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EFGWB Out: 2/23/92

To: Miller/Mays
Product Manager 23
Registration Division

From: Akiva D. Abramovitch, Ph.D., Head
Environmental Fate Review Section #3
Environmental Fate & Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Attached, please find the EFGWB review of...

Reg./File #: 008340-EI

Chemical Name: Ammonium-DL-homoalanin-4-yl methylphosphinate (Glufosinate Ammonium)

Type Product: Herbicide

Product Name: Ignite

Company Name: Hoechst Celanese Corporation

Purpose: response to EFGWB review of 6/28/90 -- submission of soil photolysis and terrestrial field dissipation data (special study in a vineyard)

Action Code: _____ EFGWB #(s): 91-0749 Total Review Time: _____ days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1			162-4			164-4			166-1		
161-2			163-1			164-5			166-2		
161-3	419201-02	Y	163-2	419201-04	Y	165-1	419201-05	O	166-3		
161-4			163-3			165-2			167-1		
162-1	419201-03	Y	164-1	419201-06	N	165-3			167-2		
162-2	419201-03	Y	164-2			165-4			201-1		
162-3			164-3			165-5			202-1		

Y = Acceptable (Study satisfied the Guideline)/Concur
P = Partial (Study partially satisfied the Guideline, but additional information is still needed)
S = Supplemental (Study provided useful information, but Guideline was not satisfied)
N = Unacceptable (Study was rejected)/Non-Concur
O = Other -- in this case, the study was acceptable, but was performed at less than maximum label rate.

1. CHEMICAL:

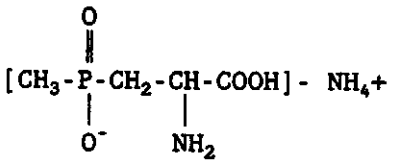
chemical name: Monoammonium 2-amino-4-hydroxymethylphosphinyl-butanoate
or ammonium-DL-homoalanin-4-yl methylphosphinate

common name: Glufosinate ammonium

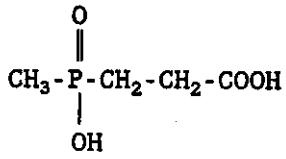
trade name: Ignite

structure:

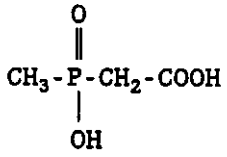
parent



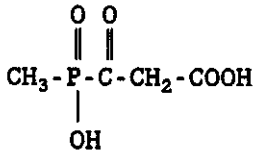
HOE 061517



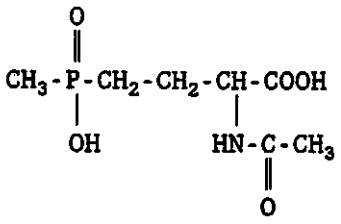
HOE 064619



HOE 086486



HOE 085355



CAS #: 77182-82-2

Shaughnessy #: 128800

characteristics: molecular weight = 198.2
white crystalline powder, faint pungent odor
melting point = 215 °C
solubility = 1370 gm/L @ 22 °C
O/W partition coefficient <0.1
pH (1% in distilled H_2O) = 4.7± .1

2. TEST MATERIAL: discussed in DERs

3. STUDY/ACTION TYPE: response to review of 6/28/90, submission of soil photolysis and vineyard field dissipaton study

4. STUDY IDENTIFICATION:

Erstfeld, K.M. **Ignite Herbicide®: Petitioner Response to the EPA Environmental Fate and Groundwater Branch Review Dated June 28, 1990 for Data Requirements for Ignite Herbicide (Glufosinate Ammonium) for Full Registration on Terrestrial Food Crops, Terrestrial Nonfood, Domestic Outdoor and Greenhouse Uses**. submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID# 419201-01

Stumpf, K. **Photolysis of HOE 039866 - ^{14}C Glufosinate Ammonium on Soil**. performed by Produktentwicklund, Hoechst Aktiengesellschaft, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID# 419201-02.

Stumpf, K. **supplement to** *HOE 061517-^{14}C, metabolite of HOE 039866 Degradation in a Sandy Loam Soil Under Aerobic Conditions at Application Rates of 0.05 and 1.0 mg/kg (MRID# 413231-18), and Degradation and Metabolism in Different Soils under Aerobic and Anaerobic Conditions at an Application Rate of 1.6 mg/kg (MRID# 413231-19).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-03.

Görlitz, G. **supplement to** *HOE 064619, Assessment of Volatilization from Soil (MRID# 413231-22).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-04.

Stumpf, K. **supplement to** *HOE 039866-^{14}C, Residue Determinations and Metabolism in Rotational Crops Sown 120 Days After Treatment of Soil (MRID# 413231-26).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-05.

Mayasich, J.M. and Czarnecki, J.J. **Determination of the Leaching Potential and Dissipation of Ignite® Residues, (Glufosinate-ammonium (HOE 039866) and Metabolites (HOE 061517 and HOE 064619) in a California Vineyard**. performed by Field Research for Hire, Porterville, CA, and EN-CAS Analytical, Winston-Salem, NC, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-06.

5. REVIEWED BY:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E. B. Conerly-Perks
JUL 23 1992

6. APPROVED BY:

Typed Name: Akiva Abramovitch
Title: Head, Review Section 3
Organization: EFGWB/EFED/OPP

JUL 23 1992

7. CONCLUSIONS:

Hydrolysis, photodegradation in water, anaerobic soil metabolism, aerobic aquatic metabolism, leaching/adsorption/desorption, and fish bioaccumulation data requirements have been fulfilled previously.

