4-12-93

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Date out of EFGWB:

TO: S. Lewis/J. Fairfax/S. Jackson/B. Sidwell/R. Gebken
Product Manager #21/#53
Registration Division (H7505C)
Special Review and Reregistration Division (H7508W)

FROM: Paul Mastradone, Ph.D., Chief
Environmental Chemistry Review Section #1
Environmental Fate and Ground Water Branch

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

Attached, please find the EFGWB review of ...
Reg./File #:

Chemical Name: 1-[2-((2,4-dichlorophenyl)4-propyl-1,3-dioxolan-2-yl)methyl] -1H-1,2,4-triazole

Type Product: Fungicide

Common Name: Propiconazole

Company Name: Ciba-Geigy Corporation

Purpose: Phase IV review and review of environmental fate studies submitted to support the following registration actions: Section 18s and Section 24(c).

Action Code: 510/580
606

EFGWB #(s): 92- 0748/1096
92-1260/93-0234

Total Review Time: 10.1 days

EFGWB Guideline/ RID Summary Table : The review in this package contains									
161-1	42238201	162-1		163-3		165-1		166-1	
161-2	41811901	162-2		164-1		165-2		166-2	
161-3	41811902	162-3	42347902	164-2	42561501 42561502	165-3		166-3	
161-4		162-4	42347901	164-3		165-4		167-1	
201-1		163-1	41727001	164-4		165-5		167-2	
202-1		163-2		164-5					

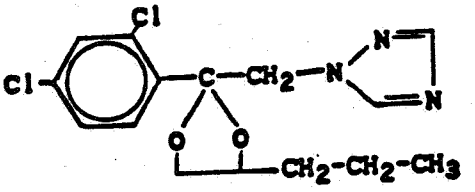
1. CHEMICAL:

Chemical name: 1-[2-((2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)-methyl]-1H-1,2,4-triazole

CAS no.: 60207-90-1

Common name: Propiconazole

Chemical structure:



Physical/Chemical properties of active ingredient:

Physical characteristics:	Colorless, odorless, viscous liquid
Molecular formula:	$C_{15}H_{18}N_3O_2Cl_2$
Molecular weight:	342.22
Vapor Pressure:	$\leq 3 \times 10^{-6}$ mm Hg at 20°C
Solubility:	110 ppm at 20°C in water
Octanol/water partition coefficient:	892

2. TEST MATERIAL:

See individual DERs.

3. STUDY/ACTION TYPE:

To review environmental fate studies submitted to support reregistration of propiconazole.

4. CITATION:

Burkhard, N. RATE OF HYDROLYSIS OF CGA-64250 UNDER LABORATORY CONDITIONS. Sponsored and Submitted by CIBA-GEIGY LIMITED, Basle, Switzerland under Project Report 07/80; Study completed 30 January 1980; Received by EPA 29 July 1981; MRID 42238201.

2

Das, Y.T. PHOTODEGRADATION OF [PHENYL(U)-^{14}C]PROPICONAZOLE IN AQUEOUS SOLUTION BUFFERED AT pH 7 UNDER ARTIFICIAL SUNLIGHT. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90070; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Protocol No. 85-90; Study completed 26 November 1990; Received by EPA 14 March 1991; MRID 41811901.

Spare, W.C. SOIL PHOTOLYSIS OF [PHENYL(U)-^{14}C]PROPICONAZOLE. Submitted by Ciba-Geigy, Greensboro, NC under Protocol No. 113-90; Performed by Agrisearch, Fredrick, MD under project No. 12194; Study completed 4 February 1991; Received by EPA 14 March 1991; MRID 41811902.

Das, Y.T. METABOLISM OF [PHENYL(U)-^{14}C]PROPICONAZOLE UNDER AEROBIC AQUATIC SOIL CONDITIONS. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90071; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Study No. 86-90; Study completed 23 May 1992; Received by EPA 10 June 1992; MRID No. 42347901.

Das, Y.T. METABOLISM OF [PHENYL(U)-^{14}C]PROPICONAZOLE UNDER ANAEROBIC AQUATIC SOIL CONDITIONS. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90072; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Study No. 87-90; Study completed 22 July 1992; Received by EPA 10 June 1992; MRID No. 42347902.

Saxena, A.M. THE ADSORPTION AND DESORPTION OF ^{14}C-PROPICONAZOLE ON REPRESENTATIVE AGRICULTURAL SOILS. Performed by Hazleton Laboratories America, Inc., Madison, WI under Laboratory Project ID: HLA 6117-140; Submitted by Ciba-Geigy Corporation, Greensboro, NC; Study completed 27 July 1988; Received by EPA 12 December 1990; MRID 41727001.

Hochman, J. 1990b. Phase 3 Summary of MRID 41727001. Propiconazole - Adsorption/desorption study: Project HLA 6117-140. Summary report prepared by Quality Associates, Inc., Ellicott City, MD, for Hazleton Laboratories America, Inc., Madison, WI.; MRID 93194056.

Krueger, H.O., Hosmer, A.J., and McIninch, S.P. DISSIPATION OF TILT IN TWO ARKANSAS RICE FIELDS. Sponsored and Submitted by Ciba-Geigy Corporation, Greensboro, NC; Performed by Wildlife International Ltd., Easton, MD and EN-CAS Analytical Laboratories, Winston-Salem, NC under Project ID 108-261; Study completed on 9 November 1992; Received by EPA 18 November 1992; MRID 42560501.

Krueger, H.O., Hosmer, A.J., and McIninch, S.P. DISSIPATION OF TILT IN TWO TEXAS RICE FIELDS. Sponsored and Submitted by Ciba-Geigy Corporation, Greensboro, NC; Preformed by Wildlife International Ltd., Easton, MD and EN-CAS Analytical Laboratories, Winston-Salem, NC under Project ID 108-262; Study completed on 6 November 1992; Received by EPA 18 November 1992; MRID 42560502.

5. REVIEWED BY:

Gail Maske
Chemist, Review section #1
OPP/EFED/EFGWB

Signature: [signature]
Date: [signature]

6. APPROVED BY:

Paul Mastradone
Chief
Review section #1
OPP/EFED/EFGWB

Signature: [signature]
Date: 12 APR 1993

7. CONCLUSIONS:

The registrant, Ciba-Geigy, submitted the following environmental fate data for review to support reregistration of propiconazole:

a. Hydrolysis (161-1)

The hydrolysis study is scientifically valid. Based on the stability of the test material at a high temperature (70°C) (plus confirmation with controls of a recent photodegradation in water study), it can be used to fulfill the hydrolysis data requirement. Furthermore, it was found acceptable in a previous review (HTA;06/17/81), but no DER was written at that time. However, the study does not meet current guidelines and normally could not be used to fulfill the data requirement for the following reasons:

Purity of the test materials (radiolabelled and non-labelled) was not furnished.

The test samples were maintained at 70°C for 28 days. Present guidelines state that a temperature of 22-25°C ± 0.5° be used. However, if the test material was stable at 70°C, it is expected stable at 22-25°C.

The pH and the sterility of the test solutions were not monitored during the testing period. However, if the test compound is stable under unsterile conditions and a pH range of ≈1 to 13, there should not be hydrolysis under sterile conditions and at pH 5, 7, and 9. The pHs were checked at 70°C prior to initiation of study.

