



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

12-17-93

EFGWB#: 94-0031  
DP Barcode: D195703  
Shaughnessy No.: 116004

**SUBJECT:** Request for a Waiver for the Photolysis on Soil (161-3),  
Aerobic Soil Metabolism (162-1), and Mobility in Soil (163-1)  
data requirements for Triclopyr Buthoxyethyl Ester

**TO:** Kathryn Davis, PM  
Accelerated Reregistration Branch  
Special Review and Reregistration Division

**FROM:** José Luis Meléndez, Chemist *José Luis Meléndez 12/16/93*  
Environmental Chemistry Review Section #2/EFGWB

**THROUGH:** Mah Shamim, Ph.D., Acting Chief *M. Shamim* DEC 17 1993  
Environmental Chemistry Review Section #2/EFGWB

and

Henry Jacoby, Chief  
Environmental Fate and Groundwater Branch  
Environmental Fate and Effects Division (H7507C), *[Signature]*

EFGWB believes that the registrant has provided sufficient bridging information on Triclopyr Buthoxyethyl Ester (BEE) and acid in natural matrices. The branch concurs with a waiver for the following data requirements for triclopyr BEE. Data provided for triclopyr acid will be used as surrogate data for the data requirements for triclopyr BEE:

Photolysis on Soil (161-3)  
Aerobic Soil Metabolism (162-1)  
Mobility in Soil (163-1)

BACKGROUND:

Triclopyr is a systemic herbicide used for the control of woody plants and broadleaf weeds on rights-of-way, forests, industrial sites, and turf. It is formulated as Triclopyr BEE (Garlon 4) and Triclopyr TEA salt (Garlon 3A). Triclopyr BEE is formulated as an emulsifiable concentrate or as a soluble concentrated liquid. Triclopyr TEA salt is formulated as a granular, an emulsifiable concentrate, a soluble concentrated liquid, or as a liquid ready-to-use. The maximum application rate for triclopyr acid is 10 kg/ha (9 lb/A). The registered use patterns are as follows:

<u>Use pattern</u>	<u>Ester</u>	<u>Salt</u>
Terrestrial feed crop	X	X
Terrestrial non-food crop	X	X
Aquatic non-food outdoor crop	--- <sup>1</sup>	X
Forestry	X	X
Outdoor residential	---	X
Indoor food	---	X

In a previous review (DP Barcode D181274, 12/01/92), EFGWB described the Environmental Fate Strategy for triclopyr and its related compounds. The strategy assumes that triclopyr TEA rapidly dissociates and triclopyr BEE rapidly hydrolyses to the free acid. Thus, salt and ester do not persist under normal environmental conditions. Therefore, the data for the acid would provide sufficient information about the environmental fate of all the related compounds.

In order to relate triclopyr BEE to triclopyr acid, the results of the hydrolysis study were evaluated. Triclopyr BEE hydrolyses to triclopyr acid with half-lives of 84.0, 8.7, 0.3, and 0.5 days in pH 5, 7, and 9 solutions, and in natural water, respectively (MRID# 134174). In the previous review, dated 12/01/92 (DP Barcode D181274), EFGWB did not concur with a waiver for any data requirements for triclopyr BEE, since triclopyr BEE showed relatively high stability in acidic (pH 5) buffered solutions.

#### REQUEST FOR A WAIVER:

The registrant has now provided<sup>2</sup> results of a number of studies that support bridging between triclopyr BEE and triclopyr acid under natural conditions as follows:

- Bidlack (1978; MRID# 134174): Triclopyr BEE degraded rapidly to triclopyr acid in aqueous buffered solutions at pH's 7 and 9, in natural water, and three soils at pH's between 5.4 and 6.8. However, it showed higher stability in pH 5 buffered sterile solutions.
- Swann & Unger (1981; MRID# 92190012): In a photolysis in soil study (found to be unreviewable), triclopyr BEE degraded to the acid in exposed and dark control soils at pH 6.4, with 80% degraded after 28 days incubation.
- Laskowski & Bidlack (1984; MRID# 00151967): In an anaerobic aquatic metabolism study, triclopyr BEE degraded to triclopyr acid

---

1. In a meeting conducted on 7/13/93, the registrant indicated that they are not seeking registration for aquatic uses for triclopyr BEE.

2. Havens, P. L. 1993. Request for Waiver of Additional Studies for Triclopyr Butoxyethyl Ester - Guidelines 161-3, 162-1, and 163-1. Submitted by DowElanco. (No MRID)

in less than one day in two sandy loam soils at pH's of 5.7 and 6.3.