1) The soil photolysis data requirement is fulfilled (MRID# 419201-02). Glufosinate ammonium is susceptible to photolysis while on a soil surface. The overall $t_{\frac{1}{2}}$ (combined effects of soil photolysis and incidental metabolism) is 8 - 9 days. Dark controls had a $t_{\frac{1}{2}}$ of 14 - 18 days. [*A calculated figure of 17 days for "pure photolysis" is reported -- EBC.*] The incubation yielded a small amount of $^{14}CO_2$ (ca. 4%) and three well known degradates:

HOE 061517 [*3-methylphosphinico-propionic acid* (up to 60% of applied radioactivity)]

HOE 064619 [*2-methylphosphinico-acetic acid (2 - 11%)*

HOE 085355 [*2-acetamido-4-methylphosphinico-butanoic acid (2 - 15%)*]

2) The aerobic soil metabolism data requirement is fulfilled by the original studies (MRID# 413231-18 and 19) together with the material received in this submission.

Glufosinate ammonium metabolizes in a variety of soils with a half-life ranging from 4 to 20 days. Higher concentrations of parent compound result in lower rates of metabolism. Major degradates are HOE 061517 and HOE 064619.

3) The volatilization from soil data requirement is fulfilled by the original study (MRID# 413231-22) together with the material received in this submission. Glufosinate ammonium does not volatilize in significant quantities.

4) The accumulation in confined rotational crops data requirement is fulfilled by the original study (MRID 413231-26) for an application rate of 1 kg a.i./ha. The maximum currently proposed label rate is 1.5 lb/A (1.68 kg/ha). In crops planted 120 days after treatment, accumulation occured in wheat, but was not detected in spinach, radishes or carrots. Some 11 - 20% (0.01 - 0.02 ppm) of the radioactivity in the wheat was recovered as HOE 061517, and the remainder as cellulosic material. [*TOX has proposed 40 ppm in the diet as a No Observed Effects Level (NOEL) based on chronic feeding and developmental toxicity studies in rats.*]

5) The previously reviewed routine terrestrial field dissipation study is still deficient. EFGWB had commented that the application rate was not confirmed, since the analyzed soil only contained 1/4 the theoretical amount. No explanation has been provided for this discrepancy. This study also included rotational crop accumulation data, which could only be validated and accepted if the field dissipation study deficiency could be resolved.

The special vineyard field dissipation study discussed in this review is not acceptable for the reasons discussed below.

a) Although the difficulty of obtaining precise measurements from field samples is well understood by EFGWB, these data appear to be more variable than is normally acceptable. EFGWB does not believe that a meaningful value can be obtained by averaging a set of results such as 0.109 ppm, 0.109 ppm, 0.052 ppm, and <0.05 ppm (four actual "replicate" values).

b) The application rate was not confirmed. Soil samples contained only a fraction of the nominally applied material even in bare-ground samples. Moreover, there was poor recovery of applied material analyzed from application cards, especially in the second and third treatments, although the applicant states that a difference in orientation of the cards accounts for these discrepancies.

One might speculate that the application, which was by boom sprayer, was faulty for some reason, giving rise both to the imprecision of the analytical values for the soil samples, and also to the failure to confirm the application rate through soil or application card analyses.

Although these data are of extremely limited usefulness in describing precisely the environmental behavior of Glufosinate ammonium, some cautious inferences can be made:

a) The mean half-lives, calculated from the three individual values for each plot, are remarkably similar for the two study sites, weeded and bare. Moreover, although they do not occur in the same order, two of the three individual values are the same for both plots. The compound appears to have a mean half-life of ca. 39 $\pm$ 23 days, possibly indicating a degree of persistence. Individual values ranged from 11.6 to 69.3 days.

b) The study did not reveal any residues below one foot depth. This indicates that leaching might not occur under these conditions.

8. RECOMMENDATIONS:

The applicant should be informed that soil photolysis, aerobic soil metabolism, and volatilization from soil requirements have been fulfilled.

The confined rotational crop accumulation data requirement has been fulfilled for a maximum application rate of 1 kg a.i./ha, but these data will not support use rates above that level. The maximum currently proposed label rate is 1.5 lb/A (1.68 kg/ha). If the applicant wishes to support a higher use rate, crop accumulation data for that use rate must be submitted. Based on the current study, a 120-day post-treatment interval seems to be adequate for crops other than wheat. For wheat, where residues are found, there are several possibilities:

1) if TOX has no concern about the residues at the 120 day level, a tolerance may not be needed, and the 120 day replanting interval might be declared appropriate for wheat as well.

2) if TOX has a concern

   a) an additional field study could be performed to establish a replanting interval long enough that no residues are detected

   b) a tolerance level for the residues could be established

The vineyard field dissipation study is seriously flawed, and cannot even be considered supplemental. These data do not allow EFGWB to predict whether (as the applicant believes) Glufosinate ammonium has a short field half-life (ca. 2 weeks), or whether it may persist more than two months. If TOX and DEB do not raise objections, a conditional registration might be in order, with the field dissipation study to be replaced within two years. The study should be performed with special attention to the following:

1) uniform application, confirmed by analytical data

2) more samples per time period, to allow for a more confident statistical treatment of the results. If the early analytical results show a reasonably uniform application, fewer samples might need to be analyzed at later periods. All samples should be retained until the study has been accepted.

