections along the root zone is not practical or an appropriate objective of this study. The only information which is needed is the average level of soil residue along the entire root zone of the rotational crop. This information is provided by a single 0-12 inch analysis.

The degradation of the residues in the soil with time is provided in the soil dissipation studies (EFGWB Study 18 - MRID 41063564-B, EFGWB Study 19 - MRID 41063564-H and EFGWB Study 20 - MRID 41063564-G) where 0-6 inch core sections were analyzed as required by the guidelines. These dissipation studies showed that the residue levels in the soil were at or below the detection limit within 90 to 176 days after application. The fall rotational crops, which were those planted at the shortest interval since application, were planted 105-128 days past treatment.

In addition, the highest possible residue in any size core section from the rotational crop study can be obtained by assuming all of the residue found in the 0-12 inch core section was located in the smaller 0-6 inch section. Since all soil residue values were <0.027 ppm, assume the residue value was 0.026 ppm and that all soil core sections had the same bulk density. Under these assumptions, the highest the residue could be in the top 0-6 inch soil core sections would be 0.052 ppm.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. Although EFGWB agrees with the registrant's reasoning, we believe that soil pesticide concentration should be reported in soil depth increments of no more than 6 inches. Since rooting depths of crops differ, smaller soil increment sampling facilitates interpretation of plant concentration.

3. EFGWB Original Comment: The storage stability data provided by the registrant were inadequate to determine if quinclorac and its degradates were stable in wheat, corn, soybeans, and sorghum samples that were stored frozen for up to 15 months, the longest period of time that crop samples in this study were stored frozen prior to analysis. In the present study, the storage stability data provided by the study authors were for rice grain and straw, corn forage, and soybean grain fortified with quinclorac at 1 ppm and stored frozen at <5°C for 8 months (Table VI). It was uncertain if quinclorac was stable under these conditions, since the study authors acknowledged that "some questionable results" were obtained.

BASF Response: Additional storage stability data is provided in Report Number A9103<sup>4</sup> (BASF Reg. Doc. No. 91/5021) which

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<sup>4</sup> Paulick, R. C. 1991. Freezer storage stability of quinclorac in rice grain and straw, corn, grain, forage, silage and fodder, soybean grain and fodder, sugarbeet roots and tops and alfalfa hay-18-19 month analyses. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417759-03.

is included in this submission. (EFGWB notes that this storage stability data has been reviewed and is listed as DER for Study 11).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment, because the storage stability data requires additional information at this time:

1. The registrant needs to provide and explain the data that shows the contamination in the control samples that occurred in numerous instances as reported in Table I (see DER for Study 11).
2. No storage stability data was provided for the sorghum and wheat matrices that were stored frozen for up to 18 months as requested in the Review of Study 24 dated 12/3/90. This additional data is required to show that quinclorac is stable in wheat and sorghum plant tissue when stored for up to 18 months prior to analyses.
4. EFGWB Original Comment: It was stated that mustard and turnips were planted as fall and annual rotational crops and that these crops were sampled; however, no analyses were conducted on these crop samples.

BASF Response: Additional residue data for these crops is provided in Report Number A9104<sup>5</sup> (BASF Reg. Doc. No. 91/5022) which is included in this submission. (EFGWB notes that this data has been reviewed and is listed as DER for Study 12).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. The study shows that no quinclorac residues were detected in the mustard or turnip plant material that exceeded the limit of detection (<0.05).

5. EFGWB Original Comment: The target application rate for the test substance was reported as 227 g/A. At the nonflooded plot, the material balance for the application rate was slightly >100%; 229 g/A was in the sediment (Table IX). The material balance for the application rate could not be determined at the flooded plot, since water samples were not

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<sup>5</sup> Paulick, R. C. January 1991. Magnitude of the residues of quinclorac (BAS 514 H) in rotational crops (mustard and turnips) following rice culture in Louisiana (RCN 87096) and Mississippi (RCN 87098). BASF Report No. A9104. BASF Registration Document No. 91/5022. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417814-28.

analyzed and <40 g/A of the test substance occurred in the sediment.

BASF Response: The material balance of 229 g/A found in the plot which was not flooded at application was very close to the expected value since the application was made directly to the soil. However, where the application was made to the flooded plot, four matrices are involved: water, rice, weeds and sediment. The material balance value of <40 g/A is the expected value for soil based on results from the Aquatic Dissipation Study (Report E8920, MRID 41063564).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The registrant needs to explain why, in this nonflood application, there was no interception of quinclorac by the rice crop that had been planted approximately 20 days before application, while in Study 19, under nonflood application, approximately 49% of the applied loss was attributable to rice plant interception.

Since no floodwater samples were analyzed in the application when flooded treatment, it is difficult to predict what the expected soil values should be based on the results of the other studies. It would have been prudent to sample the floodwater in order to verify the application amount.

