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128850

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Date Out of EFGWB: JUN 28 1990

To: Joanne Miller
Product Manager 23
Registration Division (H7505C)

From: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Groundwater Branch ~~Branch~~/EFED (H7507C)

Through: Hank Jacoby, Chief
Environmental Fate and Groundwater Branch Branch/EFED (H7507C)

Attached, please find the EAB review of . . .

Reg./File # : 8340-GR

Chemical Name : Glufosinate ammonium

Type Product : Herbicide

Product Name : Ignite

Company Name : Hoechst Celanese Corporation

Purpose : response to registration standard: additional data submitted in support of full registration on terrestrial food crops, terrestrial nonfood, domestic outdoor, and greenhouse sites

Date Received: 1/4/90

Action Code: 101

Date Completed: JUN 28 1990

EFGWB # (s): 90-~~0267~~ 0271

Monitoring Study Requested: _____

Total Reviewing time: 12.0 days

Monitoring Study Volunteered: _____

Deferrals to:

_____ Ecological Effects Branch

_____ Science Integration and Policy Staff, EFED

_____ Non-Dietary Exposure Branch, HED

_____ Dietary Exposure Branch

_____ Toxicology Branch I, HED

_____ Toxicology Branch II, HED

GLUFOSINATE AMMONIUM 90.0267 1.1

1. **CHEMICAL:** Common name:

Glufosinate ammonium

Chemical name:

parent -- Monoammonium 2-amino-4-hydroxymethylphosphinyl-butanoate or ammonium-DL-homoalanin-4-yl methylphosphinate.

degradates

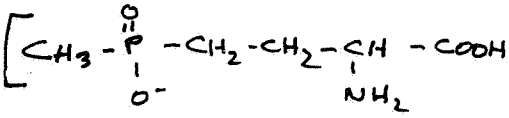
3-Methylphosphinico-propionic acid	-- HOE 061517
2-methylphosphinico-acetic acid	-- HOE 064619
3-methyl phosphinico-3-oxo-propionic acid	-- HOE 086486
2-acetamido-4-methylphosphinico-butanoic acid	-- HOE 085355

Trade name(s):

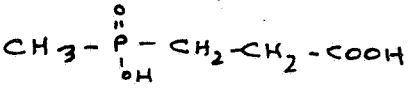
Ignite; Hoe 039866.

Structures:

parent



HOE 061517



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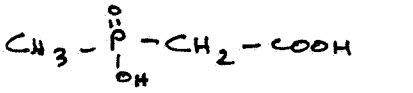
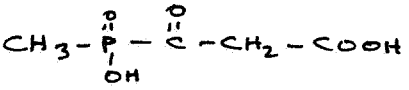
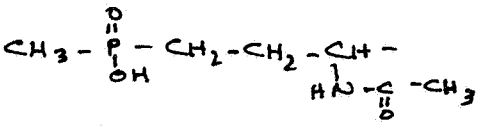


HOE 086486



HOE 085355



Formulations: 1.67 lb ai/gallon (16.22% ai) aqueous soluble.

Physical/Chemical properties:

Molecular formula: $C_5H_{15}N_2O_4P$.
Molecular weight: 198.2
Physical state: Solid.
Melting point: 215 C.
Solubility: 1370 g/L ± 11% at 22 C.
Octanol/water partition coefficient: <0.1.

2. **TEST MATERIAL:** described in individual DERs

3. STUDY/ACTION TYPE:

Response to Registration Standard, data in support of application for full registration for use on terrestrial food crop, terrestrial nonfood, domestic outdoor, and greenhouse sites.

4. STUDY IDENTIFICATION:

Horton, W.E., Mayasich, J.M. **Ignite Herbicide: Petitioner Response to the EPA Environmental Fate and Ground Water Branch Reveiew Dated October 13, 1988.** submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 11/15/89. Received EPA 12/12/89 under MRID # 413231-14.

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation in Water at pH 5, 7;, and 9.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-15.

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation on Sterile Soil.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-16.

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation on Non-Sterile Soil.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 9/6/89. Received EPA 12/12/89 under MRID # 413231-17.

Stumpf, K. **Hoe 039866 - ^{14}C, Degradation in Different Soils Under Aerobic and Anaerobic Conditions at an Application Rate of 1.6 mg/kg.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-19.

Stumpf, K. **Hoe 061517 - ^{14}C, Metabolite of Hoe 039866 Degradation in a Sandy Loam Soil under Aerobic Conditions at Application Rates of 0.5 and 1.0 mg/kg.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 3/20/89. Received EPA 12/12/89 under MRID # 413231-18.

Gildemeister, H. 1987. Hoe 039866-^{14}C: **Anaerobic soil metabolism study.** Project No. CB008/86, Report No. A36191. Unpublished study prepared by Hoechst AG, Frankfurt, Germany, and submitted by Hoechst Celanese Corp., Somerville, NJ. MRID# 405010-10

Gildemeister, H. **Hoe 039866 - ^{14}C, Anaerobic Soil Metabolism Study.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 2/2/89. Received EPA 12/12/89 under MRID # 413231-20. *supplement to Gildemeister, H., Jordan, H.J., and Schink, C. Anaerobic Soil Metabolism Study, dated 8/19/87.*

Sarafin, R., **Hoe 064619 Adsorption/Desorption in the System Soil/Water.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 2/10/89. Received EPA 12/12/89 under MRID # 413231-21.

Sarafin, R., **Hoe 064619 Assessment of Volatilization from Soil**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 12/12/89 under MRID # 413231-22.

Schwalbe-Fehl, M., Stumpf, K. **Reply to the EPA Environmental Fate Data Review Dated October 14, 1988**. developed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-25.

Schwalbe-Fehl, M., Stumpf, K. **Hoe 039866-^{14}C Residue Determinations and Metabolism in Rotational Crops Sown 120 Days After Treatment of Soil**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-26.

Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Crops Rotated After Soybeans from Geneseo, Illinois**. performed by Van Der Schaff Agricultural Research, Inc., Geneseo, IL, USA, and Dr. Specht and Partner, Hamburg, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-27.

Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Soil from Geneseo, Illinois**. performed by Van Der Schaff Agricultural Research, Inc., Geneseo, IL, USA, and Dr. Specht and Partner, Hamburg, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-23.

Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Crops Rotated After Soybeans from Salisbury, Maryland**. performed by PANAGRI, Princess Anne, MD, USA, and Bayer *Hauptversuchsansalt fuer Landvirtschaft*, Wiehenstephan, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-28.

Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Soil from Salisbury, Maryland**. performed by PANAGRI, Princess Anne, MD, USA, and Bayer *Hauptversuchsansalt fuer Landvirtschaft*, Wiehenstephan, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-24.

Schwalbe-Fehl, M., Fischer, R. **Reply to the EPA Environmental Fate Data Review Dated October 20, 1988 Hoe 039866 Bioaccumulation in Fish**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/22/88. Received EPA 12/12/89 under MRID # 413231-30.

5. REVIEWED BY:

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Date: 7/3/90

6. APPROVED BY:

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Date: JUN 28 1990

7. CONCLUSIONS:

ENVIRONMENTAL FATE ASSESSMENT

Available information indicates that glufosinate ammonium has at least the potential to persist and to migrate from application sites, although submitted field studies have not shown this to occur. The following characteristics (studies which fulfill guidelines requirements are in **BOLD AND UNDERLINED** type) are based on current data:

1) **STABLE TO HYDROLYSIS** (estimated half-life of > 300 days)
2) **STABLE TO AQUEOUS PHOTOLYSIS** (no degradation after 35 days irradiation)
3) somewhat stable to soil photolysis -- An UNACCEPTABLE soil photolysis study at much higher than use concentrations indicates a process with a 35 - 36 day half-life which is light-mediated and for which a live microbial population is also necessary
4) **SUSCEPTIBLE TO SOIL MICROBIAL METABOLISM WITH HALF-LIVES RANGING FROM 3.7 TO 30** days under various **AEROBIC CONDITIONS**, and **45 - 60 DAYS UNDER ANAEROBIC CONDITIONS** at 8.8 ppm in silt loam. These half-lives appear to be concentration dependent, with slower rates at higher concentrations
5) **SOMEWHAT SUSCEPTIBLE TO AEROBIC AQUATIC METABOLISM WITH A HALF-LIFE OF 64 DAYS** at ca. 1.8 ppm
6) **MOBILE — PARENT AND PRIMARY DEGRADATE (HOE 061517) ARE MOBILE** (highly water soluble) under laboratory conditions
7) has not been detected at depth, nor has the primary degradate, in several field dissipation studies. Half-lives of parent ranged from ca. 3 - 10 days.
8) does not accumulate into field rotational crops planted 91 - 97 days after treatment (wheat, lettuce, radishes sampled at several intervals), although a moderate amount of residue occurred in seeds and straw from the primary crop (soybeans) harvested at maturity. These data suggest a replanting interval of 3 - 4 months might be adequate for the tested crop groups.
9) **DOES NOT ACCUMULATE IN FISH** in a laboratory study.

Glufosinate ammonium is very mobile (K_ds of 0.08 to 3.48 in sand and two silt loams) to slightly mobile (K_d of 52.85 in a "volcanic ash" clay) and resistant to most degradative processes except metabolism, where half-lives vary from less than one week to two months depending on conditions. The primary degradate (HOE 061517) is very mobile (K_ds of <0.1 to 1.53 in sand and two silt loams) to somewhat immobile (K_d of 133 in a "volcanic ash" clay).

GROUND WATER ASSESSMENT

Although in the submitted field studies no residues of parent or metabolites have been detected below the surface 10 cm of soil, their persistence and mobility suggest that they could conceivably reach ground water in the most vulnerable areas, e.g., Florida citrus orchards. Once there, the primary routes of disappearance would be dilution/diffusion and metabolism. Since ground water microbial activity is typically much lower than that of soil, metabolism would be expected to be slow under these conditions. Other degradative processes, e.g. hydrolysis, would not be major factors, as indicated by the laboratory studies.