- Terrestrial Field Dissipation study: According to the registrant, in a study in progress (location unidentified), the conversion of triclopyr BEE to the acid was followed. The results show a quantitative conversion, on a soil at pH of about 6, in seven days. No quantitative data was provided to support these results.
- Fontaine (1990; MRID# 41445001): In a forestry field dissipation study in Hearst, Ontario, triclopyr BEE was aerially applied to a forested site. Triclopyr BEE in stream water degraded to the acid in a matter of hours.
- The registrant cited additional studies that provide information about the stability of triclopyr BEE in various matrices. Studies included an acute aquatic toxicity and a column leaching study. The matrices include algal assay media, fish growth media, lake water, and an acidic forest soil column leaching system. In the studies conversion of triclopyr BEE to the acid was observed.
- In addition, the registrant cited existing reports that support conversion of other herbicide esters to acids. Among others, the following chemicals were mentioned:
  - haloxyfop-methyl
  - fluoazifop-butyl
  - fluroxypyr-MHE (methylheptyl ester)
  - 2,4-D-BEE

EFGWB believes that the registrant has provided sufficient information to justify bridging of triclopyr BEE to the acid in natural matrices. It appears that triclopyr acid would be the analyte of interest under natural conditions. The data for the acid would provide sufficient information about the fate of the ester. The branch concurs with a waiver for the following data requirements for triclopyr BEE. Data provided for triclopyr acid will be used as surrogate data for the following data requirements:

Photolysis on Soil (161-3)  
Aerobic Soil Metabolism (162-1)  
Mobility in Soil (163-1)

rev87  
jlm

**REQUEST FOR WAIVER OF ADDITIONAL STUDIES FOR TRICLOPYR  
BUTOXYETHYL ESTER—GUIDELINES 161-3, 162-1, 163-1**

**AUTHOR**

Patrick L. Havens, Ph.D.  
DowElanco  
Environmental Fate Laboratory  
(317) 337-3465

**COMPLETED ON**

August 24, 1993

In a July 13, 1993 meeting in Washington, DC with EPA EFGWB representatives, DowElanco presented information describing the scientific evidence to support a waiver of several triclopyr butoxyethyl ester (triclopyr BEE) environmental fate guideline studies (161-3, 162-1, and 163-1). A previous waiver request, which had been submitted without a comprehensive assessment of the data to justify the waiver, was rejected (EFGWB#92-1252). In light of the information presented at the meeting, however, the EPA scientists present requested a formal written submission of this supportive data. The sections below are in response to that request. The data cited here were obtained from both internal DowElanco reports and articles from peer-reviewed journals.

It was the conclusion of EFGWB#92-1252 that triclopyr could be "persistent under acidic hydrolytic conditions" including soil, sediment-water, and natural water systems. Thus, new studies were required for sections 161-3 (Soil Photolysis), 162-1 (Aerobic Soil Metabolism), and 163-1 (Mobility in Soil). It is DowElanco's scientific opinion that studies performed using the acid form of triclopyr will suffice to fulfill these data requirements, and execution of additional studies using triclopyr BEE as the test substance will yield no new information. The crux of DowElanco's argument is the observation that triclopyr, in its butoxyethyl ester form, converts rapidly to triclopyr acid in soil and natural waters. This was first reported by Bidlack (1978) who applied triclopyr BEE to sterile buffer water, natural water, and soil. In the acidic, sterile buffered system, triclopyr BEE was stable. However, in three soils of pH 5.4, 6.1 and 6.8, the half-life for conversion of triclopyr BEE to triclopyr acid was not pH dependent and averaged 3 hours with 90% hydrolysis occurring in 15 hours. In that same study, triclopyr BEE introduced into natural creek water of pH 6.7 hydrolyzed with a half-life of 12 hours.

Several additional studies support the conclusions of the Bidlack study; the first, submitted in 1981 (Swann & Unger), was a soil surface photolysis study. Although this study cannot fulfill the Section 161-3 data requirements for other reasons, the observations made by the authors are valid. They observed rapid conversion of triclopyr BEE to triclopyr acid in both light-exposed and dark-control samples. The soils employed in the study had a pH of 6.4.

In another study (Laskowski & Bidlack, 1984), triclopyr BEE applied to an anaerobic soil-water system (Guideline 162-3) converted to the triclopyr acid in less than one day. This study was accepted to fulfill Guideline 162-4 for both triclopyr acid and triclopyr BEE in a review of March 4, 1993. Again, rapid conversion of the ester to the acid was observed in sediment-water systems with pH's of 5.7 and 6.3.

