Shaunessey No. 114401

Date Out EFB: FEB 3 1983

To: Montfort
Product Manager 23
Registration Division (TS-767)

From: Emil Regelman, (Acting) Chief
Review Section No. 1
Environmental Fate Branch
Hazard Evaluation Division (TS-769)

FILE COPY

Attached please find the environmental fate review of:

Reg./File No: 748-EUP-RI

Chemical: PPG-844 (carboxyethyl ester of acifluorfen)

Type Product: Herbicide

Product Name: PPG-844 2E

Company Name: PPG

Submission Purpose: preliminary application for EUP with data

ZBB Code: 3(c)(5)

ACTION CODE: 710

Date in: 11/17/82

EFB # 63

Date completed: 2/3/83

Tais (level II)	Days
52	8.0

Deferrals To:

Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

1. INTRODUCTION

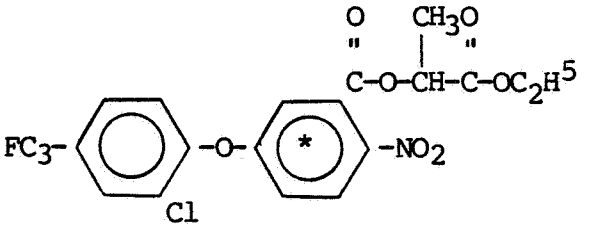
PPG Industries, Inc. has submitted an application for an EUP for the use of PPG 844 (1-carboethoxy)ethyl 5-(2-chloro-4-(trifluoromethyl) phenoxy)-2-nitrobenzoate) as a preemergence herbicide in soybeans. The EUP would cover the use of 843 lb ai on 5,000 treated acres of a total of 71,300 crop acres in 28 states.

1.1 Chemical

Chemical Name: 1-carboethoxy)ethyl 5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate

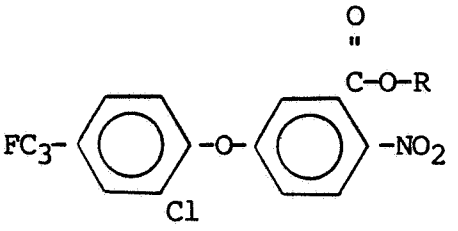
Trade Name: PPG-844 2E

Chemical Structure:



* = position of the ring label in labelled experiments

Chemical Structure of metabolites:



R = H for PPG-847 (NCTBA)
R = $CH(CH_3)CO_2H$ for PPG-947

2.0 DIRECTIONS FOR USE

See attached label

3.0 DISCUSSION OF DATA

3.1 Preliminary PPG-844 Hydrolysis Study. D.E. Hardies and D.Y. Struder, BR-21948, July 23, 1980.

Procedure:

PPG-844 in 5% aqueous acetone was added to 5% aqueous acetone solutions buffered at pH 4, 7, and 9. The flasks were stoppered and incubated in darkness in a 40°C bath. The initial concentration of PPG-844 was 1 ppm. The 5% aqueous acetone solutions was used because of the low solubility of PPG-844 in water (about 0.1 ppm).

Samples were taken over a 26 day period, extracted with methylene chloride and analyzed by HPLC.

Results:

The half life of PPG-844 was 10.7 days at pH 4, 4.6 days at pH 7, and 0.49-0.97 days at pH 9.0.

A potential hydrolysis product of PPG-844 is 5-(2-chloro-4-trifluoromethyl phenoxy)-2-nitrobenzoic acid (NCTBA). No trace of this potential product was found in the 504 hour samples by HPLC at pH 4 and pH 7. There was, however, material with the same TLC R_f value as NCTBA present in the 72 hour pH 9 sample. The identity of the material has not been confirmed by any other method.

Conclusions:

From the preliminary data, it appears that PPG-844 is fairly rapidly hydrolyzed in 5% aqueous acetone at 40°C at the 3 pH's studied.

This study does not satisfy the environmental chemistry hydrolysis data requirement.

3.2 Hydrolysis of 5-(2-chloro-4-trifluoromethylphenoxy)-2-nitrobenzoic acid (NCTBA). D.E. Hardies and D.Y. Struder, BRC-21991, August 25, 1980.

Procedure:

A buffered solution at pH 9 in 5% aqueous acetone was prepared in the same manner as those in the preliminary PPG-844 hydrolysis study in Section 3.1 and 1 ppm of NCTBA (PPG-847) added. Samples were incubated in darkness at 40°C.