SURFACE WATER ASSESSMENT

Due to high solubility and poor adsorption to most soils, parent and primary degradate could be carried into bodies of surface water by rainfall, irrigation, etc. The tendency would be for these compounds to remain in solution, where the primary routes of disappearance would be dilution and relatively slow metabolism. An acceptable aerobic aquatic metabolism study indicated a half-life of ca. two months in the water layer, and small but persistent levels in sediment. Hydrolysis and unsensitized aqueous photolysis are not major routes of disappearance for glufosinate ammonium, as indicated by the laboratory studies.

DATA BASE ASSESSMENT

Additional information is necessary on the following:

- soil photolysis -- a ***NEW STUDY*** under conditions more nearly approximating actual use rates
- soil metabolism -- information needed on MRID # 413231-18 and 19 -- comparisons of experimental soils with US soils -- e.g. Deutschland soil # 2 is similar to soil found in the northeast quadrant of Smalltown, MD, USA
- laboratory volatility -- information on the modeling scheme used. Present information does not support granting a waiver.
- field dissipation
  - Since there is a vineyard use, a **field dissipation study** is required in this special area.
  - Due to the as yet undetermined potential for contamination of ground water in highly vulnerable orchard sites such as Florida citrus, a **field dissipation study** in one of these areas is required.
  - Further data requirements, such as a ground water monitoring study, may be imposed as a result of these data.
  - The sensitivity of the analytical method in the current studies is 0.04 ppm, and for these studies to be fully acceptable, the applicant should demonstrate that the method is the best currently available. Also, a sample chromatogram showing separation of the three reference (authentic) compounds is necessary for complete acceptability.
- field rotational crop accumulation -- The sensitivity of the analytical method in the current studies is 0.04 ppm, and for these studies to be fully acceptable, the applicant should demonstrate that the method is the best currently available. Also, a sample chromatogram showing separation of the three reference (authentic) compounds is necessary for complete acceptability.

8. **RECOMMENDATIONS:**

The necessary information to complete the data base (as listed above) should be supplied with all due speed. Supporting information relative to the request for a waiver of laboratory volatility data should be submitted.

9. BACKGROUND:

Glufosinate ammonium is a nonselective foliage-applied herbicide used to control a broad spectrum of emerged annual and perennial grass and broadleaf weeds on field and vegetable crops, orchards, vineyards, terrestrial nonfood sites (including dry ditches and canals, and ditch banks), domestic outdoor sites, and greenhouses. It will also control or suppress certain woody and herbaceous plant. Glufosinate ammonium is primarily a contact herbicide with limited systemic activity; plants that have not emerged will not be controlled and there is reported to be no residual activity. Glufosinate ammonium is formulated as a 1.67 lb/gallon (16.22%) aqueous soluble, and it may be tank-mixed with numerous other pesticides. There appear to be no tolerances for glufosinate or its primary metabolite as of the 1989 40CFR.

The status of data requirements is as follows:

Hydrolysis -- fulfilled -- One study (Goerlitz et al., MRID # 403456-56) was previously reviewed and fulfills data requirements. Glufosinate ammonium did not hydrolyze in sterile aqueous solutions buffered to pH 5, 7, and 9. The hydrolytic half-life of glufosinate was estimated by the registrant to be >300 days.

Photodegradation in water -- fulfilled -- **Stumpf (MRID # 413231-15, *reviewed in this document*) investigated photolysis under a xenon lamp and found that no compounds except the test substance were found in the buffers after termination of irradiation, and practically no formation of CO_2 or other volatile degradates. Glufosinate ammonium is photolytically stable in sterile aqueous solutions.**

One previously reviewed study (Stumpf and Schink, MRID # 403456-57) did not fulfill data requirements because it was terminated after 120 hours, and the artificial light source was not similar to sunlight. [^{14}C]Glufosinate did not degrade under these conditions.

Photodegradation on soil -- not fulfilled -- **Stumpf, K. (MRID # 413231-16 and 17, *reviewed in this document*) -- In this study, dark controls indicated a (soil metabolic) half-life of some 300 days, which is in sharp contrast to other studies discussed below. Since they were done at a much higher concentration than those for soil metabolism, and high concentrations are known to result in slower relative rates of degradation, these results cannot be compared to the metabolism studies discussed below. A new study is required, under conditions which closely compare to a normal use rate and conditions. The study does indicate that glufosinate ammonium is subject to some type of light-mediated degradation on the surface of a sandy loam soil treated at 30 ppm and containing an active microbial population, but not on a "sterile" soil. Half-life under these conditions was 35 - 36 days natural sunlight equivalent (moderately labile).**

A previously reviewed study (Stumpf and Schink, MRID # 403456-58) did not fulfill data requirements because the study was terminated after 45 hours. The major degradate was 3-methyl phosphonicopropionic acid (HOE 061517).

Aerobic soil metabolism -- partially fulfilled -- **Stumpf *et al* performed additional studies (MRID # 413231-18 and 19) *reviewed in this document* for the reasons given below. For these studies to be completely acceptable, soil characteristics must be supplied.**

MRID # 413231-19 -- to establish the rate of degradation of HOE 039866 at the normal application rate (1.6 ppm) since prior studies have showed some concentration effects. E.g., at 2.3 mg/kg (2.3 ppm), the half life was 5 - 10 days; above 5 ppm it was 15 - 30 days. In this study, DT-50 [*time to 50% disappearance*] values of 3.7 -10 days for HOE 039866, 13 - 22 days for HOE 061517, and approximately 20 days for HOE 064619.

MRID # 413231-18 -- to determine the DT-50 and DT-90 values for HOE 061517 independent of HOE 039866. The only degradation product detected was HOE 064619. From the decline curves, DT-50 values of 7 -14 days were estimated for HOE 061517, and 20 - 30 days for HOE 064619 [*agreeing with the above study*].

Four studies were previously reviewed. One study (Smith, MRID # 405010-18) was unacceptable and one study (Gildemeister and Jordan, MRID # 403456-59-C and D) provided supplemental information only. A third study (Stumpf, MRID # 403456-59-A) was scientifically sound and partially fulfills data requirements by providing information on the aerobic soil metabolism of glufosinate ammonium. However, the study was terminated after 120 days, before the patterns of formation and decline of the degradates 3-methylphosphinico-propionic acid and 2-methylphosphinico-acetic acid were established.

A fourth previously reviewed study (Stumpf, MRID # 403456-59-B) was scientifically sound and partially fulfills data requirements by providing information on the aerobic soil metabolism of 3-methylphosphinico-propionic acid, the major degradate of glufosinate ammonium. The pattern of decline of 2-methylphosphinico-acetic acid has not been established by this study. Results from these two studies were as follows:

1) [^{14}C]Glufosinate degraded with a half-life of ≈8-16 days in a silt loam and two sandy loam soils treated at ≈7.5 ppm. The [*registrant-calculated*] half-lives were 20.7-23.3 days for the three soils.

2) [3-^{14}C]3-Methylphosphinico-propionic acid (Hoe 061517) at ≈1.6 kg/ha (1.42 ppm), degraded with a half-life of >120 days in sandy loam soil.

Various values for half-lives are as follows:

<u>HOE 039866</u>
study 3 -- previously reviewed
8 - 16 days at 7.5 ppm in silt loam, and two sandy loams
study 5 -- discussed in this review
3.7 - 10 days at 1.6 ppm in sandy loam, silt loam, loamy sand, marshy soiland peat soil
5 - 10 days at 2.3 ppm, reported in this study, data not presented
15 - 30 days above 5 ppm, reported in this study, data not presented

<u>HOE 064619</u>
study 5 -- discussed in this review-- 20 days at 1.6 ppm **<u>parent</u>** in loamy sand

HOE 061517

study 4 -- previously reviewed -- >120 days at 1.42 ppm **of degradate**

study 5 -- discussed in this review -- 13 - 22 days at 1.6 ppm **parent** in loamy sand

Anaerobic soil metabolism -- fulfilled -- A previously reviewed study (Gildemeister, MRID # 405010-14) did not fulfill data requirements because two degradates detected at ≈0.04 ppm [*ca 0.5% -- EBC*] were not identified. [^{14}C]Glufosinate degraded with a half-life of 45-60 days in a silt loam soil treated with at approximately 8.8 ppm and incubated anaerobically (flooding plus N_2 atmosphere) after 30 days of aerobic incubation. The [*registrant-calculated*] half-life was 56 days.

In Gildemeister's subsequent investigation (MRID # 413231-20 *discussed in this review)*, the two degradates have been identified according to their HPLC retention times. M1 is HOE 064619 (2-methylphosphinico-acetic acid), and M3 is HOE 086486 (3-methyl phosphinico-3-oxo-propionic acid). In the aerobic study, these compounds were isolated by their retention times and their structures confirmed by GC/MS. They have not been specifically confirmed for this study.

Aerobic aquatic metabolism -- fulfilled -- A previously reviewed study (Gildemeister et al., MRID # 403456-60) fulfills data requirements by providing information on the degradation of glufosinate ammonium in a gravel-pit water:sand sediment system maintained under aerobic conditions. [^{14}C]glufosinate degraded with a half-life of 64 days in a gravel-pit water:sand sediment system that had been treated at approximately 2 kg/ha. The [*registrant-calculated*] half-life was 29.1-35.2 days.

Mobility - Leaching and adsorption/desorption -- fulfilled for parent and two degradates. **In a study discussed in this review, (Sarafin, MRID # 413231-21), HOE 064619 was not mobile when tested with a silt loam soil.**

Two studies were previously reviewed. One study (Gildemeister and Scheinkoenig, MRID # 403456-61) was unacceptable because the soils were sieved through 250-500 µm mesh screens, which removes a portion of the sand fraction and may cause the pesticide to appear less mobile.

A second study (Goerlitz, MRID # 403456-62) was acceptable and partially fulfills data requirements by providing information on the mobility (batch equilibrium) of unaged glufosinate and unaged 3-methylphosphinico-propionic acid (Hoe 061517) in a sand, two silt loam, and a "volcanic ash" clay soil.