6. EFGWB Original Comment: A deviation in protocol occurred in the treatment of the nonflooded plot; the adjuvant BAS 090 025 was not included in the spray solution. The principal investigator believed that this deviation had no limiting effect on achieving the objective of the protocol, since the test substance was intercepted by the rice crop prior to the planting of the target (rotational) crops. The lack of adjuvant in the treatment mixture would restrict foliar uptake of the test substance by the rice crop, creating a potential for movement of greater amounts of the test substance to the soil surface via precipitation and/or rainfall. The principal investigator concluded that this net effect would not be expected to restrict quantities of test substance available for uptake by subsequent rotational crops.

BASF Response: The absence of the adjuvant (BAS 090 015) would result in a worse case example in the sense that more residue would reach the soil and hence be available for rotational crops.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

7. EFGWB Original comment: It appears that two erroneous air temperature readings were recorded in the meteorological data; the maximum air temperature for October 28, 1987, was reported as 56°C (132.8°F) and for June 26, 1988, was 68°C (154.4°F). The reviewer did not include these values in reporting the range of air temperature data for the test site.

BASF Response: The maximum temperature values for these days seem to be instrument printing errors. The mean temperature values recorded on these days are, however, commensurate with values recorded on days both before and after these dates and are assumed accurate.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

8. EFGWB Original Comment: Although it was reported that a 1-gallon sample of irrigation water was collected at 1 day postflooding from the plot that had been treated with quinclorac prior to flooding, no data for this water sample was provided.

BASF Response: The analysis of this water sample was not necessary to accomplish the objectives of the study.

EFGWB Rejoinder: EFGWB concludes that since the target application rate of quinclorac was confirmed by sediment analysis, analysis of the floodwater probably was not necessary; therefore, EFGWB accepts this response as resolving the original comment. However, it would be prudent to analyze this sample to determine the concentration of quinclorac that had partitioned into the water at this time.

EFGWB CONCLUSIONS: After reviewing the responses to related to quinclorac concentration in this field rotational crop study, EFGWB concludes that the study still does not satisfy the data requirements for the following reasons:

1. Target application of quinclorac to the flooded field plot was not confirmed.
2. Additional information is needed in regards to the storage stability data submitted.
3. Disparate results in plant interception of applied quinclorac between the three field rotational crops studies.

10.9.2. BASF response (MRID 417814-30) to EFGWB review of Study 23: Fall and annual rotational crop study for quinclorac following aquatic use (MRID 41063567)

1. EFGWB Original Comment: Soil samples were taken from the 0- to 6- and 6- to 12-inch depths and composited prior to analysis. However, Subdivision N guidelines specify that soil samples should be taken in increments no greater than 6 inches. The study authors stated that this was done because it "better modeled the rotational crop zone". This logic is incorrect because plants are capable of obtaining material only from the soil microsites directly adjacent to the root, not from the bulk of the soil. The most accurate assessment of potential plant exposure would be obtained by decreasing the volume of soil analyzed; for example, plant uptake can be interpreted more accurately if it is reported that the surface 1-inch of soil contains a concentration of 1 ppm and the 1- to 12-inch segments contain no pesticide than to state that the concentration of the pesticide in the 0- to 12-inch depth was 0.08 ppm.

BASF Response: Subdivision N guidelines regarding rotational crops, series 165-2, Field Accumulation Studies on Rotational Crops, EPA 540/9-82-021, October 1982 or EPA 540/9-86-149, Addendum 1 on the Data Reporting, November 1986, do not specify any soil core or soil core section size. The first mention of the 6-inch (15 cm) soil core section was printed in the Environmental Fate and Effects Division Standard Evaluation Procedure-Terrestrial Field Dissipation, EPA 540-09:90-073, December 1989, which was made available 8 months after this study was completed and reported (March 1989).

Knowing the disposition of the residue in small sections along the root zone is not practical or an appropriate objective of this study. The only information which is needed is the average level of soil residue along the entire root zone of the rotational crop. This information is provided by a single 0-12 inch analysis.

The degradation of the residues in the soil with time is provided in the soil dissipation studies (EFGWB Study 18 - MRID 41063564-B, EFGWB Study 19 - MRID 41063564-H and EFGWB Study 20 - MRID 41063564-G) where 0-6 inch core sections were analyzed as required by the guidelines. These dissipation studies showed that the residue levels in the soil were at or below the detection limit within 90 to 176 days after application. The fall rotational crops, which were those planted at the shortest interval since application, were planted 105-128 days past treatment.