In another experiment, a 1.95 ppm, pH 9, 5% aqueous acetone solution of ^{14}C-NCTBA was incubated in darkness at 40°C.

Although NCTBA is more soluble in water than PPG-844, these conditions were used to compare with the preliminary PPG-844 hydrolysis study.

Samples from both experiments were taken over a 21 day period, extracted with methylene chloride and analyzed by either HPLC or TLC/AR and LSC.

Results:

No hydrolysis was seen during the 21 day study. At time 0 there was 1.58 ppm of NCTBA by HPLC analysis, at 4 hours 1.63 ppm, and at 76 hours 1.72 ppm. After a two dimensional TLC analysis 98.33% - 100% of the ^{14}C counts were found at the R_f's of NCTBA.

Conclusion:

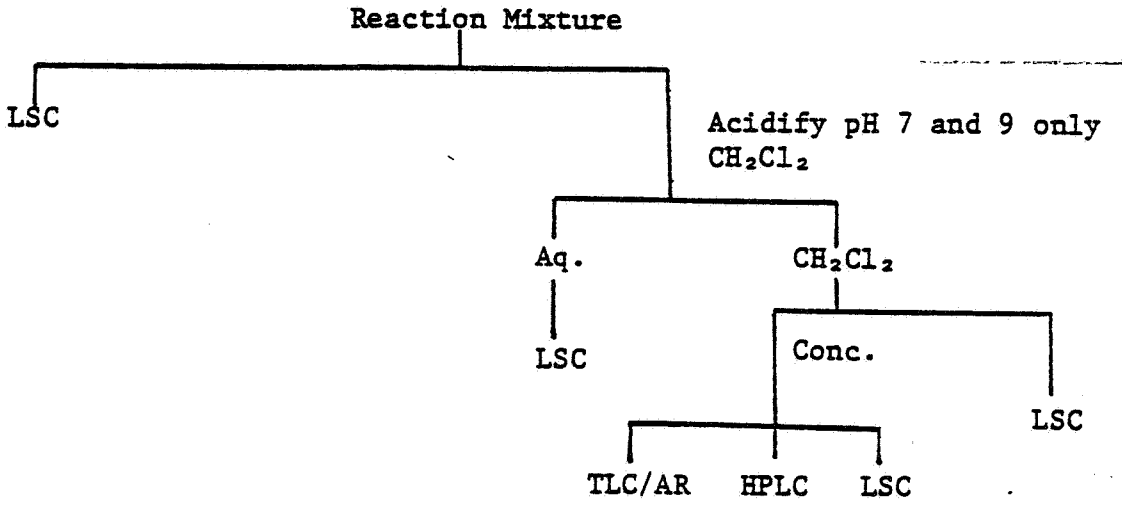
NCTBA or PPG-847 is hydrolytically stable at pH 9 in 5% aqueous acetone.

3.3 PPG-844 Hydrolysis Study -- A Progress Report. D.E. Hardies and D.Y. Struder, BRC-22798, October 14, 1982.

Procedure:

Buffered 1% aqueous methanol solutions at pH 5, 7 and 9 were amended with 0.1 ppm ^{14}C-labelled PPG-844 in methanol. The flasks were stoppered and incubated in darkness in a 25°C bath.

Samples were taken at 0, 1, 2, 4, 6, 14, 24, and 48 hours at pH 9, at 0, 2, 4, 7, 14, and 21 days at pH 5, at 0, 4 hr, 14 hr, 1 da, 2 da, 4 da, 7 da, 14 da, and 21 da for pH 7 study I and at 0, 2 hr, 4 hr, 6 hr, 12 hr, 1 da, 2 da, 6 da, 9 da, and 14 da for pH 7 study II. The samples were processed by the following scheme and analyzed by LSC, HPLC, and TLC/AR.



Results:

A summary of the ^{14}C-PPG-844 hydrolysis is shown on page 3A. After 48 hours, the pH 9 sample contained 2.5% parent. After 21 days the pH 7 sample contained 32.6% parent and the pH 5 sample contained 88.1% parent.

Conclusion:

Hydrolysis of PPG-844 is pH dependent with faster hydrolysis at higher pH. The halflife of PPG-844 is 8.7 hr at pH 9, 9.5 - 11.5 days at pH 7, and 112 days at pH 5.

3.4 Microbial Transformation of Xenobiotic Compounds. III. Relative Rates of Hydrolysis of 1'-(Ethoxycarbonyl)ethyl 5-(2-chloro-4-alpha, alpha, alpha-trifluoromethylphenoxy)-2-nitrobenzoate Analogs in Soil Solutions. R.E. Betts and J.K. Pifer, BRC-22168, January 20, 1981.