9. BACKGROUND:

Per the attached position paper from TOX dated May 13, 1992, 40 ppm is proposed as the dietary NOEL, based on chronic feeding and developmental toxicity studies in rats and using a 100X safety factor. Per the attached position paper from Dietary Exposure Branch (dated 1990), a proposed tolerance for parent was not acceptable at that time (0.50 ppm on almond hulls, 0.05 ppm on soybean seed, grapes, field corn grain, forage, fodder, and silage). Their concern was related to the possibility of secondary residues in cattle kidney and liver and poultry kidney resulting from preemergent treatment, which is not proposed at this time.

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 plants. Glufosinate ammmonium 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 an aqueous soluble liquid, and may be tank mixed with numerous other pesticides.

ENVIRONMENTAL FATE ASSESSMENT

The data base is relatively complete and reliable. Glufosinate ammonium is rapidly degraded by photolysis on soil ($t_{½}$ = 8 - 9 days on sandy loam), aerobic soil metabolism ($t_{½}$ = 4 - 23 days), and to a lesser extent, by anaerobic soil metabolism ($t_{½}$ = 56 days) and aerobic aquatic metabolism ($t_{½}$ = 64 days). It is non volatile. It is resistant to hydrolysis and aqueous photolysis under sterile conditions in the laboratory. Mobility varies from extremely mobile (k_d = 0.08, k_{oc} = 9.6 in sand) to immobile (k_d = 52.85, k_{oc} = 1229 in clay). The soils tested were all slightly acid (sand, pH 6.8; volcanic ash clay, pH 5.8; silt loams, pH 5.9 and 6.4), and, except for the clay, had less than 1% organic matter. Degradates tend to be highly polar and mobile. In a study of confined rotational crops (wheat, radishes, carrots, spinach) planted 120 days after treatment, accumulation was detected only in wheat. In this study, HOE 061517 accounted for 11-20% (0.01 - 0.02 ppm) of recovered radioactivity, while most of the residue was from the "carbon pool" and incorporated into cellulosic material. A field accumulation study which was judged supplemental by the EFGWB reviewer detected no residues after a 90 day replanting interval. Routine field studies (in loamy sand and silt loam soils) which were judged supplemental by the EFGWB reviewer indicated that Glufosinate ammonium did not persist ($t_{½}$ ca. 9.8 days) or leach below 10 cm. No accumulation occurred in laboratory fish.

GROUND WATER ASSESSMENT

The mobility of Glufosinate ammonium varies from very mobile (in sandy soils) to immobile depending on soil type. Degradates tend to be highly polar, water soluble and mobile. Therefore, ground water is vulnerable to potential contamination, especially in areas such as citrus orchards in sandy soil. Glufosinate ammonium is resistant to hydrolysis and is metabolized relatively slowly in an aerobic aquatic system. Based on the anaerobic soil metabolism study, anaerobic metabolism in an aquatic system would also be slow. Therefore, under ground water conditions, degradative processes would probably not remove parent compound quickly.

SURFACE WATER ASSESSMENT

Since the affinity of Glufosinate ammonium for soils varies so widely, it might be associated either with water or with soil particles in a run-off situation. It is likely, one way or another, that it will reach surface water. Of the degradative processes tested, the only rapid ones are aerobic soil metabolism and photolysis on soil, which would not be very effective in this situation. Photolysis mediated by sensitizers in natural waters cannot be ruled out, but EFGWB has no data on this [possible] process.

DATA BASE ASSESSMENT: The status of data requirements is as follows:

hydrolysis -- fulfilled [MRID# 403456-56 (Registration Standard 1988)] -- stable to hydrolysis at pH 5, 7, 9; estimated $t_{\frac{1}{2}}$ > 300 days

photodegradation in water -- fulfilled [MRID# 413231-15 (EBC 6/28/90)] -- stable to photolysis

photodegradation on soil -- fulfilled (MRID# 419201-02); discussed in this review -- $t_{\frac{1}{2}}$ (combined effects of soil photolysis and incidental metabolism) is 8 - 9 days. Dark controls had a $t_{\frac{1}{2}}$ of 14 - 18 days. [17 days for "pure photolysis" reported by the investigator -- EBC.] Degradates are CO_2 (ca. 4%); HOE 061517 (up to 60% of applied radioactivity)]; HOE 064619 (2 - 11%); HOE 085355 (2 - 15%)]

aerobic soil metabolism -- fulfilled [MRIDs 413231-18, -19, (EBC 6/28/90) and additional data supplied in the current submission] -- $t_{\frac{1}{2}}$ ca 4 - 23 days; degradates were HOE 064619 and HOE 061517, which peaked at ca. 30-45% of applied material within the first three weeks and then declined

anaerobic soil metabolism -- fulfilled [MRID# 413231-20 (EBC 6/28/90)] -- $t_{\frac{1}{2}}$ ca. 56 days; degradates were HOE 061517, HOE 086486

aerobic aquatic metabolism -- fulfilled [MRID# 403456-60 (Registration Standard, 1988) -- $t_{\frac{1}{2}}$ was ca. 64 days in gravel-pit water: sand sediment

mobility -- leaching/adsorption/desorption -- fulfilled [MRID# 403456-62 (Registration Standard, 1988), MRID 413231-21 (EBC 6/28/90)] for parent and two degradates:

parent -- k_ds ranged from 0.08 to 3.48 in sand and two silt loams to 52.85 in "volcanic ash" clay soil