Confirmatory analysis was not furnished.

Propiconazole appears to be stable (<5% degradation) to hydrolysis in aqueous buffered solutions at pH 5, 7, and 9 and pH 1 and 13 for 28 days. The hydrolysis studies were conducted at 70°C with propiconazole concentration of 10 ppm. The mean value of the recovered propiconazole as parent in test samples was 100 ± 3.1%.

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b. Photodegradation in water (161-2)

This study is scientifically valid and provides data on the photodegradation of the phenyl labelled propiconazole ring in water. Based on the low degradation rate (≤10% of applied radioactivity) and the present understanding of the photodegradation of propiconazole, EFGWB believes data on the triazole ^{14}C labelled ring is not needed. Therefore, no further photodegradation in water data for propiconazole are needed at this time.

Phenyl ring-labelled [^{14}C]propiconazole photodegraded slowly (≤10% of applied radioactivity) in an aqueous pH 7 solution exposed to an intermittent (12 light on/12 light off) artificial light (xenon lamp) source for 30 days at 25°C. There were no major degradates in either the light exposed or dark controls; four unidentified degradates were detected in the light exposed samples at ≤3.4% (≤0.37 ppm) of the recovered.

c. Photodegradation on soil (161-3)

This study is scientifically valid and provides data on the photodegradation of the phenyl labelled propiconazole in water. Based on the low degradation rate (<≈8% of applied radioactivity) and the present understanding of the photodegradation of propiconazole, EFGWB believes data on the triazole ^{14}C labelled ring are not needed. Therefore, no further photodegradation in water data for propiconazole is needed at this time.

Phenyl ring-labelled [^{14}C]propiconazole photodegraded slowly (<≈8% of applied radioactivity) on sandy loam soil exposed to an intermittent (12 hours on/12 hours off) artificial light (xenon lamp) source for 30 days at 25°C. In the light exposed samples, two degradates, 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl) ethanone (CGA-91304) and 1-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol (CGA-91305) were identified. These degradates were present at concentrations <10% of applied radioactivity.

d. Aerobic aquatic metabolism (162-4)

The aquatic metabolism study is scientifically valid. In addition, based on present understanding of the degradation pathway (anaerobic aquatic metabolism study, MRID 42347902) and the persistence of propiconazole ($t_{½}$=>>30 days), the study can be used to fulfill the data requirement (162-4). However, EFGWB believes that the metabolites present at concentrations ≥0.01 ppm, which the author stated could not be identified by GC/MS, can be identified by LC/MS as used in the anaerobic aquatic metabolism study.

Propiconazole had an extrapolated half-life of >>30 days when incubated under aerobic aquatic (sediment) conditions. The total concentration (in water and sediment) of parent propiconazole declined from an initial value of 94.6% to 88.79% by day 30 posttreatment. Five minor metabolites were observed using HPLC analysis. However, none of these metabolites reached concentrations greater than 2% (0.212 ppm) of

applied material. Mono-dechlorinated propiconazole was detected in the system which would suggest a dechlorination step occurred. Metabolite-5, mono-dechlorinated parent, which reached a maximum concentration of 1.8% was the only metabolite identified. There was no significant radioactivity (<0.1% of applied dose) in the volatile traps at any time during the study. The material balance was 100.3 ± 1.5%.

e. Anaerobic aquatic metabolism (162-3)

The anaerobic aquatic metabolism study is scientifically valid. In addition, it can be used to fulfill the data requirement. No further anaerobic aquatic metabolism data for propiconazole are needed at this time.

Propiconazole had a calculated half-life of 363 days when applied to an aquatic sediment system and incubated under anaerobic conditions. However, degradation appeared to slow down after the first 30 days indicating a biphasic degradation of propiconazole. The half-life calculation reported was based on the linear (kinetic) phase of the study (0 to 30 days posttreatment period).

There were no major metabolites. However, there were four minor metabolites; 1-[(2-phenyl-2-hydroxy)ethyl]-1H,1,2,4-triazole (Metabolite I), 1(2-phenyl-4-propyl-1,3-dioxalan-2-yl)-methyl alcohol (Metabolite II),1-[(2-(4-chlorophenyl)-4-hydroxymethyl-1,3-dioxalan-2-yl]methyl-1H,1,2,4-triazole (Metabolite III), and 1[((2-(4-chlorophenyl)-4-propyl-1,3-dioxalan-2-yl)methyl]-1H,1,2,4-triazole (Metabolite IV). The maximum concentration of these metabolites ranged from ≈3.6% to ≈1.5% (≤0.38 ppm) of applied test material over the 360 day posttreatment testing period. The presence of mono-dechlorinated propiconazole indicates a dechlorination step is involved during metabolism.

f. Leaching, adsorption/desorption (163-1)

This study is scientifically valid and provides data on the mobility of unaged propiconazole. Based on the following understanding of propiconazole's environmental fate, the study can be used to fulfill the unaged mobility data requirement (163-1):

a. The reported stability of propiconazole to hydrolysis, photolysis, and microbial degradation indicates that the radioactivity residue detected was unchanged parent material.

b. Previous adsorption/desorption and column leaching data (HTA; 06/17/81) suggest that propiconazole is moderately mobile to relatively immobile in most soils, as well.

Therefore, no further data on the mobility of propiconazole is needed at this time. However, data are needed on the mobility of aged propiconazole residues.

Propiconazole appears to be mobile (Kd = <5) in soils (mostly sands) with an organic matter content of ≤1.0%. In other soils propiconazole appears to be moderately mobile to relatively immobile with Kd values for silt loam, sandy loam, silty clay loam, and clay loam soils ranging

from 2.81-9.34. However, propiconazole appears to adsorb to glass (4.4 to 8.0% of applied). Adsorption of pesticide to glass may actually decrease the Kd which could make the pesticide appear to be more

mobile. Previous adsorption/desorption data (Kds ranged from 8.40 to 59.03) and column leaching data (≈80% of applied unaged and aged material found in top 8 cm of column) appear to suggest that propiconazole is moderately mobile to relatively immobile in most soils, as well.

Following desorption, 40.8-45.3% of the radioactivity that had been adsorbed to the soils was desorbed from the sand soil, 38.2-42.2% was desorbed from the silt loam soil, 23.4-32.0% from the sandy loam soil, 14.5-22.7% from the clay loam soil (Hagerstown), and 16.5-24.3% from the silty clay loam soil. Freundlich K_{des} values were 1.57 for the sand soil, 3.00 for the silt loam soil, 5.35 for the sandy loam soil, 10.3 for the clay loam soil (Hagerstown), and 10.1 for the silty clay loam soil (Arizona); respective K_{oc} values were 893, 464, 455, 703, and 1229.

g. The aquatic dissipation study is scientifically valid and provides supplemental data at this time. However, the study may be upgraded to acceptable if the registrant provides information on the identification and concentration of significant degradates (≥10% of applied and/or ≥0.01 ppm) present. These data are needed to fully understand the dissipation of propiconazole in aquatic systems.

