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

SUBJECT: CLETHODIM NEW CHEMICAL REGISTRATION STANDARD

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SUBSTANCES

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Attached is the EFGWB Science Chapter for the Clethodim New Chemical Registration Standard.

DATA BASE ASSESSMENT

Studies which are acceptable to fulfill the following registration requirements have been received:

- 1) hydrolysis
- 2) aqueous photolysis
- 3) soil photolysis
- 4) leaching
- 5) field dissipation
- 6) confined rotational crop accumulation
- 7) fish bioaccumulation

An aerobic soil metabolism study has been received which is scientifically valid and partially fulfills the registration requirements. Additional information is required for this study to be fully acceptable.

An unacceptable anaerobic soil metabolism study was submitted, but due to the nature of the deficiencies cannot be made acceptable.

Studies in the following areas are required for full registration:

- 1) aerobic soil metabolism -- additional information on the previously submitted study
- 2) anaerobic soil metabolism
- 3) rotational crop accumulation -- uptake has been observed in confined rotated crops replanted at intervals up to 365 days. Since these data cannot support a replanting interval shorter than one year, EFGWB defers to Dietary Exposure Branch, which can set tolerances for all the affected commodities, and to Toxicology Branch which can assess the significance of the expected residues.
- 4) drift field evaluation
- 5) droplet size spectrum studies

## ENVIRONMENTAL FATE ASSESSMENT

These data depict a compound which is stable to hydrolysis except in acid conditions, but highly susceptible to photolysis and metabolism. It is mobile. At exaggerated treatment rates, some uptake of radiocarbon into confined rotational crops occurred, about 1/3 in the form of closely related degradates and 2/3 from the "carbon pool".

Clethodim and degradates do not show persistence in field dissipation studies. No significant bioaccumulation occurs in fish.

In the following summaries, studies which are designated acceptable are scientifically valid and fulfill registration requirements. Partially acceptable studies are scientifically valid but do not fully satisfy registration requirements. They have the potential for being made acceptable, and generally contain useful information. Unacceptable studies are deficient such that they cannot be made acceptable, and new studies must be done to satisfy the registration requirements. They may contain some usable information.

- 1) acceptable hydrolysis studies indicate half-lives of 26 days (ring-labelled) and 42 days (allyl-labelled) at pH 5, >300 days at pHs 7 and 9, i.e. the material hydrolyzes moderately at pH 5 and is stable at higher pHs.
- 2) an acceptable aqueous photolysis study indicates half-lives of 1.5 - 9.3 days. First-order half-lives for ring-labelled compound were 1.5, 6.4, and 9.3 days at pH 5, 7, and 9 respectively for the irradiated samples. Corresponding dark controls were 12.5, 99.4, and 330.2 days. First-order half-lives for the allyl-labelled compound were 1.39, 4.05, and 5.43 days at pH 5, 7, and 9 respectively for the irradiated samples. Corresponding dark controls were 20.06, 5042.8 [sic], and 60.85 days. Although these data and the hydrolysis study all indicate stability at pH 7 and 9, the half-life estimates for the dark-incubated samples in the four studies should agree closely but do not.
- 3) an acceptable soil photolysis study indicates that degradation on soil is rapid, but metabolism is apparently the primary mechanism. A half-life for the combined processes is 1.53 - 1.82 days. Dark controls do not differ significantly from light-exposed samples.
- 4) partially acceptable aerobic soil metabolism studies indicate that the half-life of parent is ca. 1 day, generating the corresponding sulfoxide and sulfone; additional information on degradates is needed. The sulfoxide and sulfone may have half-lives of ca 1 month.
- 5) a study on anaerobic soil metabolism was unacceptable, but contained some usable information. It was not acceptable because the soil was not flooded, anaerobic conditions were not clearly established, and certain samples became aerobic during the studies. It revealed a very different pattern of degradation, including clethodim imine and imine sulfate but no carbon dioxide. No definitive anaerobic half-life for parent was calculated, since only 12% of the applied parent remained at the start of anaerobic conditions (one day after application). Approximately 2/3 of the parent present at that time had metabolized within 31 days. The two major degradates may persist, with an apparent half life of several months.
- 6) an acceptable study on leaching indicated that parent and degradates are mobile, with  $K_d$ s from  $\leq 0.1$  to 7.0, in various soils.

- 7) in acceptable field dissipation studies on cotton in two locations, parent was only found at levels at or near the level of quantitation of 0.02 ppm. Clethodim sulfoxide had an apparent half-life of ca 2.5 - 3.7 days.
- 8) an acceptable confined rotational crop study on lettuce, carrots, wheat indicated some uptake in food and fodder material at the exaggerated rate applied. Residues were detected at all replanting intervals up to 365 days. About 1/3 of the recovered material was structurally related to clethodim (imine sulfoxide and oxazole sulfoxide and sulfone derivatives), and the rest apparently came from the soil "carbon pool". At normal use rates total residue would be ca. 5 to 13 ppb in food crops (1.6 to 4 ppb clethodim related) and 60 to 160 ppb (20 to 53 ppb clethodim related) in fodder crops. In these rotational crops the individual compounds identifiable as derivatives of Clethodim would be well below the limit of quantitation of the analytical method. EFGWB defers to Tox Branch as to the significance of the expected level of residues under actual use conditions, and to Dietary Exposure Branch for tolerance setting.
- 8) Acceptable laboratory fish accumulation studies indicated maximum BCFs of 0.7 to 4.0 in various tissues, i.e. the compound does not bioaccumulate in fish.

#### GROUND WATER ASSESSMENT

Clethodim is mobile, but has a metabolic half-life of 1 - 3 days in soil under aerobic conditions. Therefore, parent compound should not be a ground water concern in most environments. In the most vulnerable areas, such as citrus orchards, it is not used at present. In the unlikely event that Clethodim did reach ground water, for example if a heavy rainfall closely followed application to areas which overlay shallow unconfined aquifers, the available routes of disappearance would be the following:

- (1) dilution/diffusion
- (2) metabolism, at a rate which is influenced by two factors, microbial activity, and aeration. Metabolism could be rapid if microbial activity is high. If, as is more typical of ground water, microbial activity is relatively low, metabolism could be much slower. In aerobic conditions, the resulting degradates would be relatively short-lived. Under anaerobic conditions, persistent degradates would be possible.
- (3) hydrolysis if the water is acid. More usually, the water would be neutral to basic, and hydrolysis would not be a significant factor.

The major degradates of clethodim under aerobic conditions (the sulfoxide and sulfone) are also mobile in soil and appear to be approximately an order of magnitude more persistent (up to 30 days). Their potential for groundwater contamination may be somewhat higher than for clethodim but would still be expected to be relatively low in most cases due to their moderately low persistence.

#### SURFACE WATER ASSESSMENT

Clethodim, and also its sulfoxide and sulfone, may migrate into surface bodies of water by run-off which occurs shortly after application (e.g. rainfall). Since they are not adsorbed readily to soil ( $K_{ds}$  of < 0.1 to 7), they are likely to remain in the aqueous phase, where they are subject to rapid photolysis and biodegradation. They may remain long enough to exert acute effects on resident biota, but are unlikely to cause chronic effects. Clethodim does not show a significant potential for bioaccumulation in aquatic organisms. Although they have not been individually tested, the primary degradates are highly polar, and would not be expected to bioaccumulate.

## TABLE OF CONTENTS

pp. ES 1.1 - ES 1.5	<b>Executive Summary</b>
pp. 1.1 - 1.3	<u>Hydrolysis study on RE-45601.</u> Pack, D.E. MRID #409745-20,
pp. 2.1 - 2.46	<u>[4,6-Ring-<sup>14</sup>C] Clethodim Photodegradation in Water.</u> Chen, Y.S. MRID # 410301-34, pp 2.1 - 2.46
pp. 3.1 - 2.46	<u>[Allyl-2-<sup>14</sup>C] Clethodim Photodegradation in Water.</u> Chen, Y.S. MRID # 410301-33
pp. 4.1 - 4.15	<u>Clethodim Photodegradation on Soil.</u> Chen, Y.S. MRID # 410301-35
pp. 5.1 - 5.5	<u>The aerobic soil metabolism of clethodim using [ring-4,6-<sup>14</sup>C]- and [allyl-2-<sup>14</sup>C] clethodim.</u> Pack, D.E. MRID # 409745-21
pp. 6.1 - 6.4	<u>The aerobic soil metabolism of [propyl-1-<sup>14</sup>C]clethodim.</u> Pack, D.E. MRID # 409745-22
pp. 7.1 - 7.24	<u>The Anaerobic Soil Metabolism of [Ring-4,6-<sup>14</sup>C] Clethodim.</u> Pack, D.E. MRID # 410301-36
pp. 8.1 - 8.3	<u>Freundlich soil adsorption/desorption coefficients of clethodim and three metabolites.</u> Pack, D.E. MRID # 409745-23
pp. 9.1 - 9.30	<u>Field Dissipation Study with Clethodim on Cotton in California.</u> Ho, B. MRID # 410302-08
pp. 10.1 - 10.31	<u>Field Dissipation Study with Clethodim on Cotton in Mississippi.</u> Ho, B. MRID # 410302-07
pp. 11.1 - 11.49	<u>Confined Rotational Crop Study of [Ring-4,6-<sup>14</sup>C] Clethodim with Carrots, Lettuce, and Wheat.</u> Gaddamidi, V. MRID # 410302-11
pp. 12.1 - 12.4	<u>Uptake, depuration and bioconcentration of [allyl-2-<sup>14</sup>C] and [cyclohexene-1-one-4,6-<sup>14</sup>C] RE-45601 to bluegill sunfish (<i>Lepomis macrochirus</i>).</u> Forbis, A.D. MRID # 409745-31
	<u>Characterization of <sup>14</sup>C residues in bluegill sunfish treated with (allyl-2-<sup>14</sup>C)-clethodim or (cyclohexene-1-one-4,6-<sup>14</sup>C)-clethodim.</u> Rose, A.F. and J.P. Suzuki MRID # 409745-24
pp. Bib1	<b>Bibliography</b>
pp. Tab1 - Tab2	<b>Table A</b>

## EXECUTIVE SUMMARY -- CLETHODIM

Clethodim is a post-emergent herbicide with a proposed label use rate of 0.125/0.25 lb ai/A (maximum application of 0.5 lb/season) for control of weeds in cotton and soybeans. Known environmental characteristics of Clethodim depict a compound which is stable to hydrolysis, except in acid conditions, but highly susceptible to photolysis and metabolism. It and its degradates are mobile. At exaggerated treatment rates, some uptake of radiocarbon into confined rotational crops occurred, about 1/3 in the form of closely related degradates and 2/3 from the "carbon pool". Clethodim and degradates do not show persistence in field dissipation studies. No significant bioaccumulation occurs in fish. Under present use patterns, it does not appear to threaten ground or surface water.

The following summarizes the data requirements.

### NOT FULFILLED -- new study required

#### Metabolism - Anaerobic Soil

MRID # 410301-36 is not acceptable to fulfill the data requirement, although it does provide some information. A new study with anaerobic conditions established by nitrogen flushing and soil flooding is required. The supplemental information from this study is as follows:

- 1) Anaerobic metabolism takes a distinctly different pathway from that under aerobic conditions.
- 2) Principal degradates at 31 days were clethodim imine (43.5% of applied) and clethodim imine sulfate (14.3% of applied), and do not include CO<sub>2</sub>.
- 3) Degradates formed by anaerobic means may persist, as indicated by 63 day values. Clethodim imine represented 33.0% of applied material, and the imine sulfate was 11.2%.

Accumulation -- Rotational Crop, Field -- no data submitted

Spray Drift Field Evaluation -- no data submitted

Droplet Size Spectrum -- no data submitted

### PARTIALLY FULFILLED -- additional information required

#### Metabolism - Aerobic Soil

Two studies were reviewed (MRID #s 409745-21 and 409745-22). If information on the deficiencies listed below is received and accepted, MRID # 409745-21 will partially satisfy the data requirement. If MRID # 409745-21 is made acceptable, together with MRID # 409745-22 it will completely satisfy the aerobic soil metabolism (162-1) data requirement.

MRID # 409745-21 provides supplemental information on ring and allyl labelled chlethodim, but is not acceptable to partially fulfill the data requirement at this time for the following reasons:

- (a) Several degradates each representing 5 - 10% of applied radioactivity were not characterized.
- (b) The time 0 samples came from soil treated separately from that of the other samples. No explanation was given.

- (c) The amount of applied radioactivity was calculated from an analysis of the stock solution and the volume of solution added instead of from the results of the time 0 samples. If a reasonable explanation for this approach cannot be provided, the study author should re-compute the applied radioactivity based upon the results of the time 0 sample.
- (d) Based on the radioactivity in the stock solution and the volume of stock solution added to the soil, the total amounts of radioactivity recovered in time 0 samples were only 90.1% (ring labeled) and 93.2% (allyl labeled). Also, total recoveries of radioactivity decreased with time to marginal levels.

MRID # 409745-22 is acceptable, and partially satisfies the data requirement by providing information on the degradation of propyl labeled [<sup>14</sup>C]-clethodim and its degradates in a sandy loam soil.

Ring and allyl[<sup>14</sup>C]-labeled incubated at 25°C at initial concentrations of 10 ppm in a sandy loam soil degraded with half-lives of approximately one day. Degradates at the end of the 4 month incubation period were:

CO<sub>2</sub> -- 52% of the ring labeled and 40% of the allyl labeled applied radioactivity

Clethodim sulfoxide -- initially the major degradate, peaked at 62-72% of the 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 the 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 [<sup>14</sup>C]-clethodim incubated at 25°C at an initial concentration of 10.3-10.7 ppm in a sandy loam soil degraded with half-life of approximately 2.6 days. The battery of reference standards did not include compounds which contained the cyclohexene ring without the propyl group nor any containing the cyclohexanene ring without the sulfur containing side chain. Therefore, it does not appear to have been possible to identify such compounds by comparison of retention times to those of the reference standards used. Degradates were:

CO<sub>2</sub> -- 54.4% of the applied radioactivity at the end of the 380 day incubation period

Clethodim sulfoxide -- initially the major degradate, 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

FULFILLED -- no further information required

Degradation - Hydrolysis

MRID # 409745-20 is acceptable to fulfill the data requirement. 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

Two studies were reviewed, are acceptable, and together fulfill the data requirement.