> **[^{14}C]glufosinate was very mobile in sand and two silt loam soils (k_{ads} 0.08 - 3.48) and slightly mobile in "volcanic ash" clay soil (k_{ads} = 52.85); respective K_{oc} values were 9.6, 156, 352, and 1229.**
>
> [^{14}C]3-methylphosphinico-propionic acid was very mobile in sand and two silt loam soils (k_{ads}s <0.1 to 1.53) and somewhat immobile in a "volcanic ash" clay soil (k_{ads} = 133). respective K_{oc} values were <10, 84.1, 158, and 3093.

Laboratory volatility studies -- not fulfilled -- the applicant has submitted information *discussed in this review* on the vapor pressure of glufosinate ammonium (measured at ca 10^{-4}, but probably much less), provided a theoretical calculation of how it partitions into various environmental compartments, and requested a waiver of this requirement. The waiver cannot be granted at this time, but EFGWB will reconsider when further information on the partitioning model is provided. The measured vapor pressure is, as the applicant states, probably a "psuedo" vapor pressure produced by decomposition of the molecule [*loss of "ammonium" -- EBC*].

Terrestrial field dissipation studies -- partially fulfilled. Available data, while not fulfilling Guidelines requirements, indicate that parent material and degradates are not persistent and are not detectable at depths below the surfacial 10 cm.

Mayasich (MRID # 413231-23, *study discussed in this review*) presents a study done on bare soil nominally treated with 1.8 lb ai./A. Analytical results on the soil did not confirm the stated treatment rate, and indicated a level approximately one-third the nominal. The chromatograms presented in the submission do not show separation of a mixture of authentic compounds. Also, the method is less sensitive than the 0.01 ppm EFGWB prefers. Validation of this method is essential to the final evaluation and acceptance of this study and the three related ones (the Maryland soil study discussed below, and the concurrent field rotational crop studies). Results were as follows:

1) A half-life of 9.8 days has been calculated for HOE-039866.
2) No HOE-039866 residues were found at any time or depth below the 10 cm level.
3) HOE-061517 occurred only at one sampling interval (0 - 10 cm, day 34, 0.06 ppm). No residues were found below 10 cm at any time.
4) HOE-064619 was not detected at any time.

Mayasich (MRID # 413231-24, *discussed in this review*) presents additional information on dissipation in a cropped plot in Salisbury, MD treated at 1.8 lb a.i./ A (120% maximum label rate).

1) A half-life of 8.0 days has been calculated for HOE-039866.
2) No HOE-039866 residues were found at any time or depth below the 10 cm level.
3) HOE-061517 began to appear in the 0 - 10 cm depth at day 0, and gradually increased to 0.17 ppm after irrigation on day 7, and were undetectable by day 61. No residues were found below 10 cm at any time.
4) HOE-064619 appeared at the 0 - 10 cm depth by day 30, was at or near the detection limit (0.05 ppm) on days 30 and 61, and undetectable thereafter. No residues were found below 10 cm at any time.

Although these two studies have limited usefulness at this time due to the deficiencies noted above, they do appear to indicate that glufosinate residues do not migrate in the field.

Three previously reviewed studies (Horton and Graney, MRID # 403456-63, 403456-64, 403456-65) provide supplemental information, but do not fulfill data requirements because the pattern of formation and decline of 2-methylphosphinico-acetic acid, a major degradate of glufosinate ammonium, was not addressed and acceptable freezer storage stability data were not provided.

Glufosinate had an initial half-life of <3 days and a second half-life of 14-30 days in three unvegetated field plots of loamy sand soil in Quantico, Maryland, [*sic*] that were treated at 3.0 lb ai/A; the [*registrant-calculated*] half-life was 20.2 days. Neither glufosinate nor 3-methylphosphinico-propionic acid were detected in soil samples taken deeper than 10 cm (soil was sampled to 75 cm) at any time during the 147 day study.

Schwalbe-Fehl and Stumpf (MRID # 413231-26, discussed in this review) found in a "field-confined" rotational crop study that significant soil residues were only found in the upper 5 cm of a plot treated at 0.87 ppm ai.

Glufosinate dissipated with a half-life of 7-14 days in unvegetated field plots of loamy sand soil in Sunnyside, Washington that were treated with glufosinate ammonium at 2.0 lb ai/A; the [*registrant-calculated*] half-life was 15.0 days. Neither glufosinate nor 3-methylphosphinico-propionic acid were detected in any soil samples taken deeper than 3 inches (soil was sampled to 24 inches) at any time during the study (duration of 90 days).

Glufosinate dissipated with a [*registrant-calculated*] half-life of 6.3 days in three unvegetated field plots of silt loam soil in Geneseo, Illinois, that were treated at 3.0 lb ai/A. Neither glufosinate nor 3-methylphosphinico-propionic acid were detected in any soil samples taken deeper than 10 cm (soil was sampled to 75 cm) at any time during the study (duration of 149 days).

Confined rotational crop accumulation -- the studies discussed below are not completely acceptable, but do not need to be repeated if the field studies become acceptable

A study by Schwalbe-Fehl and Stumpf (MRID # 405010-16) was previously reviewed and most of the comments have been answered in a reply by Schwalbe-Fehl and Stumpf (MRID # 413231-25) discussed in this review. It provides supplementary information but is still not acceptable. Accumulation is not shown to occur in the test plants.

Schwalbe-Fehl and Stumpf (MRID # 413231-26, discussed in this review) tested spinach, radishes, wheat, and carrots planted 120 days after treatment of soil with 0.87 ppm a.i [ca. 1/2 the maximum label rate]. They found that only wheat contained more than 0.04 mg/kg (0.04 ppm) of residue. The only identifiable metabolite in the wheat extracts was HOE 061517, up to 20% of the total radioactive residue. Most radioactivity was associated with cellulose or hemicellulose.

The analytical method in this study is somewhat less sensitive than is desirable. It will be acceptable if the applicant can demonstrate that it is the best available at this time. The study will then become fully acceptable, but can only support a use rate approximately half the maximum label rate. A 4 month (120 day) interval after the final treatment appears to be appropriate for planting of rotational crops based on these data.

Field rotational crop accumulation -- partially fulfilled

Mayasich (MRID # 413231-28), *discussed in this review*) found that no residues were detected in any material from rotational crops of radishes, lettuce, and wheat planted 91 - 97 days after treatment of a cropped plot in Salisbury, MD with 1.8 ppm (120% maximum label rate -- soil analyses appear to bear this

out). No residues of parent were observed in [primary crop] soybean grain or straw harvested 135 days after planting. An average of 0.06 ppm HOE-061517 was found in soybean seed, and 0.09 ppm in soybean straw. An average of 0.25 ppm HOE-061517 was found in soybean straw.

Mayasich (MRID # 413231-27), *discussed in this review*, also found that no detectable residues were measured in material sampled from any rotational crop grown in a plot in Geneseo, IL, which was bare-ground treated at a nominal 120% maximum label rate. Analytical results on the soil did not confirm the stated treatment rate, and indicated a level approximately one-third the nominal. The rotational crops, radish, leaf lettuce, and wheat were planted 91 days after treatment and examined at 1/4, 1/2, and full maturity. No residues of parent were detected in [primary crop] soybean grain or straw harvest 135 days after planting. An average of 0.06 ppm HOE-061517 was found in soybean seed and 0.09 ppm in soybean straw harvested 135 days after planting.

These data therefore support a minimum replanting interval of 3 months for radishes, lettuce, and wheat.

Two previously reviewed studies (Schwalbe-Fehl, 405010-15, 405010-16) were ruled unacceptable because the application rates could not be confirmed and the extent of pesticide uptake by the crops in relation to the concentration of pesticide in the soil was uncertain. In addition, these studies would not fulfill data requirements because [^{14}C]residues were not characterized in all plants containing >0.01 ppm of residues.

Accumulation in laboratory fish -- fulfilled -- One study (Fischer and Schwalbe-Fehl, MRID # 405010-17) was reviewed and reveals that residues did not accumulate in bluegill sunfish during 28 days of exposure at 0.1 ppm in a flow-through system. This study was originally rejected due to inappropriately applied technical criteria.

The following data requirements are deferred or are not required for presently registered uses:

Photodegradation in air studies: No data were reviewed. The data requirement is deferred pending the receipt of acceptable laboratory volatility studies.

Anaerobic aquatic metabolism studies: No data were reviewed; however, no data are required because glufosinate ammonium has no aquatic or aquatic impact use.

Field volatility studies: No data were reviewed. The data requirement is deferred pending the receipt of acceptable laboratory volatility studies.

Directions for Use: label attached

Application rates vary with the type and maturity of the weeds being controlled.

1) On terrestrial food crop sites other than minimum tillage systems, the maximum application for soybeans is 7.0 pints product [*1.46 lb a.i.*] /A, with no more than 21.6 pints product [*4.51 lb a.i.*]/A applied to other sites (e.g. vine, nut and orchard crops) in a given year.
2) On minimum tillage systems, no more than 7.2 pints product [1.50 lb a.i.]/A/year should be applied.
3) On terrestrial nonfood sites, the maximum application is 7.0 pints product [*1.46 lb a.i.*]/A, with no more than 28 pints product [*5.84 lb a.i.*]/A applied to any site in a given year.

The label states:

1) Do not graze treated soybean or corn forage, or orchard cover crops
2) Do not apply through irrigation systems or by means of aerial equipment
3) Do not apply within 14 days of nut, apple, or grape harvest
4) Do not replant treated areas with cereal grains for at least 120 days following the application of glufosinate ammonium.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: Refer to the attached reviews of individual studies.

11. COMPLETION OF ONE-LINER: attached

12. CBI APPENDIX:

All data reviewed here are considered "company confidential" by the registrant and must be treated as such.

DATA EVALUATION REVIEW 1

I. Study Type: summary responses to the 10/13/88 review

II. Citation:

Horton, W.E., Mayasich, J.M. **Ignite Herbicide: Petitioner Response to the EPA Environmental Fate and Ground Water Branch Reveiew Dated October 13, 1988.** submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 11/15/89. Received EPA 12/12/89 under MRID # 413231-14.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions: n.a.