Propiconazole was reported to dissipate from paddy water and paddy soil (≤2.4 ppb and ≤0.13 ppm by Day 28 posttreatment of second application, respectively) when aerially applied to rice paddy field plots at Walnut Ridge and Lonoke, Arkansas (AR). However, it appears that only propiconazole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at Walnut Ridge, AR were reported to be 3.4 and 6.1 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at Lonoke, AR were reported to be 5.4 and 16.1 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil. Therefore, it appears that propiconazole, which is persistent in laboratory and terrestrial field studies and is soluble in water (110 ppm in water at 20°C), may be photodegrading in the presence of a sensitizer (HTA;06/17/81) or is being diluted by irrigation water. Furthermore, propiconazole does not appear to leach through paddy soil. The concentra- in most paddy soil was <0.01 ppm at 8" throughout the testing period.

Propiconazole detected in storm drainage from the Walnut Ridge and Lonoke plots reached a maximum level of 57 and 97 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤0.01 ppb and ≤14 ppb for Walnut Ridge and Lonoke sites, respectively. Propiconazole levels in the 4-8" segment of paddy soil was ≤0.02 ppm (except for two detections, 0.17 ppm at T1 + 14 and 0.05 ppm at T2 +250 days, at the Lonoke site) at both sites. However, propiconazole was detected at slightly higher concentrations (≤0.07 and ≤0.34 ppm for Walnut Ridge and Lonoke sites, respectively) in the 0-4" soil paddy segment.

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h. The aquatic dissipation study is scientifically valid and provides supplemental data at this time. However, the study may be upgraded to acceptable if the registrant provides information on the identification and concentration of significant degradates (≥10% of applied and/or 0.01 ppm). These data are needed to fully understand the dissipation of propiconazole in an aquatic system.

Propiconazole was reported to dissipate from paddy water and paddy soil (≤13.0 ppb and ≤0.02 ppm, respectively) when aerially applied to two rice paddy field plots (B.C. and M.O.) in Bay City, TX. However, it appear that only propiconazole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at the B.C. site were reported to be 3.04 and 2.40 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at the M.O. site were reported to be 4.58 and 3.22 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil. Therefore, it appears that propiconazole, which is persistent in laboratory and terrestrial field studies and is soluble in water (110 ppm at 20°C in water), may be photodegrading in the presence of sensitizers (HTA;06/17/81) or is being diluted by irrigation water. Furthermore, propiconazole does not appear to leach through paddy soil. The concentration in most paddy soil samples was <0.01 ppm at 8"depth.

Propiconazole detected in drainage water from the B.C. and M.O. sites reached a maximum level of 26 and 149 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤2.0 ppb and ≤9.2 ppb for B.C. and M.O. sites, respectively. Propiconazole reached maximum levels of ≤0.03 ppm in the 4-8" segment of paddy soil at both sites during the testing period. However, propiconazole was detected at slightly higher concentrations (≤0.06 and ≤0.19 ppm for B.C. and M.O. sites, respectively) in the 0-4" soil paddy segment.

Environmental Fate Assessment:

Based on acceptable and supplemental environmental fate data submitted from 1986 to present, propiconazole appears to be persistent and moderately mobile to relatively immobile in most soil and aqueous environments. Propiconazole degradation appears to be dependent solely on aqueous photolysis in the presence of photo sensitizers. However, propiconazole dissipation appears to be dependent on incorportation or binding into soil organic matter content.

Laboratory and terrestrial field dissipation data indicate that propiconazole is stable in soil and aqueous environments. Propiconazole was stable to hydrolysis ($t_{1/2}$=>>30 days), aqueous photolysis (≤10% of applied degraded in 30 days), soil photolysis (<8% of applied degraded in 30 days), aerobic aquatic metabolism ($t_{1/2}$=>>30 days), aerobic soil metabolism ($t_{1/2}$=30 to 112 days), and anaerobic aquatic metabolism ($t_{1/2}$=363 days). The terrestrial field dissipation data were consistent with reported half-lives of ≥100 days for four soil textures. However, in supplemental aquatic dissipation data using basin-irrigation and flow through irrigation systems in rice fields, propiconazole was found to be dissipate rapidly

($t_{½}$=<5 days). Aqueous photolysis studies using sensitizers indicated rapid degradation ($t_{½}$=<1 day) of propiconazole which appears to be the case in rice fields. Furthermore, aquatic metabolism and dissipation studies indicate propiconazole dissipates by incorporation or binding into the organic matter content of soil/sediment.

Propiconazole mobility in soil appears to be dependent on the soil's organic matter content. In general, propiconazole appears to be moderately mobile (Kd=<5) in soils with a low organic matter content (≤1.0%). However, in soils with higher organic matter content (>1.0%), propiconazole appears to be relatively immobile (Kd=>5). Therefore, propiconazole may reach ground water in soils with low organic matter contents (e.g. pure sand). More importantly, propiconazole may contaminate surface water through off-site runoff.

There were no major metabolites because propiconazole is persistent. However, there were four minor metabolites identified in the anaerobic aquatic metabolism study; 1-[(2-phenyl-2-hydroxy)ethyl]-1H,1,2,4-triazole (Metabolite I), 1(2-phenyl-4-propyl-1,3-dioxalan-2-yl)-methyl alcohol (Metabolite II), 1-[(2-(4-chlorophenyl)-4-hydroxymethyl-1,3-dioxalan-2-yl] methyl-1H,1,2,4-triazole (Metabolite III), and 1[((2-(4-chlorophenyl)-4-propyl-1,3-dioxalan-2-yl)methyl]-1H,1,2,4-triazole (Metabolite IV). The maximum concentration of these metabolites ranged from ≈3.6% to ≈1.5% (≤0.38 ppm) of applied test material over the 360 day posttreatment testing period. The presence of mono-dechlorinated propiconazole indicates a dechlorination step is involved during metabolism. Degradates found in sensitized aqueous photolysis studies indicate the same degradation pathway. There is little data to demonstrate the rate of degradation and mobility of metabolites.

Propiconazole does not appear to accumulate in rotational crops or in bluegill fish. The BCF for the edible, viscera, and whole fish portions were 24X, 138 to 516X, and 68 to 203X, respectively.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

a. The hydrolysis, photodegradation in water, photodegradation on soil, aerobic aquatic metabolism, and anaerobic aquatic metabolism studies can be used to fulfill the respective data requirements at this time.

b. The unaged leaching, adsorption/desorption study partially fulfill the data requirement (163-1).

c. The aquatic dissipation studies (MRID 42560501 and 41560502) can not be used to fulfill the data requirement (164-2) at this time.

d. The status of the Environmental Fate Data Requirements for propiconazole for terrestrial food crop and aquatic food crop use patterns is summarized on the following page:

Environmental Fate Data Requirements		Status of data Requirement	MRID No.
Degradation Studies-lab			
161-1	Hydrolysis	Fulfilled (HTA;06/17/81) (WGM;04/06/93)	00067901 00067911 00133409 42238201
161-2	Photodegradation in water	Fulfilled (HTA;06/17/81) (WGM;04/06/93)	00067911 00133409 41811901
161-3	Photodegradation on soil	Fulfilled (HTA;06/17/81) (WGM;04/06/93)	00067902 00067908 41811902
161-1	Photodegradation in air	Not Required[1]	
Metabolism Studies-lab			
162-1	Aerobic soil	Fulfilled (AJR/10/19/89)	40424808 40963501
162-2	Anaerobic soil	Not Submitted[2]	
162-3	Anaerobic aquatic	Fulfilled[3] (AJR;06/20/89) (WGM;04/06/93)	41013001 42347902
162-4	Aerobic aquatic	Fulfilled[3] (AJR/06/20/89) (WGM;04/06/93)	41013002 42347901
Mobility Studies			
163-1	Leaching, Adsorption/ Desorption	Partially (HTA;06/17/81) (WGM;04/06/93)	00067903 00067906 00067907 41727001.
163-2	Volatility-Lab	Not Required[1]	
163-3	Volatility-field	Not Required[1]	
Dissipation Studies-field			
164-1	Soil	Fulfilled (HLB;06/20/86)	00155642 00159691
164-2	Aquatic (sediment)	Not Fulfilled[3] for rice (EBC;03/23/87) (AJR;12/15/88) (WGM/04/06/93)	40183309 42560501 42560502