HOE 086486 -- k_ds ranged from 0.1 to 1.53 in sand and two silt loams to 133 in "volcanic ash" clay soil

HOE 064619 -- not mobile (k_d ca 24) in a silt loam (MRID# 413231-21).

mobility -- laboratory volatility -- fulfilled [MRID 413231-22 (EBC 6/28/90) and additional material discussed in this review] -- Glufosinate ammonium is not volatile.

terrestrial field dissipation

not fulfilled for regular studies -- [MRID# 413231-23 (EBC 6/28/92) and additional discussion in this submission] -- The application rate was not confirmed. Glufosinate ammonium did not appear to persist or leach.

not fulfilled for vineyard -- discussed in this review (MRID# 419201-06) -- in this unacceptable study, Glufosinate ammonium appeared to have a moderately long half-life (based on the mean value of 39 days for the six individual half-lives for the three treatments in the two plots), and did not appear to leach (no residues were detected below one foot depth).

rotational crop accumulation -- confined -- fulfilled [MRID 413231-26 (EBC 6/28/92)] for an application rate of 1 kg a.i./ha (the maximum currently proposed label rate is 1.68 kg/ha) -- also discussed in this review. For crops planted 120 days post-treatment, accumulation occurred in wheat, but not in spinach, carrots, or radishes. HOE 061517 accounted for 11 - 20% (0.01 - 0.02 ppm) of the radioactivity found in the wheat, and the remainder was in the cellulosic material.

rotational crop accumulation -- field -- partially fulfilled [MRID#s 413231-27 and 28; the applicant has not resolved some deficiencies] -- at the apparent application rate of 0.37 ppm, no residues appear in crops of wheat, lettuce, or radishes planted ca. 90 days after treatment of a primary crop of soybeans.

accumulation in laboratory fish -- fulfilled [MRID# 405010-17 (Registration Standard, 1988)]; no residues accumulated during 28 days of exposure

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: n.a.

11. COMPLETION OF ONE-LINER: n.a.

12. CBI APPENDIX: attached to DERs

DATA EVALUATION REVIEW 1

I. Study Type: comments on previous reviews, not dealt with in other DERs

II. Citation:

Erstfeld, K.M. Ignite Herbicide®: Petitioner Response to the EPA Environmental Fate and Groundwater Branch Review Dated June 28, 1990 for Data Requirements for Ignite Herbicide (Glufosinate Ammonium) for Full Registration on Terrestrial Food Crops, Terrestrial Nonfood, Domestic Outdoor and Greenhouse Uses. submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID# 419201-01

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

Soil photolysis, aerobic soil metabolism, laboratory volatility, and confined rotational crop accumulation will be dealt with more fully in other DERs in this review. Other studies are discussed below.

terrestrial field dissipation

EPA comment -- *The soil analysis taken immediately after treatment appears 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.*

Applicant reply -- [discussion of measurements and dilutions]...The rate of 1.8 lb AI/A plus overage was ...applied.

EPA response -- ***While the measurements and dilutions may have been correctly carried out, the analytical results nevertheless do not confirm this. The intent of the previous EPA comment was to elicit some explanation from the applicant as to why the analytical results (0.37 ppm) were so different from the theoretical value (1.8 ppm). No such explanation was provided. This deficiency is not resolved.***

EPA comment -- *...Analyses appear to have been based on what is essentially a single soil sample...*

Applicant reply -- ...One (1) composited soil core sample from each of three replicate plots was analyzed from the study. Thus, three replicate samples were analyzed, not three analytical runs...

EPA response -- ***We appreciate the clarification. This deficiency is resolved.***

rotational crop accumulation

EPA comment -- *...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.*

Applicant reply -- The sensitivity of the analytical method for both studies is 0.05 ppm and is, in our opinion, the best currently available technology for determining residues under field environmental conditions... The level of sensitivity of the method [GC] is limited to the inherent sensitivity of the GC detector to this simple molecule....Typical GC chromatograms illustrating the separation of the mixture of authentic compounds under differing GC conditions are attached in volume 7 of 8, this submission....In addition, an updated method to determine the residues of HOE 039866 and metabolites HOE 061517 and HOE 064619 in soil ... has been validated and is attached as Volume 8 of 8, this submission.

EPA response -- ***We appreciate the clarification. This deficiency is resolved.***

V. Materials and Methods:	n.a.
VI. Study Author's Results and/or Conclusions:	n.a.
VII. Reviewer's Comments:	see above
VIII. CBI Information Addendum: attached	n.a.

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

Page_____ is not included in this copy.

Pages 12 through 15 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.

____ The document is a duplicate of page(s) _____.

____ The document is not responsive to the request.

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.

I. Study Type: soil photolysis, Guideline 161-3

II. Citation:

Stumpf, K. Photolysis of HOE 039866 - ^{14}C Glufosinate Ammonium on Soil. performed by Produktentwicklund, Hoechst Aktiengesellschaft, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-02.

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

1) The study fulfills the requirement for soil photolysis data on Glufosinate ammonium.