In addition, the highest possible residue in any size core section from the rotational crop study can be obtained by assuming all of the residue found in the 0-12 inch core section was located in the smaller 0-6 inch section. Since all soil residue values were <0.027 ppm, assume the residue value was 0.026 ppm and that all soil core sections had the same bulk density. Under these assumptions, the highest the residue could be in the top 0-6 inch soil core sections would be 0.052 ppm.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. Although EFGWB agrees with the registrant's reasoning, we believe that soil pesticide concentration should be reported in soil depth increments of no more than 6 inches. Since rooting depths of crops differ, smaller soil increment sampling facilitates interpretation of plant concentration.

2. EFGWB Original Comment: The storage stability data provided by the registrant were inadequate to determine if quinclorac and its degradates were stable in wheat, corn, soybeans, and sorghum samples that were stored frozen for up to 18 months, the longest period of time that crop samples in this study were stored frozen prior to analysis. In the present study, the storage stability data provided by the study authors were for rice grain and straw, corn forage, and soybean grain fortified with quinclorac at 1 ppm and stored frozen at <-5°C for 8 months (Table VI). It was uncertain if quinclorac was stable under these conditions, since the study authors acknowledged that "some questionable results" were obtained.

BASF Response: Additional storage stability data is provided in Report Number<sup>6</sup> A9103 (BASF Reg. Doc. No. 91/5021) which is included in this submission. (EFGWB notes that this storage stability data has been reviewed and is listed as DER for Study 12).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment, because the storage stability data requires addition information at this time:

1. The registrant needs to provide and explain the data that shows the contamination in the control samples that

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<sup>6</sup> Paulick, R. C. 1991. Freezer storage stability of quinclorac in rice grain and straw, corn, grain, forage, silage and fodder, soybean grain and fodder, sugarbeet roots and tops and alfalfa hay-18-19 month analyses. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417759-03.

occurred in numerous instances as reported in Table I (see DER for Study 12).

2. No storage stability data was provided for the sorghum and wheat matrices that were stored frozen for up to 18 months as requested in the Review of Study 24 dated 12/3/90. This additional data is required to show that quinclorac is stable in wheat and sorghum plant tissue when stored for up to 18 months prior to analyses.

3. EFGWB Original Comment: The study authors stated that a control plot was to be sampled; however, data was not presented for this control. Also, it was stated that petri dishes were placed around the levee of the treated paddy to verify the application rate; however, the results of the petri dishes analyses were not reported.

BASF Response: The analysis of these samples was not necessary to accomplish the main objective of the study. The control soil and plant material was, however, spiked and used in recovery experiments.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment, although data from the petri dishes may have helped in verifying the application rate.

4. EFGWB Original Comment: Although lettuce and sugarbeets were part of the fall rotational plantings, no data were supplied for these crops.

BASF Response: Additional residue data for these crops is provided in Report Number A9104<sup>7</sup> (BASF Reg. Doc. No. 91/5022) which is included in this submission. (EFGWB notes that this data has been reviewed and is listed as DER for Study 12).

EFGWB Rejoinder: EFGWB does not accept this response in resolving the original comment since the only data contained in Report Number A9104 (BASF Reg. Doc. No. 91/5022) is concentration of quinclorac residues in mustard and turnip plants.

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<sup>7</sup> Paulick, R. C. 1991. Magnitude of the residues of quinclorac (BAS 514 H) in rotational crops (mustard and turnips) following rice culture in Louisiana (RCN 87096) and Mississippi (RCN 87098). BASF Report No. A9104. BASF Registration Document No. 91/5022. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417814-28.



5. EFGWB Original Comment: Based on the concentration of quinclorac in the floodwater immediately post treatment and assuming a water depth of 5 inches, the study authors determined that 149 g/A of quinclorac were applied to the rice paddy. Since the target application of 0.5 lb ai/A should have resulted in a water concentration of 227 g/A, the actual application was only 65% of the nominal (Table IX).

BASF Response: The material balance calculation is an approximation which does not include the intercept of quinclorac by rice and weeds which were growing in the plot at the time of application. The 149 g/A value shows that the application was made to the plot and a 40% intercept would be a reasonable result based on the density of the vegetative cover at the time of the application.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The registrant needs to explain why, in this flood application study, 35% of the application was attributable to interception by plants, while in Study 24 >100% was recovered in the floodwater.

EFGWB CONCLUSIONS: After reviewing the responses to related to quinclorac concentration in this field rotational crop study, EFGWB concludes that the study still does not satisfy the data requirements for the following reasons:

1. Target application of quinclorac to the flooded field plot was not confirmed.
  2. Disparate results in plant interception of applied quinclorac between the three field rotational crops studies.
  3. Additional information is needed in regards to the storage stability data submitted and quinclorac concentration in lettuce and sugarbeets.
- 10.9.3. BASF response (MRID 417814-31) to EFGWB review of Study 24: Fall and annual rotational crop study for quinclorac following aquatic use (MRID 41063567)
1. EFGWB Original Comment: Soil samples were taken from the 0- to 6- and 6- to 12-inch depths and composited prior to analysis. However, Subdivision N guidelines specify that soil samples should be taken in increments no greater than 6 inches. The study authors stated that this was done because it "better modeled the rotational crop zone". This logic is incorrect because plants are capable of obtaining material only from the soil microsites directly adjacent to the root, not from the bulk of the soil. The most accurate assessment

of potential plant exposure would be obtained by decreasing the volume of soil analyzed; for example, plant uptake can be interpreted more accurately if it is reported that the surface 1-inch of soil contains a concentration of 1 ppm and the 1- to 12-inch segments contain no pesticide than to state that the concentration of the pesticide in the 0- to 12-inch depth was 0.08 p,pm.