Con't-- Environmental Fate Data Requirements		Status of data Requirement	MRID No.
Accumulation Studies			
165-1	Confined rotational crops	Fulfilled[4] (HLB;06/20/86) (EBC;03/23/87) (EBC;03/13/87)	00074498 00129915 00138266 00155645 00164802 41102001
165-3	Irrigation crops	Not Required (label restriction)	
165-4	in Fish	Fulfilled (AJR;10/19/89)	00069570 40963502

[1] Not required in the registration standard.

[2] The anaerobic aquatic metabolism study may be used to fulfill the anaerobic metabolism data requirement.

[3] This study is required for aquatic use patterns.

[4] The previously reviewed study, called a field rotational crop study (165-2) in the review (EBC;03/23/87), was determined to be a confined rotational crop study (165-1).

9. BACKGROUND:

General Background:

Propiconazole is a broad spectrum foliar fungicide with systemic and eradicative properties. It is a triazole derivative which is registered for use on pecans, wheatgrass, wheat, barley, rice, rye, sugarcane, bluegrass, fescue, orchardgrass, and ryegrass. Multiple applications may be made to non-bearing pecans and grasses. Applications are limited to six on bearing pecans, two on rice (depending on application rate), and one on wheat, barley, and rye. Propiconazole may be applied using ground spray equipment or aircraft.

Propiconazole is the only registered fungicide that with a single treatment to wheat can provide full control of all foliar diseases (letter of M. Newman, University of Tennessee, Inst. of Agriculture, to Ciba-Geigy Corporation, date 3 March 1989, submitted with 24C request).

There is an endangered species restriction for use of propiconazole to protect the endangered fat pocketbook pearly mussel and its habitat in Arkansas. Propiconazole use is not allowed in certain areas of Arkansas which are Mississippi, Poinsett, Cross, St. Francis, and Lee Counties.

Propiconazole is toxic to fish and aquatic life. However, the propiconazole is only slightly toxic to animals and humans.

11

10. DISCUSSION:

See individual DERs.

11: COMPLETION OF ONE-LINER:

See attached one-liner.

12: CBI APPENDIX:

N/A

ONE-LINER

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPICONAZOLE
Last Update on April 12, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer:	Section Head:	Date:

Common Name:PROPICONAZOLE
Smiles Code:
PC Code # :122101 CAS #:60207-90-1 Caswell #:

Chem. Name :1-[2-(2,4-DICHLOROPHENYL)-4-PROPYL-1,3-DIOXOLAN-2-YL-METHYL]-1H-1,2,4 TRIAZOLE
Action Type:FUNGICIDE

Trade Names:TILT; EMBOLDEN; BANNER
(Formul'tn):3.6 LB/GAL EC
Physical State:

Use :GRASS. PROPICONAZOLE IS ACTIVE ON DISEASES CAUSED BY ASCO-
Patterns :MYCETES, BASIDIOMYCETES, AND DEUTEROMYCETES
(% Usage) :
:

Empirical Form: $C_{15}H_{18}N_3O_2Cl_2$
Molecular Wgt.: 342.22 Vapor Pressure: 4.20E -7 Torr
Melting Point : °C Boiling Point: °C
Log Kow : pKa: @ °C
Henry's : E Atm. M3/Mol (Measured) 1.72E -9 (calc'd)

Solubility in ...					Comments
Water	1.10E	2	ppm	@20.0 °C	
Acetone	E		ppm	@ °C	
Acetonitrile	E		ppm	@ °C	
Benzene	E		ppm	@ °C	
Chloroform	E		ppm	@ °C	
Ethanol	E		ppm	@ °C	
Methanol	E		ppm	@ °C	
Toluene	E		ppm	@ °C	
Xylene	E		ppm	@ °C	
	E		ppm	@ °C	
	E		ppm	@ °C	

Hydrolysis (161-1)
[V] pH 5.0:STABLE (70C)
[V] pH 7.0:STABLE (70C)
[V] pH 9.0:STABLE (70C)
[ ] pH :
[ ] pH :
[ ] pH :

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPICONAZOLE
Last Update on April 12, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Photolysis (161-2, -3, -4)
[V] Water:Stable
[V] :<1 DAY WITH SENSITIZER
[ ] :
[ ] :

[V] Soil :STABLE
[ ] Air :

Aerobic Soil Metabolism (162-1)
[S] 60-80DA SI LM pH7.6 2.7%OC
[V] 10 WEEKS
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[ ]
[ ]
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Anaerobic Aquatic Metabolism (162-3)
[S] >12 wks --Swiss soil
[V] >>30 days
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[V] >>30 days
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPICONAZOLE
Last Update on April 12, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)
[V] 8.48 Lm Sd pH 7.8 2.2%OM
[V] 10.96 SAND pH 6.3 1.2%OM
[V] 26.2 Si Lm pH 6.1 3.6%OM
[V] 59.03 Sd Cl Lm pH 6.7 5.6%OM
[V] 1.2 to 9.34 in sand to clay loam soils
[ ]

Soil Rf Factors (163-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[V] 730 DA MISS. SILT LOAM pH7.1, 1.7%OM
[ ] 152 DA MISS. SILT CLAY LOAM pH7.2, 1.2%OM
[ ] 96-170 DA TX. SANDY LOAM pH7.2, 0.6%OM
[ ] 104-107 DA GA. LOAMY SAND pH6.7, 0.5%OM
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aquatic Dissipation (164-2)
[S] <6 days in rice paddies in Arkansas
[S] <5 day in rice paddies in Texas
[ ]
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

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Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[V] Residues did not accumulate in indicator rotation
[ ] crops

Accumulation in Rotational Crops, Field (165-2)
[ ]
[ ]

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[V] BLUEGILL 24X EDIB; 138-516X VISC; 68-203 WHOLE. DEPURATION
[ ] HALF-LIFE = 7 DAYS

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Small Scale Retrospective (166-2)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Large Scale Retrospective (166-3)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Miscellaneous Data (158.75)
[ ]
[ ]
[ ]

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PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
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Field Runoff (167-1)
[ ]
[ ]
[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

1,2,4-H triazole
Triazole acetic acid

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PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPICONAZOLE
Last Update on April 12, 1993
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Comments

Propiconazole is soluble in water but relatively immobile in most soils and is fairly persistent in the environment.

Nonextractables comprise up to 62% of the metabolites in laboratory soil after 1 year. Soil Koc= 100 (estimate)

References: EAB REVIEWS
Writer : PJH WGM DAW

TILT

Page 20 is not included in this copy.

Pages _____ through _____ are not included.