2) Glufosinate ammonium is susceptible to photolysis while on a soil surface. The overall $t_{\frac{1}{2}}$ (combined effects of soil photolysis and incidental metabolism) is 8 - 9 days. The dark controls had a $t_{\frac{1}{2}}$ of 14 - 18 days (representing aerobic soil metabolism). [*A calculated figure of 17 days for "pure photolysis" is reported by the investigator -- BCP.*] The incubation yielded a small amount of $^{14}CO_2$ (ca. 4%) and three well known degradates:

HOE 061517 [*3-methylphosphinico-propionic acid* (up to 60% of applied radioactivity)]

HOE 064619 [*2-methylphosphinico-acetic acid (2 - 11%)*

HOE 085355 [*2-acetamido-4-methylphosphinico-butanoic acid (2 - 15%)*]

V. Materials and Methods:

Materials

test compound -- 3,4-^{14}C-labelled Glufosinate ammonium; spec. act 2348.7 MBq/g (63.5 mCi/g; 140923 dpm/μg; 94% (HPLC, anion exchange column); the material was kept as the free acid until needed, and formed by adding an equimolar amount of ammonia to an aqueous solution of the free acid

test soil -- German sandy loam SL V (characteristics attached) -- until needed, stored in a container in a 15-20 cm layer at 18 $\pm$ 2 °C overgrown with chickweed and exposed to artificial sunlight with a light/dark cycle approximating natural sunshine.

test plates -- before use, the soil was sieved (2mm), made into a slurry and coated onto stainless steel plates. Soil layers were ca. 2 - 4 mm thick, and weighed 4.3 - 7.9 gm

light source -- xenon lamp, filtered to remove uv below 290 nm; measurements of spectra and light intensities before and after exposure showed no significant difference

Methods

incubation -- 11 plates were exposed at the same time in a quartz-topped box fitted for adsorption of $^{14}CO_2$ and other volatiles; four plates were the time-zero samples; eleven plates stored in a second box covered with aluminum foil provided the dark controls. Temperature was maintained at 25 ± 1 °C.

sampling -- 0, 2, 4, 8, 16, and 30 days of 12 hour light/dark cycle; adsorbent was replaced at each sampling; following the last sampling the box itself was rinsed with water/ethanol

extraction

soil -- (3 x) with H_2O @ 60 - 70 °C for one hour; extracted soil was then combusted and the released $^{14}CO_2$ was analyzed

analysis

LSC -- $^{14}CO_2$ and volatiles other than $^{14}CO_2$; $^{14}CO_2$ from combusted soil (lod 60 - 80 dpm/sample)

HPLC -- concentrated soil extracts

system 1: KH_2PO_4 acidified with phosphoric acid to a pH ca.2, containing 10% methanol; column of strong basic anionic exchanger

system 2: aqueous sodium sulfate (0.05 mol/l); column of a different strong basic anionic exchanger

TLC -- mobile phase: isopropanol/water/acetic acid; plates: silica gel/cellulose

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

ABSTRACT:

The soil photolysis of HOE 039866, 3,4-^{14}C-ammonium-DL-homoalanin-4-yl(methyl)-phosphinate, was studied to determine the route and velocity of degradation and the nature of photolytic products.

HOE 039866 was applied to the surface of a microbiologically active sandy loam soil layer coated on stainless steel plates. The plates were placed in a closed system and exposed in a test apparatus equipped with a xenon arc lamp with 290 nm cut-off filters. Suitable traps were used to collect $^{14}CO_2$ and volatiles and a material balance was determined.

The irradiations were performed under temperature control (25 ± 1 °C) for 30 days with a 12-hour light/dark cycle. The light intensity was such that one hour of irradiation corresponded to approx. 0.9 h of sunshine under outdoor conditions [experimentally determined by actinometry].

One set of soil samples was kept in darkness under the same conditions as the irradiated ones. The water content of all soil samples was supervised and water was added if necessary.

Soil residues were extracted with hot water. Extractable residues were identified and quantified by radio-HPLC. Non-extractable residues were measured by combustion of the extracted soil.

RESULTS AS DESCRIBED BY THE AUTHOR

The DT-50 for the irradiation was 8-9 days, for the dark control 14-18 days. The calculated half-life for the purely photolytic degradation of the test substance was found to be equivalent to 17 days under natural sunlight conditions.

The three degradation products were identified as the well-known soil metabolites HOE 061517 [*3-methylphosphinico-propionic acid* (up to 60% of applied radioactivity)]; HOE 064619 [*2-methylphosphinico-acetic acid (2 - 11%)*]; and HOE 085355 [*2-acetamido-4-methylphosphinico-butanoic acid (2 - 15%)*]. Formation of $^{14}CO_2$ amounted to 4% of the applied radioactivity at the end of the irradiation.

The corresponding dark controls showed a similar degradation behaviour when compared to irradiated samples in regard to the metabolic pattern, the mineralization rate and the amount of bound residues. Nevertheless, the half life was longer than for the irradiation.

Recoveries were 85.2-105.0% for the irradiated samples and 95.3 - 105.8% for the dark controls.

CONCLUSIONS OF THE AUTHOR

The degradation of HOE 039866 on microbially active soil during irradiation is due to photolytic processes caused by photosensitisation of humic acids and also to microbial degradation.

VII. Reviewer's Comments:

1) *The applicant notes that the study was done using a German soil. Per the applicant*, a dependence on the soil could not be discerned; soil types, application rates, and temperature were more important.

VIII. CBI Information Addendum: attached

RIN 5218-93

EFGWB Reviews of Glufosinate (128850)

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____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

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____ The product confidential statement of formula.

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DATA EVALUATION REVIEW 3

I. Study Type: aerobic soil metabolism, Guideline 162-1

II. Citation:

Stumpf, K. **supplement to** *HOE 061517-^{14}C, metabolite of HOE 039866 Degradation in a Sandy Loam Soil Under Aerobic Conditions at Application Rates of 0.05 and 1.0 mg/kg (MRID# 413231-18), and Degradation and Metabolism in Different Soils under Aerobic and Anaerobic Conditions at an Application Rate of 1.6 mg/kg (MRID# 413231-19).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-03.

