Shaughnessy No.: 030001, 030053, 030016, 030801, 030819

Date Out of EFGWB: MAY 24 May 24, 1991

To: Ms. Judith Coombs
Product Manager # 74
Special Review and Reregistration Division

From: Paul Mastradone, Ph.D., Chief
Environmental Chemistry Review Section #1
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File #: 030801-5/030053-3

Chemical Name: 2,4-D

Type Product: Herbicide

Product Name:

Company Name: DowElanco over 20 study summaries

Purpose: Review of photodegradation in water and soil studies, and a laboratory volatility study for 2,4-D BEE, dissociation study for 2,4-D salts, and an anaerobic aquatic metabolism study for 2,4-D.

Action Code: 660

EFGWB #(s): 90-0668, 91-0237
90-0664, 90-0624
90-0686, 90-0783

Date Received: 5/90

Total Reviewing Time: 12 days

Deferrals to:
___ Ecological Effects Branch
___ Dietary Exposure Branch
___ Non-Dietary Exposure Branch
___ Toxicology Branch I
___ Toxicology Branch II

MRIDs too many to name

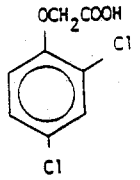
41483103
41557901
41718001
41890601
~~413~~ 41353702
41308901
41353701
41483101
41483102

2011877

1.0 CHEMICAL:

chemical name: diethanolamine salt (DEA) of (2-(2,4-dichlorophenoxy) acetic acid

trade name: N/A
structure:
CAS #:N/A
Shaughnessy #: 030016



2.0 TEST MATERIAL: N/A

3.0 STUDY/ACTION TYPE: Review of proposed environmental fate strategy for the diethanolamine salt (DEA) of 2-(2,4-dichlorophenoxy) acetic acid (2,4-D).

4.0 STUDY IDENTIFICATION:N/A

5.0 REVIEWED BY:

James A. Hetrick, Ph.D. Signature:
Chemist, ECRS # 1 Date:
EFGWB/EFED/OPP

6.0 APPROVED BY:

Name: Paul Mastradone, Ph.D. Signature:
Section Chief, ECRS # 1 Date:
EFGWB/EFED/OPP

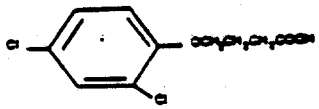
7.0 CONCLUSIONS:

General: The proposed fate strategy for 2,4-D DEA is modeled after the 2,4-D environmental fate strategy. This strategy assumes the 2,4-D DEA salt rapidly dissociates to the free acid. Therefore, the salts of 2,4-D should not persist under normal environmental conditions.

EFGWB concludes the proposed fate strategy should provide the necessary fate data for 2,4-D DEA. EFGWB believes, however, the environmental fate strategy should be conducted in a tiered approach; where the environmental bridging datum-dissociation rate of the 2,4-D DEA -is submitted and reviewed before conducting the environmental fate studies. Therefore, the data requirements for 2,4-D DEA should be reserved pending the results of an acceptable salt dissociation study. (*Note*: At this time, the dissociation rate study for 2,4-D DEA has not been reviewed by EFGWB. It is imperative the 2,4-D DEA dissociation rate study is submitted and reviewed prior to acceptance of the proposed environmental fate strategy.)

1.0 CHEMICAL:

chemical name: (4-(2,4-dichlorophenoxy) butyric acid and its dimethylamine salt (DMA)
trade name: N/A
structure:
CAS #:N/A
Shaughnessy #: 030801



2.0 TEST MATERIAL: N/A

3.0 STUDY/ACTION TYPE: Review of proposed environmental fate strategy for 4-(2,4-dichlorophenoxy) butyric acid (2,4-DB) and its dimethylamine salt (DMA). Additionally, a 2,4-DB acid dissociation study was reviewed.

4.0 STUDY IDENTIFICATION:N/A

Ruzo, Luis O. and Alan D. Ewing. 1989. Determination of pKA Value for 2,4-DB. Performed by Pharmacology and Toxicology Research Laboratory (PTRL), Richmond, CA. Submitted by Chemical Consultants Intl., Inc. Overland Park, KS for the 2,4-DB Task Force. MRID 41890601.

5.0 REVIEWED BY:

James A. Hetrick, Ph.D. Signature:
Chemist, ECRS # 1 Date:
EFGWB/EFED/OPP

6.0 APPROVED BY:

Name: Paul Mastradone, Ph.D. Signature:
Section Chief, ECRS # 1 Date:
EFGWB/EFED/OPP

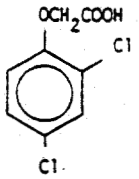
7.0 CONCLUSIONS:

General: The proposed fate strategy for 2,4-DB acid and 2,4-DB DMA salt is modeled after the 2,4-D environmental fate strategy. This strategy assumes the salt rapidly dissociates to the free acid. Therefore, 2,4-DB DMA should not persist under normal environmental conditions.