BASF Response: Subdivision N guidelines regarding rotational crops, series 165-2, Field Accumulation Studies on Rotational Crops, EPA 540/9-82-021, October 1982 or EPA 540/9-86-149, Addendum 1 on the Data Reporting, November 1986, do not specify any soil core or soil core section size. The first mention of the 6-inch (15 cm) soil core section was printed in the Environmental Fate and Effects Division Standard Evaluation Procedure-Terrestrial Field Dissipation, EPA 540-09:90-073, December 1989, which was made available 8 months after this study was completed and reported (March 1989).

Knowing the disposition of the residue in small sections along the root zone is not practical or an appropriate objective of this study. The only information which is needed is the average level of soil residue along the entire root zone of the rotational crop. This information is provided by a single 0-12 inch analysis.

The degradation of the residues in the soil with time is provided in the soil dissipation studies (EFGWB Study 18 - MRID 41063564-B, EFGWB Study 19 - MRID 41063564-H and EFGWB Study 20 - MRID 41063564-G) where 0-6 inch core sections were analyzed as required by the guidelines. These dissipation studies showed that the residue levels in the soil were at or below the detection limit within 90 to 176 days after application. The fall rotational crops, which were those planted at the shortest interval since application, were planted 105-128 days past treatment.

In addition, the highest possible residue in any size core section from the rotational crop study can be obtained by assuming all of the residue found in the 0-12 inch core section was located in the smaller 0-6 inch section. Since all soil residue values were <0.027 ppm, assume the residue value was 0.026 ppm and that all soil core sections had the same bulk density. Under these assumptions, the highest the residue could be in the top 0-6 inch soil core sections would be 0.052 ppm.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. Although EFGWB, in general, agrees with the registrant's reasoning, we believe that soil pesticide concentration should be reported in soil depth

increments of no more than 6 inches. Since rooting depths of crops differ, smaller soil increment sampling facilitates interpretation of plant concentration.

2. EFGWB Original Comment: The storage stability data provided by the registrant were inadequate to determine that quinclorac and its degradates are stable in crop (wheat, sorghum, and soybeans) and water samples that were stored frozen prior to analysis in the present study.

BASF Response: Additional storage stability data is provided in Report Number A9103<sup>8</sup> (BASF Reg. Doc. No. 91/5021) which is included in this submission. (EFGWB notes that this storage stability data has been reviewed and is listed as DER for Study 11).

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment since the registrant did not provide or explain the data that shows the contamination in the control samples that occurred in numerous instances as reported in Table I. Also no storage stability data was provided for the sorghum and wheat matrices that were stored frozen for up to 18 months as requested in the Review of Study 24 dated 12/3/90. This additional data is required to show that quinclorac is stable in wheat and sorghum plant tissue when stored for up to 18 months prior to analyses. See DER for Study 12 for additional details.

3. EFGWB Original Comment: The target application rate for the test substance was reported as 227 g/A. In the plot treated after flooding, the study author estimated that the concentration of quinclorac in the water was equivalent to 255 g/A, based on a 4-inch water depth (Table IX). In the plot treated prior to flooding, the concentration of quinclorac in the soil immediately posttreatment was only 50 g/A.

BASF Response: The material balance of 255 g/A found in the plot which was flooded at application shows that almost all of the Facet ended up in the water and was not intercepted by the rice growing in the plot. This was due to the size of

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<sup>8</sup> Paulick, R. C. January 1991. Freezer storage stability of quinclorac in rice grain and straw, corn, grain, forage, silage and fodder, soybean grain and fodder, sugarbeet roots and tops and alfalfa hay, 18-19 month analyses. BASF Report No. A9103. BASF Registration Document No. 91/5021. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417759-03.

the rice and the depth of the water at the time of application. In the plot treated prior to flooding, the material balance of 50 g/A was lower than expected due to a dense cover of rice and weeds at the time of application.

EFGWB Rejoinder: EFGWB does not accept this response as resolving the original comment. The registrant needs to explain why, in the flood application study, none of the material was intercepted by plants resulting in >100% verification of the amount applied, while in study 23, 35% of the amount applied was attributable to plant interception.

4. EFGWB Original Comment: It was stated that mustard and turnips were planted as fall and annual rotational crops and that these crops were sampled; however, no analyses were conducted on these crop samples.