This study is not an environmental fate data requirement.

3.5 Microbial Transformation of Xenobiotic Compounds. II. Conversion of 1'-(Ethoxycarbonyl)ethyl 5-(2-chloro-4-alpha, alpha, alpha-trifluoromethylphenoxy)-2-nitrobenzoate by Nine Bacterial Species. R.E. Betts and J.K. Pifer, BRC-22169, February 10, 1981.

This study is not an environmental fate data requirement.

3.6 Microbial Transformation of Xenobiotic Compounds. IV. Metabolism of PPG-844 by Soil Organisms. R.E. Betts and J.K. Pifer, BRC-22389, August 25, 1981.

This study is not an environmental fate data requirement.

3.6.1 While these studies do not fulfill any environemental fate data requirements, they do show that PPG-844 is degraded to PPG-847 with both fungi and bacteria. The rate is rapid with fungi and slower with bacteria. In a sterile control experiment PPG-844 was stable.

Conclusion:

Biological degradation is the major metabolic pathway in the soil degradation of PPG-844

3.7 Progress Report on a Laboratory Soil Degradation Study of Carbon-fourteen Labeled PPG-844. D.E. Hardies and D.Y. Struder, BRC 22816, October 25, 1982.

Procedure:

A Wooster silty clay loam (18.4% Sand, 53.2% Silt, 28.4% Clay, 2.0% OM, CEC = 11.0, pH = 4.9, water holding capacity = 23.32%, and bulk density = 1.3 g/cm^3) was fortified with ring labelled ^{14}C-PPG-844 to a concentration of 10 ppm. The soil was incubated in the dark at room temperature (approximately 21°C). Soil moisture was maintained by the addition of distilled water at least twice a week. Four flasks with caustic traps were used to assess CO_2 production.

Soil samples were taken at 0, 1, 3, 7, 14, and 30 days and analyzed according to the scheme on the next page (4A).

Wooster silty clay loam soil fortified as above was also used to isolate metabolites of PPG-844. Four samples were prepared. Two samples were processed after aging for 1 day and the other two were processed after 3 days aging. The isolation scheme is shown on page 4B.

Results:

This is a progress report on a study that was designed to cover a 90 day period and include an anaerobic study. This report only covers the first 30 days of the complete study.

Acifluorfen

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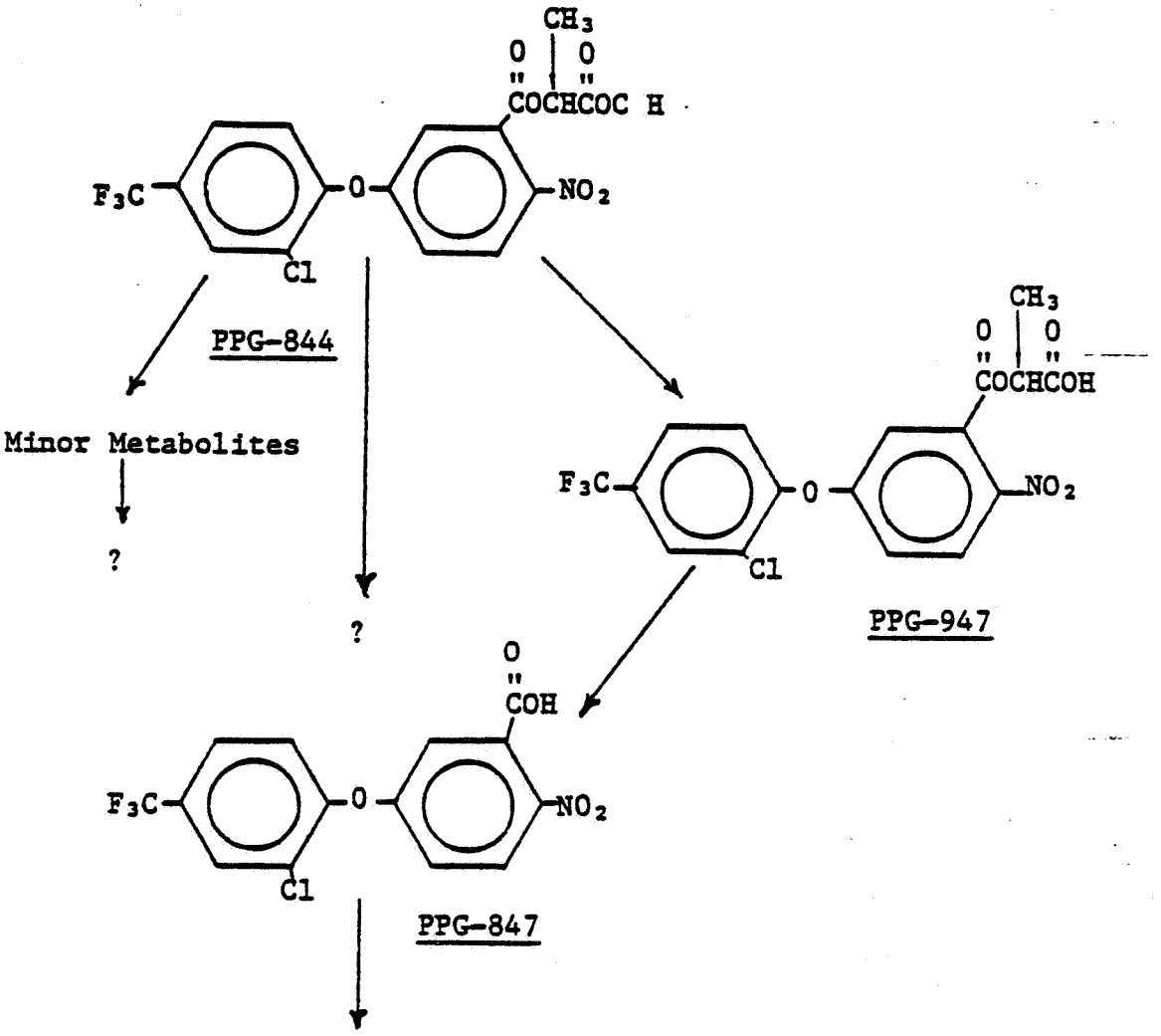
PPG-844 was slowly degraded to carbon dioxide while being rapidly degraded to PPG-947 and PPG-847 with 2.3 days being the halflife of PPG-844. The following is the proposed pathway for degradation of PPG-844:



