Shaughnessy Number: 129001

Date out of EFGWB: APR 15 1991

To: M. Erumsale-Matzer
Product Manager 23
Registration Division (H7505C)

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

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

Hank Jacoby

Attached, please find the EFGWB review of...

Reg./File #: 59639-G

Chemical Name: Clethodim

Type Product: herbicide

Product Name: Select 2-EC

Company Name: Valent U.S.A. Corporation

Purpose: submission of additional discussion on aquatic metabolism study

Date Received: 03/05/91

Action Code: n.a.

EFGWB#(s): 91-0501

Total Reviewing Time (decimal days): 0.5

Deferrals to: ___Ecological Effects Branch, EFED

___Science Integration and Policy Staff, EFED

___Non-Dietary Exposure Branch, HED

___Dietary Exposure Branch, HED

___Toxicology Branch

1

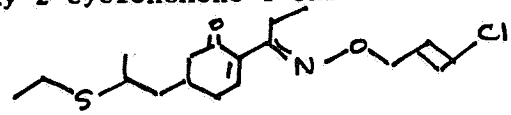
1. CHEMICAL:

chemical name: 2-[1-[[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexene-1-one

common name: Clethodim

trade name: Select

structure:



CAS #: not known

Shaughnessy #: 129001

2. TEST MATERIAL: see DER

3. STUDY/ACTION TYPE:

submission of additional information on a previously submitted anaerobic aquatic metabolism study (offered *in lieu of* the anaerobic soil study)

4. STUDY IDENTIFICATION:

additional information in support of:

Tucker, B.V., The Anaerobic Aquatic Metabolism of [Ring-4,6-^{14}C] Clethodim. dated August 29, 1990. performed and submitted by Chevron Chemical Company Agricultural Chemicals Division, Richmond CA. received EPA 10/19/90, under MRID# 416523-01. previously submitted and reviewed

5. REVIEWED BY:

Typed Name: E. Brinson Conerly

Title: Chemist, Review Section 3

Organization: EFGWB/EFED/OPP

E.B. Conerly 4/10/91

6. APPROVED BY:

Typed Name: Akiva Abramovitch

Title: Section Head, Review Section 3

Organization: EFGWB/EFED/OPP

Akiva Abramovitch

APR 11 1991

7. CONCLUSIONS:

1) The anaerobic aquatic metabolism study is acceptable to fulfill the requirement for anaerobic aquatic metabolism with the additional information supplied. The applicant has supplied soil comparisons [attached] and an acceptable explanation for the choice of Canadian test matrixes -- they were chosen to represent both U.S. and Canadian oil crop soils. The study can serve to fulfill the requirement for anaerobic soil metabolism as well. It provides the following information:

   Clethodim has a half-life of ca. 150 days (per the applicant) under these conditions. [This reviewer calculates 128 days in the aqueous phase and 214 days in the sediment].

   The degradates formed are metabolized approximately as rapidly as they are formed, and do not appear to accumulate.

8. RECOMMENDATIONS:

The applicant should be informed that the new information taken together with the original study is now acceptable. No further data are required on anaerobic metabolism at this time. Spray drift data should be submitted as soon as possible.

9. BACKGROUND:

Clethodim is a post-emergent herbicide with a proposed label use rate of 0.125/0.25 lb ai/A (max. appl. 0.5 lb/season) to control weeds in cotton and soybeans. Known available environmental data for Clethodim depict a compound which is stable to hydrolysis, except in acid conditions, but susceptible to photolysis and aerobic metabolism. Parent and degradates are mobile. At exaggerated treatment rates, some uptake of radiocarbon into confined rotational crops occurred. About 1/3 of the residues were closely related degradates and 2/3 were from the "carbon pool". Clethodim and degradates do not show persistence in field dissipation studies. No significant bioaccumulation occurs in fish. Since it is easily degraded both by photolysis and aerobic microbial action, Clethodim does not seem likely to threaten surface water. Under present use patterns and in most circumstances, it does not appear likely to threaten ground water. However, if Clethodim should reach an anaerobic region in the soil, e.g., if a heavy rainfall occurred immediately after application, it could persist and contaminate ground water. Data requirements are summarized below.

NOT FULFILLED

Accumulation -- Rotational Crop, Field -- no data submitted -- EFGWB reserves imposition of this data requirement at this time

Spray Drift Field Evaluation -- no data submitted

Droplet Size Spectrum -- no data submitted

FULFILLED -- no further information required

Degradation - Hydrolysis -- **MRID # 409745-20** -- **Propyl-labeled [14C]-clethodim** degraded with half-lives of 26 days (pH 5) and approximately 300 days (pHs 7 and 9). **Allyl-labeled clethodim** degraded with half-lives of 42 days (pH 5) and 360 days (pH 7). The major degradates were **clethodim oxazole** and **1-chloropropen-3-ol**.