BASF Response: Additional residue data for these crops is provided in Report Number A9104<sup>9</sup> (BASF Reg. Doc. No. 91/5022) which is included in this submission. (EFGWB notes that this data has been reviewed and is listed as DER for Study 13).

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. The study shows that no quinclorac residues were detected in the mustard or turnip plant material that exceeded the limit of detection (<0.05). For the complete review of this study see the DER for Study 13.

EFGWB CONCLUSIONS: After reviewing the responses to related to quinclorac concentration in this field rotational crop study, EFGWB concludes that the study still does not satisfy the data requirements for the following reasons:

1. Target application of quinclorac to the flooded field plot was not confirmed.
2. Disparate results in plant interception of applied quinclorac between the three field rotational crops studies.

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<sup>9</sup> Paulick, R. C. January 1991. Magnitude of the residues of quinclorac (BAS 514 H) in rotational crops (mustard and turnips) following rice culture in Louisiana (RCN 87096) and Mississippi (RCN 87098). BASF Report No. A9104. BASF Registration Document No. 91/5022. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC, MRID 417814-28.

3. Additional information is needed in regards to the storage stability data submitted.

10.10. ANCILLARY DATA - STORAGE STABILITY

10.10.1. New data in support of storage stability of quinclorac and its metabolites in soil and water:

1. Eswein, R. P. January 1991. Freezer storage stability of quinclorac (BAS 514 H) in water - 15-17 month analysis Interim report of an ongoing storage stability study. Presents data from the 17 month time period. Registration Document No. 91/5015. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplements: Eswein, R. P. 1988. Freezer storage stability of quinclorac in water. BASF Registration Document No. 89/5015, MRID 41063571. (MRID 417814-33).

Quinclorac was stable in uncharacterized pond water stored frozen at  $<-5^{\circ}$  C for 17 months. This study is scientifically sound; however, the value of these data is currently limited to this particular set of pond water samples as the registrant did not characterize the pond water beyond stating where it was obtained.

The registrant should submit detailed characterization of the pond water so that it can be determined if the physical, chemical, and biological parameters are within normal ranges. If water from this site is "typical", no additional information on the storage stability of quinclorac in water is required unless quinclorac is stored frozen in water for longer than 17 months prior to analysis.

See attached DER No. 9 for the complete review of this study.

2. Stewart, J. January 1991. Freezer storage stability of quinclorac and its metabolites in soil - 0, 17, 21 month analysis. This is an interim report of a 36-month storage stability study. Registration Document No. 91/5016. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-32).

Quinclorac was stable in clay soil stored frozen at  $<-5^{\circ}$  C for 21 months. This study is scientifically sound. Based on the information provided in this study, clay soil samples containing quinclorac may be stored frozen for up to 21 months prior to analysis.

No additional information on storage stability of quinclorac in clay soil is required at this time. However, if quinclorac in clay soil is stored for longer than 21 months prior to analysis, additional storage stability information will be required.

See attached DER No. 10 for the complete review of this study.

10.11 163-2--LABORATORY VOLATILITY STUDY

- 10.11.1. The registrant has submitted a waiver request for a laboratory volatility study with quinclorac. This waiver request is based on the reported vapor pressure of quinclorac of  $1 \times 10^{-7}$  mbar ( $0.76 \times 10^{-7}$  mm Hg) at  $20^{\circ}$  C and the Henry's Law Constant of  $1.22$  to  $24.3 \times 10^{-15}$  atm.  $\text{m}^3 \text{mol}^{-1}$ . The registrant indicates that these two parameters indicate that there is no reasonable expectation of volatility and therefore request a waiver.

EFGWB CONCLUSIONS: EFGWB has no objection to granting a waiver for the laboratory volatility study, since the vapor pressure of quinclorac, reported to be  $1 \times 10^{-7}$  mbar ( $0.76 \times 10^{-7}$  mm Hg) at  $20^{\circ}$  C, and Henry's Law Constant both indicate a low possibility of volatilization.

11.0 COMPLETION OF ONE-LINER: Updated to include the data from acceptable studies reviewed within the framework of this action.

12.0 CBI APPENDIX: No claim of confidentiality was made for any information contained in this submission on the basis of its falling within the scope of FIFRA Section 10 (d)(1)(A), (B), or (C).

REFERENCES

The following documents were reviewed to assist EFGWB in understanding the environmental fate of quinclorac:

I. Summary Document

1. Nelsen, T. R. January 1991. An overview of the environmental fate of quinclorac. Registration Document No. BASF: 91/5134. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-01).