V. Materials and Methods: n.a.

VI. Study Author's Results and/or Conclusions:

photolysis, aqueous -- glufosinate-ammonium does not degrade photolytically. There was no measurable degradation after the equivalent of 35 to 39 days of irradiation in buffered (pH 5, 7, or 9) sterile aqueous solution. No compounds except parent were found at any time period or pH. There was practically no formation of $^{14}CO_2$ or other volatile degradates.

photolysis, soil -- glufosinate-ammonium does not degrade photolytically on a sterile soil surface. There was no measurable degradation after the equivalent of 32 days of continuous irradiation. However, glufosinate-ammonium is subject to photodegradation on a non-sterile soil surface. When irradiated with a 12 hour light/dark cycle equivalent to 48 days of natural sunlight, it degrades with an estimated half-life of 37 days.

metabolism, aerobic soil -- the half-life of glufosinate-ammonium in sandy loam soil was determined to be 7 and 14 days respectively for 0.50 and 1.0 mg/kg treatments. Between 63 and 69% of the total radioactive residue was CO_2. No other volatile components could be identified. One other degradation product was detected, 2-methylphosphinico-acetic acid (HOE-064619), accounting for between 31 and 38% at 21 days after application. HOE-064619 has an estimated half-life of between 20 and 30 days.

Another study tested sandy loam, silt loam, loamy sand, marsh soil, and peat with 120 days aerobic incubation followed by anaerobic incubation. Between 20 and 40% of the applied radioactivity was measured as CO_2 at the termination of the study. Aerobic half-lives were as follows:

sandy loam -- 3.7 days
silt loam -- 8.3 days
loamy sand -- 6.4 days
marsh soil -- 6.6 days
peat -- 10 days

metabolism, anaerobic soil -- The anaerobic portion of the study above demonstrated that mineralization was suppressed. Degradation of the parent was rapid, but that of the degradates was very slow.

Based on another study, degradates were identified by HPLC as 2-methylphosphinico-acetic acid (HOE-064619) and 3-methyl-phosphinico-3-oxopropionic acid (HOE-086486).

mobility -- leaching/adsorption/desorption -- 2-methylphosphinico-acetic acid (HOE-064619) showed higher adsorption than 3-methyl phosphinico-propionic acid (HOE-061517) or parent (HOE-039866). The K_{ads}s were >100, 3.48, and 1.56 respectively. Significant leaching of HOE-064619 seems highly unlikely.

volatility, laboratory -- The herbicide -- since it is a salt -- has an extremely low vapor pressure and an extremely high solubility in water. The petitioner requests a waiver for the field and laboratory volatility studies.

field dissipation, terrestrial -- Ignite herbicide was applied at 1.8 lb/A ai to bare ground subsequently planted to soybeans in Geneseo, IL. The average HOE-039866 residues in the 0-10 cm core decreased rapidly from 0.37 ppm immediately after application to non-detectable levels by day 34. No detectable residues of HOE-039866 were found below the 10 cm zone at any depth or any time period. No detectable residues of HOE-064619 were found at any depth or time period. HOE-061517 was only found in the 0-10 cm core on day 34, and at no other time or depth. [lod 0.05]

In a separate study in Salisbury, MD, Ignite was applied at 1.8 lb/A ai to weed-containing plots which were planted to soybeans. Residues of HOE-039866 declined from 0.81 ppm immediately after treatment to non-detectable levels at day 61. No detectable residues were detected below the 10 cm zone at any depth or time. HOE-016517 began to appear at day 0 (0.05 ppm), increased to 0.17 ppm (day 7), and were not detectable by day 61. No detectable residues were found below the 10 cm zone.

rotational crop accumulation, confined -- ^{14}-C HOE-039866 was applied to sandy loam soil at 1.0 kg/ai/ha (0.45 ppm), and the system was aged for 120 days. Radishes and carrots (root), spinach (leafy), and wheat (small grain) were planted and grown to maturity. Residues were as follows: wheat straw -- 0.19 ppm total; wheat stubble --0.20 ppm; wheat chaff-- 0.07 ppm; wheat grain-- 0.05 ppm. Identifiable extractable residues were exclusively HOE-061517, and the majority of unextractable residues were associated with cellulose or hemicellulose. Analysis of soil samples yielded a half-life of 20 days for HOE-039866, 45 days for HOE-064617, and 30 days for HOE 064619.

rotational crop accumulation, field -- HOE-039866 was applied to a plot where soybeans and accompanying weeds were growing. At day 91 post-treatment, the soybeans were removed and rotational crops of leaf lettuce (leafy), radishes (root), and wheat (small grain) were planted. No detectable residues were found in any rotational crop.

fish bioaccumulation, laboratory -- Observed BCFs were fractional, i.e. concentration of glufosinate ammonium in the fish was less than that in the water. Based on water solubility and K_{OW} values, this study is not required.

VII. Reviewer's Comments: These responses will be more fully discussed in specific DERs. The applicant is correct that a new fish bioaccumulation study should not be required.

VIII. CBI Information Addendum: n.a.

DATA EVALUATION REVIEW 2

I. Study Type: Photolysis, Aqueous (161-2)

II. Citation:

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation in Water at pH 5, 7;, and 9.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-15.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions:

1) Glufosinate ammonium does not photodegrade under Guidelines conditions.
2) The study fulfills data requirements.

V. Materials and Methods:

test material -- ^{14}-C labelled glufosinate-ammonium at ca. 1.5 ppm
test buffers -- 0.01 M acetate (pH 5), phosphate (pH 7), borate (pH 9)
light source -- xenon arc
light intensity -- 2.16 $\pm$ 0.5 x natural sunlight
test conditions -- 25 $\pm$ 2° C (light exposed samples), 21 $\pm$ 2° (dark controls)
test duration -- 192 hrs (equivalent of 16 twelve-hour periods) for pH 5 and 7; 216 hours (equivalent to 18 twelve-hour periods) for pH 9. At the reported intensity, 196 hours is equivalent to 35 days natural sunlight (2.16 x 16 = 34.56)
volatiles trapping -- "suitable" per applicant
organics -- 0.5 gm resin in 10 ml water adjusted to pH 3 with H_2SO_4
CO_2 -- 10 ml alkylamine
both -- 20 ml methanol + 1 ml 1N NaOH cooled in dry ice
sterility testing -- before and after each irradiation series
sampling schedule
pH 5 and 7 -- 6, 24, 48, 72, 96, and 192 hours
pH 9 -- 6, 24, 48, 72, 96, 216 hours
analytical methods
volatiles -- resins from traps were extracted and analyzed by LSC
buffer solutions
total radioactivity by LSC
products by HPLC vs authentic compounds (HOE 039866, 064619, and 061517) -- lod 0.05 ppm vs 1.5 ppm total

VI. Study Author's Results and/or Conclusions: No compounds except the test substance were found in the buffers after termination of irradiation, and practically no formation of CO_2 or other volatile degradates. Glufosinate ammonium is photolytically stable in sterile aqueous solutions.

VII. Reviewer's Comments: The investigator's conclusions are supported. Glufosinate ammonium does not photodegrade under test (Guidelines) conditions.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 17 through 38 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION REVIEW 3

I. Study Type: photolysis, soil

II. Citation:

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation on Sterile Soil**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-16.

Stumpf, K. **Hoe 039866 - ^{14}C, Photodegradation on Non-Sterile Soil**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 9/6/89. Received EPA 12/12/89 under MRID # 413231-17.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E. B. Conerly 5/10/90

IV. Conclusions: The study is not acceptable to fulfill the requirement for soil photolysis data, for reasons detailed below. A new study is required under conditions more nearly approximating use rates. The current study does provide some information:

1) Glufosinate ammonium is subject to light-mediated degradation on the surface of a soil containing an active microbial population, but not on a "sterile" soil.
2) Under the experimental conditions, the half-life in a sandy loam soil was 35 - 36 days natural sunlight equivalent (moderately labile).
3) The percentage of unextractable radioactivity increased over time to ca 30%.

V. Materials and Methods:

test compound -- ^{14}-C labelled in the 3 and 4 positions
sterile soil -- sandy loam "which had been sterilized"
non-sterile soil -- the same, but not sterilized
plate preparation -- soil was passed through a 2 mm sieve, made into a slurry, and coated onto 4 x 4 cm stainless steel plates which were dried overnight. The approximate weight of soil on one plate was 1.5 gm, and bulk density was 1.15 g/cm^3 [Therefore the soil layer was 1.5/1.15 cm^3 = 1.30 cm^3. The thickness of the soil layer was 1.30 cm3 volume /16 cm^2 surface area = .08cm =0.8 mm]. 51 ug of test compound (ca 30 ppm)
light source -- xenon arc lamp with 290 nm cut-off filters
exposure conditions -- 25±5°C, 120 hours (corresponding to 32 days). The experimental set up provided irradiation which was approximately 1.5 x more intense than sunlight

VI. Study Author's Results and/or Conclusions:

The soil photolysis of HOE 039866 was studied to determine the route and velocity of degradation and the nature of photolytic products.

RESULTS:

Sterile soil -- Formation of $^{14}CO_2$ amounted to about 2.3% of the applied radioactivity at the end. No further degradation products were observed. Dark controls showed no release of $^{14}CO_2$.

Non-sterile soil -- the calculated half life was 35 - 36 days under natural sunlight. Of the six degradation products detected, three were identified as the soil metabolites HOE 061517, HOE 064619, and HOE 085355. Three other degradates were each less than 10% of applied. Formation of CO_2 amounted to 7.6% of the applied at the end of irradiation. Corresponding dark controls did not release CO_2, and HOE 061517 was measured at 0 - 8%.

CONCLUSIONS:

HOE 039866 is subject to photodegradation on soil surfaces with a half life of 35 - 36 days under outdoor conditions. Mineralization to CO_2 and six metabolites shows that photodegradation takes place. The fact that HOE 039866 shows photolytic breakdown on soil surfaces, in contrast to its behavior in sterile buffer solution and on a sterile soil surface, is best explained by photoactivation by compounds (such as humic acid) in the soil, since HOE 039866 has no UV absorption at wavelengths >290 nm.