EFGWB concludes the proposed fate strategy should provide the necessary fate data for 2,4-DB acid and 2,4-DB DMA. EFGWB believes, however, the environmental fate strategy should be conducted in a tiered approach; where the environmental bridging datum-dissociation rate of the 2,4-DB DMA salt-is submitted and reviewed before conducting the environmental fate studies. Therefore, the data requirements for 2,4-DB DMA should be reserved pending the results of an acceptable salt dissociation rate study.

1.0 CHEMICAL:

chemical: 2,4-dichlorophenoxyacetic acid (2,4-D)
2,4-D-2-butoxyethyl ester (2,4-D BEE)
2,4-D-isopropylamine salt (2,4-D IPA)
2,4-D-triisopropanolamine salt (2,4-D TIPA)
2,4-D-dimethylamine (2,4-D DMA)
structure:
CAS #:
Shaughnessy #: 30001



2.0 TEST MATERIAL: discussed in DER

3.0 STUDY/ACTION TYPE:

3.1 Review of dissociation studies for 2,4-D salts.

3.2 Review of hydrolysis studies, photodegradation studies in air and water, and a laboratory volatility study for 2,4-D BEE.

3.3 Review of an anaerobic soil metabolism study for 2,4-D.

4.0 STUDY IDENTIFICATION:

Reim, R. E. 1989. Dissociation of 2,4- Dichlorophenoxyacetic acid (2,4-D), 2,4-D Isopropylamine Salt (IPA), and 2,4-D Triiso-propanolamine Salt (TIPA) in Water. performed and submitted by Analytical Science Department, Dow Chemical U.S.A., Midland Michigan. MRID# 413537-02.

Reim, R. E. 1989. Dissociation of 2,4-Dchlorophenoxyacetic acid (2,4-D) and 2,4-D Dimethylamine Salt (DMA) in Water. performed and submitted by Analytical Science Department, Dow Chemical U.S.A., Midland, Michigan. MRID# 413089-01.

Racke, K.D. 1989. Hydrolysis of 2,4-Dichlorophenoxyacetic Acid-2-Butoxyethyl Ester to 2,4-Dichlorophenoxyacetic Acid in a Soil/Water System. performed by Pharmacology and Toxicity Research West (PTRL), Richmond, CA and submitted by DowElanco, Midland, Michigan. MRID# 413537-01.

Shepler, K., B.S. Estigoy, and L. Ruzo. 1990. Hydrolysis of 2,4-Dichloro-phenoxyacetic Acid-2-Butoxyethyl Ester (2,4-D BEE) at pH 5,7 and 9. performed by Pharmacology and Toxicity Research West (PTRL), Richmond, CA and submitted by DowElanco, Midland, Michigan. MRID# 414831-01.

Marx, M. and K. Shapler. 1990. Sunlight Photodegradation of [^{14}C]-2,4-Dichlorophenoxyacetic, Butoxyethyl Ester [2,4-D BEE] in Buffered Aqueous Solution at pH 5. performed by Pharmacology and Toxicity Research East (PTRL), Richmond, Kentucky and submitted by DowElanco, Midland, Michigan. MRID# 414831-02.

Marx, M. and K. Shapler. 1990. Vapor Phase Photolysis of [^{14}C]-2,4-Dichlorophenoxyacetic, Butoxyethyl Ester [2,4-D BEE]. performed by Pharmacology and Toxicity Research West (PTRL), Richmond, California and submitted by DowElanco, Midland, Michigan. MRID# 414831-03.

Cohen, S.P. and V. V. Rama. 1990. Anaerobic Aquatic Metabolism of 2,4-Dichlorophenoxyacetic Acid. performed by Center of Hazardous Materials Research, Pgh., PA and submitted by 2,4-D Industry Task. MRID 415579-01.

Kesterson, B.A., Steve Johnson, and Lowell J. Lawrence. 1990. Laboratory Volatility of [^{14}C] 2,4-D 2 Butoxyethyl Ester. performed by Pharmacology and Toxicity Research East (PTRL), Richmond, Kentucky and submitted by DowElanco, Midland, Michigan. MRID# 417180-01.

5.0 REVIEWED BY:

James A. Hetrick, Ph.D. Signature: James A. Hetrick
Chemist, ECRS # 1 Date: MAY 24
EFGWB/EFED/OPP

6.0 APPROVED BY:

Name: Paul Mastradone, Ph.D. Signature: Paul J Mastradone
Section Chief, ECRS # 1 Date:
EFGWB/EFED/OPP

7.0 CONCLUSIONS:

■ The 2,4-D salt dissociation studies are acceptable and fulfill the environmental fate bridging data for 2,4-D IPA, 2,4-D TIPA, and 2,4-D DMA. At this time, the requested waiver for environmental fate testing on 2,4-D DMA cannot be granted without environmental fate data on the dimethylamine moiety.