II. 161-2 Photodegradation in Water

Response to Reviewer's Comments:

2. Ellenson, J. L. January 1991. Response to reviewer's comments (EFGWB # 2 - MRID 41063560) for photolysis of BAS 514 H in aqueous solution. Registration Document No. 91/5000. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-06).
3. Clark, J. R. January 1991. Response to reviewer's comments (EFGWB Study # 3 - MRID 41063564-A) for photodegradation of quinclorac in aqueous solution. Registration Document No. 91/5001. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-07).
4. Clark, J. R. January 1991. Response to reviewer's comments (EFGWB Study # 4 - MRID 41063564-B) for the study of biodegradation of quinclorac by microorganisms in activated sludge under sunlight. Registration Document No. 91/5002. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-08).

New Data in Support of Response to Reviewer's Comments to Photodegradation in Water Study:

5. Ellenson, J. L. January 1991. Photolysis of <sup>14</sup>C-BAS 514 H in water sensitized with hydrogen peroxide. Registration Document No. 91/5003. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplement to: Photolysis of BAS 514 H in pH 7 aqueous solution at 25° C, BASF Report M8806, MRID 41063560. (MRID 417814-02).

6. Huber, R. November 1990. Preliminary investigation of the humic acid sensitized aqueous photolysis of quinclorac. Registration Document No. 90/0487. Unpublished study performed by BASF Akteingesellschaft, Product Safety Crop Protection, Limburgerhof, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-03, supplements MRID 41063560).
7. Goto, S. May 1989. Solar photolysis of quinclorac in aqueous solutions. Registration Document No. 89/0191. Unpublished study performed by The Institute of Environmental Toxicology, Tokyo University of Agriculture and Technology, Tokyo, Japan. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-04, supplements MRID 41063560).

Literature Review in Support of Response to Reviewer's Comments to Photodegradation in Water Study:

8. Clark, J. R. January 1991. Impact of aqueous photolysis on FACET field dissipation: An overview. Registration Document No. 91/5004. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-05).

III. 161-2 Photodegradation on Soil

New Study:

9. Goetz, A.J. and V. W. Winkler. February 1991. Photolysis of <sup>14</sup>C-BAS H in soil. Registration Document No. 91/5005. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-09).

IV. 162-1 Aerobic Soil Metabolism

Response to Reviewer's Comments:

10. Winkler, V. W. January 1991. Response to review's comments (EFGWB Study # 6 - MRID 4140356) for respiration of live soil treated with <sup>14</sup>C-Quinclorac. Registration Document No. 91/5006. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-15).

New Data in Support of Response to reviewers's Comments to Aerobic Soil Metabolism Study:

11. Schmider, D. R. April 1988. Studies on the behavior of quinclorac in soil. Registration Document No.



88/0642. Unpublished study performed by BASF Aktiengesellschaft, Agricultural Research Stationm Ludwigshafen, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-10, supplements MRID 412473-01).

12. Mittelstaedt, W. and F. Fuhr. September 1988. BASF 514 H - Degradation according to the German Federal Biological Institute of Agricultural and Forestry (modified in accordance with leaflet 36). Registration Document No. 88/0426. Unpublished study performed by Institute for Radio Agronomy, Nuclear Research Facility at Julich, Julich, west germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-11, supplements MRID 41247301).

Literature Reviews in Support of Response to Reviewer's Comments to Aerobic Soil Metabolism Study:

13. Bicki, T. J. January 1991. Review of literature relating variability of microbial degradation to environmental variables, soil properties and pesticide concentration. Registration Document No. 91/5131. Unpublished study performed by Roux Associates, Inc. Huntington, NY. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-12, supplements MRID 41247301).
14. Akkari, K.H. January 1991. Literature review of some biochemical factors affecting the degradation of organic chemicals in soil. Registration Document No. 91/5030. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-13).

V. 162-3 Anaerobic Aquatic Metabolism

Response to Reviewer's Comments:

15. Winkler, V. W. January 1991. Response to reviewer's comment (EFGWB study # 7 - MRID 41063561) for BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: Anaerobic aquatic system. Registration Document No. 91/5007. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-16).

VI. 162-4 Aerobic Aquatic Metabolism

Response to Reviewer's Comments:

16. Winkler, V. W. January 1991. Response to reviewer's comment (EFGWB Study # 8 - MRID 403208-17) for BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: Aerobic aquatic system. Registration Document No. 91/5008. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-19).

New Data in Support of Response to Reviewer's comments to Aerobic Aquatic Metabolism:

17. Wood, N. F. and V. W. Winkler. February 1991. Further identification studies on quinclorac aerobic soil/sediment metabolites. Registration Document No. 91/5009. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplement to: Clark, J. R., BAS 514 H-<sup>14</sup>C laboratory soil metabolism study: aerobic aquatic metabolism, MRID 40320817, BASF registration document No. 87/5034, Report No. M8716. (MRID 417814-17).
18. Brode, S. January 1991. The determination of the electronic properties of quinclorac and its important metabolite BH 514-1 and intermediate E by quantum mechanical Ab initio calculations. Registration Document No. 91/5132. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-18, supplements 40320817).