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TABLE OF CONTENTS

PROPICONAZOLE

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DATA EVALUATION RECORD

STUDY 1

CHEM 128834 PROPICONAZOLE §161-1

STUDY ID 42238201

Burkhard, N. RATE OF HYDROLYSIS OF CGA-64250 UNDER LABORATORY CONDITIONS. Sponsored and Submitted by CIBA-GEIGY LIMITED, Basle, Switzerland under Project Report 07/80; Study completed 30 January 1980; Received by EPA 29 July 1981.

DIRECT REVIEW TIME = 1.0 day

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 305-5245

SIGNATURE: Carl D. Maske 16 Apr '93

APPROVED BY: Paul Mastradone, Chief
Review section #1
OPP/EFED/EFGWB

Signature: Paul J. Mastradone

Date: [illegible] 1993

CONCLUSIONS:

The hydrolysis study is scientifically valid. Based on the stability of the test material at a high temperature (70°C) (plus confirmation with controls of a recent photodegradation in water study), it can be used to fulfill the hydrolysis data requirement. Furthermore, it was found acceptable in a previous review (HTA;06/17/81), but no DER was written at that time. However, the study does not meet current guidelines and normally could not be used to fulfill the data requirement for the following reasons:

Purity of the test materials (radiolabelled and non-labelled) was not furnished.

The test samples were maintained at 70°C for 28 days. Present guidelines state that a temperature of 22-25°C ± 0.5° be used. However, if the test material was stable at 70°C, it is expected to be stable at 22-25°C.

The pH and the sterility of the test solutions were not monitored during the testing period. However, if the test compound is stable under unsterile conditions and a pH range of ≈1 to 13, there should not be hydrolysis under sterile conditions and at pH 5, 7, and 9. The pHs were checked at 70°C prior to initiation of study.

Confirmatory analysis was not furnished.

Propiconazole appears to be stable (<5% degradation) to hydrolysis in aqueous buffered solutions at pH 5, 7, and 9 and pH 1 and 13 for 28 days. The hydrolysis studies were conducted at 70°C with propiconazole concentration of 10 ppm. The mean value of the recovered propiconazole as parent in test samples was 100 ± 3.1%.

MATERIALS AND METHODS:

Test Material: ^{14}C-triazolring labelled propiconazole with specific activity of 59.6μCi was used.

Reference Standards: Unlabeled propiconazole

Buffered Solution: 0.1N HCl for pH 1
0.1N NaOH for pH 13
See Table 1 for buffered solutions

Sampling: Samples were taken at 0, 7, 14, 21, and 28 days post-treatment.

Test System: Not furnished.

METHODOLOGY:

Solutions of 10 ppm ^{14}C-triazolring labelled propiconazole were prepared in the following aqueous solutions: 0.1N HCl, 0.1N NaOH, and buffered solutions of pH 5, 7, and 9, respectively. Thirty mL aliquots of each solution were transferred to separate sample flask. The sample flask were kept in thermostatically controlled water baths and shaken at a temperature of 70°C

Samples were taken at 0, 7, 14, 21, and 28 days posttreatment.

Each test sample was extracted with isopropylether. The extracted aliquots were analyzed by gas chromatograph using a borosilicate glass column filled with 10% DC-200 on gas chrom Q.

DATA SUMMARY:

Propiconazole appears to be stable (<5% degradation) to hydrolysis in aqueous buffered solutions at pH 5, 7, and 9 and pH 1 and 13 for 28 days. The hydrolysis studies were ran at 70°C with propiconazole concentration of 10 ppm. The mean value of the recovered propiconazole as parent in test samples was 100 ± 3.1%.

COMMENTS:

1. Purity of the radiolabelled and non-labelled test material was not furnished.

2. It was not clear from the submission whether the samples were analyzed immediately. Storage stability data were not furnished for test samples. However, because compound is stable, storage stability data is not an issue.

3. The test samples were maintained at a temperature of 70°C for 28 days. Present guidelines state that a temperature of 22-25°C ± 0.5° be used. However, if the test material was stable at 70°C, it is expected to be stable at 22-25°C.

4. EFGWB prefers that [^{14}]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

In this study, the samples were analyzed using GC. Reference standards were used for confirmation.

5. The pH and the sterility of the test solutions were not monitored during the testing period. Since the test compound is stable in non-sterile solutions and at a pHs range of ≈1 to 13, there should not be hydrolysis under sterile conditions and at pH 5, 7, and 9. The pHs was check at 70°C prior to initiation of study.

6. Radiolabelling position of the test material was the triazol ring. Normally EFGWB would needed data from both the phenyl ring and triazol ring labelled positions to fulfill the data requirement. However, due to the stability of the test material, EFGWB concludes that additional data is not needed to understand the environmental fate of propiconazole.

7. This study was reviewed in 1981 (HTA;06/17/81) and was determined to fulfill the data requirement because of propiconazole's stability in the photolysis system. However, no DER was written at that time.

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____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

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Y FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 2

CHEM 122101 PROPICONAZOLE §161-2

STUDY ID 41811901

Das, Y.T. PHOTODEGRADATION OF [PHENYL(U)-^{14}C]PROPICONAZOLE IN AQUEOUS SOLUTION BUFFERED AT pH 7 UNDER ARTIFICIAL SUNLIGHT. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90070; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Protocol No. 85-90; Study completed 26 November 1990;; Received by EPA 14 March 1991.

DIRECT REVIEW TIME = 9 hours

REVIEWED BY: L. Mickley TITLE: Staff Scientist

Edited BY: W. Martin TITLE: Staff Scientist
K. Ferguson Task Leader

APPROVED BY: W. Spranger TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: G. Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 305-5245

SIGNATURE: G. Maske 12 Apr '93

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study can be used to fulfill the photodegradation in water data requirement.

2. Phenyl ring-labelled [^{14}C]propiconazole photodegraded slowly (≤10% of applied radioactivity) in an aqueous pH 7 solution exposed to an intermittent (12 light on/12 light off) artificial light (xenon lamp) source for 30 days at 25°C. There were no major degradates in either the light exposed or dark controls; four unidentified degradates were detected in the light exposed samples at ≤3.4% (≤0.37 ppm) of the recovered.

3. This study is scientifically valid and provides data on the photodegradation of the phenyl labelled propiconazole ring in water. No further photodegradation in water data for propiconazole are needed at this time.

4. Based on the low degradation rate (≤10% of applied radioactivity) and the present understanding of the photodegradation of propiconazole, EFGWB believes data on the triazole ^{14}C labelled ring is not needed at this time.

METHODOLOGY:

Uniformly phenyl ring-labelled [^{14}C]propiconazole (radiochemical purity >95%, specific activity 40 μCi/mg, Ciba-Geigy), in acetonitrile, was aseptically added at 10.8 ppm to screw-cap borosilicate glass vials containing filter-sterilized (0.2 μm) aqueous buffer solution (0.02 M phosphate, pH 7). The test solutions completely filled the vials, which were sealed with Teflon-lined septa; the acetonitrile concentration was approximately 0.15% (reviewer-calculated). Twelve treated vials were placed into a photolysis chamber and irradiated on a 12-hour photoperiod (total irradiation time 360 hours) using a xenon arc lamp (Heraeus Suntest Accelerated Exposure Unit; Figure 5). The artificial light source, positioned 23 cm above the test solutions, was equipped with a glass filter to remove wavelengths <290 nm; and the irradiance was measured with a spectral radiometer at 300-8;00 nm. The xenon arc lamp had a spectral distribution comparable to that of natural sunlight (Figure 6). During the course of the study, the total intensity of the artificial light was 506.0 W/m^2. The photolysis chamber was maintained at 24.2 - 25.5 °C by means of a temperature-controlled circulating water bath (Figure 7). Twelve additional vials were prepared in an identical manner were placed in a biological incubator to serve as dark controls. Duplicate vials were removed from both the irradiated and dark control systems at 0, 1, 3, 7, 14, 21, and 30 days posttreatment.