■ The hydrolysis study (MRID# 41357-01) is actually an aborted desorption/adsorption study. This study provides supplemental data on 2,4-D BEE degradation, but it cannot be used to fulfill the 161-1 data requirement.

■ The hydrolysis study (MRID# 414831-02) provides supplemental data for 2,4-D BEE. At this time, the study cannot be fully evaluated without a complete explanation on the methods used to correct for microbially contaminated samples. (Please refer to DER for complete details.)

■ The photodegradation in water study (MRID# 414831-02) provides acceptable data and fulfills the photodegradation in water (161-2) data requirement.

■ This photodegradation in air study (MRID# 414831-03) provides supplemental data for 2,4-D BEE. At this time, the study cannot be

fully evaluated without a detailed explanation on air sampling methods. (Please refer to DER for more details.)

■ This soil laboratory study (MRID# 417180-01) is unacceptable because volatile 2,4-D BEE residues were not identified by a confirmatory methods.

■ The anaerobic aquatic study (MRID# 415579-01) provides supplemental data for 2,4-D. The study cannot fulfill the anaerobic aquatic metabolism (162-3) data requirement because the material balance was incomplete.

■ The waiver request of the adsorption/desorption-leaching (163-1) data requirement for 2,4-D EH cannot be granted without a full review of 2,4-D EH environmental fate data. Additionally, EFGWB notes the 2,4-D 2-EH will have forestry use patterns. As per Subdivision N guidelines, two forest dissipation studies are required for 2,4-D-2-EH in typical use areas.

7.1 2,4-D Salts

■ The salt dissociation study (MRID# 413537-0) provides acceptable data. The data can be used to bridge the dissociation of 2,4-D IPA and 2,4-D TIPA to 2,4-D.

Based on acceptable data, 2,4-D IPA and 2,4-D TIPA rapidly dissociated in distilled water. Therefore, 2,4-D IPA and 2,4-D TIPA should not persist under normal environmental conditions.

■ The salt dissociation study (MRID# 413537-0) provides acceptable data. The data can be used to bridge the dissociation of 2,4-D DMA to 2,4-D.

Based on acceptable data, 2,4-D DMA rapidly dissociated in distilled and deionized water. Therefore, 2,4-D DMA should not persist under normal environmental conditions.

7.2 2,4-D BEE

■ The hydrolysis study (MRID# 41357-01) is actually an aborted desorption/adsorption study. This study provides supplemental data on 2,4-D BEE degradation, but it cannot be used to fulfill the 161-1 data requirement.

Based on supplemental data, 2,4-D BEE rapidly degrades in nonsterile, soil slurries. The actual route of 2,4-D BEE degradation is unknown because the experiment was conducted under non-sterile conditions. Therefore, the degradation of 2,4-D BEE may be a combination of hydrolysis and microbial metabolism.

■ The hydrolysis study (MRID# 414831-02) provides supplemental data. At this time, the study cannot be fully evaluated without a complete explanation on the methods used to correct for microbially contaminated samples. (Please refer to DER for complete details.)

Based on supplemental data, the hydrolysis rate of 2,4-D BEE is dependent on solution pH; where the hydrolysis rate was 196 days (R^2=0.30) at pH 5, 47.5 hours (R^2=0.88) at pH 7, and 55 minutes (R^2=0.99) at pH 9. The major hydrolytic degradate was 2,4-D.

■ The photodegradation in water study (MRID# 414831-02) provides acceptable data and fulfills the photodegradation in water (161-2) data requirement.

Based on acceptable data, the half-life for 2,4-D BEE was estimated at 74 days in both irradiated and dark control samples (R^2=0.76 and 0.67 respectively). The major degradate was identified as 2,4-D (≤ 17% of applied 2,4-D BEE). The reported data indicate 2,4-D BEE does not photodegrade in slightly-acidic, aqueous environments.

■ The photodegradation in air study (MRID# 414831-03) provides supplemental data. At this time, the study cannot be fully evaluated without a detailed explanation on the air sampling methods. (Please refer to DER for more details.)

Based on supplemental data, the nonvolatile nature of 2,4-D BEE prevented an estimation of the photodegradation rate in air; where < 1.4% of the applied 2,4-D BEE volatilized. No photodegradates were identified.

The reported data suggest 2,4-D BEE photodegrades in air.

■ The soil laboratory study (MRID# 417180-01) is unacceptable because volatile 2,4-D BEE residues were not identified by a confirmatory methods.

Based on unacceptable data, the rate of 2,4-BEE volatilization was 2.4 to 1.3 X 10^{-4} $\mu g\ cm^{-2}\ hr^{-1}$. (Please note the volatilization rates are expressed as 2,4-D equivalents.) The major soil extractable degradate was 2,4-D; however, volatile residues were not identified.