Abstract of a Ph. D. Thesis in support of Aerobic Aquatic Metabolism Study No. 8, MRID 40320817:

19. Huber, R. November 1988. Microbial degradation of the quinclorac metabolite 3-chloroquinoline-8-carboxylic acid: An abstraction of a Ph.D. Thesis by P. Tibble. University of Hohenheim. Registration Document No. 91/5135. Unpublished study performed by The Institute of Microbiology, University of Hohenheim, West Germany. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-14, supplements MRID 40320817).

Translation of a Ph. D. Thesis in support of Aerobic Aquatic Metabolism Study No. 8, MRID 40320817:

20. Tibbles, P. 1988. The microbial degradation of 3-chloroquinoline-8-carboxylic acid and 5-chloro-2-hydroxynicotinic acid. BASF Registration Document No. 88/0647. Unpublished Ph.D. dissertation performed at the Institute of Microbiology of Hohenheim University, Germany. Submitted by BASF Corporation, Research Triangle Park, NC. (MRID 41919601)

VII. 163-2 Laboratory Volatility

21. Nelsen, T. February 1991. Waiver request for a laboratory volatility study with quinclorac (FACET). Registration Document No. 91/5136. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (No MRID Number ???).

VIII. 164-1 Terrestrial Field Dissipation

Response to Reviewer's Comments:

22. Winkler, V. W. January 1991. Response to reviewer's comments (EFGWB Study #11 - MRID 414321-01) for confined field <sup>14</sup>C-quinclorac (BAS 514 H) dissipation study. Registration Document No. 91/5010. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-20).

IX. 164-2 Aquatic Field Dissipation

Response to Reviewer's Comments:

23. Cargile, N. L. January 1991. Response to reviewer's comments (EFGWB study # 17 - MRID 41063565) for <sup>14</sup>C-quinclorac confined field aquatic dissipation study in rice paddy water. Registration Document No. 91/5011. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-21).
24. Panek, E. J. January 1991. Response to reviewer's comments (EFGWB Study # 18 - MRID 41063564-A, 41063564-B, 41063564-C, 41063564-F, 41063564-I, 41063568, 410635669, 41063570) for quinclorac aquatic field dissipation study in Chico, CA. Registration Document No. 91/5012. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-22).
25. Panek, E. J. January 1991. Response to reviewer's comments (EFGWB Study # 19 - MRID 41063564-A, 41063564-B, 41063564-C, 41063564-E, 41063564-H, 410635669, 41063570) for quinclorac aquatic field dissipation study in Leland, MS. Registration Document No. 91/5013. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417924-01).
26. Response to reviewer's comments ((EFGWB Study # 20 - MRID 41063564-A, 41063564-B, 41063564-C, 41063564-D, 41063564-G, 410635668, 41063570) for quinclorac aquatic

field dissipation study in East Bernard, TX. Registration Document No. 91/5014. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-23).

27. Response to reviewer's comments (EFGWB Study # 28 - MRID 41063572) for freezer storage stability study of quinclorac residues (BAS 514 H) and its metabolite (BH 514-1) in aquatic sediment. Registration Document No. 91/5023. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-24).

Literature Review in Support of Response to reviewer's Comments to Aquatic Field Dissipation Study:

28. Blasland and Bouck Engineers. January 1991. Assessment of quinclorac potential to leach to groundwater from labelled uses on rice in the Southern United States. Registration Document No. 91/5133. Unpublished study performed by Blasland and Bouck Engineers, Syosset, NY. Submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-25). Supplementary data.
29. McAvoy, W. J. January 1991. FACET herbicide and rice water management. Registration Document No. 91/5140. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-26).

X. 165-1 Confined Rotational Crops

Response to Reviewer's Comments:

30. Response to reviewer's comments (EFGWB Study # 21 - MRID 41063566) for <sup>14</sup>C-quinclorac confined accumulation study in fall and spring rotation crops. Registration Document No. 91/5017. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-27).

XI. 165-2 Field Rotational Crops

Response to Reviewer's Comments:

31. Clark, J. R. January 1991. Response to reviewer's comments (EFGWB Study # 22 - MRID 41063567) for fall and annual rotational crop study following aquatic uses. Registration Document No. 91/5018. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-29).

32. Clark, J. R. January 1991. Response to reviewer's comments (EFGWB Study # 23 - MRID 41063567) for fall and annual rotational crop study for quinclorac (FACET Herbicide) following aquatic use. Registration Document No. 91/5019. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-30).
33. Clark, J. R. January 1991. Response to reviewer's comments (EFGWB Study # 24 - MRID 41063567) for fall and annual rotational crop study for quinclorac (FACET Herbicide) following aquatic use. Registration Document No. 91/5020. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-31).