The phenomenon of ester to acid conversion has been observed recently under field conditions. In a terrestrial field dissipation study now in progress to fulfill Guideline 164-1 data requirements, a concerted attempt was made to specifically follow the conversion of triclopyr BEE to triclopyr acid (R.C. Gardner, personal communication). A number of samples were taken from the field, frozen immediately, extracted and analyzed in-toto without any sample processing. The in-toto samples, as well as samples processed normally, showed rapid and identical conversion of triclopyr BEE to triclopyr acid, with nearly quantitative conversion in seven days. The soil on the site was acidic with a pH of about 6.

In another field study, triclopyr BEE was intentionally oversprayed onto a stream as part of a forestry dissipation study (Fontaine, 1990) carried out in Hearst, Ontario. After sampling, water samples were partitioned immediately by a validated solid-phase extraction technique into ester and acid portions. Analysis demonstrated the rapid hydrolysis of the ester to the acid within hours.

Further studies performed in The Dow Chemical Company toxicology laboratories have demonstrated the rapid conversion of triclopyr BEE to triclopyr acid. The results of an aquatic plant phytotoxicity study (Milazzo, *et al.*, 1993) show that triclopyr BEE was completely converted to triclopyr acid after seven days (the first sampling point) of incubation in standard Algal Assay Medium at pH 7.5. In addition, a stability study with standard fish growth media (Lehr & Piasecki, 1991) demonstrated half-lives of 7 to 29 hours.

Additional published studies have examined the stability of triclopyr BEE in environmental matrices. Two examples include an acute aquatic toxicity study (Servizi, *et al.*, 1987) and a laboratory column leaching study (Lee, *et al.*, 1986). Servi and his co-workers at the... Canadian Department of Fisheries observed a half-life for triclopyr BEE hydrolysis of about 3 to 4 days; lake water with a pH of 7.8 was employed. In a very acidic forest soil system (pH 3.4), Lee and his colleagues at Simon Fraser University (British Columbia, Canada) applied triclopyr BEE to the top of soil column and applied leaching water at a rate of 2.5 centimeters every other day. After 54 days, the columns were sectioned, extracted and analyzed. Even at these extremely acidic conditions, no residues of triclopyr BEE were detected; only triclopyr acid and its metabolites were present.

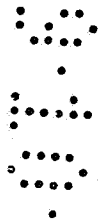
A significant body of additional evidence for the hydrolysis of other herbicide esters to acids exists, both as DowElanco reports and peer-reviewed journal articles. These include studies on haloxyfop methyl ester (Swann & Hertel, 1983; Smith, 1985; and Woodburn, *et al.*, 1987), fluazifop butyl ester (Negre, *et al.*, 1988), and fluroxypyr methylheptyl ester (Lehmann, *et al.*, 1993). In each of these studies the various esters were rapidly converted into their corresponding acids in a variety of environmental matrices. Various ester forms of 2,4-dichlorophenoxyacetic acid (2,4-D) have been studied extensively since the 1970's with similar results. Representative citations include Racke (1989), Smith (1972), Grover (1973), Smith (1976), Stewart & Gaul (1977), and Birmingham & Colman (1985).

The above descriptions demonstrate that there is a great weight of scientific evidence supporting DowElanco's waiver request. Herbicide esters in general appear to be hydrolytically unstable in environmental matrices. This is a result of surface and catalytic interactions with the humic substances that are ubiquitous in natural systems and, in the case of triclopyr BEE, occur whether the bulk pH is acid, neutral, or basic or if the system is biologically active or sterile. In EFGWB#92-1252 and subsequent reviews, only the results of the sterile, buffered system are cited although the information on naturally occurring (and acidic) environmental matrices was provided. A deeper examination of the data presented, combined with the information delineated above, should lead to the conclusion that triclopyr acid is the analyte of interest in these matrices.

In summary, data have been presented to support a waiver request for Guidelines 161-3, 162-1, 163-1 data requirements of triclopyr BEE. Introduction of triclopyr BEE into a soil or soil-water system would result in rapid conversion of triclopyr BEE to triclopyr acid. Thus, the studies submitted using triclopyr acid as the test substance should also fulfill the data requirements for triclopyr BEE.

All cited references are listed on the attachment. For previously submitted internal studies (with MRID numbers), abstracts are attached; for open literature studies, complete copies are attached for the reviewers' convenience.