Degradation - Aqueous Photolysis -- **MRID # 410301-34**, done with **Ring - labelled compound** and **MRID # 410301-33**, with **Allyl-labelled compound:**

Ring labelled -- First-order half-lives were 1.5, 6.4, and 9.3 days at pH 5, 7, and 9 respectively for irradiated samples. Corresponding dark controls were 12.5, 99.4, and 330.2 days. Major photoproducts were clethodim sulfoxide, imine, imine sulfoxide, and DME sulfoxide. Minor photoproducts were trione sulfoxide, oxazole, oxazole sulfoxide, and imine ketone. After 30 days the major products remaining are imine sulfoxide and DME sulfoxide. Most photoproducts are rapidly formed and then degraded, except DME sulfoxide. Material balance ranged from 88.2% to 108.1%. Very little volatile material was produced.

Allyl labelled -- First-order half-lives were 1.39, 4.05, and 5.43 days at pH 5, 7, and 9 respectively for the irradiated samples. Dark controls were 20.06, 5042.8, and 60.85 days. The major initial photoproducts were clethodim sulfoxide, chloroallyl alcohol, and 3-chloropropenal, with lesser amounts of oxazole, oxazole sulfoxide, imine, imine sulfoxide, and DME sulfoxide. After 30 days the major products remaining are chloroallyl alcohol and 3-chloropropenal. Most of the photoproducts are rapidly formed and then degraded. Total material balance ranged from 86.8% to 103.5%. Very little volatile material was produced.

Degradation - Soil Photolysis -- **MRID # 410301- 35** -- Photolysis of clethodim on soil will not be a major pathway of degradation, since metabolism is so rapid. Less than 6.8% of parent remained after 7 days. Little or no volatile material, organic or CO_2, was produced. The single major product was clethodim sulfoxide. Minor products ranged from 0.2 to 2.6%. Half-lives of 1.87 and 1.96 days for the dark samples (agreeing with the independent soil metabolism study), and 1.53 and 1.82 days for light samples in two runs were statistically identical. Therefore, the degradates detected were probably metabolites, not photoproducts.

Metabolism - Aerobic Soil -- **MRID # 413768-01** (ring and allyl labelled) and **MRID # 409745-22** (propyl labelled)

Ring and allyl[^{14}C]-labeled incubated at 25°C at initial concentrations of 10 ppm in sandy loam soil degraded with half-lives of ca. 1 day. Degradates at the end of 4 months were: CO_2 -- 57% of ring labeled and 45% of allyl labeled applied radioactivity; **Clethodim sulfoxide** Peaked at 62-72% of applied radioactivity at 3-7 days post-treatment and then declined (half-life approximately 30 days) to 0.2-0.5% of applied at 121 days post-treatment; **Clethodim sulfone**, formed by oxidation of sulfoxide, peaked at 15% of applied at 30 days post-treatment and then declined to 5-7% of applied at 121 days post-treatment.

Propyl-labeled [^{14}C]-clethodim incubated at 25°C at an initial concentration of 10.3-10.7 ppm in sandy loam soil degraded with half-life of approximately 2.6 days. Degradates were: CO_2 -- 54.4% of the applied radioactivity at the end of 380 days; **Clethodim sulfoxide** peaked at 60.7-64.6% of the applied at 7 days posttreatment, decreased to 12.8-16.5% at 62 days, and was ≤0.3% at 120-380 days; **Clethodim sulfone**, formed from the oxidation of the sulfoxide peaked at 10.1-11.7% of the applied at 62 days post-treatment, declined to 3.7-5.0% at 90 days post-treatment, and was ≤ 0.6% at 180-380 days post-treatment.

Metabolism - Anaerobic Soil -- fulfilled by the anaerobic aquatic study, MRID # 416523-01. Satisfactory additional information has been received. Anaerobic metabolism takes a distinctly different pathway from that under aerobic conditions. Principal degradates were **clethodim imine** and **clethodim imine sulfate**, and do not include CO_2. Degradates formed by anaerobic means do not appear to persist.

Mobility - Leaching and Adsorption/Desorption -- **MRID # 409745-23** -- Clethodim and its sulfoxide, sulfone, and oxazole sulfone degradates were weakly adsorbed onto 2 sandy loam soils, a clay loam, a sandy clay loam, and a sandy soil. The following ranges of Freundlich K_{ads} values were reported for the 5 test soils at 25°C: clethodim (0.08-1.6), clethodim sulfoxide (≤ 0.2), clethodim sulfone (≤ 0.1), and clethodim oxazole sulfone (0.3-7.0).