VII. Reviewer's Comments:

1) The study was performed at a concentration many times higher than the expected label rates and also approximately three time the highest rate used in the metabolism studies. The rate of metabolism is known to decrease with increasing concentration of Glufosinate ammonium, and this could be due to adverse effects on the soil microbes.
2) The dark, non-sterile, control is in effect a soil metabolism specimen and should reflect that process. Accordingly, it should yield a half-life somewhere in the range observed for soil metabolism studies, 3 - 30 days. Instead, it indicates a half-life somewhere around 300 days, pointing to an almost complete lack of metabolism in these specimens. This could be more evidence of an adverse effect on soil microbiota.
3) On the other hand, the observed decomposition cannot be explained solely by chemical photosensitization due to compounds in the soil, since degradation does not occur in the "sterile" light-exposed samples.
4) Both light and microbial presence are apparently required to produce any significant degradative effect under these conditions.
5) Since this study is inconsistent with, and even contradictory to, other studies, in both experimental conditions and results, and was done under conditions very different from expected use, it is not acceptable.

Although the report does not so state, the most likely sterilization method is autoclaving (steam heat under pressure). Besides inactivating microorganisms, this alters soil properties unpredictably, and the results from such a study are not necessarily useful predictors of environmental behavior. A curious result is that a small amount of radioactive CO_2 was apparently detected, but no other degradates -- the compound remaining after this release should also contain radiocarbon label and be distinguishable from parent. The applicant should provide a clarification of this observation.

The metabolites HOE 064619 and 085355 were formed only in light. HOE 061517 was formed in both light and dark, but represented a greater proportion of applied material in the light-exposed sample (0 - 8% vs 6 - 21%).

HOE 085355 (the first degradate in the proposed chain) is the parent **plus** an acetyl group added to the amino and **minus** the ammonium ion.

HOE 061517 (next in the chain) has a carbonyl group substituted for the amino group.

HOE 064619 (third in the chain) is HOE 061517 minus a methylene group.

Reported results can be summarized as follows:

sterile dark -- produced no detectable degradates

sterile light-exposed -- produced a small amount of CO_2

non-sterile dark -- extrapolated half life ca 300 days -- produced HOE 061517 (0 - 8%), no CO_2

non-sterile light-exposed -- extrapolated half-life 35 days -- produced HOE 061517 (6 - 21%), 064619, 085355, and CO_2

Since a new study must be performed, the applicant should note the following:

1) temperature should be controlled within closer tolerances, usually $\pm$ 1 °C <u>on the average</u>, although it is recognized that wider fluctuations may occur at the beginning and end of irradiation periods.

2) a study using sterile soil is additional information and may be useful, but is not required.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION REVIEW 4

I. **Study Type:** Metabolism, Aerobic Soil (162-1) and Anaerobic Soil (162-2)

II. Citation:

Study 1) Stumpf, K. **Hoe 039866 - ^{14}C, Degradation in Different Soils Under Aerobic and Anaerobic Conditions at an Application Rate of 1.6 mg/kg.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-19.

Study 2) Stumpf, K. **Hoe 061517 - ^{14}C, Metabolite of Hoe 039866 Degradation in a Sandy Loam Soil under Aerobic Conditions at Application Rates of 0.5 and 1.0 mg/kg.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 3/20/89. Received EPA 12/12/89 under MRID # 413231-18.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions:

V. Materials and Methods:

Study 1

test material -- 3,4-^{14}C-glufosinate ammonium, applied at a rate of 1.6 mg/kg (1.6 ppm)

test soils -- sandy loam, silt loam, loamy sand, marshy soil, and peat soil taken from the upper 10 - 15 cm of agricultural fields, stored with a "cover crop" of chickweed, exposed to artificial sunlight and irrigated when required. Before use they were sieved (<2 mm) and adjusted to approximately 75% of 1/3 bar.

incubation protocol

aerobic -- in the dark at 21 ± 2° C; both open and closed systems were used. In the closed system, CO_2 was trapped in 2-aminoethanol/2-methoxyethanol (3/7 vv), and other volatiles were trapped in 2-methoxyethanol. Vessels were sampled at days 0, 1,4, 7, 14, 20, 29, 60, 90, 120 days.

anaerobic -- sandy loam incubated for 7 days aerobically, then flooded with water and purged with nitrogen. Although redox potential and oxygen content did not reach their minimum values until day 11, CO_2 evolution was suppressed, and the conditions were considered to be anaerobic from the conversion point [day 7] on. Vessels were sampled at 11, 26, 46, and 71 days after conversion

soil extraction -- with hot water (60 - 70° C)

analytical methods

HPLC -- lod 0.008 ppm
GC/MS -- on acetylated/methylated derivatives
GC/FPD
combustion followed by LSC

Study 2 -- as above, except as noted

test material -- HOE 061517 (3-^{14}C-3-methylphosphinico-propionic acid), the main metabolite of HOE 039866, applied at 0.5 and 1.0 ppm
test soil -- sandy loam as above
sampling protocol -- days 0, 1, 3, 7, 21, 30, 63, 90, and 120

Study 3 -- supplemental material to a previously submitted study

VI. Study Author's Results and/or Conclusions:

Study 1
The objective of study 1 was to establish degradation rate at the normal application rate since prior studies have showed concentration effects. E.g., at 2.3 mg/kg, the half life was 5 - 10 days; above 5 ppm it was 15 - 30 days.

RESULTS
Aerobic
DT-50 values of 13 - 22 days were found for HOE 061517, and DT-50 of approximately 20 days for HOE 064619. HOE 039866 was quantitatively extractable from the sandy soils, but less so from silt, peat, and marsh.

Unextractable residues increased to 30 - 43% then decreased slowly.

The only volatile degradate detected in quantity was CO_2, although trace amounts of radioactivity were seen at 0.1 - 1.0% of applied in some day 43 [sic] samples.

In open vessels, recovery was 50 - 75% at day 120, but was 80 -90% in the closed vessels.

Anaerobic
Total mineralization was suppressed. Only 3.4% of $^{14}CO_2$ was formed. The disappearance time of the active ingredient was rapid with a DT-50 of 5 - 10 days, but both main metabolites were degraded very slowly. 69 - 82% of applied radiocarbon was still extractable at the end of the study (78 days after application).

CONCLUSIONS

The degradation of the herbicide glufosinate-ammonium is very fast in microbially active soils under aerobic conditions when the active ingredient is added at rates occurring in agricultural practice.

The aerobic degradation occurred *via* oxidative deamination and decarboxylation, forming HOE 061517 and HOE 064619. The metabolites too undergo rapid degradation to CO_2 and smaller molecules, and are incorporated into the microbial biomass of the soil, or adsorbed strongly to the soil.

HOE 039866 is degraded rapidly under aerobic and anaerobic conditions. It is therefore unlikely that, under normal agricultural conditions, either the active ingredient or metabolites will accumulate in the upper soil layer. The risk of transport to deeper soil layers is minimized and ground water contamination will not occur.

The decrease in bound residues after an initial increase means that these residues can also be degraded. The low level of extractable compounds at the end of the study indicates the rapid degradation of parent and metabolites.

DER 4.2

Degradation is slower in the closed systems, and the rate of degradation and CO_2 evolution is similar for open systems.

Study 2
The objective of the study was to determine the DT-50 and DT-90 values for HOE 061517 independent of HOE 039866.

RESULTS
Only one degradation product could be detected, HOE 064619, representing maximum of 38% (at 0.5 ppm) and 31% (at 1.0 ppm) of the applied material after 21 days. From the decline curve the metabolite has a DT-50 of 20 -30 days.

CONCLUSIONS
The degradation of both HOE 061517 and HOE 064619 is fast, and there is no risk of accumulation of these metabolites from the use of HOE 039866. The risk of transport to deeper soil layers is minimal.

VII. Reviewer's Comments:

Study 1

Additional information on the soils is needed. The country of origin of the soils is not given. The silt loam (Mississippi 2) is probably from the U.S.A.

The report refers to DT-50 and DT-90, rather than the more usual **half-life**. This terminology avoids any implications about kinetics of the system.

Although this does not invalidate the study, the method of soil extraction is not typical of studies reviewed by EFGWB. Hot water extraction is not exhaustive, and some of the unrecovered residues from this procedure may yield to another relatively mild technique. Some of this "bound" material is apparently bioavailable and may also be taken up by crops.

Study 2 -- The above comments apply.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

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DATA EVALUATION RECORD 5

STUDY 1) Gildemeister, H. 1987. Hoe 039866-^{14}C: Anaerobic soil metabolism study. Project No. CB008/86, Report No. A36191. Unpublished study prepared by Hoechst AG, Frankfurt, Germany, and submitted by Hoechst Celanese Corp., Somerville, NJ. MRID# 405010-10

STUDY 2) Gildemeister, H. **Hoe 039866 - ^{14}C, Anaerobic Soil Metabolism Study**. performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 2/2/89. Received EPA 12/12/89 under MRID # 413231-20. *Supplement to Gildemeister, H., Jordan, H.J., and Schink, C. Anaerobic Soil Metabolism Study, dated 8/19/87.*

STUDY 1 REVIEWED BY: L. Binari TITLE: Staff Scientist
EDITED BY: K. Patten TITLE: Task Leader
DER APPROVED BY: W. Spangler TITLE: Project Manager
ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

DER APPROVED BY: P. Datta
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-9733

STUDY 2 Reviewer:
Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

CONCLUSIONS:

The original study is scientifically sound and provides supplemental information towards the registration of glufosinate ammonium. The second study provides the additional information necessary to fulfill EPA Data Requirements for Registering Pesticides by identifying the two degradates M1 and M3.

SUMMARY OF DATA BY REVIEWER:

STUDY 1

[^{14}C]Glufosinate degraded with a half-life of 45-60 days in a silt loam soil treated with [3,4-^{14}C]glufosinate ammonium (radiochemical purity 99.5%) at approximately 8.8 ppm and incubated anaerobically (flooding plus N_2 atmosphere) at 22 ± 2 C in the dark for 60 days following 30 days of aerobic incubation. The registrant-calculated half-life was 56 days. After 60 days of anaerobic incubation, glufosinate comprised 12.8% of the applied radioactivity, 3-methyl-phosphinico-propionic acid comprised 41.2% of the applied, and two unknowns each were approximately 5% (≈0.04 ppm) of the applied.