Conclusions:

PPG-844 is degraded in this soil with a halflife of 2.3 days. The initial major metabolite was PPG-947, peaking at 16.2% on day 1 and falling to 2.1% by day 30. PPG-847 was the second major metabolite produced peaking at 52.3% on day 7 and falling to 38.2% by day 30. PPG-844 slowly degraded to CO_2 reaching 2.7% CO_2 production by day 30.

3.8 Determination of PPG-844 Residues in Soil After a Preemergence Treatment with C-14 PPG-844. J. L. Wiedmann, J. Pensyl and P. Marsden, BRC 22817, October 25, 1982.

This study is not needed to fulfill the data requirements for an EUP and has not been evaluated.

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3.9 Dissipation of PPG-844 and Its Metabolites From Soil 1981 and 1982 Crop Years. J. L. Wiedmann, J. Pensyl and P. Marsden, BRC 22808, October 20, 1982.

This study is not needed to fulfill the data requirements for an EUP and has not been evaluated.

3.10 Determination of Residues in Rotational Crops Planted at Different Intervals After 14-C-PPG-844 Soil Application. PPG-844 Rotational Crop Studies I. J. L. Wiedmann, D. R. Coffman and P. Marsden, BRC 22807, October 20, 1982.

Procedure:

A silty loam soil (24.8% Sand, 52.8% Silt, 22.4% Clay, 2.5% OM, CEC = 5.7 and pH = 5.5) in three 27 inch growing tubes was seeded to soybeans (2 tubes, #10 and #11) and corn (1 tube, #14) and treated with 0.92 lb ai/A of ^{14}C-ring labelled PPG-844 on August 20, 1981. The highest recommended rate is 0.2 lb ai/A. Corn plant samples were taken for analysis at 20, 32, 42 and 50 days. No corn samples were taken at harvest as the corn was killed by frost prior to harvest. Soybean plant samples were taken for analysis at 26, 42, 61 days.

Winter wheat was planted in tubes #11 and #14 on October 30, 1981 (71 days after treatment). Green wheat plants were sampled on May 27, 1982. Mature wheat was harvested on July 8, 1982. Control wheat was planted on May 27, 1982, but was not harvested as it was eaten by birds.

Radish and lettuce were planted on April 29, 1982 in the area of tube #11 where the wheat had winter killed. The lettuce was crowded out by the wheat and radish. Radishes were harvested on July 8, 1982. Control radish and lettuce was planted on May 27, 1982. Control lettuce was harvested on July 21, 1982 and control radishes were harvested on July 22, 1982. Lettuce was planted in tube #14 on July 8, 1982 after the wheat was harvested and harvested on August 27, 1982.