Field Dissipation -- fulfilled -- **MRID # 410302-08** (cotton in California) and **MRID # 410302-07** (cotton in Mississippi) -- Clethodim and its degradates do not persist in California. The parent clethodim was only found at or near the 0.02 ppm limit of quantitation (loq). Both parent and metabolites disappeared rapidly. 21 day samples showed no residues of any kind. No vertical movement of the residues was observed as all measurable residues were confined to the top 20 cm of the soil. Results in Mississippi were similar to those in California. In all cases, the 28 day samples showed no residues of any kind. All measurable residues were confined to the top 20 cm of the soil.

Accumulation -- Confined Rotational Crop -- **MRID # 410302-11** -- lettuce, carrots, and wheat grown as confined rotational crops. Some uptake and concentration were detected at an exaggerated rate of application (4 x the maximum single application). Closely related metabolites accounted for around 1/3 of the total radioactivity observed in the plants. The remaining labelled material may derive from the soil "carbon pool". EGWB understands at this time that the residues which could be expected from use at legal label rates would not be of concern to TOX or Dietary Exposure Branches.

Laboratory Accumulation - Fish -- **MRID #s 409745-31 and 409745-24** taken together -- Maximum bioconcentration factors reported for total[^{14}C]-in bluegill sunfish exposed to 0.06 ppm [^{14}C]clethodim for 28 days at 21^{0}C were 0.7-2.1X for edible tissues, 3.0-4.0X for non-edible tissues, and 2.3-3.6X for whole fish.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: See individual DERs.

11. COMPLETION OF ONE-LINER: new information added

112. CBI APPENDIX: attached

Con ob
9/3

DP Barcode :D 162019

PC Code No. : ____________

Date Out : ____________

TO: ______________________________
Product Manager ______
Registration Division (H7505C)

FROM: Akiva Abramovitch, Head
Chemistry Review Section #3
Environmental Fate and Groundwater Branch

THRU: Hank Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Attached, please find the EFGWB review of...

Reg./File # : ______________________________

Chemical Name : Clethodim

Type Product : ______________________________

Product Name : ______________________________

Company Name : ______________________________

Purpose : ______________________________

: ______________________________

: ______________________________

Date Received: ___/___/___ EFGWB#: 91-0501 Time (days): ____.___

Deferrals to:

____ EEB/EFED ____ DEB/HED ____ TB1/HED

____ SIPS/EFED ____ OREB/HED ____ TB2/HED

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(202) 872-4688
FAX (202) 872-4689

VALENT

March 4, 1991

SELECT 2EC 59639-G
Clethodim Tech 59639-E
Anaerobic Soil & Aquatic
Metabolism Studies
EFGWB Review Dated
Feb. 24, 1991, Soil Types

Ms. Joanne I. Miller, Product Manager
Registration Division (H7505C)
U.S. EPA
Crystal Mall 2
1921 Jefferson Davis Highway
Arlington, VA 22202

Dear Joanne:

Thank you for the subject review, we appreciate the timely response. In the discussion the reviewer asked for additional information on the choice of a Canadian pond sediment for the Anaerobic Aquatic Metabolism study. In this context we would like to provide the following information:

1) The soil used in this study was chosen to represent as closely as possible both U.S. soybean and Canadian oil crop soils, as these are target crops. A comparison of the Saskatchewan soil type used in the Anaerobic Aquatic study with U.S. soils indicates that the soil characteristics match several U.S. cotton and soybean soils. Soils are compared in Table 1 and in more detail in Appendix A.

Table 1 Comparison of Saskatchewan Pond Sediment with U.S. Agricultural Soils

	Subject Soil (Pond Sediment)	Acuff[1]	Cuero[2]	Wadena[3]
Classification	Sandy Clay Loam	Sandy Clay Loam	Sandy Clay Loam	Loam
% Sand	56	53	55	35-51
% Silt	23	24	19	19-47
%Clay	21	23	26	18-30
% Org. Matter	3.8	2.1	1-3	2.9-5.9
pH	7.8	7.6	6.1-7.8	6.6-7.3
Bulk Density	0.72	1.42	1.4-1.65	1.3-1.4

Valent U.S.A. Corporation

[1]Data obtained from Neitsch, 1991; USDA, 1976. (Texas Cotton Soil).

[2]Data obtained from Neitsch, 1991. (Texas Cotton & Soybean Soil).

[3]Data obtained from USDA, 1975a; and data adapted from the SCS/Iowa State University SOILs5 database by Arnold et al, 1990. (Iowa/Minnesota Soybean Soil).

As can be seen the pond sediment used in this study is very similar to several U.S. agricultural soils. Further detail is provided in Appendix A. It should be noted that this Anaerobic Aquatic Metabolism study was conducted with a pond sediment as required in the EPA guidelines. Pond sediments can be expected to differ slightly from soils with respect to bulk density. This is due to the different structure of organic matter seen in many aquatic sediments (peat).