MRID # 410301-34, done with Ring - labelled compound:

First-order half-lives were 1.5, 6.4, and 9.3 days at pH 5, 7, and 9 respectively for the irradiated samples. Corresponding dark controls were 12.5, 99.4, and 330.2 days. Corresponding sensitized samples gave half lives of 0.87, 1.2, and 0.52 days. The 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 of the 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.

MRID # 410301-33, done with Allyl-labelled compound:

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. Sensitized samples gave half lives of 0.2, 0.61, and 0.33 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 was reviewed and is acceptable. 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<sub>2</sub>, 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 the light samples in the two runs were statistically identical. Therefore, it can be concluded that the degradates detected were metabolites, rather than photoproducts. Although the study was done with radioactive label in only one portion of the molecule, further investigation is not necessary, since studies on metabolism have been performed with appropriate labelling in different parts of the molecule.

## Mobility - Leaching and Adsorption/Desorption

✓  
MRID # 409745-23 is acceptable and fulfills EPA Data Requirements. 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 ( $\leq 0.2$ ), clethodim sulfone ( $\leq 0.1$ ), and clethodim oxazole sulfone (0.3-7.0).

## Field Dissipation

Cotton in California -- MRID # 410302-08 is acceptable and provides information on field dissipation on a cotton crop in California. The data indicate that clethodim and its degradates do not persist under these conditions. The parent clethodim was only found at levels at or near the 0.02 ppm limit of quantitation. The major metabolite, clethodim sulfoxide, showed a maximum concentration of 0.04 ppm and quickly dissipated such that none was detected at 7 days; a half-life of 2.5 days was calculated for this degradate. The metabolites, clethodim sulfone, clethodim oxazole sulfoxide, and clethodim oxazole sulfone, were only found at levels at or below the 0.02 ppm limit of quantitation. 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.

Cotton in Mississippi -- MRID # 410302-07 -- Results were similar to that for California. Clethodim sulfoxide, showed a maximum concentration of 0.01 ppm and none was detected at 14 days; a half-life of 3.7 days was calculated for this degradate. Clethodim sulfone, clethodim oxazole sulfoxide, and clethodim oxazole sulfone were only found at levels at or below the 0.02 ppm limit of quantitation. 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 is acceptable, and provides data on lettuce, carrots, and wheat grown as confined rotational crops. Some uptake and concentration were detected at this exaggerated rate of application. Metabolites with structures closely related to the parent compound accounted for around 1/3 of the total radioactivity observed in the plants. The remaining labelled material may derive from the "carbon pool" of soil organic matter into which clethodim has been incorporated.

Bare sandy loam soil was treated with the equivalent of 1 ppm [ring-4,6- $^{14}C$ ]-Clethodim in a single application. After fallow periods of 30, 120, and 365 days in the greenhouse, crops of lettuce (leafy crop), carrot (root crop), and wheat (small grain) were planted in the treated soil. The ordinary maximum application is two postemergence treatments of 0.25 ppm (0.25 lb ai/A) for a total of 0.5 ppm.

Soil residue decreased from 1.0 ppm (present in the form of >85% clethodim and 9-15% clethodim sulfate) measured immediately after application to 0.15 ppm at 30 days, 0.19 ppm at 120 days, and 0.09 ppm at 365 days. Clethodim was rapidly metabolized. At all replanting intervals, clethodim was undetectable in the soil, and at each interval a total of approximately 0.05 ppm was detected as imine sulfoxide, oxazole sulfoxide, and oxazole sulfone. The remaining radioactivity had become incorporated in soil organic matter, or mineralized.

Edible crop total residues were below 0.05 ppm except for 30-day lettuce, containing 0.08 ppm [table says 0.05 - EBC], and no further identification was done. The lettuce contained 0.025 ppm total of the three clethodim metabolites, imine sulfoxide, oxazole sulfoxide, and oxazole sulfone.

Fodder crop total residues were approximately an order of magnitude higher than those of edible crops. 40 - 70% of the <sup>14</sup>C could not be extracted by dichloromethane followed by aqueous methanol. Imine sulfoxide, oxazole sulfoxide, and oxazole sulfone were isolated at 0.06, 0.06, and 0.03 ppm respectively, accounting for roughly 1/3 of the total.

#### Laboratory Accumulation - Fish

MRID #s 409745-31 and 409745-24 together are acceptable and fulfill EPA Data Requirements for Registering Pesticides. Maximum bioconcentration factors reported for total [<sup>14</sup>C]-in bluegill sunfish exposed to 0.06 ppm [<sup>14</sup>C]clethodim for 28 days at 21°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.

DATA EVALUATION RECORD

STUDY 1 (Hydrolysis -- 161-1)

Pack, D.E. 1988d. Hydrolysis study on RE-45601. Laboratory Project ID MEF-0013/8703899. prepared and submitted by Chevron Chemical Company, Richmond, CA. MRID #409745-20

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CONCLUSIONS:

- (1) This study is acceptable, and satisfies the hydrolysis (161-1) data requirement by providing information on the transformation of clethodim at 25°C in light-shielded sterilized aqueous buffers at pHs 5, 7, and 9.
- (2) Propyl-labeled <sup>14</sup>C]clethodim incubated in the dark at 25°C in sterilized aqueous buffers 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.

MATERIALS AND METHODS:

The E-isomer (RE-45601) of clethodim (a designation for the stearic position of the chloropropenyl group) is the predominant, if not exclusive, form of both the technical product and the analytical standard.

[Propyl-1-<sup>14</sup>C]clethodim (E isomer; radiochemical purity 98%, specific activity 56 mCi/mMol, Chevron Chemical Co.) dissolved in acetonitrile was added to filter-sterilized aqueous buffer solutions to make a final concentration of 5 ppm [<sup>14</sup>C]clethodim and 0.1% acetonitrile. The buffered solutions were made using commercial "pHydron" pH 5, 7, and 9 buffers that were diluted 1:5 with water. Aliquots of the three buffer solutions were placed in HPLC autoinjector vials, capped, and incubated at 25 ± 1°C in the dark. Two vials of each solution were sampled at 0, 1, 4, 7, 14, and 32 days posttreatment. The solutions were analyzed for total [<sup>14</sup>C]residues by LSC and for specific compounds by reverse-phase HPLC with radioactive flow and UV detection. The solutions were cochromatographed with unlabeled reference standards using an isocratic solvent system of deionized water:20% acetic

acid (95:5, v:v).

After the hydrolysis rate study using propyl-labeled [ $^{14}\text{C}$ ]clethodim was completed, the study was repeated using [allyl-2- $^{14}\text{C}$ ]clethodim (E isomer; radiochemical purity 98%, specific activity 40.3 mCi/mMol, Wizard Laboratories, purified by Chevron Chemical Co.). [ $^{14}\text{C}$ ]Clethodim dissolved in acetonitrile was added to pH 5 and 7 buffer solutions to make a final concentration of 10 ppm [ $^{14}\text{C}$ ]clethodim and 0.1% acetonitrile; the study author stated that hydrolysis in a pH 9 solution was not examined with the allyl label because there was no difference in the behavior of propyl-labeled [ $^{14}\text{C}$ ]clethodim between the pH 7 and 9 solutions. Aliquots of both pH solutions were placed in HPLC autoinjector vials, capped, and incubated at  $25 \pm 1^\circ\text{C}$  in the dark. Two vials of each solution were sampled at 0, 1, 3, 7, 14, 21, and 30 days posttreatment. The solutions were analyzed for total [ $^{14}\text{C}$ ]residues by LSC and for specific compounds by reverse-phase HPLC with radioactive flow and UV detection. The solutions were cochromatographed with unlabeled reference standards using a solvent system gradient from deionized water:20% acetic acid (70:5, v:v) to 20% acetic acid:acetonitrile (5:95, v:v).

For confirmation of degradate structures by GC/MS following hydrolysis of [propyl-1- $^{14}\text{C}$ ]clethodim, a 50 ppm solution in pH 5 buffer was maintained in the dark at  $25^\circ\text{C}$  for 42 days. Following LSC of aliquots, the solution was saturated with ammonium sulfate, extracted with methylene chloride, dried with anhydrous sodium sulfate, and distilled. The residue was dissolved in acetone for further purification and identification. Aliquots were chromatographed alone and with reference standards of clethodim and clethodim oxazole using two-dimensional TLC on silica gel plates developed in chloroform:acetic acid (9:1, v:v) and chloroform:acetic acid (40:1, v:v). Following autoradiography and UV-quenching to locate the radioactive areas and the nonlabeled standards, respectively, the [ $^{14}\text{C}$ ]degradate comprising >10% of the applied was eluted from the silica gel with acetone. An aliquot of the acetone solution was rechromatographed with the clethodim oxazole standard; the remainder of the solution was analyzed by GC/MS.

For confirmation of degradate structures by GC/MS following hydrolysis of [allyl-2- $^{14}\text{C}$ ]clethodim, a 500 ppm solution in pH 5 buffer was maintained in the dark at  $25^\circ\text{C}$  for 14 days. Four 2-mL aliquots were subjected to HPLC using the isocratic solvent system, and the radioactive fractions were combined. Following LSC of aliquots, the solution was saturated with ammonium sulfate, extracted with methylene chloride, dried with anhydrous sodium sulfate, and distilled. The residue and a suspected degradate standard were analyzed by GC/MS.

## RESULTS:

Propyl-labeled [ $^{14}\text{C}$ ]clethodim (E isomer; radiochemical purity 98%), at 5 ppm, degraded with half-lives of 25.7 days (reviewer-calculated) at pH 5 and approximately 300 days at pH 7 and 9 in sterile aqueous buffered solutions incubated in the dark at  $25^\circ\text{C}$  (Tables 1-3, Figures 16-18). Allyl-labeled [ $^{14}\text{C}$ ]clethodim (E isomer; radiochemical purity 98%), at 10 ppm, degraded with half-lives of 42.1 days at pH 5 and 360 days at pH 7 under similar conditions (Tables 4 and 5). The major degradates of [ $^{14}\text{C}$ ]clethodim were: clethodim oxazole (Product 2; RE-47365) from the propyl portion of the molecule and E-1-chloropropen-3-ol (Product 1; RE-46261) from the allyl portion of the molecule (Figures 1 and 21). Clethodim sulfoxide (RE-45924) was detected in both the propyl- and allyl-labeled [ $^{14}\text{C}$ ]clethodim solutions at up to 5.3% of the applied (maximum in the pH 9 solution). Three unidentified degradates, each  $\leq 2.5\%$  of the applied, were isolated from the propyl-labeled solution and three were isolated from the allyl-labeled solution; because of differences in the analytical procedures for the two labels, it was uncertain if the unidentified degradates associated with the different labels were identical. During the entire

study, the material balance ranged from approximately 99 to 101%.

#### DISCUSSION:

- (1) The study author did not address the fact that propyl-labeled [<sup>14</sup>C]clethodim degraded more rapidly than allyl-labeled [<sup>14</sup>C]clethodim in the pH 5 solution. Using linear regression equations and the tabular data (Tables 1 and 4), this reviewer determined the half-life of propyl-labeled [<sup>14</sup>C]clethodim to be 25.7 days and the half-life of allyl-labeled [<sup>14</sup>C]clethodim to be 42.1 days. The 28-day half-life of clethodim that is reported by the study author was calculated using only data from the propyl-labeled [<sup>14</sup>C]clethodim portion of the study; the study author used data from the allyl-labeled [<sup>14</sup>C]clethodim experiment only to identify the degradate 1-chloropropen-3-ol.

Besides differences in label position, the allyl-labeled [<sup>14</sup>C]clethodim experiment was conducted at a higher concentration (10 ppm rather than 5 ppm) than the propyl-labeled [<sup>14</sup>C]clethodim experiment; it is possible that the degradation rate of clethodim is not pseudo first order and is therefore concentration-dependent. The allyl-labeled [<sup>14</sup>C]clethodim experiment was also conducted after the propyl-labeled [<sup>14</sup>C]clethodim experiment had been completed rather than concurrently; it is possible that incubation conditions were slightly different. The study author should resolve why different degradation rates were observed in the two experiments.

- (2) Discrepancies exist between the tabular and graphic data for the allyl-labeled [<sup>14</sup>C]clethodim experiment. When the tabular data in Table 1 (propyl-labeled [<sup>14</sup>C]clethodim) for duplicate analyses are averaged, the results agree with the data points on Figure 11. However, similar averaging of the data in Table 4 (allyl-labeled [<sup>14</sup>C]clethodim) and comparisons to the corresponding Figure 14 reveal significant differences in all recovery values for time periods >4 days, e.g., ~65% parent is the mean value obtained from Table 4 for 30 days, but the data point plotted in Figure 14 is ~79%. Also, Figure 14 has data points for 4 days, but none for 3 days whereas Table 4 has values for 3 days, but none for 4 days.
- (3) Material balance data were not supplied by the study author, but were calculated by the reviewer from the tabular data (Tables 1-5) on the assumption that these data represented percent of applied radioactivity and not percent of total recovered radioactivity.
- (4) The molarity of the buffer solutions was not specified.
- (5) Isomers (geometrical and optical isomers; tautomers) of clethodim resulted in multiple HPLC peaks. The isomerization of the [<sup>14</sup>C]compounds was discussed at length by the study author.
- (6) The study author stated that the isocratic rather than gradient solvent system had to be used to isolate 1-chloropropen-3-ol because: in the gradient system 1-chloropropen-3-ol eluted too close to the void volume to insure separation and reliable retention times; and the acetic acid in the gradient solvent system interfered with the UV detection of 1-chloropropen-3-ol.
- (7) The study authors point out that the abiotic reactions that clethodim undergoes in water are technically not "hydrolysis" because OH is not substituted for any leaving group. In addition, the reactions are also observed under heated anhydrous conditions.

DATA EVALUATION RECORD

Study 2

I. Study Type: Aqueous Photolysis (161-2)

II. Citation:

Chen, Y.S. [4,6-Ring-<sup>14</sup>C] Clethodim Photodegradation in Water.  
performed and submitted by Chevron Chemical Company, Richmond, CA.  
dated 12/28/88, received EPA 3/6/89 under MRID # 410301-  
34

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E. B. Conerly*  
6/28/90

IV. Conclusions:

This study is acceptable. It provides data on photodegradation of ring-- labelled clethodim, and partially fulfills the data requirement set forth in 161-2. Clethodim is readily photolyzed, even without sensitizers.