New Data in Support of Response to Reviewer's Comments to Field Rotational Crops Study:

34. Paulick, R. C. January 1991. Magnitude of the residue of quinclorac (BAS 514 H) in rotational crops (mustard and turnips) following rice culture in Louisiana (RCN 87096) and Mississippi (RCN 87098). Registration Document No. 91/5022. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplements Panek, et. al. 1989. Fall and annual rotational crop study for quinclorac (FACET Herbicide) following aquatic use. MRID 41063567-A-C). (MRID 41784-28)

XII. 171-4 Storage Stability

New Data:

35. Stewart, J. January 1991. Freezer storage stability of quinclorac and its metabolites in soil - 0, 17, 21 month analysis. This is an interim report of a 36-month storage stability study. Registration Document No. 91/5016. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-32).
36. Eswein, R. P. January 1991. Freezer storage stability of quinclorac (BAS 514 H) in water - 15-17 month analysis. Interim report of an ongoing storage stability study. presents data from the 17 month time period. Registration Document No. 91/5015. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. Supplements : Eswein, R. P. 1988. Freezer storage stability of

quinclorac in water. BASF Registration Document No. 89/5015. MRID 41063571. (MRID 417814-33).

XIII. Reference Document

The following document contains published and unpublished documents referenced in the BASF Corporation studies listed above.

37. Huntsinger, D. February 1991. A compilation of published and unpublished documents referenced in BASF corp. studies. Registration Document No. 91/5024. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. (MRID 417814-34).

APPENDIX A

TABLE 2. <sup>14</sup>C-BAS 514 H EQUIVALENTS FOLLOWING APPLICATION OF 0.75 LB AI/A TO NON-FLOODED RICE AT GRENVILLE, MISSISSIPPI (PLOT 2)

Date	Days After Treatment	PPM, Water <sup>b</sup>	PPM Soil <sup>c</sup>			PPM, Soil (Average)		
			0-4"	4-8"	8-12"	0-4"	4-8"	8-12"
06/05/84	0	N/A	0.424	-	-	0.424	-	-
06/13	8 <sup>a</sup>	0.013	-	-	-	-	-	-
06/14	9	0.005	-	-	-	-	-	-
06/15	10	0.007	-	-	-	-	-	-
06/16	11	0.009	-	-	-	-	-	-
06/17	12	0.013	-	-	-	-	-	-
06/18	13	0.008	-	-	-	-	-	-
06/19	14	0.009	-	-	-	-	-	-
06/20	15	0.011	-	-	-	-	-	-
06/27	22	0.011	-	-	-	0.056	-	-
07/03	28	0.004	0.056	-	-	-	-	-
07/11	36	0.002	-	-	-	-	-	-
07/18	43	0.002	-	-	-	-	-	-
07/23	48	0.002	-	-	-	-	-	-
08/03	59	0.001	-	-	-	-	-	-
08/07	63	0.001	-	-	-	-	-	-
08/14	70	0.001	-	-	-	-	-	-
08/21(to 9-5)	77 (to 92)	<0.001	-	-	-	-	-	-
09/01	88	-	0.029	-	-	0.029	-	-
10/04	121	-	0.040	0.025	0.020	0.040	0.025	0.020
12/09	187	-	0.051	-	-	0.045	0.041	0.032
			0.034	0.021	0.018			
			0.051	0.063	0.047			
			0.039	0.038	-			
04/02/85	303	-	0.063	0.028	0.021	0.063	0.028	0.021
04/04	305	-	0.020	0.022	0.023	0.040	0.024	0.021
			0.063	0.028	0.021			
			0.037	0.021	0.019			



TABLE 2. (Continued)

Date	Days After Treatment	PPM, Water <sup>b</sup>	PPM Soil <sup>c</sup>			PPM, Soil (Average)		
			0-4"	4-8"	8-12"	0-4"	4-8"	8-12"
04/17	319	-	0.052	0.057	0.036	0.047	0.046	0.029
04/24	326	-	0.041	0.034	0.021	0.030	0.064	0.038
05/12	344	-	0.123	0.107	0.058	0.065	0.089	0.032
05/20	352	-	0.037	0.022	0.019	0.036	0.027	0.024
05/21	353	-	0.065	0.089	0.032	0.067	0.036	0.012
06/08	368	-	0.036	0.027	0.024	0.042	0.029	0.017
06/25	385	-	0.079	0.026	0.023	0.060	0.038	0.020
			0.055	0.047	<0.002			
			0.039	0.019	0.017			
			0.045	0.039	NA			
			0.076	0.037	0.011			
			0.043	0.039	0.029			

<sup>a</sup>Plot was flooded at 7 DAT (6-12).

<sup>b</sup>Water data from Reference 3, p. 12.

<sup>c</sup>Soil data from Reference 4, pp. 19, 25 and 26.

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