DISCUSSION:

1. Two degradates, each comprising ≈5% of the applied (0.04 ppm), were not identified. Further investigations were said to be underway.
2. The decline in material balance at day 45 of anaerobic incubation (due to a cracked incubation flask) did not appear to significantly affect the results.

3. Although it was not clearly stated in the Materials and Methods section of the original report, the data indicate that corresponding water samples and soil extracts were combined prior to HPLC analysis.
4. The detection limit for the HPLC method was not specified.

MATERIALS AND METHODS:

Experiment 1 (Soil analysis)
Air-dried silt loam soil (8.7% sand, 73.1% silt, 18.2% clay, 1.0% organic matter, pH 5.9, CEC 16.1 meq/100 g) was sieved (1 mm), moistened to 80% of field capacity, and maintained in the dark at 22 ± 2 C for 2 weeks. The soil was then treated with [3,4-^{14}C]glufosinate ammonium (Hoe 039866; radiochemical purity 99.5%, specific activity 16.8 mCi/g, Hoechst AG) at ≈8.8 ppm. The treated soil was incubated in the dark at 22 ± 2 C in flasks sealed with cotton-wool plugs for 30 days. Following the 30-day aerobic incubation, anaerobic conditions were established by flooding the soil with distilled water containing peptone (1:15 w/v). The flasks were purged with nitrogen and sealed with ground-in stoppers. Soil samples were taken after 0 and 30 days of aerobic incubation and soil:water samples were taken after 0, 15, 30, 45, and 60 days of anaerobic incubation (30, 45, 60, 75, and 90 days posttreatment).

Soil samples taken during the aerobic portion of the study were extracted with distilled water for 6 hours at temperatures not exceeding 75 C. The extracts were analyzed for total [^{14}C]residues by LSC and for specific compounds by HPLC with radioactivity detection. Unextractable [^{14}C]residues remaining in the soil were quantified by LSC following combustion.

Samples taken during the anaerobic portion of the study were separated into water and soil fractions. The water fraction was analyzed for total radioactivity by LSC. The soil fraction was extracted with water, and the extract and extracted soil were analyzed as described above. Corresponding water samples and soil extracts were combined and analyzed for glufosinate and its degradates by HPLC with radioactivity detection.

Experiment 2 (Volatile determination)
Silt loam soil was treated with [3,4-^{14}C] glufosinate ammonium as described in Experiment 1. The system was incubated aerobically for 30 days in the dark at 22 ± 2 C in flasks attached to a gas collection system having 3 successive traps containing sulfuric acid, ethylene glycol, and methanol:ethanolamine (7:3) (Figure 1). The flasks were purged with air (flow rate unspecified) daily for 8 hours. Following the 30-day aerobic incubation, anaerobic conditions were established and the flasks were reattached to the gas collection system; the flasks were purged with nitrogen daily for 1 hour. Gas trap solutions were sampled after 8, 15, 21, and 30 days of aerobic incubation, and at various intervals up to day 60 of anaerobic incubation. The solutions were analyzed for total radioactivity by LSC.

STUDY 2
The two degradates have been identified according to their HPLC retention times. M1 is HOE 064619 (2-methylphosphinico-acetic acid), and M3 is HOE 086486 (3-methyl phosphinico-3-oxo-propionic acid). In the aerobic study, these compounds were isolated by their retention times and their structures confirmed by GC/MS.

CBI INFORMATION ADDENDUM: attached

DER 5.2

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 154 through 156 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION REVIEW 6

I. Study **Type:** Leaching/Adsorption/Desorption

II. Citation:

Sarafin, R., **Hoe 064619 Adsorption/Desorption in the System Soil/Water.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 2/10/89. Received EPA 12/12/89 under MRID # 413231-21.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions: HOE 064619 was not mobile when tested with a silt loam soil.

V. Materials and Methods:

The adsorption/desorption of HOE 064619, a principal metabolite of HOE 039866, to allow assessment of its leaching potential.

test compound -- HOE 064619 labelled with ^{14}C in the 2-position, 97.5% radiopurity, 25.05 mCi/gm (55608 dpm/ug)
test soil -- silt loam, Hoechst Roussel Agri-Vet research farm, Leland, MS
test system -- 10 gm (dry weight equivalent) of soil in 25 ml solution. Because preliminary experiments using $CaCl_2$ solution gave unexpectedly high K_ds, and K_ds showed dependence on Ca^{++} concentration [data not presented], the definitive experiment was done in double distilled H_2O.
adsorption -- at 20 $\pm$ 1° C in the dark. After equilibration, the solutions were centrifuged, and the supernatant filtered. The resulting aqueous phase was analyzed by LSC for total radioactivity.
desorption -- the volume of solution removed in the adsorption phase was replaced with 25 ml fresh distilled water, and the mixture equilibrated. After centrifugation and filtration the aqueous phase was analyzed for total radioactivity. Desorption was performed three times.

VI. Study **Author's Results** and/or Conclusions:

RESULTS

The adsorption behavior of HOE 064619 is characterized by several peculiar features: dependence of K on the concentration of calcium ions, $K_{des} > K$, and high adsorption relative to HOE 039866 and HOE 061517. $K_d$ads was 23.29 in double distilled water, and the $K_d$des was 13.5.

VII. Reviewer's Comments:

1) The "unexpectedly high" K_ds using $CaCl_2$ solution may more nearly reflect behavior in the environment than the results from distilled water since

Ca would routinely be found in soils. In any case, HOE 064619 does not appear to be highly mobile in silt loam.

VIII. CBI Information Addendum: attached

DER 6.2

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 159 through 167 are not included.

The material not included contains the following type of information:

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION REVIEW 7

I. Study Type: Volatility, Soil (163-2)

II. Citation:

Sarafin, R., **Hoe 064619 Assessment of Volatilization from Soil.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 12/12/89 under MRID # 413231-22.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions:

The measured vapor pressure reported in this document does not meet the criterion for waiving the requirement for soil volatility data. If the applicant supplies information on the modeling program, and other information discussed below, EFGWB can reconsider.

V. Materials and Methods: n.a.

VI. Study Author's Results and/or Conclusions:

Glufosinate ammonium decomposed in the measuring device (vapor pressure balance), yielding a "pseudo" vapor pressure of 5.9×10^{-4} at 22° C. This was taken as a "worst-case" upper limit for the theoretical real value. The aqueous solubility is extremely high, at 1.37 kg/L [3 lb/qt]. This parameter is an indicator of partition between soil and air. The partitioning of glufosinate ammonium was modeled using MACKAY level 1, with the following results:

water	--	69.83%
soil	--	28.16%
sediment	--	2.01%
air	--	**0.00%**
suspended sediment	--	0.00%
aquatic biomass	--	0.00%

Based on the low vapor pressure and high aqueous solubility, volatility of glufosinate ammonium from soil is expected to be minimal. A waiver of this data requirement is requested.

VII. Reviewer's Comments:

Upon request of an applicant, EFGWB will usually waive the volatility requirement for a compound with vapor pressure < 10^{-7}. Glufosinate ammonium does not meet this criterion. Although the observed vapor pressure may result from loss of ammonia, this has not been demonstrated in the submission.

The stated solubility value of 1.37 kg/l is indeed extremely high, but is somewhat less than that known for other compounds, e.g., sucrose (2 kg/l, per

Merck index). For the record, the applicant should verify that this is not a typographical error -- e.g. mg where ug is intended.

EFGWB staff are not familiar with the specific model used. The applicant should provide the equations upon which the model is based, if known, so that it may be evaluated as supporting evidence to justify the requested waiver.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 170 through 176 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

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____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION REVIEW 8

I. Study Type: Rotational Crop Accumulation, Confined (165-1)

II. Citation:

STUDY 1
Schwalbe-Fehl, M., Stumpf, K. **Reply to the EPA Environmental Fate Data Review Dated October 14, 1988.** developed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-25.

STUDY 2
Schwalbe-Fehl, M., Stumpf, K. **Hoe 039866-^{14}C Residue Determinations and Metabolism in Rotational Crops Sown 120 Days After Treatment of Soil.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-26.

III. Reviewer:

Typed Name:	E. Brinson Conerly
Title:	Chemist, Review Section 2
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

STUDY 1

Most, but not all, of the previous EFGWB comments have been satisfactorily answered, but the study has been replaced by more recent ones. We note that control plants were said to have taken in radioactive CO_2 from experimental plants kept near them. This would certainly have made interpretation of the results more difficult.

STUDY 2

The analytical method is somewhat less sensitive than is desirable. It will be acceptable if the applicant can demonstrate that it is the best available at this time. The study will then become fully acceptable, but can only support a use rate approximately half the maximum label rate. A 4 month (120 day) interval after the final treatment appears to be appropriate for planting of rotational crops based on these data. The description of the formulation is not readily apparent in EFGWB files.

V. Materials and Methods:

STUDY 1 -- n.a.

STUDY 2

test formulation -- 17.9% active ingredient, spec. act. 4.7 MCi/gm, formulated from 7.5 mg 99.6% radiopure HOE 039866-^{14}C (labelled in the 3 and 4 positions), 62.6 mg unlabelled HOE 039866, and 320.0 "Blank Formulation" [designated by a company code, but not otherwise described]

spray mixture -- 390 mg test formulation plus 35 ml H_2O

test protocol -- spray mixture was applied at 0.87 ppm a.i. to soil which had been aged 2 mos. in a container 1.0 m x 0.7 m x 0.5 m. d. Rotational crops of radish, spinach, wheat, and carrots were sown 120 days after treatment. Prior to sowing, the upper layer of the soil was loosened, but weeds which were present at the time of treatment were not removed. They covered approximately 1/3 of the surface. Growing conditions were as follows:

sowing -- April 14, 1987
greenhouse -- April 14 - 20, 1987
outdoors but under a roof -- April 20 - 27, 1987
outdoors without a roof -- April 27 - Sept. 8, 1987

Temperature and irrigation details are attached.

sampling protocol -- mature crops were harvested as follows:

radishes -- 43 days after sowing (163 days after treatment)
spinach -- 43 days after sowing
wheat and carrots -- 147 days after sowing

analytical methods -- level of quantitation (loq) 0.0007 - 0.04 ppm

plant samples -- homogenization, followed by water extraction. Clean-up of the concentrated extracts was by (1) methanol extraction, or (2) anion exchange chromatography followed by 10% formic acid elution, or (3) dialysis. Purified extracts were subjected to HPLC/TLC or derivitization followed by GC/MS. Total radioactivity was determined by LSC. Samples were analyzed within one week, but the quantity and nature of residues were stable for at least 6 months (data not included). There were no data presented indicating the level of recovery from fortified samples.

soil samples -- repeated extraction with hot distilled water. The concentrated water extract was analyzed for radioactivity by LSC. Total and unextracted radioactivity were determined by combustion followed by LSC. There were no data presented indicating the level of recovery from fortified samples. Total radioactivity was determined by combustion, and was relatively constant throughout. There were no data presented indicating the level of recovery from fortified samples. Recoveries in various fractions (extracted, bound, etc.) ranged from 94.1 to 104.5% of total, with no evidence of time dependency.