V. Materials and Methods:

Photolysis of approximately 10 ppm [4,6-ring <sup>14</sup>C]-clethodim was studied in sterile buffer solutions at pH 5, 7, and 9. Samples were exposed within a thermally controlled apparatus at 25 C ± 1 C to natural sunlight. The intensity of the light was monitored throughout exposure. Traps for possible volatile degradates contained NaOH for CO<sub>2</sub>, and xylene [or ethylene glycol -- see below] for organics. Sample analysis and identification techniques were:

TLC -- preparative isolation  
chloroform:acetic acid (20:1)  
acetone:chloroform (2:1)

LSC -- quantitation of radioactivity from isolated TLC spots  
HPLC -- separation of parent and products, compound  
identification by cochromatography  
MS -- compound identification

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

RESULTS:

- 1) First-order half-lives were 1.5, 6.4, and 9.3 days at pH 5, 7, and 9 respectively for the irradiated samples. Corresponding dark controls were 12.5, 99.4, and 330.2 days. Corresponding sensitized samples gave half lives of 0.87, 1.2, and 0.52 days.
- 2) The major photoproducts were clethodim sulfoxide, imine, imine sulfoxide, and DME sulfoxide. Minor photoproducts

were trione sulfoxide, oxazole, oxazole sulfoxide, and imine ketone.

- 3) After 30 days the major products remaining are imine sulfoxide and DME sulfoxide. Most of the photoproducts are rapidly formed and then degraded, except DME sulfoxide.
- 4) Total material balance ranged from 88.2% to 108.1%.
- 5) There was very little volatile material produced.

#### CONCLUSIONS:

Clethodim is readily photolyzed in aqueous solutions under natural sunlight. These results also imply that clethodim would be degraded faster under natural conditions, since photosensitizers are known to be present in natural waters. The half-lives of photolysis range from 1.5 to 9.6 days depending on pH and the presence of photosensitizers. Sulfoxidation and elimination of the chloroallyl sidechain are two major initial photolytic reactions. The initial photoproducts are clethodim sulfoxide and imine, which are then further photolyzed to form imine sulfoxide and DME sulfoxide. In another study with allyl labelled material the rate of photodegradation was similar, and produced chloroallyl alcohol and 3-chloropropenal. Both these products are readily degraded under sunlight in the presence of a photosensitizer.

#### VII. Reviewer's Comments:

The conclusions of the author are supported, and demonstrate that aqueous photolysis is a rapid process for clethodim. It is not clear what the trapping solution was in the definitive study [contrast p. 10 para 2 under Experimental Design, vs para 4], although no significant amount of volatile material was produced. Please clarify.

#### VIII. CBI Information Addendum: attached

TABLE I

CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES  
OF POSSIBLE CLETHODIM METABOLITES

DESIGNATION	CHEMICAL NAME	STRUCTURE
CLETHODIM (RE-45601)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFOXIDE (RE-45924)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFONE (RE-47253)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFOXIDE (RE-47718)	2-[[1-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFONE (RE-47719)	2-[[1-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
5-OH SULFOXIDE (RE-51229)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-5-hydroxy-3-hydroxy-2-cyclohexen-1-one	
5-OH SULFONE (RE-51228)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-5-hydroxy-3-hydroxy-2-cyclohexen-1-one	
AROMATIC SULFONE (RE-50419)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-1,3-dihydroxybenzene	
OXAZOLE SULFOXIDE (RE-47795)	6,7-dihydro-6-[2-(ethylsulfoxo)propyl]-2-ethyl-4(5H)-benzoxazolone	

TABLE I (CONTINUED)

CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES  
OF POSSIBLE CLETHODIM METABOLITES

DESIGNATION	CHEMICAL NAME	STRUCTURE
OXAZOLE SULFONE (RE-47797)	6,7-dihydro-6-[2-(ethylsulfonyl)propyl]- 2-ethyl-4(5H)-benzoxazolone	
TRIONE SULFOXIDE (RE-47386)	2-[1-one]propyl]-5-[2-(ethylsulfoxo) propyl]-3-hydroxy-2-cyclohexen-1-one	
DME SULFIDE (RE-52420)	3-[2-(ethylthio)propyl] pentanedioic acid	
DME SULFOXIDE (RE-52453)	3-[2-(ethylsulfoxo)propyl] pentanedioic acid	
IMINE KETONE	2-[1-[imino]propyl]-5- [propyl-2-one]-3-hydroxy-2- cyclohexen-1-one	
IMINE (RE-47686)	2-[[1-imino]propyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexen-1-one	
OXAZOLE (RE-47365)	6,7-dihydro-6-[2-(ethylthio)propyl]- 2-ethyl-4(5H)-benzoxazolone	

Clethodim environmental fate review

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Pages 17 through 58 are not included in this copy.

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- Identity of product inert ingredients
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  - Identity of the source of product ingredients
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DATA EVALUATION RECORD

STUDY 3

I. Study Type: Aqueous Photolysis (161-2)

II. Citation:

Chen, Y.S. [Allyl-2-<sup>14</sup>C] Clethodim Photodegradation in Water. performed and submitted by Chevron Chemical Company, Richmond, CA. dated 12/28/88, received EPA 3/6/89 under MRID # 410301-33

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E. B. Conerly*  
6/28/90

IV. Conclusions:

This study is acceptable. It provides data on photodegradation of allyl-labelled clethodim, and partially fulfills the data requirement set forth in 161-2. Clethodim is readily photolyzed, even without sensitizers.

V. Materials and Methods:

Photolysis of approximately 10 ppm [allyl-2-<sup>14</sup>C]-clethodim was studied in sterile buffer solutions at pH 5, 7, and 9. Samples were exposed within a thermally controlled apparatus at 25 ± 1° C to natural sunlight. The intensity of the light was monitored throughout exposure. Volatile materials were trapped within NaOH and xylene scrubbers. Sample analysis and identification were by means of the following:

TLC -- preparative isolation  
chloroform:acetic acid (20:1)  
chloroform  
chloroform:methanol (5:1)  
methylene chloride:acetic acid (10:1)  
methylene chloride  
LSC -- quantitation of radioactivity from isolated TLC spots  
HPLC -- separation of parent and products, compound identification by  
cochromatography  
MS -- compound identification  
derivitization -- 3-chloropropenal was converted to the 2,4-dinitrophenyl hydrazole, and then isolated and purified by preparative TLC

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

**RESULTS:**

- 1) First-order half-lives were 1.39, 4.05, and 5.43 days at pH 5, 7, and 9 respectively for the irradiated samples. Corresponding dark controls were 20.06, 5042.8, and 60.85 days. Corresponding sensitized samples gave half lives of 0.2, 0.61, and 0.33 days.
- 2) 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.

- 3) After 30 days the major products remaining are chloroallyl alcohol and 3-chloropropenal. Most of the photoproducts are rapidly formed and then degraded.
- 4) Total material balance ranged from 86.8% to 103.5%.
- 5) There was very little volatile material produced.

**CONCLUSIONS:**

Clethodim is readily photolyzed in aqueous solutions under natural sunlight. These results also imply that clethodim would be degraded faster under natural conditions, since photosensitizers are known to be present in natural waters. The half-lives of photolysis range from 0.2 to 6 days depending on pH and the presence of photosensitizers. Sulfoxidation and elimination of the chloroallyl sidechain are two major initial photolytic reactions. The initial photoproducts are clethodim sulfoxide, imine, imine sulfoxide, chloroallyl alcohol and 3-chloropropenal which are then further photolyzed to form carbon dioxide and DME sulfoxide. In another study with ring labelled material the rate of photodegradation was similar, and produced imine sulfoxide and DME sulfoxide.

VII. Reviewer's Comments:

The conclusions of the author are supported. The author observes that light intensity was somewhat greater during this experiment than in the parallel experiment with ring-labelled material, and consequently half-lives were somewhat shorter.

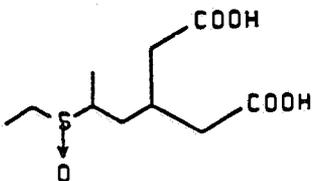
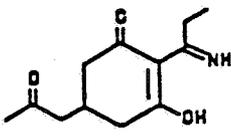
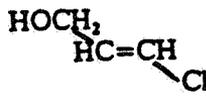
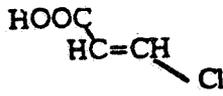
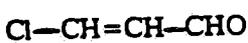
VIII. CBI Information Addendum: attached

TABLE I  
CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES  
OF POSSIBLE CLETHODIM METABOLITES

DESIGNATION	CHEMICAL NAME	STRUCTURE
CLETHODIM (RE-45601)	2-[1-[[[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFOXIDE (RE-45924)	2-[1-[[[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE (RE-47686)	2-[[1-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFOXIDE (RE-47718)	2-[[1-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
OXAZOLE (RE-47365)	6,7-dihydro-5-[2-(ethylthio)propyl]-2-ethyl-4(5H)-benzoxazolone	
OXAZOLE SULFOXIDE (RE-47796)	6,7-dihydro-6-[2-(ethylsulfoxo)propyl]-2-ethyl-4(5H)-benzoxazolone	
DME SULFIDE (RE-52420)	3-[2-(ethylthio)propyl]pentanedioic acid	

TABLE I (CONTINUED)

CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES  
 OF POSSIBLE CLETHODIM METABOLITES

DESIGNATION	CHEMICAL NAME	STRUCTURE
DME SULFOXIDE (RE-52453)	3-[2-(ethylsulfoxy)propyl] pentanedioic acid	
IMINE KETONE	2-[1-[imino]propyl]-5- [propyl-2-one]-3-hydroxy-2- cyclohexen-1-one	
CHLOROALLYL ALCOHOL (RE-46261)	trans-3-chloroallyl alcohol	
CHLOROACRYLIC ACID (CAS#:2345-61-1)	trans-3-chloroacrylic acid	
3-CHLOROPROPENAL	trans or cis-3-chloro- propenal	

Clethodim environmental fate review

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  - Identity of the source of product ingredients
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DATA EVALUATION RECORD

Study 4

I. Study Type: Soil Photolysis (161-3)

II. Citation:

Chen, Y.S. Clethodim Photodegradation on Soil. performed and submitted by Chevron Chemical Company, Richmond, CA. dated 4/8/88, received EPA 3/6/89 under MRID # 410301-35

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E.B. Conerly* 6/28/90

IV. Conclusions:

The study is acceptable and fulfills the requirement for soil photolysis data. Photolysis of clethodim on soil will not be a major pathway of degradation.

V. Materials and Methods:

The surface of a sandy loam (Crevasse, from Greenville, MS) was treated with ring-labelled <sup>14</sup>C-clethodim at a rate equivalent to 0.25 lb/A. It was then exposed within borosilicate vessels to natural sunlight under outdoor conditions for 0, 1, 2, 3, 4, and 7 days. Foil wrapped control flasks were identically treated. Temperatures ranged from 11 - 18° C and 2 - 17° C in two separate runs. Volatile materials were trapped in xylene and NaOH scrubbers.

Analyses were by the following methods:

TLC

chloroform:acetic acid (8:1)  
chloroform:acetic acid:isopropanol (9:1:1)  
chloroform:acetic acid (20:1)

HPLC

MS

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

**RESULTS:**

Less than 6.8% of parent remained after 7 days. Little or no volatile material, organic or CO<sub>2</sub>, was produced. The single major product was clethodim sulfoxide. Minor products ranged from 0.2 to 2.6%. All products were detected in both light and dark flasks. Least square analysis of the data gave 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 the light samples in the two runs.

**CONCLUSIONS:**

Since the dark and light-exposed flasks yielded statistically identical results, it can be concluded that the degradates detected were

metabolites, rather than photoproducts. Soil metabolism predominates under these experimental conditions. Clethodim does not photolyze on soil.

VII. Reviewer's Comments:

Although the study was done with radioactive label in only one portion of the molecule, further investigation is not necessary. The metabolism of clethodim is so rapid that photolysis on soil will not be a major pathway of degradation, and studies on metabolism have been performed with appropriate labelling.

VIII. CBI Information Addendum: attached

TABLE I  
SOIL CHARACTERISTICS

Soil Reference No.	6073-48
Origin	Greenville, MS
Classification	Sandy Loam
% Sand	70
% Silt	17
% Clay	13
% Organic	1.0
pH	7.1
Cation Exchange Capacity(Meq/100g)	7.5
1/3 Bar Value	13.4
Bulk Density	1.23
Laboratory Analysis Number	58567
Analysis was done by A&L Midwest Agricultural Laboratories, Omaha, NE	

TABLE II

CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES  
OF POSSIBLE PRODUCTS

DESIGNATION	CHEMICAL NAME	STRUCTURE
CLETHODIM (RE-45601)	2-[1-[[[ <u>E</u> -3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFOXIDE (RE-45924)	2-[1-[[[ <u>E</u> -3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFONE (RE-47253)	2-[1-[[[ <u>E</u> -3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFOXIDE (RE-47718)	2-[1-imino]propyl]-5-[2-(ethylsulfoxo)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFONE (RE-47719)	2-[1-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
OXAZOLE (RE-47365)	6,7-dihydro-6-[2-(ethylthio)propyl]-2-ethyl-4(5H)-benzoxazolone	
OXAZOLE SULFOXIDE (RE-47796)	6,7-dihydro-6-[2-(ethylsulfoxo)propyl]-2-ethyl-4(5H)-benzoxazolone	
IMINE (RE-47686)	2-[1-iminopropyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	

Clethodim environmental fate review

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- (c) The time 0 samples were collected from soil that had been treated separately from the soil from which the day 1 and subsequent samples were collected. No explanation was given.
  - (d) The computation of applied radioactivity was based upon an analysis of the stock solution and the volume of solution added instead of the results of the time 0 samples. No explanation was provided. If a reasonable explanation cannot be provided, the study author should recompute the applied radioactivity based upon the results of the time 0 sample.
  - (e) The total radioactivities recovered from the time 0 soil samples were only 90.1% (ring labeled) and 93.2% (allyl labeled) of that nominally applied to the soil based upon the radioactivity in the stock solution and the volume of stock solution added to the soil. No explanation was provided.
  - (f) The total radioactivity recovered decreased with time to marginal levels (see discussion). The gradual decrease in total radioactivity recovered could possibly be due to inefficient trapping of volatile organic degradates or inefficient extraction of the polyurethane plugs used for the trapping since no significant radioactivity was detected in extracts from the plugs. Therefore, further discussion is needed on the trapping efficiency of polyurethane plugs and on the efficiency of the method used to extract the plugs. (Since no organic volatiles were identified, trapping and extraction efficiency data on such compounds can obviously not be provided. Therefore, a general discussion may suffice.)
- (2) Given the somewhat complex chemistry of clethodim and its degradates, this study was a very good one despite the deficiencies listed above. This study can probably be made to partially satisfy the aerobic soil metabolism data requirement by the submission of acceptable information addressing at least most of the above listed deficiencies. If this study is made to partially satisfy the data requirement, it will together with study 3 (40974522) completely satisfy the aerobic soil metabolism (162-1) data requirement.
- (3) Ring and allyl <sup>14</sup>C labeled incubated at 25°C at initial concentrations of 10 ppm in a sandy loam soil degraded with half-lives of approximately one day. The major degradate at the end of the 4 month incubation period was CO<sub>2</sub> which represented 52% of the ring labeled and 40% of the allyl labeled applied radioactivity. Clethodim sulfoxide which was initially the major degradate peaked at 62-72% of the 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 which was formed from the oxidation of the sulfoxide peaked at 15% of applied at 30 days post-treatment and then declined to 5-7% of applied at 121 days post-treatment. The proposed degradative pathway for clethodim in soil under aerobic conditions is given in Figure 17.