Carrots were planted on July 8, 1982 in tube #14 and only a few small carrots were harvested on September 24, 1982.

Six inch soil samples were taken in 4 inch cores, air dried and screened with an 8 inch screen to remove rocks. Samples were analyzed by combustion-LSC and EC-GC.

Plant samples were extracted into methanol and analyzed by LSC. The unextracted plants and solids were oxidized and analyzed by LSC. From the remaining methanol extract, the methanol was removed and the extract transferred to a Clin Elute extraction column. The organo soluble fraction was eluted with methylene chloride and quantitated by LSC. The remaining organo soluble extract had the methylene chloride removed and was transferred to a C_{10} Bond Elute column and eluted with methanol/water and analyzed by EC-GC.

Results:

The residue method for PPG-844 has a limit of quantitation of 0.05 ppm. Consequently, crop samples with ^{14}C levels less than 0.02 ppm were not analyzed further. The ^{14}C remaining in the soil over the length of the study is summarized in the table on the next page (7A).

The results of crop analyses are summarized below:

Crop	Days Exposure	Days from treatment to planting	^{14}C ppm
Corn	20	—	0.09
Corn	32	—	0.07
Corn	42	—	0.12
Corn (frost damage)	50	—	0.07
Corn Control	—	—	<0.01
Soybean	26	—	0.26
Soybean	42	—	0.29
Soybean	61	—	0.31
Lettuce Control	—	—	<0.02
Lettuce	372	291	<0.02
Radish Root Cntl	—	—	<0.02
Radish Root	322	221	<0.02
Radish Top	322	221	<0.02
Wheat Plant	280	72	0.12
Wheat Straw	322	72	0.27
Wheat Grain	322	72	0.10
Carrot Top	400	291	<0.02
Stems			
Leaves			
Carrot Root	400	291	<0.02

The only significant ^{14}C uptake in rotational crops was by wheat. All other rotational crops had no (<0.02 ppm) uptake. The wheat samples were further analyzed to determine if the ^{14}C represented PPG-844. No detectable residues were found in wheat plant parts with EC-GC.

Conclusion:

No significant residues of PPG-844 were taken up by rotational crops treated with greater than 4 times the maximum recommended rate. No rotational crop restrictions are needed.

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3.11 Determination of PPG-844 Residues in Rotational Crops Planted After the Preemergence Treatment of PPG-844 Applied to Corn or Soybeans. 1981-1982 Crop Years. PPG-844 Rotational Crop Studies II. J. L. Wiedmann, P. Marsden and D. R. Coffman, BR 22818, October, 1982.

This study is not needed to fulfill the data requirements for an EUP and has not been evaluated.

3.12 Uptake, Depuration and Bioconcentration of ^{14}C-PPG-844 by Bluegill Sunfish (Lepomis macrochirus). A. D. Forbis, ABC Progress Report #29377, Obtober 11, 1982.

This study is not needed for an EUP and is only a progress report. Therefore it has not been evaluated.

4.0 CONCLUSIONS

4.1 Although the hydrolysis study is not fully complete, the progress report demonstrates that aqueous hydrolysis is not a major pathway for degradation of PPG-844 due to the low solubility in water. The full report should, however, be submitted for review when completed.

4.2 Aqueous hydrolysis is pH dependent with faster hydrolysis at more alkaline pH's.

4.3 The aqueous halflife of PPG-844 is 9 hours at pH 9, 10 days at pH 7, and 112 days at pH 5.

4.4 The major aqueous hydrolysis metabolite is stable to further hydrolysis at pH 9 in 5% aqueous acetone at 40°C over 21 days.

4.5 Although the soil degradation study is only a progress report, it demonstrates that PPG-844 is rapidly degraded in soil (halflife 2.3 days) with the major degradative pathway being biological. The full report should, however, be submitted for review when completed.

4.6 A rotational crop restriction is not needed for PPG-844 for this use.

5.0 RECOMMENDATION

EFB concurs with this EUP. Partially complete studies should, however, be submitted for final review when completed. The field dissipation, field rotational crop, and fish accumulation studies were not reviewed due to time constrains. These should be resubmitted for a full review with the registration request.

Norma Kay Whetzel
February 3, 1983
Review Section No. 1
Environmental Fate Branch
Hazard Evaluation Division

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