VI. Study Author's Results and/or Conclusions:

STUDY 1 -- *[Reply to comment of previous review]*

Confined 30 days study:
Soil was treated with a small hand-spraying device. Direct mixing of pesticide into the soil would also have been practicable ... but is not usually carried out in agricultural practice. ... Spray application was preferred, ... [but] generally results in greater variations of the soil concentrations directly after treatment ... especially if only few soil samples are taken... One special circumstance probably enhanced the variability of the soil concentrations in the confined 30 days study: weeds covered the soil surface of the test container to approx. [sic] one third of the container surface ... [and] ... were not removed prior to the treatment. In agricultural practice, HOE 039866 is never applied to bare soil but only to soil covered with weeds, because ... [it] ... acts only via contact with the green parts of the weeds. As the damaged weeds were kept in the container throughout the study, the increase of the radioactivity concentrations in the

spray mixture -- 390 mg test formulation plus 35 ml H_2O

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spinach -- 43 days after sowing
wheat and carrots -- 147 days after sowing

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plant samples -- homogenization, followed by water extraction. Clean-up of the concentrated extracts was by (1) methanol extraction, or (2) anion exchange chromatography followed by 10% formic acid elution, or (3) dialysis. Purified extracts were subjected to HPLC/TLC or derivitization followed by GC/MS. Total radioactivity was determined by LSC. Samples were analyzed within one week, but the quantity and nature of residues were stable for at least 6 months (data not included). There were no data presented indicating the level of recovery from fortified samples.

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soil at later sampling dates is understandable. Although this procedure probably led to an increased variability of soil residues, it simulates what generally happens in practice.

...It was impossible to collect volatile degradation products because of the size of the container. ... [This] is generally not necessary ... because the results can be provided from the aerobic soil degradation laboratory studies which are carried out with the same soil ... It was observed, however, that soil degradation in containers was slower than in the corresponding standard laboratory degradation studies. Consequently the confined crop rotation studies provide the worst case scenarium [sic] for soil degradation.

From the results of the control plants kept in the same room as the treated ones, it can be clearly proved that CO_2 from soil was evolved; otherwise control plants could not contain radioactive residues at the measured level.

The study was carried out using the normal water-soluble concentrate formulation SL18 which was used in all studies that had to be carried out with formulated material. Consequently, a further description of the formulation is not necessary.

Plants were not sampled immature because neither radishes nor spinach, carrots or wheat are used as feed or food items when immature.

Fortifications of soil samples were not carried out because the use of radiolabeled material allowed the determination of recoveries per se. Moreover, the extraction and clean-up procedure for soil samples was identitical [sic] with that of the routine residue method which is routinely validated by determining the recovery of fortified soil samples.

Confined 120 days Study:
Residues in soil were only characterized at the time of harvest. This deficiency is overcome by the new 120 days confined crop rotation study which is submitted together with this answer.

The one unidentified degradate at day 158 ... proved to be HOE 064619 after GC-MS analysis and comparison with the authentic reference compound. Its appearance in soil was ... confirmed in the new 120 days ... study.

Plant and soil samples were always stored deep frozen (-20°C) until analysis.

[Blank formulation, immature plant sampling, and fortification of soil samples are discussed under the 30 day study.]

STUDY 2

Results

Plant residues (details attached)
All plant samples except those of wheat contained less than 0.04 mg/kg (0.04 ppm) and were not investigated further. Following clean-up, the only identifiable metabolite in the extracts was HOE 061517. Most radioactivity was associated with cellulose or hemicellulose. From 11 to 20 % (0.01 to 0.02 ppm) of the residues were identified as HOE 061517.

Soil residues (details attached)
Significant soil residues were only found in the upper 5 cm. At day 0, total residues were 0.745 mg ai equiv./kg (86% of applied). The 5-10 cm layer contained residues above the limit of quantification (0.039 mg ai equiv/kg = 39 ppb) only at 120 days after treatment.

Day 0 extracts only contained HOE 039866. HOE 061517 and, later, HOE 064619 were detected in subsquent samples. HOE 039866 was completely undetected by days 163 and 267. Calculated half-lives are 20 days for HOE 039866, 45 days for HOE 061517, and 30 days for HOE 064619. HOE 039866 is degraded to significant amounts of CO_2.

Conclusions

The nature of the residues in rotated crops is fully understood. Incorporation of most of the recovered radioactivity in cellulose and hemicellulose indicates complete metabolism of parent to degradates such as CO_2 or those degradates shortly before it such as succinic or acetic acid [i.e., it becomes part of the "carbon pool" -- EBC]. Plants then use it to form glucose, fatty and amino acids, cellulose, etc, which are found in all parts. HOE 061517 (3-methylphosphinicopropionic acid) is the only residue of concern in plants.

Taking into account that soil degradation depends largely on growing conditions (temperature, moisture, etc.), calculated half-lives are in good agreement with those from the aerobic soil metabolism study: 3 - 10 days for HOE 039866, 7 - 22 days for HOE 061517, and 18 - 30 days for HOE 064619.

VII. Reviewer's Comments:

STUDY 1 -- see section IV, "Conclusions", above.

STUDY 2

1) The investigator's conclusions are supported for the rate tested, which is approximately half the maximum label rate for a single application. However, this does not provide information on the maximum use rate.

2) The study is an "outdoor confined" study, which could be expected to yield results more closely related to those observed in a true field study.

3) Direct uptake of the parent and closely related degradates seems to be insignificant at the level tested.

4) The HPLC method appears to separate the parent and major degradate satisfactorily. The sensitivity (limit of quantitation or loq) as calculated by the investigator is 0.04 ppm for soil, rather than 0.01. This value for the loq in soil is based on 3σ counts (99% confidence level) above the mean of the control soil ("background") value for the LSC analysis. Sensitivities for the various plant material ranged from 0.7 to 27 ppb. Some of these do not meet the "10 ppb" criterion established by EFGWB. The guidelines mention 0.01 ppm as desirable, but not an absolute requirement. The investigator may be able to demonstrate that the method is the best available, and it would then be fully acceptable.

4) Soil bound residues increased over time, to ca. 70% of the original material at day 267.

5) HOE 061517 constituted 90% of extractable material in the top 5 cm of soil at day 267. Although this was not a soil dissipation study, if

additional soil analyses were done for HOE 061517, EFGWB would like them as part of the record. This degradate is somewhat persistant, and is therefore a matter for attention.

6) The presentation of data is less than ideal, since pertinent information is given in several tables, rather than in one.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 183 through 211 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

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✓ FIFRA registration data.

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DATA EVALUATION REVIEW 9

I. Study Type: terrestrial field dissipation, field rotational crop accumulation

II. Citation:

STUDY 1
Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Crops Rotated After Soybeans from Geneseo, Illinois.** performed by Van Der Schaff Agricultural Research, Inc., Geneseo, IL, USA, and Dr. Specht and Partner, Hamburg, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-27.

STUDY 2
Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Soil from Geneseo, Illinois.** performed by Van Der Schaff Agricultural Research, Inc., Geneseo, IL, USA, and Dr. Specht and Partner, Hamburg, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-23.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E. B. Conerly
6/18/90

IV. Conclusions:

The studies have serious deficiencies including the following:

1) The application rate supported by the analytical data is apparently much lower (ca. 1/3) than that claimed by the applicant. This discrepancy may be resolved by a satisfactory explanation by the applicant.

2) EFGWB strongly recommends **against** compositing of soil or other sample material into a single sample for analysis. The value obtained from such a composited sample is a "grand average" of the values which would have resulted from analysis of several samples. This does not provide information on application variability or other factors which are of importance to EFGWB. Further, if a single composite is somehow flawed or aberrent, it will give misleading results. Without independent samples, the investigator has no means of identifying these faulty data.

3) The analytical method may become acceptable, but additional information should be submitted to show that sensitivity is the best obtainable and to demonstrate the separation of authentic compounds, so that EFGWB may complete validation of the method. These results appear to indicate that residues of concern do not occur in the tested crops when replanted at 91 days at ca. 0.4 ppm.

V. Materials and Methods:

STUDY 1 -- plant residues
test material -- Ignite[tm] Herbicide containing glufosinate ammonium

Methods
test protocol -- test material was applied at 1.8 lb/A ai (120% expected maximum label rate for soybeans) to a bare plot which was ready to plant. During the test, irrigation was used to provide 120% of the 10-year average rainfall. The plot was immediately planted with soybeans. After 90 days some of the growing soybeans were removed, and typical rotational crops (leaf lettuce, radishes, and wheat) were planted. These rotational crops were examined at 1/4, 1/2, and full maturity:

for radishes -- planted 91 days after treatment; harvested 113, 119, and 124 days after treatment, or 22, 28, and 33 days after planting

for lettuce -- planted 91 days after treatment; harvested 124, 138, and 154 days after treatment, or 33, 47, and 63 days after planting

for wheat -- planted 91 days after treatment; harvested 335, 364, and 401 days after treatment, or 224, 273, and 310 days after planting

Remaining soybean seed and straw were harvested at maturity, 135 days after treatment and planting.

analyses -- samples were analyzed for HOE-039866, HOE-061517, and HOE-064619. Plant material was extracted with water, the extract concentrated and derivatized with trimethyl-orthoacetate. The derivatives were then analyzed by gas chromatography (phosphorus sensitive flame photometric detector). The level of detection was 50 ppb.