#### MATERIALS AND METHODS:

Fifty-gram samples of sandy loam soil (0.9% organic matter, pH 7.5)(Tables II and III) were weighed into biometer flasks, moistened to 75% of field capacity, and treated at a nominal concentration of 10 ppm with either [ring-4,6-<sup>14</sup>C]clethodim dissolved in acetone or [allyl-2-<sup>14</sup>C]clethodim dissolved in ethanol (radiochemical purities ≥99%; specific activities 56.5 and 57.1 mCi/mMole, respectively; Wizard Labs). The treated soil samples were stirred with a spatula to mix. A "low pressure"

oxygen source was connected to the biometer flasks; volatiles were trapped in a polyurethane foam plug located in the connecting arm and a 0.5 N sodium hydroxide solution located in the side well. The flasks were maintained in dark at 25°C. Duplicate flasks of soil were collected for analysis at 0, 1, 3, 7, 14, 30, 60-62, 94-99, and 121-125 days posttreatment; the sodium hydroxide trapping solutions were changed at each sampling interval.

The soils were extracted once with methanol containing unlabeled clethodim on an Omni-Mixer for 5 minutes, followed by three extractions with clethodim-free methanol; the samples were centrifuged and the extract removed after each extraction. The extracts were combined, and aliquots were analyzed for total radioactivity by LSC. The remainder was concentrated in a vacuum rotary evaporator at ambient temperature; the solvent vapors were condensed onto a dry ice-cooled cold finger trap to insure that no material was lost during condensation. The concentrated residues were diluted with methanol and again concentrated, this time under a stream of nitrogen. Aliquots of the methanol concentrate and the trapped distillates were analyzed for radioactivity by LSC. The methanol-extracted soils were further extracted three times with a clethodim-free 10 mM calcium sulfate solution on an Omni-mixer as described; the calcium sulfate extracts were combined and analyzed for radioactivity by LSC. The methanol concentrate and calcium sulfate extract were analyzed using reversed-phase HPLC with radioactive flow detection. Reference compounds were cochromatographed with the extracts, and retention times for the standards were determined by UV detection. In addition, the methanol concentrates were analyzed using TLC on silica gel plates developed in either chloroform:acetic acid (9:1) or hexane:acetone:acetic acid (50:50:1). Radioactive areas on the plates were detected by autoradiography. Reference compounds were cochromatographed with the samples and visualized by quenching of UV fluorescence. The twice-extracted soils were analyzed for unextractable radioactivity by LSC following combustion.

The polyurethane foam plugs were extracted three times using sonication with methanol; aliquots of the combined methanol extracts were analyzed by LSC. Aliquots of the sodium hydroxide solutions were analyzed for total radioactivity by LSC.

The detection limit appeared to be 0.1% of the applied.

## RESULTS:

Ring- and allyl-labeled [<sup>14</sup>C]clethodim (radiochemical purities ≥99%), at a theoretical application rate 10 ppm, degraded with half-lives of approximately 1 day in sandy loam soil incubated in the dark at 25°C and 70-75% of field capacity for 4 months (Figure 15). At the end of the 4-month study, evolved <sup>14</sup>CO<sub>2</sub> was the major degradate and totaled 52% of the ring-labeled radioactivity and 40% of the allyl-labeled radioactivity (Table IV and Figure 16). Nonvolatile degradates included clethodim sulfoxide, clethodim sulfone, clethodim imine sulfoxide, clethodim oxazole sulfoxide, and clethodim oxazole sulfone.

In the soil treated with ring-labeled [<sup>14</sup>C]clethodim, [<sup>14</sup>C]clethodim decreased from 89% of the applied at day 0 to 49% at day 1, 17% at day 3, and 0.2% at day 121-125 (Table V). [<sup>14</sup>C]Degradates isolated from the soil included (Table V and Figure 16):

- clethodim sulfoxide (maximum concentration 64% of the applied at 7 days posttreatment)
- clethodim sulfone (15% at 30 days posttreatment);
- clethodim imine sulfoxide (2% at 7-14 days posttreatment);
- clethodim oxazole sulfoxide (2% at 7 through 125 days posttreatment);
- clethodim oxazole sulfone (8% at 125 days posttreatment).

At 121-125 days posttreatment,  $^{14}\text{CO}_2$  totaled 52% of the applied radioactivity and unextractable [ $^{14}\text{C}$ ]residues were 11% of the applied. Throughout the study, the material balance ranged from 75 to 90% of the applied. In the soil treated with allyl-labeled [ $^{14}\text{C}$ ]clethodim, [ $^{14}\text{C}$ ]clethodim decreased from 94% of the applied at day 0 to 58% at day 1, 10% at day 3, and 0.2% at day 121-125 (Table V). [ $^{14}\text{C}$ ]Degradates isolated from the soil included (Table V and Figure 16):

clethodim sulfoxide (maximum concentration of 70% of the applied at 3 days posttreatment)  
clethodim sulfone (15% at 30 days posttreatment).

At 121-125 days posttreatment,  $^{14}\text{CO}_2$  totaled 40% of the applied radioactivity and unextractable [ $^{14}\text{C}$ ]residues were 26% of the applied. Throughout the study, the material balance ranged from 72 to 92% of the applied.

#### DISCUSSION:

- (1) All data were expressed by the study author in terms of "% of the applied radioactivity", but the source of the application rates used in calculating these values was unclear. The application rates were apparently not determined using the typical procedure, which is to analyze treated soil at time 0 (although there was a time 0 soil sample) and set the resulting concentration as "100% of the applied". In this study, the [ $^{14}\text{C}$ ]clethodim application rates of 10.1 and 10.4 ppm were reportedly determined by pipetting (automatic pipette) aliquots of the stock solution at the start and finish of the soil treatment into 250-mL volumetric flasks, diluting the samples to volume, and analyzing the diluted stock solution. The application rates in terms of "dpm" that were used by the study author to convert soil data into "% of the applied" (Appendix Tables II-A and II-B) were:

ring-labeled: 177950000 dpm--0 time;  
181550000 dpm--all samples except 0 time;  
allyl-labeled: 171950000 dpm--0 time;  
177950000 dpm--all samples except 0 time.

No explanation was given time 0 samples being collected from soil that had been treated separately from the soil from which the day 1 and subsequent samples were collected.

- (2) At time 0, an average of only 90.1% of the applied radioactivity was recovered from the soil treated with ring-labeled [ $^{14}\text{C}$ ]clethodim (Appendix Table II-A) and an average 93.2% from the soil treated with allyl-labeled [ $^{14}\text{C}$ ]clethodim (Appendix Table II-B).
- (3) The material balances were incomplete; up to 25.8% of the allyl-labeled and 25.4% of the ring-labeled radioactivity that was applied to the soil (applied computation based upon an analysis of stock solutions) were not recovered. However, at time 0, only 90.1-93.2% of the applied radioactivity was recovered. Therefore, if the amount of applied had been computed from time 0 samples instead of from the stock solutions, recovery numbers for other times would have been much higher. The fact that no volatiles other than  $\text{CO}_2$  were trapped suggests that the lower than expected recoveries may be at least partially due to inefficient trapping of volatile organics by the polyurethane plugs.

- (4) All degradates >0.01 ppm ( $\approx$ 0.1% of the applied) were not identified (Appendix Tables V-A and V-B). In the HPLC analysis of the ring-labeled [ $^{14}\text{C}$ ]clethodim-treated soil, eleven [ $^{14}\text{C}$ ]compounds each representing 0.2-5.9% of the applied were isolated but not identified. In the HPLC analysis of the allyl-labeled [ $^{14}\text{C}$ ]clethodim-treated soil, twelve [ $^{14}\text{C}$ ]compounds were isolated at 0.1-9.4% of the applied but not identified. Of special concern is Peak 18 in the ring-label, which comprised up to 5.9% of the applied (0.59 ppm), and Peaks 16 and 18 in the allyl-label, which comprised up to 9.4 and 6.0% of the applied (0.94 and 0.60 ppm), respectively.

Also, it was unclear whether peak numbers in Appendix Table V-A (ring label) were intended to correspond to peak numbers in Appendix Table V-B (allyl label). In both tables, clethodim is peak 23, clethodim sulfoxide is peaks 12, 13, and 17, and clethodim sulfone is peaks 15 and 19. However, peaks 6-11 are identified in Table V-A as clethodim imine sulfoxide, clethodim oxazole sulfoxide, and clethodim oxazole sulfone, but these peaks are not similarly identified in Table V-B. If the peak numbers do correspond, then the unidentified [ $^{14}\text{C}$ ]compound measured by peak 18 is an important degradate of both labels.

- (5) Recovery efficiencies from fortified soil samples were not reported.
- (6) The study was terminated before patterns of decline of the degradates clethodim oxazole sulfoxide and clethodim oxazole sulfone were established. However, a second aerobic soil metabolism study (Study 6) submitted in this data package was conducted for 1 year and provides the additional necessary information on the formation and decline of these two degradates.
- (7) It appeared that the accountability for the HPLC analysis was >100%, based on a comparison between the HPLC totals (Appendix Tables V-A and V-B) and the total extractable radioactivity (Table IV).
- (8) Isomers (geometrical and optical isomers; tautomers) of clethodim and its degradates resulted in multiple HPLC peaks and streaking on the TLC plates. A very thorough discussion on the possible isomers of clethodim and its degradates was provided in the Appendix.
- (9) The study author stated (Studies 5 and 6) that when low concentrations of clethodim are present in soil, considerable oxidation of clethodim to clethodim sulfoxide occurs during extraction. Methanol gave the lowest amount of conversion of the solvents tested, and the addition of unlabeled clethodim to the extracting solution repressed air oxidation completely. No numerical data were provided to support these statements.



The treated soils were moistened to 75% of field capacity with deionized water and mixed. Humidified air was pumped continuously (flow rate not specified) into the flasks to maintain aerobic conditions; volatiles were not trapped. The flasks were maintained in dark at 25°C beginning on May 6, 1986. Duplicate flasks of soil were collected for analysis at 0, 1, 3, 7, 14, and 30 days posttreatment.

A second set of soils was fortified at 10.7 ppm with propyl-labeled [<sup>14</sup>C]clethodim (radiochemical purity 99.5%; specific activity 161743 dpm/ug; Chevron Chemical Company) on April 9, 1987, and incubated as previously described. Again, volatiles were not trapped. Duplicate flasks of soil were collected for analysis at 30, 62, 90, 120, 180, 270, and 380 days posttreatment.

The soils were extracted once with methanol containing unlabeled clethodim on an Omni-Mixer for 10 minutes, followed by three extractions with clethodim-free methanol; the samples were centrifuged and the extract removed after each extraction. The extracts were combined, and aliquots were analyzed for total radioactivity by LSC. The remainder was concentrated in a vacuum rotary evaporator at ambient temperature; the solvent vapors were condensed onto a dry ice-cooled cold finger trap to insure that no material was lost during condensation. The concentrated residues were diluted with methanol and again concentrated, this time under a stream of nitrogen. Aliquots of the methanol concentrate and the trapped distillates were analyzed for radioactivity by LSC. The methanol concentrate was analyzed using reversed-phase HPLC with radioactive flow detection. Reference compounds were cochromatographed with the extracts, and retention times for the standards were determined by UV detection. In addition, the methanol concentrates were analyzed using TLC on silica gel plates developed in chloroform:acetic acid (9:1). Radioactive areas on the plates were detected by autoradiography. Reference compounds were cochromatographed with the samples and visualized by quenching of UV fluorescence. The methanol-extracted soils were further extracted twice with a clethodim-free 10 mM calcium sulfate solution; the calcium sulfate extracts were combined and analyzed for radioactivity by LSC. The twice-extracted soils were analyzed for unextractable radioactivity by LSC following combustion.

Volatile Trapping -- One 50-g sample of sandy loam soil was weighed into an Erlenmeyer flask and treated at a nominal concentration of 10.7 ppm with [propyl-1-<sup>14</sup>C]clethodim (radiochemical purity 99.5%; specific activity 161743 dpm/ug; Chevron Chemical Company) dissolved in acetone. The treated soil was moistened to 75% of field capacity with deionized water and mixed. Humidified air was pumped continuously (flow rate not specified) into the flask, then sequentially through pseudocumene and 2-ethanolamine:2-methoxyethanol (4:6, v:v) trapping solutions; the outlet of the last trap was under slight negative pressure to prevent the loss of <sup>14</sup>CO<sub>2</sub>. The flask was maintained in dark at 25°C. The trapping solutions were sampled at approximately 1 to 7 day intervals until 441 days post-treatment. Aliquots of the trapping solutions were analyzed for total radioactivity by LSC.