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

This submission supplies the missing information on soil characteristics which had been requested. The original study together with this information satisfies the data requirement.

V. Materials and Methods: n.a.

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

VII. Reviewer's Comments:

This supplement contains administrative material and a two-page summary comparing soil characteristics and half-lives among several soil metabolism studies. The German soil SLV was used in five of the studies, which were done at several different concentrations. Two studies done at similar concentrations yielded similar results. At higher concentrations, metabolism was significantly slower.

VIII. CBI Information Addendum: attached

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DATA EVALUATION REVIEW 4

I. Study Type: Volatility from Soil, Guideline 163-2

II. Citation:

Görlitz, G. **supplement to** *HOE 064619, Assessment of Volatilization from Soil (MRID# 413231-22).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-04.

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

The current submission supplies the requested information on modeling techniques used by the applicant. The original study together with the current submission satisfy the data requirement.

V. Materials and Methods: informational material attached

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

VII. Reviewer's Comments:

The applicant has supplied the reference material to support the environmental model used in the original study.

VIII. CBI Information Addendum: attached

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Pages 50 through 71 are not included.

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DATA EVALUATION REVIEW 5

I. Study Type: residue accumulation in rotational crops, Guideline 165-1

II. Citation:

Stumpf, K. **supplement to** *HOE 039866-^{14}C, Residue Determinations and Metabolism in Rotational Crops Sown 120 Days After Treatment of Soil (MRID# 413231-26).* performed by Hoechst AG, Frankfurt, FRG, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-05.

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

The submitted material removes one of the two deficiencies, that of the method sensitivity. However, the data will only support an application rate of 1 kg a.i./ha.

V. Materials and Methods: n.a.

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

VII. Reviewer's Comments:

One of the previous comments had to do with sensitivity of the method. The applicant has provided a discussion of the limitations of sensitivity, which are in part imposed by legal regulations restricting the amount and specific activity of radioisotope which could be used. This deficiency is resolved.

However, a second deficiency is not satisfactorily resolved. The application rate for wheat (1 kg a.i./ha) was roughly half of the maximum label rate (1.68 kg a.i./ha), and therefore the study will only support the rate tested. A similar study done on corn at 1.9 kg a.i./ha, which is described in the submission, cannot substitute.

VIII. CBI Information Addendum: attached

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Pages 73 through 102 are not included.

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DATA EVALUATION REVIEW 6

I. Study Type: field dissipation (vineyard)

II. Citation:

Mayasich, J.M. and Czarnecki, J.J. Determination of the Leaching Potential and Dissipation of Ignite® Residues, (Glufosinate-ammonium (HOE 039866) and Metabolites (HOE 061517 and HOE 064619) in a California Vineyard. performed by Field Research for Hire, Porterville, CA, and EN-CAS Analytical, Winston-Salem, NC, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-06.

III. Reviewer:

Typed Name:	E. Brinson Conerly-Perks
Title:	Chemist, Review Section 3
Organization:	EFGWB/EFED/OPP

IV. Conclusions:

1) The study is unacceptable.

a) The data are too variable. EFGWB does not believe that a meaningful value can be obtained by averaging a set of results such as 0.109 ppm, 0.109 ppm, 0.052 ppm, and <0.05 ppm (four actual "replicate" values).

b) The application rate was not confirmed. Soil samples contained only a fraction of the nominally applied material even in bare-ground samples. Moreover, there was poor recovery of applied material analyzed from application cards, especially in the second and third treatments, although the applicant states that a difference in orientation of the cards accounts for these discrepancies.

2) Although these data are of extremely limited usefulness in describing precisely the environmental behavior of Glufosinate ammonium, some cautious inferences can be made:

The half-lives determined in the study are remarkably similar for the two study sites, weeded and bare. The compound appears to have a mean half-life of ca. 39 ± 23 days, indicating a certain degree of persistence.

The study did not disclose any detectable residues below the 1 foot depth. This indicates that leaching might not occur under these conditions.

V. Materials and Methods:

Materials

test compound -- Ignite Herbicide containing 200 gm Glufosinate ammonium (1.67 lb ai/gal)

test site -- vineyard in CA, planted with grapes, sandy loam surface soil

test plots -- each 80 x 120 feet, sandy loam surface soil (characteristics included in data following DER)

weed-grown, untreated -- upwind and upslope from treated plots
weed-grown, treated
bare ground, treated

Methods

treatment -- material was applied by boom spray @ 1.5 lb ai/A, on 1/14/88, 5/14/88, and 8/1/88. Additional chemicals [*including paraquat*] applied are listed in attached data

irrigation -- furrow, with sprinkler supplementation when needed to adjust the rainfall to $\geq$ 120% of the 10 year average

climatic conditions -- monitored daily from CIMIS station located ca. 25 miles NW of the site.

sampling -- 5 types (schedule and details attached):

soil cores
soil spikes
weeds
application cards
spray mixture

extraction

soil cores -- a representative sample of soil was extracted by blending in 0.004 M $Ca(OH)_2$. The extract was clarified by settling or centrifugation, cleaned up by successive passage through cation and anion exchange resins. The analytes were eluted from the anion column using 10% aqueous formic acid. Water was removed from the eluant by rotary evaporation, and the analytes were derivatized by refluxing for 4-6 hours in a mixture of acetic acid and trimethyl orthoacetate (TMOA). Excess reagents were removed by solvent exchange into toluene, which was in turn removed by a solvent exchange into methyl acetate.

analysis

derivatized soil extracts -- GC - flame photometric detector with a 526 nm phosphorous filter

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

ABSTRACT:

Three ground applications of Ignite herbicide were made to each of two plots supporting grapes. One plot contained weeds and the other was bareground. The rate for each of the three applications was 1.5 lb ai/A. An untreated control plot was also included in the study.