Triplicate aliquots (10 μL) of each sample were analyzed by LSC. Additional aliquots (100μL) were analyzed by HPLC on a reverse phase RP 100A5U column eluted with a mobile phase of acetonitrile:water (50:100,v/v) using radioactivity and UV (254 nm) detection. Reference standards of proiconazole , CGS-136735, CGA-118245, CGA71019, CGA-91304, and CGA-91305 were cochromatographed with the samples. Eluant fractions from the HPLC column representing the parent peak were collected and the identity of parent propiconazole was confirmed by GC/MS. Additional aliquots from the 30-day posttreatment solutions were analyzed by two-dimensional TLC on silica gel plates developed in either chloroform:isopropanol (9:1,v/v) in the first direction and acetonitrile in the second direction, or acetonitrile:benzene (9:1,v/v) and chloroform:methanol (9:1,v/v) (Table VI). Reference standards of propiconazole, CGA-91304, CGA-91305, and CGA-118245 were cochromatographed with the samples and visualized under UV light. The [^{14}C]compounds were visualized by autoradiography. All analyses were conducted immediately following collection.

DATA SUMMARY:

Uniformly phenyl ring-labelled [^{14}C]propiconazole (radiochemical purity 95%), at 10.8 ppm, photodegraded slowly (≤10% at 30 days posttreatment) in sterile aqueous pH 7 buffered solutions that were exposed to an intermittent light source (xenon arc lamp) having a total light intensity of 506.0 Ws/m_2 at 300-800 nm for 30 days at 25 ± 1°C. [^{14}C]Propiconazole did not degrade in the dark control (Tables X and XI). In the light exposed solutions, [^{14}C]propiconazole declined from 97.9% of the recovered applied radioactivity at Day 0 posttreatment to 88.4% of the recovered applied radioactivity at Day 30 posttreatment. There were four uncharacterized degradates, none of which exceeded 3.4% (ranging from 0.11 to 0.37 ppm) of the recovered radioactivity. Additional [^{14}C]residues, classified as "other" in the data, reach a maximum of 2.0% of recovered radioactivity (Table XI).

During the study, the pH of the test solutions was 6.99-7.04. The material balances of the light exposed and dark control solutions were 94.9-104.1 and 94.9 -105.3% of the applied radioactivity, respectively (Table VII).

COMMENTS:

1. The registrant-calculated half-life of propiconazole was 249 days. Since this half-life exceeds the time limits of the study, it is of limited value. Data are often incapable of accurately predicting trends outside of their ranges because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

2. The irradiance value of the xenon arc lamp, measured at the beginning and end of the experiment, was 508.0 W/m^2 and 504.1 Wm^2, respectively. The irradiance of natural sunlight was determined to be 545.8 W/m^2 on 17 June 1990 at 11:53 AM at the performing laboratory in Piscataway, NJ (40°30' N, 74°25' W).

3. The water solubility of propiconazole was reported to be 110 ppm at 20°C.

4. The absorption spectrum (190-800 nm) of propiconazole at pH 7 is provided in Figure 3.

5. The reference standard for the possible degradate, CGA-136735, was "eventually left out of consideration since it did not meet the requirements of GLP standards".

6. To confirm sterility of the test solutions, triplicate aliquots of the time 0 and 30 Day posttreatment test samples were added to beef extract and peptone. The samples were incubated for 7 days at 25°C. The study author stated that "The test solutions were found to be devoid of any microbial contamination and remained sterile throughout the study, as

revealed by the culture tests of the solutions at 0 and 30 days post-treatment".

7. The pH of all samples was monitored during the test period.

8. The direct discrepancy ($t_{1/2}$=1 day vs ≈2545 days) between the previous photodegradation in water studies (MRID Nos. 00067911/00133409) and this study (MRID 41811901) appears to be due to a combination of the following factors in the earlier (1980) studies:

    - higher light intensity
    - lack of sterility and temperature monitoring
    - inadequate filtration of wavelengths below 290 nm (There is adsorption from 280 to 290 nm shown on the propiconazole emission spectrum.)

Title

Page_____ is not included in this copy.

Pages 34 through 45 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

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____ Description of the product manufacturing process.

____ Description of quality control procedures.

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____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 3

CHEM 122101 PROPICONAZOLE §161-3

STUDY ID 41811902

Spare, W.C. SOIL PHOTOLYSIS OF [PHENYL(U)-^{14}C]PROPICONAZOLE. Submitted by Ciba-Geigy, Greensboro, NC under Protocol No. 113-90; Performed by Agrisearch, Fredrick, MD under project No. 12194; Study completed 4 February 1991; Received by EPA 14 March 1991.

DIRECT REVIEW TIME = 9 hours

REVIEWED BY: L. Mickley TITLE: Staff Scientist

Edited BY: W. Martin TITLE: Staff Scientist
K. Ferguson Task Leader

APPROVED BY: W. Spranger TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: G. Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 305-5245

SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation on soil

1. This study can be used to fulfill the photodegradation on soil data requirement.

2. Phenyl ring-labelled [^{14}C]propiconazole photodegraded slowly (<≈8% of applied radioactivity) on sandy loam soil exposed to an intermittent (12 hours on/12 hours off) artificial light (xenon lamp) source for 30 days at 25°C. In the light exposed samples, two degradates, 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl) ethanone (CGA-91304) and 1-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol (CGA-91305) were idenfied at concentrations <10% of applied radioactivity.

3. This study is scientifically valid and provides data on the photodegradation of the phenyl labelled propiconazole ring in water. No further photodegradation in water data for propiconazole is needed at this time.

4. Based on the low degradation rate (<≈8% of applied radioactivity) and the present understanding of the photodegradation of propiconazole, EFGWB believes data on the triazole ^{14}C labelled ring is not needed.

METHODOLOGY:

Uniformly phenyl ring-labeled [^{14}C]propiconazole (radiochemical purity 99.8%, specific activity 40.0 uCi/mg, Ciba-Geigy) was added at 9.8 ppm to quartz glass test tubes containing subsamples (2 g dry weight) of sieved (2 mm) sandy loam soil (63.2% sand, 20.0% silt, 16.8% clay, 1.9% organic matter, pH 7.5, CEC 6.1 meq/100 g) moistened to 75% of 0.33 bar, and the tubes were sealed with a Teflon-coated rubber stopper. The tubes to be irradiated were placed in a sample holding tray and partially immersed in an ethylene glycol "bath". The tray was then placed on a cooling table; an ethylene glycol:water mixture was used to maintain the samples at 24.7 ± 0.9 C (Figure 2). The samples were irradiated on a 12-hour photoperiod for up to 30 days with a xenon arc lamp (Heraeus Suntest Unit); the light source, positioned 2.75 inches above the soil samples, was equipped with a filter to remove wavelengths <290 nm. The light intensity, measured over 300-800 nm, was 413.3-489.5 W/cm^2 during the course of the study. To serve as dark controls, seven additional tubes were wrapped in foil and incubated in the dark at 25 ± 1 C. Duplicate irradiated tubes and single dark control tubes were collected for analysis at 1, 2, 4, 7, 15, 21, and 30 days posttreatment; a single tube was analyzed immediately posttreatment. In addition, three tubes containing sterilized soil were treated at 10 ppm; two of these samples were irradiated as previously described and one was incubated with the dark controls. Samples were not stored prior to analysis.