#### RESULTS:

Propyl-labeled [<sup>14</sup>C]clethodim (radiochemical purity >97%), at 10.3-10.7 ppm, degraded with an observed half-life of 1-3 days (registrant-calculated 2.6 days) in sandy loam soil incubated in the dark at 25°C and 70-75% of field

capacity for 380 days (Figure 14). [<sup>14</sup>C]Clethodim decreased from 99.8% of the applied at day 0 to 46% at 3 days and 2.8% at 14 days; 0.4% of the [<sup>14</sup>C]clethodim applied to the soil remained undegraded at 380 days (Tables 5 and 6, Figure 15). The major nonvolatile degradate was **clethodim sulfoxide** (RE-45924). It accumulated to a maximum 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.

Other nonvolatile degradates identified during the study were:  
**clethodim sulfone** (RE-47253; maximum concentration 10.1-11.7% of the applied at 62 days posttreatment)  
**clethodim oxazole sulfone** (RE-47797; 9.3-10.4% at 180-380 days)  
**clethodim oxazole sulfoxide** (RE-47796; 5.9-6.1% at 90 days)  
**clethodim oxazole** (RE-47365; 2.0-2.1% at 3 days)  
**clethodim imine sulfoxide** (RE-47718; 1.0-1.1% at 14-30 days)

At 380 days post-treatment, <sup>14</sup>CO<sub>2</sub> was the major degradate and totaled 54.4% of the applied, organic volatiles totaled 0.27%, total extractable [<sup>14</sup>C]-residues were 18.1-18.6%, and unextractable [<sup>14</sup>C]residues were 13.8-18.2% (Table 4, Figure 1). During the 380-day study, the material balance ranged from 84.8 to 95.9% of the applied.

#### DISCUSSION:

- (1) This aerobic soil metabolism study was, in fact, three separate experiments: volatilization from a single sample over a 441-day period; degradation of clethodim and formation and decline of its degradates between 0 and 30 days posttreatment; and degradation of clethodim and formation and decline of its degradates between 30 and 380 days posttreatment. The study author combined the three experiments to obtain complete material balances and to establish the pattern of formation and decline of degradates. The 0-30 and 30-380 day soil analysis data overlap on day 30 and are in agreement, and the volatilization data appear to complete the material balance, so that although it is preferable that a single experiment be conducted, in this case the combination appears to be acceptable.
- (2) The study author did not state whether the soil application rates for the 30-380 days and volatilization studies were confirmed by analysis or was assumed. Since the material balance is approximately 5% of the applied lower on day 30 for the 30-380 day study than for the 0-30 day study, it is possible that the actual application rate for the 30-380 day experiment was lower than the theoretical application rate.
- (3) It could not be determined from the methodology whether the soil in the volatilization study was analyzed after the last sampling interval to provide a complete material balance (data in the "% left" column of Table 3 appear to have been obtained by subtraction) and confirm that radioactivity that was not volatilized was still in the system.
- (4) All degradates >0.01 ppm (approximately 0.1% of the applied) were not identified. The calcium sulfate extracts (aqueous extracts) which together comprised up to 8.7% of the applied (approximately 0.9 ppm) were not analyzed except by LSC. However, the aqueous soluble polar degradates appear to undergo rapid degradation down to CO<sub>2</sub>. In the HPLC analysis of the methanol extracts of the treated soil, unidentified

[<sup>14</sup>C]compounds with retention times of 2.8 minutes comprised up to 0.3% of the applied; 4.0 minutes, up to 0.5%; 17.6 minutes, up to 2.5%; 24.5 minutes, up to 0.3%; 29.2 minutes, up to 0.8%; 31.7 minutes, up to 2.7%; and 32.7 minutes, up to 0.4%.

- (5) The study author supplied data demonstrating the freezer storage stability of the methanol extracts. An extract of the 3-day posttreatment soil sample was analyzed before and after 13 months of storage at -20°C. During storage, clethodim decreased from 52.4 to 51.1% of the recovered, clethodim sulfoxide increased from 45.3 to 46.2%, and clethodim oxazole increased from 2.3 to 2.4%.
- (6) In Table 4 (Extraction Data), the column labeled "CO<sub>2</sub>" should be labeled "CO<sub>2</sub> plus Organic Volatiles". The CO<sub>2</sub> data in Table 4 are the sum of the "CO<sub>2</sub>" and "Organic" columns in Table 3.
- (7) Isomers (geometrical and optical isomers; tautomers) of clethodim and its degradates resulted in multiple HPLC peaks and streaking on the TLC plates. The isomerization of the [<sup>14</sup>C]compounds was thoroughly discussed in the Appendix.
- (8) Recovery efficiencies from fortified soil samples, and method detection limits were not reported.
- (9) The study author stated (Studies 5 and 6) that when low concentrations of clethodim are present in soil, considerable oxidation of clethodim to clethodim sulfoxide occurs during extraction. Methanol gave the lowest amount of conversion of the solvents tested, and the addition of unlabeled clethodim to the extracting solution repressed air oxidation completely.

DATA EVALUATION REVIEW

Study 7

I. Study Type: Anaerobic soil metabolism (162-2)

II. Citation:

Pack, D.E. The Anaerobic soil metabolism of [ring-4,6-<sup>14</sup>C]- Clethodim. Lab Project ID MEF-0063. Unpublished study performed and submitted by Chevron Chemical Company, Richmond CA. MRID # 410301-36

Pomidor, P. B. correspondence dated May 7, 1990 including memorandum re anaerobic soil metabolism of clethodim. submitted by Valent USA Corporation. no MRID #.

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E. B. Conerly* 6/28/90

IV. Conclusions:

- 1) The study (MRID # 410301-36) did not address the intent of the data requirement, which is to establish the behavior of the compound in flooded soil.
- 2) This study cannot be repaired by additional information, and therefore a new study is required.
- 3) The parent compound has a short half-life, and was largely degraded when "anaerobic conditions" were established.
- 4) Imine and imine sulfoxide degradates may persist -- at day 63, ca. 45% of recovered radioactivity was recognizable as clethodim derivatives.

The useful information which can be gained from the current study is described below:

- a) "Anaerobic" metabolism on dry soil appears to take a distinctly different pathway from that under aerobic conditions.
- b) Principal degradates at 31 days were clethodim imine (43.5% of applied) and clethodim imine sulfate (14.3% of applied), and do not include CO<sub>2</sub>.
- c) Degradates formed by anaerobic means may persist, as indicated by 63 day values. Clethodim imine represented 33.0% of applied material, and the imine sulfate was 11.2%.

V. Materials and Methods:

Incubation and sampling -- Fifty-gram samples of sandy loam soil (0.9% organic matter, pH 7.5)(Tables II and III) in biometer flasks was moistened to 75% of field capacity and treated at 10 ppm with ring-4,6-<sup>14</sup>C]clethodim dissolved in ethanol (radiochemical purity ≥99%; specific activity 56.5 mCi/mMole). The flasks were maintained in the dark at 25°C. Volatiles were trapped in a polyurethane foam plug and in 0.5 N sodium hydroxide. After 1 half-life (1 day) anaerobic conditions were established by flushing with nitrogen. Duplicate samples of soil were collected for analysis at 0 and 1 day (aerobic) and 30 and 63 days (anaerobic).

Extraction -- soils were extracted 1x with methanol containing unlabeled clethodim, followed by 3 extractions with clethodim-free methanol were combined. The remainder was concentrated, diluted with methanol and again concentrated. The methanol-extracted soils were further extracted 3x with clethodim-free 10 mM calcium sulfate; Extracted soils were combusted to release remaining radioactivity.

Analysis -- the detection limit appeared to be 0.1% of the applied (10 ppb).

LSC -- for total radioactivity -- soil extracts (methanol and Calcium sulfate), extracted soils after combustion, volatile trap materials

reverse-phase HPLC -- soil extracts

TLC -- soil extracts

chloroform:acetic acid (9:1)

hexane:acetone:acetic acid (50:50:1)

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

### RESULTS

The only volatile metabolite found during the aerobic phase was a small amount of CO<sub>2</sub>. CO<sub>2</sub> evolution virtually stopped under anaerobic conditions. At 1 half-life (1 day), clethodim sulfate was the only major aerobic metabolite. After 30 days in anaerobic conditions, most of the clethodim and clethodim sulfate had formed clethodim imine (not detected under aerobic conditions) and clethodim imine sulfoxide (a minor aerobic metabolite). Average recoveries ranged from 101% at day 0 to 81% at day 31. An initial study under anaerobic conditions resulted in 1 out of the 4 replicates going aerobic, as indicated by <sup>14</sup>CO<sub>2</sub> evolution. A second test was set up ... and one of the samples released 19.9 percent of the <sup>14</sup>C treatment as CO<sub>2</sub> indicating it was not anaerobic [Reviewer's emphasis added]. Essentially no <sup>14</sup>C organic volatile material was recovered in the polyurethane plug.

### CONCLUSIONS:

Under anaerobic conditions, clethodim is metabolized primarily to clethodim imine, which appears to be relatively stable (33% of applied radioactivity at day 62).

The clethodim sulfoxide that was formed under aerobic conditions goes to clethodim imine sulfoxide under anaerobic conditions.

Recoveries from the soil extraction decrease over time, seemingly due to increasing binding by the soil.

### ADDITIONAL DISCUSSION FROM CORRESPONDENCE

Guidelines do not require measuring redox potential in this study.

- 1) Lack of CO<sub>2</sub> liberation and differences in the identity and amounts of metabolites formed when compared to the aerobic study are valid measures of anaerobicity.
- 2) In the submitted study, there were at least two anaerobic samples at each sampling time. Thus results were verified.
- 3) There are only two major metabolites, clethodim imine and clethodim imine sulfoxide. No clethodim imine and only a slight amount of the clethodim imine sulfoxide are detected in the aerobic study. These are products of a reductive (anaerobic)

process and thus would not be expected to form under oxidative (aerobic) conditions. This is specific evidence of the anaerobicity of this study.

- 4) Clethodim is not persistent under anaerobic soil conditions, having a half-life between one and two weeks.
- 5) The anaerobic metabolites, clethodim imine and clethodim imine sulfoxide, are somewhat more persistent, based on this 60 day study. However, they too will completely degrade within a reasonable time frame.

VII. Reviewer's Comments:

- 1) The intent of the study is to investigate the behavior of parent compound under simulated flooding, and, for this reason, anaerobicity is to be established by a combination of flooding (waterlogging) the soil and flushing the system with nitrogen. Providing measurements of redox potential to confirm that the specimens were anaerobic is not a requirement, although that information is welcome, nor is it expected that extraordinary efforts will be made to remove the last molecule of oxygen from the system.
- 2) The absence of CO<sub>2</sub> production provides a strong indication that some samples were anaerobic, but is not necessarily definitive proof. Since one sample from each run is said *by the applicant* to have become aerobic, conditions were marginal at best.
- 3) In addition, there is potential for hydrolysis at acid pHs, and the "dry" study does not establish the rate and patterns of disappearance for the hydrolytic degradates. These degradates, clethodim oxazole and 1-chloropropen-3-ol, do not arise through metabolism but might occur under flooding.
- 4) Also, the parent compound was largely metabolized at the induction of "anaerobicity". In a new study, more information will be gained by initiating anaerobic conditions immediately.
- 5) The present data are not only difficult to interpret, they do not provide the necessary information. They do indicate a different pattern of degradation from that of aerobic studies.

VIII. CBI Information Addendum: attached

Clethodim environmental fate review

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Pages 149 through 169 are not included in this copy.

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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 product quality control procedures
  - Identity of the source of product ingredients
  - Sales or other commercial/financial information
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  - Information about a pending registration action
  - FIFRA registration data
  - The document is a duplicate of page(s) \_\_\_\_\_
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348,504 dpm/ug, Wizard Laboratories);  
**clethodim sulfoxide** (RE-45924 or SOX; ring-labeled [<sup>14</sup>C], radiochemical purity 88%, specific activity 333,670 dpm/ug);  
**clethodim sulfone** (RE-47253 or ONE; ring-labeled [<sup>14</sup>C], radiochemical purity 91%, specific activity 320,048 dpm/ug); and  
**clethodim oxazole sulfone** (RE-47797 or OXONE; ring-labeled [<sup>14</sup>C], radiochemical purity 87%, specific activity 418,963 dpm/ug).

The soil:solution slurries (2.5 g soil:5 mL of 10 mM calcium sulfate solution) were equilibrated with shaking for a total of 3 hours at 25 ± 1°C. Equilibration was established in ≤0.5 hours; an equilibration time of 1 hour was selected for the definitive study.

The definitive adsorption study was conducted in duplicate as separate experiments for [<sup>14</sup>C]clethodim and each of the three degradates at four concentrations (0.1, 0.2, 0.5, and 1 ug/mL) in 10mM calcium sulfate solutions with each of the four soils. The soil:solution slurries (2.5 g soil:5 mL solution) were shaken in centrifuge tubes at 25 ± 0.1°C for 1 hour. After the shaking period, the tubes were centrifuged and the supernatant was removed and its volume determined. Aliquots of the supernatant were analyzed by LSC for total radioactivity. Additional aliquots were analyzed for degradates using reverse-phase HPLC with radioactive flow monitoring. Because of the existence of isometric forms of clethodim and its suspected degradates, only the major peaks of the HPLC chromatograms were integrated for [<sup>14</sup>C]activity.

Desorption of the four chemicals was determined by adding 5 mL of pesticide-free 0.01 M calcium sulfate to the soil residue (from the adsorption experiments), shaking for 1 hour at 25 ± 0.1°C, centrifuging, and sampling as with the adsorption studies. The soils were then dried overnight at 50°C, ground in a mill to a fine powder, and analyzed for total radioactivity by LSC following combustion.

## RESULTS:

Ring-labeled [<sup>14</sup>C]**clethodim** (radiochemical purity 97.7%) at 0.1-1.0 ppm based on batch equilibrium studies, was determined to be very mobile in two loamy sand soils, a sandy clay loam, a sand, and a clay loam soil when equilibrated at 25°C in 1:2 soil:calcium sulfate solution slurries. Freundlich  $K_{ads}$  values were 1.57 for a high organic matter loamy sand (1.0% organic matter), 0.15 for a low organic matter loamy sand (0.4% organic matter), 0.46 for a sandy clay loam, 0.51 for a sand, and 0.08 for a clay loam soil; 1/n values were 0.49-1.90.  $K_{des}$  values were 4.15 for a high organic matter loamy sand soil and 380 (possibly an error-see discussion) for a low organic matter loamy sand;  $K_{des}$  values for the other soils were 1.40-22.60. Desorption 1/n values for all soils were 0.83-1.77.