The study was primarily designed to evaluate the leaching potential of the parent (HOE-039866) compound and the primary (HOE-061517) and secondary (HOE-064619) metabolites. Even under the worst-case conditions established by the irrigation and cultural practices used in this study (i.e. rainfall + irrigation was 340% of the ten-year average), quantifiable residues were not found below a soil depth of one foot.

The secondary objective of the study was to determine the dissipation rate of the parent and elucidate the formation and decline patterns of the metabolites. Due to the complexity of the study design and the confounding effects of live and dead weed cover, a number of half-life determinations ranging from 11.6 to 59.3 days were calculated. Given the paucity of confounding effects associated with the first application to the bareground plot, the Sponsor considers the corresponding half-life determination of 11.6 days to be the most accurate.

In total, the study provides additional evidence that Ignite herbicide residues are not persistent in the environment and do not tend to leach.

RESULTS AS DESCRIBED BY THE AUTHOR

spray deposition cards -- [results are presented in detail in attachments (table 8)]. The results associated with application one are considered to be adequate validation for an application of 1.5 lb ai/A. The results of applications two and three do not appear to validate this application as directly. However, the sponsor believes that they are adequate due to the following rationale:

1) For application one the entire surface of the cards was analyzed, and ... the data were adequate.

2) Only 24% of the surface of the cards was analyzed for applications two and three. This resulted in an apparent decrease in collection efficiency of nearly two-fold. Considering the critical relationships between orientation and design of any deposition card and the application equipment used, it is not surprising that this decrease in collection efficiency was not strictly proportional to the associated decrease in surface area analyzed. The decrease in collection efficiency was remarkably precise ... and therefore key to the sponsor's belief that - while all three applications were accurately made at a rate of 1.5 lb ai/A, the surface area of the samples analyzed for applications two and three... [did]... not reflect the accuracy of these applications.

3) Calibration data on file corroborate an application rate of 1.5 lb ai/A for all three applications.

field fortifications -- when corrected for procedural recoveries, 83 ± 17% (HOE-039866), 82 ± 11% (HOE-061517), and 78 ± 10% (HOE-064619) of nominal fortified values were recovered. In addition these data provide adequate storage stability data for all three analytes, since storage times ranged from 192 to 577 days. The maximum of the range exceeds the storage time of the actual field samples.

soil core analysis -- details presented in attachments (tables 9 -- 16)

Weedy plot, application 1

At the 0 - 4" level, HOE-039866 mean residues reached a peak at 0.153 ppm 7 days after treatment (d.a.t.), rapidly declined to negligible levels by 29 d.a.t., and remained so through day 119. Maximum levels of HOE-061517 and HOE-064619 occur 7 and 29 d.a.t. respectively. The half-life of HOE-039866 was calculated to be 34.7 days.

At the 4 - 8" level, HOE-039866 mean residue levels peaked at 0.240 ppm 4 d.a.t., declined to just above the limit of quantitation (loq) by 7 d.a.t., and remained below the loq through day 119. The primary metabolite, HOE-061517, had a single residue above the loq at 4 d.a.t. The secondary metabolite, HOE-064619, had a single mean residue level equal to the loq at 29 d.a.t.

In the 8 - 12" soil horizon, a single mean residue level of 0.053 ppm HOE-039866 was detected 7 d.a.t. The remaining mean residue levels of HOE-039866 and all mean residue levels of the metabolites were below the loq. Analysis of deeper soil horizons indicated that HOE-039866 and its metabolites do not leach beyond a depth of one foot.

Weedy plot, application two

In the 0 - 4" soil horizon, a maximum mean residue of 0.214 ppm HOE-039866 was detected 3 d.a.t. After an immediate decline to negligible levels 7 d.a.t., the mean HOE-039866 residues rose to 0.083 ppm at 20 d.a.t., then declined to and remained at negligible levels through 77 d.a.t. The mean residue levels of HOE-061517 also were bimodal, but staggered from that of HOE-039866, with a maximum mean level of 0.114 ppm being detected 77 d.a.t. The mean levels of HOE-064619 rose from 0.086 ppm on application day to about 0.1 ppm 3 days later, then declined and remained negligible from 7 through 77 d.a.t. The half-life of HOE-039866 was calculated to be 17.3 days. The mean residue levels of each analyte never exceeded the limit of quantitation when soil horizons deeper than 0 - 4" were analyzed.

Weedy plot, application three

In the 0 - 4" soil horizon, the mean residue levels of HOE-039866 reached equivalent maxima of about 0.11 ppm 0 and 7 d.a.t., and then gradually declined to and remained at very low levels through 63 d.a.t. The low mean residue levels of HOE-039866 associated with the 3 d.a.t. sampling may again be attributed to heavy weed cover in the subplots samples. The half-life of HOE-039866 was calculated to be 69.3 days. There was no evidence of any analyte leaching beyond the 0 - 4" soil horizon. Therefore the aggregate results of all samples analyzed clearly indicate that residues of Ignite[R] did not leach beyond one foot.