At each sampling interval, hypodermic needles were inserted through the stopper and the headspace of the tubes was flushed with air; the volatile compounds were drawn by vacuum sequentially through ethylene glycol and 10% KOH trapping solutions. Aliquots of each trapping solution were analyzed by LSC.

The soil samples were extracted using a combination of three procedures to extract ≥90% of the applied radioactivity. The soil samples were initially extracted three times by sonicating with methanol:water (8:2, v:v). If needed, the extracted soil was then extracted three times by sonicating with methanol:water:acetonitrile (8:2:5, v:v:v) and/or further extracted three times by sonicating with acetone:acetonitrile (1:1, v:v). The extracts were combined and aliquots of the extracts were analyzed by LSC. Additional aliquots of the extracts were analyzed by two-dimensional TLC on silica gel plates developed in chloroform:methanol (9:1, v:v) in the first direction and in acetonitrile:toluene (9:1, v:v) in the second direction. Reference standards of propiconazole and the degradates CGA-91304, CGA-91305, and CGA-118245 were cochromatographed with the extracts. Radioactive areas were quantitated by radioscanning; the standards were located with UV light. In order to confirm the iden-

tity of propiconazole, additional aliquots of the extracts were analyzed by reverse phase HPLC using a Zorbax ODS column eluted with a linear acetonitrile:water (50:50, v:v) to 100% acetonitrile gradient, with radioactivity and UV (254 nm) detection. Subsamples of the extracted soil were analyzed by LSC following combustion. The detection limits were 0.007 ppm for the extract solutions, 0.005 ppm for the soil combustion, and 0.0004 ppm for the volatile traps.

DATA SUMMARY:

Uniformly phenyl ring-labeled [^{14}C]propiconazole (radiochemical purity 99.8%), at 9.8 ppm, degraded slowly on sandy loam soil that was exposed to an intermittent (12 hours on/12 hours off) artificial light source (xenon arc lamp) for 30 days at 24.7 $\pm$ 0.9 C. The intensity of the lamp between 300-800 nm was 413.3-489.5 W/cm^2 during the course of the study (Table III). In the light exposed samples, propiconazole was 100.0-107.3% of the applied immediately posttreatment, 96.6-103.6% at 1-7 days, and decreased to 84.7-96.4% at 30 days posttreatment. In the dark controls, propiconazole was 104.9% of the applied at 1 day posttreatment, and declined to 90.4% at 30 days posttreatment (Table VII). The degradate,

1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)ethanone (CGA-91304)

was 0.6% of the applied in the dark control at 30 days posttreatment;

1-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol (CGA-91305)

was 0.4% of the applied in one of the irradiated samples at 30 days posttreatment. Uncharacterized [^{14}C]residues ("remainder") were 1.0-2.0% in the irradiated samples at 30 days posttreatment. [^{14}C]-Compounds remaining at the origin were a maximum of 6.1% of the applied in the light exposed samples and 2.3% in the dark controls.

In the sterile samples, propiconazole was 90.8-94.1% of the applied at 30 days posttreatment. The only degradate identified in the sterile samples was CGA-91304, which was 0.7% of the applied in the dark control. Uncharacterized [^{14}C]residues were 0.8-1.9%, and [^{14}C]-compounds remaining at the origin were 2.1-2.4% of the applied.

Material balances were 100.0-111.7% for the irradiated samples and 96.0-109.3% for the dark controls.

COMMENTS:

1. The registrant-calculated half-lives of propiconazole were 150 days and 265 days for the light exposed and dark control samples, respectively. Since these half-lives exceed the time limits of the study, they are of questionable value. Data are often incapable of accu-

rately predicting trends outside of their ranges because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

2. The soil was extracted using combinations of three extraction procedures to "release ≥90% of the dosed radiocarbon". The study author did not state which extraction procedures were used for specific soil samples.

3. The study author reported that the intensity of the xenon lamp ranged from 4.1 to 4.9 x 10^{-5} W/cm^2, and stated that the intensity of natural sunlight was approximately 2.0 to 2.6 x 10-5 W/cm^2. Measurements taken with a longwave UV meter were indicated that natural sunlight and the xenon lamp were comparable. The author also stated that the 12-hour exposure period was considered to be equivalent to 1 day of natural sunlight exposure.

4. EFGWB prefers that [^{14}]residues in samples be separated by chromatoraphic methods (such as TLC, HPLC, and GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

   In this study, two dimensional TLC analysis and HPLC were used for analysis. Reference standards were used for confirmation.

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Page_____ is not included in this copy.

Pages 51 through 55 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

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DATA EVALUATION RECORD

STUDY 4

CHEM 122101 PROPICONAZOLE §162-4

STUDY ID 42347901

Das, Y.T. METABOLISM OF [PHENYL(U)-^{14}C]PROPICONAZOLE UNDER AEROBIC AQUATIC SOIL CONDITIONS. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90071; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Study No. 86-90; Study completed 23 May 1992; Received by EPA 10 June 1992.

DIRECT REVIEW TIME = 1.8 day

REVIEWED BY: G. Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 305-5245

SIGNATURE: G. Maske 12 Apr '93

APPROVED BY: Paul Mastradone, Chief
Supervisory Chemist
Review section #1
OPP/EFED/EFGWB

Signature: Paul J Mastradone

Date:

CONCLUSIONS:

The aerobic aquatic metabolism study is scientifically valid. In addition, based on present understanding of the degradation pathway (anaerobic aquatic metabolism study, MRID 42347902) and the persistence of propiconazole ($t_{1/2}$=>>30 days), the study can be used to fulfill the data requirement (162-4). However, EFGWB believes that the metabolites present at concentrations ≥0.01 ppm, which the author stated could not be identified by GC/MS, can be identified by LC/MS as used in the anaerobic aquatic metabolism study.

Propiconazole had an extrapolated half-life of >>30 days when incubated under aerobic aquatic (sediment) conditions. The total concentration (in water and sediment) of parent propiconazole declined from an initial value of 94.6% to 88.79% by day 30 posttreatment. Propiconazole did appear to readily bind to soil/sediment, as well. As the radioactivity in the aqueous phase dropped from an initial concentration of 92.8% to 10.0% of applied at 30 days posttreatment, the radioactivity in the soil extracts increased from an initial concentration of 6.5% to 84.7% of applied at 30 day posstreatment.

Five minor metabolites were observed using HPLC analysis. However, none of these metabolites reached concentrations greater than 2% (0.212 ppm) of applied material. Mono-dechlorinated propiconazole was detected in the system which would suggest a dechlorination step occurred. Metabolite-5, mono-dechlorinated parent, which reached a maximum concentration of 1.8% was the only metabolite identified. There was no significant radioactivity (<0.1% of applied dose) in the volatile traps at any time during the study. The material balance was 100.3 ± 1.5%.