Reference List  
Attachments



References Cited:

- Bidlack, H.D. (1978). *The Hydrolysis of Triclopyr EB Ester in Buffered Deionized Water, Natural Water, and Selected Soils*. Unpublished report of DowElanco; GH-C 1106; MRID 134174.
- Birmingham, B.C. & Colman, B. (1985). Persistence and Fate of 2,4-D Butoxyethanol Ester in Artificial Ponds; *J Environ Qual* 14, 100-104.
- Fontaine, D.D. (1990). *Dispersal and Degradation of Triclopyr Within a Canadian Boreal Forest Ecosystem Following an Aerial Application of Garlon\* 4*. Unpublished report of DowElanco; GH-C 2314; MRID 41445001.
- Grover, R. (1973). The Adsorptive Behaviour of Acid and Ester Forms of 2,4-D on Soils; *Weed Res* 13, 51-58.
- Laskowski, D.A. and Bidlack, H.D. (1984). *Anaerobic Degradation of Triclopyr Butoxyethyl Ester*; Unpublished report of DowElanco; GH-C 1697; MRID 151967.
- Lee, C.H.; Oloffs, P.C.; Szeto, S.Y. (1986). Persistence, Degradation, and Movement of Triclopyr and Its Ethylene Glycol Butyl Ether Ester in a Forest Soil; *J Agric Food Chem* 34, 1075-1079.
- Lehmann, R.G.; Miller, J.R.; Cleveland, C.B. (1993). Fate of Fluroxypyr in Water; *Weed Res* 33, 197-204.
- Lehr, K.M. & Piasecki, D.A. (1991). *Triclopyr Butoxyethyl Ester and GARLON 4 Herbicide: Determination in Dilution Waters Used in Static Acute Toxicology Studies with Bluegill and Rainbow Trout*; Unpublished report of the Dow Chemical Company; ES-2394.
- Milazzo, D.P.; Servinski, M.F.; Weinberg, J.T.; Rick, D.L.; Martin, M.D. (1993). *Triclopyr Butoxyethyl Ester: Toxicity to the Aquatic Plant Duckweed, Lemna gibba L. G-3*; Unpublished report of the Dow Chemical Company; DECO-ES-2592; MRID 416337-09.
- Negre, M.; Gennari, M.; Cignetti, A.; Zanini, E. (1988). Degradation of Fluazifop-butyl in Soil and Aqueous Systems; *J Agric Food Chem* 36, 1319-1322.
- Racke, K.D. (1989). *Hydrolysis of 2,4-dichlorophenoxyacetic acid-2-butoxyethyl ester to 2,4-dichlorophenoxyacetic acid in a Soil/Water System*. Unpublished report of DowElanco; GH-C 2198; MRID 41353701.

---

\* Trademark of DowElanco

- Servizi, J.A.; Gordon, R.W.; Martens, D.W. (1987). Acute Toxicity of Garlon 4 and Roundup Herbicides to Salmon, Daphnia, and Trout; *Bull Environ Contam Toxicol* **39**, 15-22.
- Smith, A.E. (1972). The Hydrolysis of 2,4-Dichlorophenoxyacetate Ester to 2,4-Dichlorophenoxy Acid in Saskatchewan Soils; *Weed Res* **12**, 364-372.
- Smith, A.E. (1976). The Hydrolysis of Herbicidal Phenoxyalkanoic Esters of Phenoxyalkanoic Acids in Saskatchewan Soils; *Weed Res* **16**, 19-22.
- Smith, A.E. (1985). Transformation and Persistence of the Herbicide [14-C]Haloxypop-Methyl in Soil Under Laboratory Conditions; *J Agric Food Chem* **33**, 972-976.
- Stewart, D.K.R. & Gaul, S.O. (1977). Persistence of 2,4-D, 2,4,5-T and Dicamba in a Dykeland Soil; *Bull Environ Contam Toxicol* **18**, 210-218.
- Swann, R.L. & Hertel, J.A. (1983). Anaerobic Soil Degradation of Carbon-14 Labeled Dowco 453 (Methyl Ester); Unpublished report of DowElanco; GH-C 1621; MRID 00128680.
- Swann, R.L. & Unger, S.M. (1981). Photodecomposition of Triclopyr Butoxy Ethyl Ester on Soil Surfaces. Unpublished report of DowElanco; GH-C 1399R2; MRID 151966.
- Woodburn, K.B.; Laskowski, D.A.; Richards, J.F.; Schultz, M.R. (1987). Aerobic Soil Degradation of 14-C Phenyl-Labeled Haloxypop Methyl Ester; Unpublished report of DowElanco; GH-C 1965; MRID 40560403.