7.3 2,4-D Acid

■ The anaerobic aquatic study (MRID# 415579-01) provides supplemental data. The study cannot fulfill the anaerobic aquatic metabolism (162-3) data requirement because the material balance was incomplete.

Based on supplemental data, the half-life for 2,4-D in anaerobic (Eh=-220 mv) aquatic environments was 41 days (R^2=0.91). The extractable soil/water residues were identified as 2,4-D,chlorophenol and 2-chlorophenol; and the volatile residue was tentatively identified as CO_2.

The reported data indicate 2,4-D appears to be moderately stable in anaerobic aquatic environments.

7.4 Environmental Fate Assessment

2,4-D Salts

Based on acceptable data, 2,4-D TIPA, 2,4-D IPA, and 2,4-D DMA rapidly dissociate in water. Therefore, these 2,4-D salts should not persist under normal environmental conditions. There are insufficient data to address the fate of the 2,4-D moieties including TIPA, IPA, and DMA.

2,4-D BEE

At this time, there are insufficient data to assess the fate of 2,4-D BEE in soil and water. Based on supplemental and acceptable environmental fate data (Section 9), 2,4-D BEE appears to degrade by microbial and hydrolytic processes. The hydrolysis half-life for 2,4-D BEE ranged from 196 days at pH 5 to 55 minutes at pH 9. In aquatic field studies, parent 2,4-D BEE had a dissipation half-life of < 3 days. The dissipation of 2,4-D BEE does not appear to be dependent on volilization.

2,4-D

At this time, a complete environmental assessment cannot be made because of insufficient environmental fate data. Based on acceptable and supplemental data (Section 9), 2,4-D had an average soil metabolism half-life of < 8 days in six aerobic, mineral soils. Additionally, 2,4-D had a dissipation half-life of < 3 days in aquatic field studies. The major route of degradation in aerobic soils appears to be controlled by microbial mineralization to CO_2 with subsequent residue incorporation in nonlabile soil organic matter.

Batch equilibrium and soil TLC studies indicate 2,4-D has a low binding affinity in soil and, therefore, appears to be mobile in terrestrial environments. The adsorption coefficient (K_{ad}) for 2,4-D was < 3 in four soils. The desorption coefficient (K_{de}) for parent 2,4-D was < 1 in four soils. .

The reported data indicate that 2,4-D appears to be mobile in soil, but it appears to rapidly degrade by microbially mediated processes.

8.0 <u>RECOMMENDATIONS:</u>

8.1 Inform the registrant the hydrolysis study (MRID# 414831-01) provides supplemental data on 2,4-D BEE hydrolysis in water. This study may fulfill the 161-1 data requirement by explaining the procedures used to repeat contaminated samples.

8.2 Inform the registrant the photdegradation in air (MRID# 414831-03) provides supplemental data on 2,4-D BEE photolysis in air. This study may fulfill the 161-4 data requirement by giving a detailed explanation on the sampling procedures.

8.3 Please refer to Section 7 for recommendation of other studies.

9.0 BACKGROUND:

Data Requirements[1]	Status
161-1 Hydrolysis	Not Satisfied
161-2 Photodegradation in Water	Satisfied[2]
161-3 Photodegradation in Soil	Not Satisfied
161-4 Photodegradation in Air	Not Satisfied
162-1 Aerobic Soil Metabolism	Partially Satisfied
162-2 Anaerobic Soil Metabolism	Not Satisfied
162-3 Anaerobic Aquatic Metabolism	Not Satisfied
162-4 Aerobic Aquatic Metabolism	Not Satisfied
163-1 Leaching/Adsorption-Desorption	Partially Satisfied
163-2 Lab Volatility	Not Satisfied
163-3 Field Volatility	Not Satisfied
164-1 Soil Dissipation	Not Satisfied
164-2 Aquatic Dissipation	Not Satisfied
164-3 Forest Dissipation	Not Satisfied
165-5 Long-term, Soil Dissipation	Reserved
165-1 Rotational Crop Accumulation	Not Satisfied
165-2 Field Rotational Crop Accumulation	Reserved
165-3 Irrigated Crops	Not Satisfied
165-4 Fish Accumulation	Partially Satisfied
165-5 Aquatic Non-Target	Partially Satisfied
201-1 Spray Drift-Droplet Size	Not Satisfied
201-2 Spray Drift-Drift Field	Not Satisfied

1-Generic Data Requirements for 2,4-D Acid and its [X]-2,4-D [X = salts, amines, and esters] compounds

2-The data requirement satisfies the data requirement for 2,4-D BEE.

10.0 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: Please refer to attached DER's

11.0 COMPLETION OF ONE-LINER:

12.0 CBI APPENDIX: There is no CBI used in this review.