Ring-labeled [<sup>14</sup>C]**clethodim sulfoxide** (radiochemical purity 88%), at 0.1-1.0 ppm, was determined to be very mobile in the same five soils equilibrated under similar conditions. Freundlich  $K_{ads}$  and 1/n values were 0.22 and 0.47, respectively, for a 1% organic matter loamy sand soil; respective desorption values ( $K_{des}$  and 1/n) were 1.06 and 0.66. Freundlich  $K_{ads}$  values were <0.2 for the other four soils; desorption values could not be reliably calculated because the amount of pesticide absorbed was too low to accurately evaluate its desorption.

Ring-labeled [<sup>14</sup>C]**clethodim sulfone** (radiochemical purity 91%), at 0.1-1.0 ppm, was determined to be very mobile in the same five soils equilibrated under similar conditions. Freundlich  $K_{ads}$  and 1/n values were 0.11 and 1.27, respectively, for a 1% organic matter loamy sand soil; respective desorption values ( $K_{des}$  and 1/n) were 1.37 and 0.86. Freundlich  $K_{ads}$  values were <0.1 for the other four soils; desorption

values could not be reliably calculated because the amount of pesticide absorbed was too low to accurately evaluate its desorption.

Ring-labeled [ $^{14}\text{C}$ ]clethodim oxazole sulfone (radiochemical purity 87%), at 0.1-1.0 ppm, was determined to be mobile to very mobile in the clay loam soil and very mobile in two loamy sand soils, the sandy clay loam, and the sand soil equilibrated under similar conditions. Freundlich  $K_{\text{ads}}$  values were 0.29 for a 1% organic matter loamy sand, 1.79 for a 0.4% organic matter loamy sand, 1.60 for a sandy clay loam, 1.02 for a sand, and 6.96 for a clay loam soil;  $1/n$  values were 0.82-1.09.  $K_{\text{des}}$  values were 0.72 and 3.30 for the loamy sand soils;  $K_{\text{des}}$  values for the other soils were 5.69-25.30.

#### DISCUSSION:

- (1) The guideline distinction between unaged and aged equilibrium studies may be inappropriate in the case of clethodim because the aerobic soil metabolism study indicated that clethodim is readily degraded (half-life of approximately 1 day) in the presence of soil to clethodim sulfoxide, clethodim sulfone, and clethodim oxazole sulfone; therefore, it is probable that any mobility study would produce data for a mixture of parent and degradates. The study author has apparently elected to conduct mobility studies using three soil degradates of clethodim in lieu of an aged clethodim mobility study.
- (2) In the summary data table (Table XLVIII), the study author refers to a silt loam soil. The number reference to this soil, 8149-35, is characterized as a loamy sand soil in Table II, (Soil Char's). The loamy sand classification is correct, based on the textural analysis of the soil that is reported in Table II. This soil is also incorrectly labeled as a silt loam in the Tables XI, XV, XX, XXV, XXXI, XXXV, XL, and XLV.
- (3) In Table XXXI (and XLVIII), the Freundlich  $K_{\text{des}}$  value for clethodim on soil 8149-35 (loamy sand) is presented as 380 which appears to be a computational error for the following reasons: (a) simple averaging of the individual distribution coefficients ( $K_d$  values; ug/g soil  $\div$  ug/mL solution) gives a mean value of approximately 17 which is well within an order of magnitude of a Freundlich  $K_{\text{des}}$  that would have been obtained from a regression analysis, and (b) the Freundlich  $K_{\text{des}}$  reported in Table XXIX (and XLVIII) for the other loamy sand soil (#8419-14), having similar physical characteristics, is 4.15 which is almost two orders of magnitude less than the reported value of 380 for soil #8149-35.
- (4) The range of Freundlich  $K_{\text{ads}}$  presented in the Summary (page 10 of the original report) for clethodim oxazole sulfone (RE-47797) is incorrect. The range of values should be 0.3-7.0 rather than 1.0-6.7.

DATA EVALUATION REVIEW

Study 9

I. Study Type: Field Dissipation (164-1) -- cotton in California

II. Citation:

Ho, B. Field Dissipation Study with Clethodim on Cotton in California.  
performed and submitted by Chevron Chemical Company, Richmond CA. dated  
1/23/89, received EPA under MRID # 410302-08

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E. B. Conerly*  
*6/28/90*

IV. Conclusions:

This study is acceptable and provides information on field dissipation on a cotton crop in California. The data indicate that clethodim and its degradates do not persist under these conditions.

V. Materials and Methods:

field protocol -- The cotton crop was at the 2nd square growth stage at application 1 (July 6, 1988), and at the late flowering stage at the second application (July 20, 1988). Each of four 7500 sq. ft. treated sectors of the test plot was further subdivided into 25 subplots. Samples consisting of 5 90-cm soil cores were collected as follows:

pre-treatment  
day 0-treatment 1  
day 0-treatment 2  
1, 2, 3, 4, 7, 14, 21, 28 days, 2, 3, and 4 months after treatment  
2

Specimens were taken from designated subplots according to a randomized schedule. A control plot was also sampled at each interval. Samples from each subplot were segmented by depth -- 0-5, 5-10, 10-20, 20-30, 30-50, 50-70, and 70-90 cm -- and corresponding depth segments combined. Samples were analyzed by an HPLC method which differentiates between clethodim, clethodim sulfoxide, clethodim sulfone, oxazole sulfoxide, and oxazole sulfone.

soil extraction and analysis -- Samples were analyzed by an HPLC method which differentiates between clethodim, clethodim sulfoxide, clethodim sulfone, oxazole sulfoxide, and oxazole sulfone.

Soil was extracted with methanol/water followed by partitioning into hexane, then methylene chloride. Parent clethodim partitions into hexane, and the four metabolites into methylene chloride.

Combined extracts were derivatized with diazomethane to form O-methyl ethers of clethodim, clethodim sulfoxide, and clethodim sulfone, and analyzed by HPLC.

Since clethodim forms clethodim sulfoxide after partition into hexane, this fraction was analyzed for both parent and sulfoxide and the results combined for a total clethodim value.

During freezer storage for three months, clethodim oxidizes to clethodim sulfoxide; therefore the value reported represents the combined total of these two compounds. This is considered to further demonstrate the instability of clethodim under field conditions.

The limit of detection is defined as 0.01 ppm for each compound, and the limit of quantitation set at twice this value.

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

The data from this study indicates [sic] clethodim residues are low following application of SELECT 2EC to cotton. The parent clethodim was only found at levels at or near the 0.02 ppm limit of quantitation. The major metabolite, clethodim sulfoxide, showed a maximum concentration of 0.04 ppm and quickly dissipated such that none was detected at 7 days; a half-life of 2.5 days was calculated for this degradate. The metabolites, clethodim sulfone, clethodim oxazole sulfoxide, and clethodim oxazole sulfone, were only found at levels at or below the 0.02 ppm limit of quantitation. In all cases, the 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.

VII. Reviewer's Comments:

The data support the investigator's conclusions. The complex chemistry involved in this study has been well addressed. Although the cores from each subplot were combined, there were four independent analytical samples representing the four quadrants of the test plot. We note that the statement "no vertical movement of residues was observed" does not mean that none occurred. What it probably means is that levels of residue were undetectable due to the low initial levels of clethodim applied, together with the rapid rate of metabolism of clethodim and its degradates. Laboratory studies show that leaching might be a concern if the compound were persistent.

VIII. CBI Information Addendum:

TABLE I (CONT'D)

CHEVRON  
1641-88-7226  
Page 20

TERM	CHEMICAL IDENTITY	REMARKS
Clethodim Oxazole (RE-47365)		Metabolite CAS No. 111059-49-5
Clethodim Oxazole Sulfoxide (RE-47796)		Metabolite CAS No. 111031-20-0
Clethodim Oxazole Sulfone		Metabolite CAS No. 111031-21-1

Clethodim environmental fate review

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  - Identity of product impurities
  - Description of the product manufacturing process
  - Description of product 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
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DATA EVALUATION REVIEW

Study 10

I. Study Type: Field Dissipation (164-1) -- cotton in Mississippi

II. Citation:

Ho, B. Field Dissipation Study with Clethodim on Cotton in Mississippi. performed and submitted by Chevron Chemical Company, Richmond CA. dated 1/23/89, received EPA 3/6/89 under MRID # 410302-07

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

*E.B. Conerly* 6/28/90

IV. Conclusions:

This study is acceptable and provides information on field dissipation on a cotton crop in Mississippi. The data indicate that clethodim and its degradates do not persist under these conditions.

V. Materials and Methods:

field protocol -- The cotton crop was at the fruiting stage at both applications (July 18, 1988 and August 1, 1988). Each treatment was at the rate of 0.25 lb ai/A. Each of four 625 sq. ft. treated sectors of the test plot was further subdivided into 25 subplots. Samples consisting of 5 90-cm soil cores were collected as follows:

pre-treatment  
day 0-treatment 1  
day 0-treatment 2  
1, 2, 3, 4, 7, 14, 21, 28 days and 2, 3, and 4 months after the last treatment.

Specimens were taken from designated subplots according to a randomized schedule. A control plot was also sampled at each interval. Samples from each subplot were segmented by depth -- 0-5, 5-10, 10-20, 20-30, 30-50, 50-70, and 70-90 cm -- and corresponding depth segments combined.

soil extraction and analysis -- Samples were analyzed by an HPLC method which differentiates between methyl derivatives of clethodim, clethodim sulfoxide, clethodim sulfone, oxazole sulfoxide, and oxazole sulfone.

Soil was extracted with methanol/water followed by partitioning into hexane, then methylene chloride. Parent clethodim partitions into hexane, and the four metabolites into methylene chloride.

Combined extracts were derivatized with diazomethane to form O-methyl ethers of clethodim, clethodim sulfoxide, and clethodim sulfone, and analyzed by HPLC.

Since clethodim forms clethodim sulfoxide after partition into hexane, this fraction was analyzed for both parent and sulfoxide and the results combined for a total clethodim value.

During freezer storage for three months, clethodim oxidizes to clethodim sulfoxide; therefore the value reported represents the combined

total of these two compounds. This is considered to further demonstrate the instability of clethodim under field conditions. The limit of detection is defined as 0.01 ppm for each compound, and the limit of quantitation set at twice this value.

In cases where apparent residues determined by the compound-specific method were inconsistent with those of adjacent quadrants, the "common moiety" method which detects all cyclohexane residues was also used. This would be expected to give values equal to or greater than the sum of the individual values.

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

The data from this study indicates [sic] clethodim residues are low following application of SELECT 2EC to cotton. The parent clethodim was only found at levels at or near the 0.02 ppm limit of quantitation. The major metabolite, clethodim sulfoxide, showed a maximum concentration of 0.01 ppm and quickly dissipated such that none was detected at 14 days; a half-life of 3.7 days was calculated for this degradate. The metabolites, clethodim sulfone, clethodim oxazole sulfoxide, and clethodim oxazole sulfone, were only found at levels at or below the 0.02 ppm limit of quantitation. In all cases, the 28 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.

VII. Reviewer's Comments:

The data support the investigator's conclusions. The complex chemistry involved in this study has been well addressed. Although the cores from each subplot were combined, there were four independent analytical samples representing the four quadrants of the test plot. We note that the statement "no vertical movement of residues was observed" does not mean that none occurred. What it probably means is that levels of residue were undetectable due to the low initial levels of clethodim applied, together with the rapid rate of metabolism of clethodim and its degradates. Laboratory studies show that leaching might be a concern if the compound were persistent.

VIII. CBI Information Addendum:

FIELD DISSIPATION STUDY WITH CLETHODIM  
ON COTTON IN MISSISSIPPI - T7227

LIST OF TABLES

Table I.	Nomenclature and Structures
Table II.	Residues of Clethodim in Soil.
Table III.	Residues of Clethodim Sulfoxide in Soil.
Table IV.	Residues of Clethodim Sulfone in Soil.
Table V.	Residues of Clethodim Oxazole Sulfoxide i.. Soil.
Table VI.	Residues of Clethodim Oxazole Sulfone in Soil.
Table VII.	Total Clethodim Related Residues in Soil.
Table VIII.	Soil Characteristics
Table IX.	Rainfall/Irrigation
Table X.	Recovery of Clethodim and Metabolites
Table XI.	Sample Analysis Dates

TABLE I

CHEVRON  
1641-88-7227  
Page 21

## NOMENCLATURE AND STRUCTURES

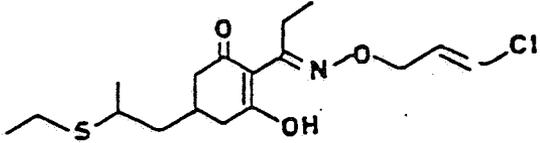
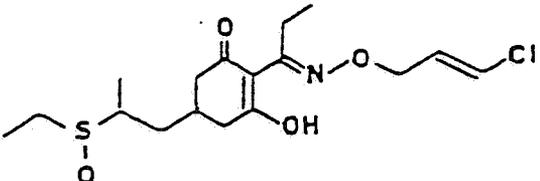
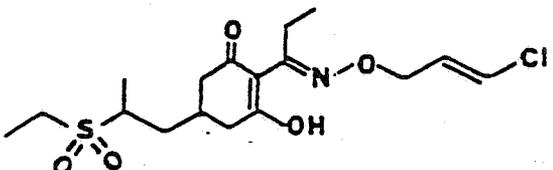
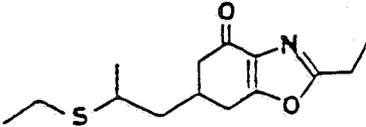
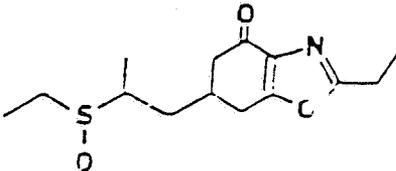
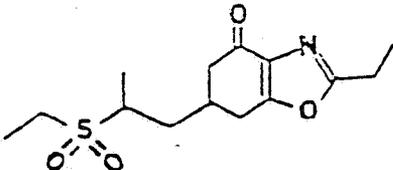
TERM	CHEMICAL IDENTITY	REMARKS
SELECT	Clethodim plus manufacturing impurities	Clethodim Technical
		