2) The Anaerobic Aquatic Metabolism study which was run on Canadian soil confirms results of the earlier Anaerobic Soil Metabolism study, which was run on typical U.S. soils. EPA questioned whether the earlier anaerobic study (MRID 410301-36), conducted according to Guideline 162-2 with a U.S. soil, was truly conducted under anaerobic conditions. Consequently, the new aquatic anaerobic study was submitted to satisfy EPA's anaerobic requirement. This new aquatic study confirms that the previous study conducted with a U.S. soil was anaerobic. Both anaerobic studies had the same metabolites, which differed from those found under aerobic conditions, in addition $^{14}CO_2$ was not released from either anaerobic study, but was released under aerobic conditions.

Thus, clethodim's anaerobic metabolic pathway has been confirmed in two different soil systems, including a U.S. soil.

We trust that this additional information should allow you to consider the Anaerobic Soil and Aquatic Metabolism data requirements to be fulfilled. Please contact Rick Stanton or John Finegan at (202) 872-4688 if you have any additional questions.

Sincerely,

Richard H. Stanton
Federal Registration and
Regulatory Affairs Mgr.

RHS:ap/M29

APPENDIX A

Comparison of Saskatchewan Pond Sediment with U.S. Agricultural Soils

Comparison of American Cotton/Soybean Soils to the Saskatchewan Soil Sample

There are numerous soil series which possess characteristics similar to the subject soil, based on literature review and contact with various SCS soil scientists. These soils support significant cotton and/or soybean production in different parts of the country. The majority of these soils are from the Glaciated Central region and the High Plains region. Many soils throughout Georgia and Mississippi in the Atlantic Gulf Coastal Plain are also similar in many respects to the subject soil except that the pH values are generally in the range of 4.5 to 5.5. Listed below are 11 example soil series that have characteristics (including pH) similar to the Saskatchewan soil sample and support significant production of cotton and/or soybean crops.

Soil Series	Geographic Location
Acuff sandy clay loam	Texas - High Plains
Amarillo sandy clay loam	Texas - High Plains
Ankeny fine sandy loam	Iowa - Glaciated Central
Clarion loam	Minnesota - Glaciated Central
Crosier loam	Indiana - Glaciated Central
Cuero sandy clay loam	Texas - Gulf Coastal Plain
Cylinder loam (over s.c.l.)	Iowa - Glaciated Central
Dickenson fine sandy loam	Iowa - Glaciated Central
Fox sandy loam, loam	Wisconsin - Glaciated Central
Miami loam	Indiana/Wisconsin - Glac Central
Wadena loam (over s.c.l.)	Iowa/Minnesota - Glac Central

(over s.c.l.) = substratum is a sandy clay loam

The Saskatchewan soil sample described in the February 27, 1991 correspondence as a Weyburn Loam is classified by texture as a sandy clay loam. The 56% sand, 23% silt, 21% clay distribution borders very closely to two other soil textural classes: sandy loam and loam. For example, if the clay fraction were only 2% less (19%) then the soil would be classified as a sandy loam. And if the sand fraction was decreased by 5% and that portion added to the silt fraction then the soil would be a loam. This explains why several different soil series can be similar to the subject soil.

Listed below is a more detailed comparison of three of the soils to the sample Saskatchewan soil. The Acuff sandy clay loam is found throughout Lynn County, Texas which according to the 1987 Agricultural Census is the #6 cotton producing county in Texas (US Dept. of Commerce, 1989). The Cuero sandy clay loam is located throughout DeWitt County and Washington County, Texas in the Gulf Coastal Plain region. These counties are highly productive of cotton and soybean (Neitch, 1991). The Wadena loam is found in

Nobles County, Minnesota and Webster County, Iowa which are respectively the #8 and #1 soybean producing counties in each state (Lorenzen, 1975; Koppen, 1975; US Dept. of Commerce, 1989).

	Subject Soil	Acuff[1]	Cuero[2]	Wadena[3]
Classification	sandy clay loam	sandy clay loam	sandy clay loam	loam
% Sand	56	53	55	35-51
% Silt	23	24	19	19-47
% Clay	21	23	26	18-30
% Org Matter	3.8	2.1	1-3	2.9-5.9
pH	7.8	7.6	6.1-7.8	6.6-7.3
Bulk Density	0.72	1.42	1.4-1.65	1.3-1.4

1 Data obtained from Neitsch, 1991; USDA, 1976.
2 Data obtained from Neitsch, 1991.
3 Data obtained from USDA, 1975a; and data adapted from the SCS/Iowa State University SOILS5 database by Arnold et al, 1990.

References

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