Bareground Plot, application one -- *the sponsor feels this portion of the study is most representative of the overall metabolic fate of HOE-039866, reflecting the absence of a key confounding factor (weeds) and also the absence of influence of previous applications of Ignite[R] on the soil microflora.*

In the 0 - 4" soil horizon, mean residues of HOE-039866 rapidly declined from a maximum of 0.267 ppm on day 0 to below the loq by 29 d.a.t. and remained so through day 119. mean levels of HOE-061517 increased to a 0.140 ppm maximum 15 d.a.t. and gradually declined to negligible levels by 119 d.a.t. The formation and decline of HOE-064619 is as expected. The half-life of HOE-039866 was calculated to be 11.6 days.

In the 4 - 8" and 8 - 12" soil horizons, considerable levels of both HOE-039866 and HOE-061517 are present 4 d.a.t. These results coincide with the occurence of precipitation over days immediately following this application. By 7 d.a.t. the mean residue levels of all analytes in all depths analyzed declined to less than quantifiable levels and remained negligible through day 119. The leaching potential of HOE-039866 and its metabolites defined in the weed covered plot as one foot is now verified in the bareground plot.

Bareground plot, application 2

In the 0 - 4" soil horizon gradually increased to a maximum of 0.318 ppm 7 d.a.t., immediately declined to less than the loq 16 d.a.t., then rose slightly and returned to negligible levels by 77 d.a.t. Mean residues of HOE-061517 exceeded the loq once at 31 d.a.t. and then declined to negligible levels by 77 d.a.t. Mean residue levels of HOE-064619 never exceeded the loq. The half-life of HOE-039866 was calculated to be 34.7 days.

In the 4 - 8" soil horizon, a single mean residue of HOE-039866, barely above the loq is the only evidence of leaching associated with this portion of the study.

Bareground plot, application 3

In the 0 - 4" soil horizon, mean residues of HOE-039866 gradually declined from a maximum of 0.168 ppm on application to negligible levels 16 and 29 days later. The mean level increased slightly to 0.065 ppm 42 d.a.t. and then declined to below the loq 63 d.a.t. The mean residue levels of HOE-061517 remained very low until a maximum of 0.078 ppm was reached 42 d.a.t. by 63 d.a.t. the mean level of HOE-061517 declined to slightly above the loq. Mean residue levels of HOE-064619 never exceeded the loq. a half-life of 69.3 days was calculated for HOE-039866.

In the 4 - 8" horizon, very low levels of HOE-039866 and HOE-061517 were detected 63 d.a.t. Analysis of deeper horizons collected 63 d.a.t. did not detect any analyte at a mean residue level above the loq.

CONCLUSIONS OF THE AUTHOR

The irrigation and overall cultural practices, specific to this study, defined a worst-case scenario for evaluating the leaching potential of Ignite herbicide residues. For example, it should be emphasized that total precipitation (rainfall + irrigation) for the study was 340% of the ten year average. The results indicate that HOE-039866 and its metabolites (HOE-061517 and HOE-064619) are not mobile beyond a depth of one foot.

A key factor which tended to confound the dissipation results of the study was weed cover. This cover was represented by live weeds in one treated plot and dead weed trash in the other treated plot. The plot with live weeds was included in the study to represent the use scenario for Ignite herbicide as a component of a typical herbicide program for vineyards. This cover was of sufficient density to intercept considerable quantities of test material by the time the second and third applications were made. A significant source of test material therefore remained poised for introduction to the soil matrix upon any precipitation or irrigation event. The half-life calculations associated with applications two and three are, therefore, considered to be semi-accurate. The most accurate estimation of the half-life of HOE-039866 was calculated to be 11.6 days (Application I, Bareground, 0-4" soil)

VII. Reviewer's Comments:

The data are too variable to establish a pattern of disappearance of parent and appearance and disappearance of degradates. The variability inherent in field work does not appear to account for values as divergent as 0.2 ppm and <0.05 ppm (non-detect) in a cohort of samples which are supposed to be replicates. It is unacceptable to take such imprecise data and use the mean as the "correct" value.

The actual application rate claimed is not supported by available data. The highest observed level in soil samples from the bare-ground study (ca. 0.27 ppm in a 4" soil layer) is far below the nominal application rate (0.75 ppm for a 6" soil layer). Also, application card data is less than convincing in establishing the actual application rate, although the applicant has supplied a rationale for those results.

The study results imply that *detectable* residues of Glufosinate ammonium and its metabolites do not appear lower than one foot below the soil surface.

The data do not define a reliable half-life value, but may be useful for establishing an order of magnitude for the half-life. The data are consistent with a certain amount of persistence. Despite the highly variable data, the author-calculated results from the two plots are remarkably similar. Indeed, two of the three half-life values (for treatments 1, 2, and 3) are identical for both plots, although they do not occur in the same sequence in the two cases. For the weedy plot the value of the $t_{\frac{1}{2}}$ is 40.43 $\pm$ 20.61 days, and for the bare ground plot, it is 38.53 $\pm$ 23.71 days. The two plots combined give a $t_{\frac{1}{2}}$ of 39.48 $\pm$ 22.71 days.

The monitoring of climatological conditions from 25 miles away is insufficient. Particularly in hilly country such as typical grape-growing areas, micro-climates can differ greatly in only a short distance.

VIII. CBI Information Addendum: attached

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