STUDY 2 -- soil residues
Materials
test material as described above

Methods
test protocol as described above
sampling protocol -- day 0, pre and post application; days 6, 9, 34, 65, 91, 121, and 180 days post application -- ten cores were taken at each interval, sectioned into 10 cm portions, and composited
analyses -- samples were analyzed for HOE-039866, HOE-061517, and HOE-064619

VI. Study **Author**'s Results and/or Conclusions:

STUDY 1 -- plant residues
Results

No detectable residues were measured in any rotational crop sampled. No detectable residues of parent were found in soybean grain or straw harvest 135 days after planting. An average of 0.06 ppm HOE-061517 was found in soybean seed, and 0.09 ppm in soybean straw.

Conclusions

1) The analytical method selected is capable of analyzing all residues of environmental concern.

2) The residue trial represents normal climatological conditions for the area.
3) There is no potential for residues of HOE-039866 to be assimilated in crops rotated after soybeans when treated according to the label directions.
4) HOE-064619 residues are not encountered in substrates analyzed.
5) [This statement was included by the applicant.] The residue trial was conducted in full compliance with the guidelines for Rotational Crop Studies.

STUDY 2 -- soil residues

Results

1) The average HOE-039866 residues in the 0 - 10 cm core decreased rapidly from 0.37 ppm immediately after application through day 34 to non-detectable levels. No HOE-039866 residues were found at any time or depth below the 10 cm level.
2) A half-life of 9.8 days has been calculated for HOE-039866.
3) HOE-061517 occurred only at one sampling interval (0 - 10 cm depth, day 34, 0.06 ppm). No residues were found below 10 cm at any time.
4) HOE-064619 was not detected at any time.

VII. Reviewer's Comments:

The soil analyses of samples taken immediately after treatment appear to establish that the level of treatment was incorrect. It is given as 0.37 ppm in a 4 inch soil layer, but should be in the order of 1.8 ppm for a three inch soil layer or 1.4 ppm for the four inch core analyzed. Unless the applicant can demonstrate otherwise, the conclusion is inevitable that the application rate was less than stated

Analyses appear to have been based on what is essentially a single soil sample (i.e. a composite of all samples obtained for a given time and depth), although three analytical runs were done. This becomes a secondary issue, given the uncertainty about the application rate. EFGWB strongly recommends that at least three independent samples be analyzed at each time period. This prevents the possibility of a single aberrent analytical value distorting the data and its interpretation, as well as demonstrating the "natural" variability of the whole analytical system.

EFGWB recommends, but does not absolutely require, that an analytical method have a sensitivity of 0.01 ppm. The method used in this study does not meet that criterion. If the applicant can demonstrate that the method is the best available, the method may be acceptable. Further, the chromatograms presented in the submission do not show separation of a mixture of authentic compounds. This information is also essential to the final evaluation and acceptance of the method.

The residues do not appear to be significant, but the data cannot be used to support an application rate of 1.8 lb a.i./A.

VIII. CBI Information Addendum: included

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 215 through 253 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION REVIEW 10

I. **Study Type:** Terrestrial Field Dissipation, Rotational Crop Accumulation, Field

II. Citation:

STUDY 1
Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Crops Rotated After Soybeans from Salisbury, Maryland**. performed by PANAGRI, Princess Anne, MD, USA, and Bayer *Hauptversuchsansalt fuer Landvirtschaft*, Wiehenstephan, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-28.

STUDY 2
Mayasich, J.M. **Determination of the Residues of Glufosinate-Ammonium (Hoe 039866), Its Free Acid (Hoe 035956), and Its Metabolites (Hoe 061517 and Hoe 064619) in Soil from Salisbury, Maryland**. performed by PANAGRI, Princess Anne, MD, USA, and Bayer *Hauptversuchsansalt fuer Landvirtschaft*, Wiehenstephan, West Germany. sponsored and submitted by Hoechst Celanese, Somerville, NJ, USA. dated 5/1/89. Received EPA under MRID # 413231-24.

III. Reviewer:

Typed Name:	E. Brinson Conerly
Title:	Chemist, Review Section 2
Organization:	EFGWB/EFED/OPP

E. B. Conerly 6/18/90

IV. Conclusions: The studies may become acceptable, but additional information is necessary to the validation of the analytical method. The applicant must show that the analytical method sensitivity is the best available at this time, and demonstrate that the method separates authentic compounds. These results appear to indicate that residues of concern do not occur in the tested rotational crops at a replanting interval of 91-97 days.

V. Materials and Methods:

STUDY 1
Materials
test material -- Ignite[tm] Herbicide containing glufosinate ammonium

Methods
test **protocol** -- test material was applied at 1.8 lb/A ai (120% expected **maximum** label rate for soybeans) to weed-containing plots (loamy sand) **planted** to soybeans . Irrigation was used to maintain the equivalent of 120% 10-year average rainfall. After 91 days some of the soybeans were removed, and leaf lettuce, radishes, and wheat were planted. Remaining soybean seed and straw were examined at harvest (135 days after application). Rotational crops were examined at 1/4, 1/2, and full maturity:

for radishes -- planted 91 days after treatment; harvested 111, 121, and 139 days after treatment, or 20, 30, and 38 [*sic* -- from the dates given, the figure should be 48 days -- EBC]

for lettuce -- planted 97 days after treatment; harvested 124, 138, and 154 days after treatment, or 55, 72, and 86 days after planting

for wheat -- planted 91 days after treatment; harvested 335, 364, and 401 days after treatment, or 109, 265, and 304 days after planting

analyses -- samples were analyzed for HOE-039866, HOE-061517, and HOE-064619. Plant material was extracted with water, the extract concentrated and derivatized with trimethyl-orthoacetate. The derivatives were then analyzed by gas chromatography (phosphorus sensitive flame photometric detector). The level of detection was 50 ppb.

STUDY 2

Materials

test material as described above

Methods

test protocol as described above

sampling protocol -- day 0, pre and post application; days 7, 30, 61, 90, 120, 186, and 244 days post application

analyses -- samples were analyzed for HOE-039866, HOE-061517, and HOE-064619

VI. Study Author's Results and/or Conclusions:

STUDY 1 -- plant residues

Results

No detectable residues were measured in any rotational crop sampled. No detectable residues of parent were found in soybean grain or straw harvest 135 days after planting. An average of 0.25 ppm HOE-061517 was found in soybean straw.

Conclusions

1) Uptake of IGNITE residues following application to soybeans is improbable.
2) The analytical method selected is capable of analyzing all residues of environmental concern.
3) The residue trial represents normal climatological conditions for the area.
4) There is no potential for residues of HOE-039866 to be assimilated in crops rotated after soybeans when treated according to the label directions.
5) HOE-064619 residues are not encountered in substrates analyzed.
6) [Included by the applicant] The residue trial was conducted in full compliance with the guidelines for Rotational Crop Studies.

STUDY 2 -- soil residues

Results

1) The average HOE-039866 residues in the 0 - 10 cm core decreased rapidly from 0.81 ppm initially through day 61 to non-detectable levels. No HOE-039866 residues were found at any time or depth below 10 cm.
2) A half-life of 8.0 days has been calculated for HOE-039866.
3) HOE-061517 began to appear in the 0 - 10 cm depth at day 0, and gradually increased to 0.17 ppm after irrigation on day 7, and were undetectable by day 61. No residues were found below 10 cm at any time.
4) HOE-064619 appeared at the 0 - 10 cm depth by day 30, were at or near the detection limit (0.05 ppm) on days 30 and 61, and were undetectable thereafter. No residues were found below 10 cm at any time.

VII. Reviewer's Comments:

The sensitivity of the method is not as good as the 0.01 ppm EFGWB strongly recommends. If the applicant can demonstrate that it is the best currently available, it can be accepted. Also, the chromatograms presented in this as well as three related studies do not show separation of a mixture of authentic compounds by the stated analytical method. This information is crucial to the acceptance of the investigator's conclusions and final evaluation of the study.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

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Pages 257 through 275 are not included.

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✓ FIFRA registration data.

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DATA EVALUATION REVIEW 11

I. Study Type: fish bioaccumulation

II. Citation:

Schwalbe-Fehl, M., Fischer, R. **Reply to the EPA Environmental Fate Data Review Dated October 20, 1988 Hoe 039866 Bioaccumulation in Fish.** performed by Hoechst AG, Frankfort am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/22/88. Received EPA 12/12/89 under MRID # 413231-30.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions:

Due to its very high water solubility, Glufosinate ammonium will not bioaccumulate.

V. Materials and Methods: described in previous report

VI. Study Author's Results and/or Conclusions:

1) ***Characterization of radioactive residues in fish*** -- Accumulation behavior of a test substance is in general independent from the concentration in the flow through system. Therefore bioaccumulation factors are generally not influenced by the treatment level. The study proved -- as predicted from the physico-chemical parameters -- that HOE 039866 did not accumulate in fish tissues. Consequently, residues in fish are not of concern for the evaluation of HOE 039866.

2) ***Plateau of residues*** -- Although a real plateau was not reached, the total radioactive residues are only marginal. Even after exposure for 28 days, the maximum residue concentration (0.034 mg/kg in non-edible tissues) was three times lower than the concentration in the flow-through system (0.1 mg/l).

A theoretical plateau of approx. 0.03 $\pm$ 0.01 mg/kg in the non-edible tissues can be calculated if first-order kinetics for uptake and elimination of HOE 039866 are assumed. In edible tissues and for the whoe fish analyses, no plateau can be calculated because there i no significant increase in the concentration during the uptake phase but only varying concentrations slightly above the limit of quantification.

3) ***Nature of the residues in the water at days 3 and 21*** -- ... the radio-HPLC chromatograms of the water samples together with the authentic reference compound ...[proves] that HOE 039866 was the only detectable radioactive compound in the water.

4) ***Radioactivity in the control samples*** -- [data attached]

5) ***Bioconcentration factors at all sampling times*** -- [data attached]

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VII. Reviewer's Comments: The water solubil
obtained in the original study serve to
will not bioaccumulate in fish.

VIII. CBI Information Addendum: n.a.

DE