Clethodim (RE-45601)	2-[1-[[[(3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	Active Ingredient CAS No. 99129-21-2
		
Clethodim Sulfoxide (RE-45924)	2-[1-[[[(3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfinyl)propyl]-3-hydroxy-2-cyclohexen-1-one	Metabolite CAS No. 111031-14-2
		
Clethodim Sulfone (RE-47253)	2-[1-[[[(3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	Metabolite CAS No. 111031-17-5

TABLE I (CONT'D)

TERM	CHEMICAL IDENTITY	REMARKS
Clethodim Oxazole (RE-47365)		Metabolite CAS No. 111059-49-5
Clethodim Oxazole Sulfoxide (RE-47796)		Metabolite CAS No. 111031-20-0
Clethodim Oxazole Sulfone (RE-47797)		Metabolite CAS No. 111031-31-1

Clethodim environmental fate review

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DATA EVALUATION REVIEW

Study 11

I. Study Type: Confined Rotational Crop (165-1)

II. Citation:

Gaddamidi, V. Confined Rotational Crop Study of [Ring-4,6-<sup>14</sup>C]Clethodim with Carrots, Lettuce, and Wheat. performed and submitted by Chevron Chemical Company, Richmond, CA. dated 12/28/88. received EPA under MRID # 410302-11

III. Reviewer:

Typed Name: E. Brinson Conerly  
Title: Chemist, Review Section 2  
Organization: EFGWB/EFED/OPP

E.B. Conerly 6/26/90

IV. Conclusions:

The study is acceptable, and provides data on lettuce, carrots, and wheat grown as confined rotational crops. Some uptake and concentration do occur. Metabolites with structures closely related to the parent compound accounted for around 1/3 of the total radioactivity observed in the plants. The remaining labelled material may derive from the "carbon pool" of soil organic matter into which clethodim has been incorporated.

The following is speculative: Extrapolating linearly from the exaggerated rate on bare soil to ordinary application rates on a cropped field, the expected residues could be lower by a factor of 4 - 6 based on an application rate of 2 x 0.25 ppm and 1/3 to 1/2 the applied material reaching the soil. This projection predicts residues of some 4 - 140 ppb total. The three clethodim-related compounds, together representing approximately 1/3 of the total label, could be as much as 47 ppb. When this amount is divided among the 3 compounds, each individual value would be well below the level of detection of 0.05 ppm (50 ppb), the current limit of the enforcement method.

V. Materials and Methods:

field protocol -- Bare sandy loam soil was treated with the equivalent of 1 ppm [ring-4,6-<sup>14</sup>C]-Clethodim in a single application. After fallow periods of 30, 120, and 365 days in the greenhouse, crops of lettuce (leafy crop), carrot (root crop), and wheat (small grain) were planted in the treated soil. The ordinary maximum application is two postemergence treatments of 0.25 ppm (0.25 lb ai/A) for a total of 0.5 ppm. [This is intended to be a worst case situation -- EBC].

extraction and analysis

extraction of plants -- dichloromethane/methanol (DCMM 1:1), followed by methanol/water (MW 3:1). Details are attached.

extraction of soil -- methanol, for all soils other than 0-time. 0-time soils were extracted with dichloromethane and dichloromethane/methanol.

preparation for analysis

acid hydrolysis -- aqueous methanol plant extracts were refluxed with 2N HCl, saturated with NaCl and extracted 3x with ethyl acetate.

analysis

total <sup>14</sup>C -- combustion followed by LSC  
metabolites

HPLC on the extracts described above, including samples  
spiked with authentic compounds

LC/MS

TLC in chloroform/isopropyl alcohol/acetic acid (250/50/1)

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

Results:

Soil residue decreased from 1.0 ppm (>85% clethodim and 9-15% clethodim sulfate) measured immediately after application to 0.15 ppm at 30 days, 0.19 ppm at 120 days, and 0.09 ppm at 365 days. Clethodim was rapidly metabolized. At all replanting intervals, clethodim was undetectable in the soil, and at each interval a total of approximately 0.05 ppm was detected as imine sulfoxide, oxazole sulfoxide, and oxazole sulfone. The remaining radioactivity had become incorporated in soil organic matter, or mineralized.

Edible crop total residues were below 0.05 ppm except for 30-day lettuce, containing 0.08 ppm [table says 0.05 - EBC], and no further identification was done. The lettuce contained 0.025 ppm total of the three chletodim metabolites, imine sulfoxide, oxazole sulfoxide, and oxazole sulfone.

Fodder crop total residues were approximately an order of magnitude higher than those of edible crops. 40 - 70% of the <sup>14</sup>C could not be extracted by dichloromethane followed by aqueous methanol. The three metabolites mentioned above (imine sulfoxide, oxazole sulfoxide, and oxazole sulfone) were isolated at 0.06, 0.06, and 0.03 ppm respectively, accounting for roughly 1/3 of the total.

Results are summarized below:

follow crop days		total ppm <sup>14</sup> C as Clethodim	<sup>14</sup> C crop/soil
30	carrot root	0.021	0.021/0.15 = 0.14
120		0.033	0.033/0.19 = 0.17
365		0.005	0.005/0.09 = 0.05
30	lettuce leaf	0.050	0.050/0.15 = 0.33
120		0.045	0.045/0.19 = 0.24
365		0.016	0.016/0.09 = 0.17
30	wheat grain	0.025	0.025/0.15 = 0.17
120		0.012	0.012/0.19 = 0.06
356		0.021	0.021/0.09 = 0.23
30	wheat straw	0.48	0.48/0.15 = 3.20
120		0.65	0.65/0.19 = 3.42
365		0.42	0.42/0.09 = 4.67
30	wheat hulls	0.30	0.30/0.15 = 2.00
120		0.57	0.57/0.19 = 3.00
365		0.36	0.36/0.09 = 4.00

## Conclusions

The results of this study indicate that rotational crops grown in fields that had been previously planted with crops sprayed with clethodim would not take up detectable clethodim or clethodim metabolite residues. The clethodim that is not intercepted by the crop and reaches the soil would be rapidly metabolized. Minor metabolites present in the soil can be taken up by plants, but would not result in levels that could be detected by the residue enforcement method.

## VII. Reviewer's Comments:

From an application rate of 1 lb ai/A which produced soil <sup>14</sup>C residues of 0.15 ppm at 30 days post-treatment, there were residues of 0.021 - 0.48 ppm detected in various plant materials. Results were similar for the other two intervals, and were fairly consistent for a given tissue. This study shows that there is considerable uptake of radiolabelled material, but only about 1/3 of this radiolabel is parent Clethodim or closely related degradates.

### THE FOLLOWING IS SPECULATION:

If the results of this study are projected back to a normal dosage and application to a cropped plot instead of bare soil, the expected residues would be as listed below. There would probably not be measurable residues of individual clethodim derivatives even in fodder portions of wheat. However, whether these levels of residue might still have toxicological significance has not yet been determined by Tox Branch.

follow crop days		total ppm <sup>14</sup> C (calculated as Clethodim)	total <sup>14</sup> C present as Clethodim metabolites
30	carrot root	0.005	0.0016
120		0.008	0.0026
365		0.00120	0.0004
30	lettuce leaf	0.0012	0.0004
120		0.011	0.004
365		0.0040	0.0013
30	wheat grain	0.006	0.002
120		0.003	0.001
356		0.005	0.0015
30	wheat straw	0.12	0.04
120		0.16	0.06
365		0.11	0.04
30	wheat hulls	0.075	0.025
120		0.15	0.05
365		0.09	0.03

Of the possible degradative routes for Clethodim, only metabolism is rapid. Therefore, if it is applied in an ordinary manner, it could be intercepted by foliage, where it would not photolyze or hydrolyze. It could persist and reach the soil undegraded for a considerable time after the last application. For this reason, the "effective" half-life might be longer in the field than would be predicted from the laboratory studies.

## VIII. CBI Information Addendum: attached

**TABLE I. CHEMICAL NAMES, DESIGNATIONS AND STRUCTURES OF POSSIBLE CLETHODIM METABOLITES.**

DESIGNATION (RE-NUMBER)	CHEMICAL NAME	STRUCTURE
CLETHODIM (RE-45601)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFOXIDE (RE-45924)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfoxy)propyl]-3-hydroxy-2-cyclohexen-1-one	
CLETHODIM SULFONE (RE-47253)	2-[1-[(E-3-chloro-2-propenyl)oxy]-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFOXIDE (RE-47718)	2-[1-imino]propyl]-5-[2-(ethylsulfoxy)propyl]-3-hydroxy-2-cyclohexen-1-one	
IMINE SULFONE (RE-47719)	2-[1-imino]propyl]-5-[2-(ethylsulfonyl)propyl]-3-hydroxy-2-cyclohexen-1-one	
OXAZOLE SULFOXIDE (RE-47796)	6,7-dihydro-6-[2-(ethylsulfoxy)propyl]-2-ethyl-4(5H)-benzoxazolone	
OXAZOLE SULFONE (RE-47797)	6,7-dihydro-6-[2-(ethylsulfonyl)propyl]-2-ethyl-4(5H)-benzoxazolone	

TABLE II. SOIL CLASSIFICATION ANALYSIS<sup>(a)</sup>

Analysis	Results
pH	6.50
Bulk Density	1.43 g/cm <sup>3</sup>
Cation Exchange Capacity (meq/100 g)	6.50
Organic Matter (%)	0.3
Estimated Field Capacity (%)	9.00
Mechanical Analysis	
Type	Sandy loam
Sand (%)	58
Silt (%)	27
Clay (%)	15

<sup>(a)</sup> Analyses by A&L Western Agricultural Laboratories,  
1010 Carver Road, Modesto, CA. Report date:  
April 21, 1987.

Clathodim environmental fate review

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DATA EVALUATION RECORD

Studies 12 and 13 (Fish Bioaccumulation -- 165-4)

Forbis, A.D. 1987. Uptake, depuration and bioconcentration of [allyl-2-<sup>14</sup>C] and [cyclohexene-1-one-4,6-<sup>14</sup>C]RE-45601 to bluegill sunfish (*Lepomis macrochirus*). Laboratory Project ID No. S-2827. prepared by ABC Laboratories, Inc., Columbia, MO, and submitted by Chevron Chemical Co., Richmond, CA. MRID #409745-31

Rose, A.F. and J.P. Suzuki. 1988. Characterization of <sup>14</sup>C residues in bluegill sunfish treated with (allyl-2-<sup>14</sup>C)-clethodim or (cyclohexene-1-one-4,6-<sup>14</sup>C)-clethodim. Laboratory Project Identification No. MEF-0020. Unpublished study prepared and submitted by Chevron Chemical Company, Richmond, CA. STUDY ID 40974524

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REVIEWED BY:	J. Harlen	TITLE:	Staff Scientist
EDITED BY:	K. Tatten	TITLE:	Task Leader
APPROVED BY:	W. Spangler	TITLE:	Project Manager

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APPROVED BY: H. Nelson, Ph.D.  
TITLE: Chemist  
ORGANIZATION: EFGWB/EFED/OPP  
TELEPHONE: 557-2505

SIGNATURE:

---

CONCLUSIONS:

- (1) This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the accumulation of allyl- and cyclohexene-labeled [<sup>14</sup>C]clethodim in laboratory fish.
- (2) Maximum bioconcentration factors reported in terms of total <sup>14</sup>C for bluegill sunfish exposed to 0.06 ppm [<sup>14</sup>C]clethodim for 28 days at 21°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.

MATERIALS AND METHODS:

Bluegill sunfish (*Lepomis macrochirus*, mean weight 6 g, mean length 55 mm) were held in culture tanks on a 16-hour daylight photoperiod for at least 14 days prior to the initiation of the study. Flow-through aquatic exposure systems were prepared using three 100-L glass aquaria. Aerated well water (pH 7.8-8.3, dissolved oxygen 9.2-10.1 ppm, alkalinity 325-375 ppm as CaCO<sub>3</sub>, hardness 225-275 ppm as CaCO<sub>3</sub>, temperature 15-20°C; Table 1) was provided to each aquarium at a rate of 7.3 turnovers per day. The aquaria were placed in a water bath and maintained at 22 ± 2°C.

Bluegill sunfish (120) were placed in each aquarium, and one aquarium each was treated with either [allyl-2-<sup>14</sup>C] or [cyclohexene-1-one-4,6-<sup>14</sup>C]clethodim (radiochemical purities 98%; specific activities 3.73 x 10<sup>9</sup> dpm/g and 3.43 x 10<sup>9</sup>

dpm/g, respectively; Wizard Laboratories) at 0.05 ppm. The third aquarium served as an untreated control. Following a 28-day exposure period, the water in the treated aquaria was siphoned down to a depth of three inches and replaced with 70 L of uncontaminated well water (22°C). The fish were maintained in the aquaria for a 14-day depuration period. Water and fish (6, 15 or 25) were sampled from the treated and control aquaria after 0.17, 1, 3, 7, 14, 21, and 28 days of exposure. During the depuration period, water and fish were sampled on 1, 3, 7, 10, and 14 days. Water and fish samples were stored frozen at  $-10^{\circ}\text{C}$  prior to analysis.

Radioactivity in the water samples was quantified using LSC. The detection limit was 0.00077 and 0.000842 ppm for the allyl- and cyclohexene-1-one-labeled water samples, respectively. Additional water samples were taken on days 21 and 28 of the exposure period in order to characterize degradates. Aliquots (500 mL) were adjusted to pH 2-4 and extracted with methylene chloride. The aqueous fraction was saturated with sodium chloride or ammonium sulfate. The allyl-labeled samples only were extracted with diethyl ether. The aqueous fractions from both radiolabeled samples were then extracted with diethyl ether:ethanol. The methylene chloride and diethyl ether:ethanol extracts were analyzed by TLC on silica gel plates developed in chloroform:2-propanol:glacial acetic acid (250:50:1), n-hexane:acetone:glacial acetic acid (50:50:1), and chloroform:acetic acid (10:1). Following development, radioactive areas were located by autoradiography. Reference compounds were co-chromatographed with the samples and, following development, were visualized under UV light. Clethodim and its degradates were quantified by LSC of radioactive zones removed from the TLC plates following visualization. Degradate characterizations were confirmed by reverse phase HPLC. The total extraction efficiency for [cyclohexene-1-one- $4,6\text{-}^{14}\text{C}$ ]-related metabolites was reported to be >97%. The extraction efficiency for [allyl-2- $^{14}\text{C}$ ]-related metabolites using diethyl ether:ethanol was >60%.

Pooled samples (3 fish each) from each sampling interval were dissected into edible tissues (body, muscle, skin, skeleton) and nonedible tissues (fish, head, internal organs). The pooled edible and nonedible tissue samples and additional whole fish samples (3 fish/sampling interval) were analyzed for total radioactivity by LSC following combustion. For the allyl-labeled tissue samples, the detection limits for whole fish, edible tissues, and nonedible tissues were 0.0335, 0.032, and 0.0336 ppm, respectively. For the cyclohexene-1-one-labeled samples, the detection limits for whole fish, edible tissues, and nonedible tissues were 0.0364, 0.0358, 0.0358, and 0.0365 ppm, respectively.

In order to characterize clethodim and its degradates, samples of the 21- and 28-day edible, nonedible, and whole fish tissues were extracted three times with chloroform:methanol (2:1); the chloroform:methanol extracts were combined and separated using counter-current partitioning into acetonitrile and hexane fractions. Both fractions were analyzed for total radioactivity by LSC. The chloroform:methanol - extracted fish tissues were reextracted three times with methanol:water; the resulting extracts were combined and analyzed for total radioactivity by LSC. The acetonitrile and methanol:water extracts were analyzed by TLC as described above. Unextractable radioactivity remaining in the extracted tissues was quantified by LSC following combustion.

In an attempt to characterize the residual radioactivity that was present in the chloroform:methanol/methanol:water extracted tissues from the 28-day allyl-labeled and 21-day cyclohexene-labeled fish, acid hydrolysis was performed. The extracted fish tissues were further extracted with methanol:1 N hydrochloric acid (2:1) at room temperature; the resulting extract was analyzed for total radioactivity by LSC. The methanol:hydrochloric acid extracted tissues were refluxed in 6 N hydrochloric acid for six hours. The samples were centrifuged, extracted three times with ethyl acetate, and the organic extracts were combined and brought to a known volume. Total radioactivity in the ethyl acetate and aqueous acid fractions was quantified by LSC

following combustion. An aliquot of the aqueous acid solution was fortified with [cyclohexene-1-one-4,6-<sup>14</sup>C]clethodim sulfoxide and then extracted with methylene chloride. An attempt was made to adsorb radiolabel from the aqueous acid onto activated carbon. The small amount of [<sup>14</sup>C]residues present prevented further characterization of this radioactivity.

## RESULTS:

[<sup>14</sup>C]clethodim residues did not significantly accumulate in bluegill sunfish exposed to [<sup>14</sup>C]clethodim at 0.06 ppm for 28 days. Maximum bioconcentration factors were 2.1x (0.13 ppm) for the edible tissues, 4x (0.25 ppm) for the nonedible tissues, and 3.6x (0.23 ppm) for the whole fish. Allyl-labeled [<sup>14</sup>C]residues that did accumulate in the fish were depurated gradually; in contrast, cyclohexene-labeled [<sup>14</sup>C]residues that did accumulate in the fish were depurated rapidly. Despite exhaustive extraction of the tissues, no [<sup>14</sup>C]compound was isolated in sufficient quantity to permit characterization.

Total [<sup>14</sup>C]clethodim residues did not readily accumulate in bluegill sunfish during 28 days of exposure to [allyl-2-<sup>14</sup>C]clethodim at 0.06 ppm in a flow-through system maintained at 21°C. Maximum bioconcentration factors were 2.1, 4, and 3.6x in edible tissues (body, muscle, skin, skeleton), nonedible tissues (fish, head, internal organs), and whole fish, respectively. During the exposure period, accumulation of [<sup>14</sup>C]residues was greatest in nonedible tissues and was the lowest in edible tissues. Maximum concentrations of [<sup>14</sup>C]residues (observed on day 21 for all fish samples) were 0.13 ppm in edible tissues, 0.25 ppm in nonedible tissues, and 0.23 ppm in whole fish. Exhaustive extraction of the tissue samples failed to generate sufficient radioactivity for degradate characterization. Residues accumulated at day 28 were depurated gradually; at day 14 of depuration, [<sup>14</sup>C]residues were 0.06 ppm in edible tissues, 0.05 ppm in nonedible tissues, and 0.06 ppm in whole fish, representing 49% depuration in edible tissues, 75% in nonedible tissues, and 72% in whole fish.

Additional bluegill sunfish were exposed to [cyclohexene-1-one-<sup>14</sup>C]clethodim at 0.06 ppm during 28 days of exposure in a flow-through system maintained at 21°C. Total [<sup>14</sup>C]residues did not readily accumulate in the fish; maximum bioconcentration factors were 0.7, 3, and 2.3x in edible tissues (body, muscle, skin, skeleton), nonedible tissues (fish, head, internal organs), and whole fish, respectively. During the exposure period, accumulation of [<sup>14</sup>C]residues was the greatest in nonedible tissues and was the lowest in edible tissues. Maximum concentrations of [<sup>14</sup>C]residues were 0.067 ppm in edible tissues (day 3), 0.19 ppm in nonedible tissues (day 7), and 0.15 ppm (day 7) in whole fish. Exhaustive extraction of the fish samples did not generate sufficient radioactivity for degradate characterization. Residues accumulated by day 28 of the exposure period were rapidly depurated. By day 3 of the 14-day depuration period, [<sup>14</sup>C]residues were nondetectable in edible tissues (<0.0358 ppm), nonedible tissues (<0.0365 ppm), and whole fish (<0.0364 ppm), indicating rapid depuration rates in the fish tissues (>19% in edible tissues, >80% in nonedible tissues, and >70% in whole fish).

Throughout the study, the temperature of the treated water was 21°C, the pH ranged from 8.0 to 8.4, and the dissolved oxygen content ranged from 6.3 to 9.0; values were comparable to the control aquarium. During the exposure period in the treated aquarium, total [<sup>14</sup>C]residues in the water ranged from 0.058-0.073 ppm. Of the total [<sup>14</sup>C]residues in the 21-day allyl label-treated water samples, clethodim was 0.048 ppm (79%) and the degradate, clethodim sulfoxide, was 0.013 ppm (21%). In the 28-day allyl label-treated water sample, clethodim sulfoxide was 0.071 ppm (100%) of the total [<sup>14</sup>C]residues. Of the total [<sup>14</sup>C]residues in the 21- and 28-day cyclohexene label-treated water samples, clethodim was 0.038-0.040 ppm (54-60%) and the degradate, clethodim sulfoxide, was 0.021-0.024 ppm (31-34%).

## DISCUSSION:

- (1) In the original document (Study ID 40974524), the study authors suggested that the 21-day allyl-labeled fish samples may have been interchanged with the 21-day cyclohexene-1-one-labeled fish samples because the data for day 21 for both labels were inconsistent with data from other intervals. Based on the data provided in Table III, the 21-day allyl-labeled edible tissues contained nondetectable (<0.032 ppm) residues, which is inconsistent with the data provided for the 3, 7, 14, and 28-day samples, in which residues were detectable (0.047-0.120 ppm). Discrepancies were also noted for the 21-day allyl-labeled nonedible tissue and whole fish samples. Inconsistencies were noted in the cyclohexene-labeled 21-day tissue samples (Table 4); edible tissues contained 0.13 ppm total residues compared to residue levels at or below the detection limit (0.0358 ppm) for edible tissues taken at the remaining sampling intervals. Similar discrepancies were noted for the 21-day cyclohexene-labeled nonedible tissue and whole fish samples. The suggestion that the 21-day labeled samples may have been interchanged was also supported by the tissue solvent extraction data presented in Table VIII. The study authors stated while such an explanation would make the data "fit", no evidence of a sample mix-up was found by ABC Laboratories. However, since the data provided in Tables 3-6 and 8 support the likelihood that the 21-day labeled fish samples were interchanged, the data reported by this reviewer (including re-calculation of bioconcentration factors for the 21-day fish samples) reflects the assumption that the 21-day fish samples were interchanged.
- (2) Despite exhaustive extraction of the fish samples, including acid hydrolysis of the unextractable radioactivity, degradate characterization was not possible due to the low amount of radioactivity present in the samples. It appears that the registrant made sufficient attempts to identify possible degradates in the fish tissues.
- (3) Residues in the water were characterized in only the 21- and 28-day samples; it is preferable that residues in the water be characterized at more frequent sampling intervals. However, based on the hydrolysis study (Study 1, STUDY ID 40974520), clethodim degrades with a half-life of approximately 300 days; therefore, it is unlikely that significant degradation of the test substance would have occurred at the earlier sampling intervals of the exposure period.
- (4) Data from the control aquarium (water and fish) were not provided.
- (5) The mortality and general health of the treated and control fish during the study was not adequately described.
- (6) Mean recoveries for tissue sample combustion (edible tissues, nonedible tissues, and whole fish) averaged 96% for fish treated with [allyl-<sup>2</sup><sup>14</sup>C]clethodim and 98% for [cyclohexene-1-one-4,6-<sup>14</sup>C]clethodim.
- (7) Acid hydrolysis of the unextractable residues in the fish samples failed to generate radioactivity that was ethyl acetate extractable. The study authors suggested since fish have a high protein content, this radioactivity may have been incorporated into proteins (amino acids).
- (8) A preliminary study was conducted to determine the toxicity of clethodim to bluegill sunfish. The 7-day no-observed effect concentration of clethodim was 5 ppm, based on the lack of mortality and abnormal effects at this concentration. In view of these results, the study authors chose a nominal concentration of 0.05 ppm for the bioaccumulation study, (which represents 1/100 of the 7-day no-observed effect concentration). The actual concentration used in the study was 0.06 ppm.

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TABLE A -- GENERIC DATA REQUIREMENTS FOR CLETHODIM TERRESTRIAL FOOD USE

Data Requirement	Composition <sup>1</sup>	Use Pattern	Does EPA have data to satisfy this requirement	Bibliographic Citation	Must additional data be submitted?
<b>158.290 Environmental Fate</b>					
<b><u>DEGRADATION STUDIES-LAB:</u></b>					
161-1 - Hydrolysis	TGAI or PAIRA	A	Yes	409745-20	No
Photodegradation					
161-2 - In Water	TGAI or PAIRA	A	Yes	410301-33, -34	No
161-3 - On Soil	TGAI or PAIRA	A	Yes	410301-35	No
161-4 - In Air	TGAI or PAIRA	A	No		Reserved <sup>3</sup>
<b><u>METABOLISM STUDIES-LAB:</u></b>					
162-1 - Aerobic Soil	TGAI or PAIRA	A	Partial	409745-21, -22	<u>YES</u> <sup>4</sup>
162-2 - Anaerobic Soil	TGAI or PAIRA	A	Partial	410301-36	<u>YES</u> <sup>5</sup>
162-3 - Anaerobic Aquatic	TGAI or PAIRA	N.A.	No		No
162-4 - Aerobic Aquatic	TGAI or PAIRA	N.A.	No		No
<b><u>MOBILITY STUDIES:</u></b>					
163-1 - Leaching/ads/des unaged and aged	TGAI or PAIRA	A	Yes	409745-23	No
163-2 - Volatility (Lab)	TEP	A	No		Reserved <sup>3</sup>
163-3 - Volatility (Fld)	TEP	A	No		Reserved <sup>3</sup>
<b><u>DISSIPATION STUDIES-FIELD:</u></b>					
164-1 - Soil	TEP	A	Yes	410302-07, -08	No
164-2 - Aquatic (Sed)	TEP	N.A.	No		No
164-3 - Forestry	TEP	N.A.	No		No
164-4 - Cmbn/Tank Mixes	TEP	N.A.	No		No
164-5 - Soil, Long-term	TEP	N.A.	No		No
<b><u>ACCUMULATION STUDIES:</u></b>					
165-1 - Rotational Crops (Confined)	PAIRA	A	Yes	410302-11	No
165-2 - Rotational Crops (Field)	TEP	A	No		Reserved <sup>6</sup>

Tab 1

TABLE A -- GENERIC DATA REQUIREMENTS FOR CLETHODIM TERRESTRIAL FOOD USE

Data Requirement	Composition <sup>1</sup>	Use <sup>2</sup> Pattern	Does EPA have data to satisfy this requirement?	Bibliographic Citation	Must additional data be submitted?
<u>ACCUMULATION STUDIES:</u>					
165-3 - Irrigated Crops	TEP	N.A.	No		No
165-4 - In Fish	TGAI or PAIRA	A	Yes	4097545-24, -31	No
165-5 - In Aq. Nontarget	TEP		No		No
<u>158.440 Spray Drift</u>					
201-1 - Drift Field Evaluation	TEP	A	No		<u>YES</u>
202-1 - Droplet Size Spectrum	TEP	A	No		<u>YES</u>

FOOTNOTES:

- 1/ Composition: TGAI = Technical grade of the active ingredient; PAIRA = Pure active ingredient, radiolabeled; TEP = Typical end-use product.
- 2/ The use patterns are coded as follows: A = Terrestrial, Food Crop; B = Terrestrial, Non-Food; C = Aquatic, Food Crop; D = Aquatic, Non-Food; E = Greenhouse, Food Crop; F = Greenhouse, Non-Food; G = Forestry; H = Domestic Outdoor; I = Indoor.
- 3/ These data are required if the vapor pressure of the compound so indicates. The vapor pressure of Clethodim (per personal communication via M. Erumsale) is less than  $1 \times 10^{-7}$  torr @ 25° C, and therefore this requirement does not apply.
- 4/ Some degradate identification is required to make existing studies fully acceptable to fulfill guidelines.
- 5/ The soils were not flooded and it was uncertain whether anaerobic conditions actually existed in the cited study.
- 6/ The applicant should petition for a tolerance through Dietary Exposure Branch.