MATERIALS AND METHODS:

Test Material: [Phenyl(U)-^{14}C]propiconazole with a reported specific activity of 40 μCi/mg was used. The radiochemical purity was verified by HPLC and reported to be 97.0%.

Reference Standards: See Figure 3.

The reference standards were stored in a freezer at -20°C. The parent appeared to be stable during the test period.

Test Solution: A test solution of ^{14}C-propiconazole was prepared in acetonitrile. The solution was assayed by LSC and reported to be 3.8612 μg/μL (88,800 dpm = 1 μg) ^{14}C-propiconazole.

A 55 μL aliquot of the test solution was transferred to each of the test sample's water layer (10.6 μg/mL).

Soil and Water: See Table I and II.

The Sharkey Clay soil and natural water from a flooded rice field in Washington County, Mississippi were collected by Ciba-Geigy on 28 June 1990.

Sampling: Test samples were taken for analyses at 0, 1, 3, 7, 14, 21, and 30 days posttreatment.

Trapping was performed at least once a week and at each sampling interval.

The aerobicity and microbial viability of the soil was determined at the beginning and termination of the study.

Test System: See Figure 5.

METHODOLOGY:

A Sharkey Clay soil and natural water was collected from a flooded rice field in Washington County, Mississippi. They were immediately stored in a refrige-

rator at 5°C. In addition, the physical characteristics of the soil and water were determined prior to use.

Prior to treatment with the test material the soil-water samples were acclimatized at 25°C in an incubator for 7 weeks. At termination of the acclimatized phase, the microbial viability was determined.

Individual 40 mL test vessels were used to contain the soil and water. Each test vessel contained 20 g of soil (dry weight) and a total of 20 mL of water. Fifty-five mL of test solution was into each individual test vessel which resulted in a 10.6 ppm propiconazole concentration.

There was a total of 26 test vessels: 2 for each 7 scheduled sampling intervals, 4 for the microbiological assays and aerobically measurements, and 8 for structural analysis of propiconazole and its metabolites by GC/MS.

The test vessels were individually wrapped in aluminum foil to exclude light. The wrapped test vessels were placed in a biological incubator. The incubator was maintained at 25 ± 1°C under dark conditions. The temperature was measured with an electronic thermometer and recorded every 10 minutes using data acquisition (Table IV). In addition, the temperature data was recorded manually every day (Table III).

The test vessels were collected at 0, 1, 3, 7, 14, 21, and 30 days posttreatment. Analyses were performed immediately after collection of sample. Therefore, samples were not stored prior to analyses.

LSC was used to determine radioactivity. Aliquots of soil extracts or volatile trapping solutions were mixed with liquid scintillation cocktail and counted for 5 minutes. A minimum amount of 0.34 ng of [^{14}C]propiconazole, or 0.0032% of the applied test material (0.00034 ppm) could be detected using this LSC methodology.

The headspace of each test vessel was flushed out into a series of traps comprised of ethylene glycol, 1.0N sulfuric acid and 1.0N potassium hydroxide, alternating with an empty trap (Figure 5). Traps were sampled at least once a week and at each sampling interval. Traps were sampled for 10 minutes under negative pressure with air. The radioactivity in each trap was measured by counting triplicate 1 mL aliquots with LSC.

After the headspace analysis, the test vessel was centrifuged. The water layer was decanted into a glass tube and assayed for [^{14}C]propiconazole with LSC.

The soil layer in the test vessel was extracted. Fifteen mL of methanol-water mixture (90:10;v/v) was added to the soil and agitated. The vessel was again centrifuged. The solvent/water layer was decanted into another tube. The soil was subjected to 2 more identical extractions using fresh 15 mL and 10 mL aliquots of methanol-water mixtures, respectively. The 3 extracts were combined and assayed for radioactivity by LSC.

Following the above extraction, the soil was transferred into a longer vessel and extracted with 100 mL of methanol. After centrifugation, the solvent/water was decanted into a separate vessel. The soil was then finally extracted with 60 mL of acetonitrile-water mixture (80:20;v/v). These two extracts were combined and assayed by LSC for radioactivity.

After the above extractions, the sediment portion was allowed to dry at room temperature. The unextractable radioactivity was then measured by combustion analysis on triplicate samples. After oxidation for 4 minutes, the $^{14}CO_2$ trapped in the cocktail was assayed by LSC. The BMO efficiency was determined to be 98.4%.

Separation of [^{14}C]residues found in the water layer and soil extracts of each sample was done by a reversed phase column HPLC. In addition, a mobile phase solvent was used. A solvent system of 50% acetonitrile in water to 100% acetonitrile provided separation of parent and degradates of interest. An aliquot of 100 μL of water layer or soil extract was injected into the system. The separated ^{14}C-residues were identified by retention times of ^{14}C-propiconazole and reference standards. Individual residues were quantitated by integration of area under the peak.

A detection limit of 0.01% of applied was reported by the author.

Confirmation of the identity of compounds of interest (parent and degradates) was attempted using GC/MS. Identification of compounds of interest were based on unlabeled reference standards of propiconazole and expected degradates, retention time, presence of nitrogen and chlorine, and selected ions in the spectra.

The aerobicity of the test sediment was measured with an oxygen meter. Measurements were made at the initiation and termination of the study.

The microbial population was determined by using suitable dilutions in sterile pH 7.4 buffer for lacing the culture media. Measurements were made at the initiation and termination of the study.

DATA SUMMARY:

Propiconazole had a calculated half-life of 426.8 days under aerobic aquatic (sediment) conditions. The total concentration (water and soil) of parent propiconazole declined from an initial value of 94.6% to 88.79% by day 30 posttreatment. Propiconazole did appear to readily bind to soil/sediment, as well. As the radioactivity in the aqueous phase dropped from an initial concentration of 92.8% to 10.0% of applied at 30 days posttreatment, the radioactivity in the soil extracts increased from an initial concentration of 6.5% to 84.7% of applied at 30 day posstreatment.

Five minor metabolites were observed using HPLC analysis. None of these metabolites reached concentrations greater than 2% (0.212 ppm) of applied material. However, mono-dechlorinated propiconazole was detected which would suggest a dechlorination step did occurr. Metabolite-5, mono-dechlorinated

parent, which reached a maximum concentration of 1.8% was the only metabolite identified.

The five metabolites were designated as metabolites 1, 2, 3, 4, and 5. In an attempt to identify these metabolites in the combined extracts, the extracts were concentrated using nitrogen air flow and subjected to HPLC fraction collection. The fractions representing the 5 metabolites and parent were then analyzed by isobutane-DCI-MS.

The mass spectra indicated that fraction 5, metabolite 5, was the mono-dechlorinated parent. In addition, fraction 6 was confirmed as the structure of the parent. Fractions 1, 2, 3, and 4, which represented metabolites 1, 2, 3, and 4, could not be identified. The authors attributed this to their presence at low concentrations (0.01 to 0.191 ppm).

There was no significant radioactivity (<0.1% of applied dose) in the volatile traps at any time during the study.

The test samples were aerobic throughout the study. The oxygen content values were 10.0 mg/L at the initiation of the study and 9.9 mg/L at the termination of the study.

The material balance was 100.3 ± 1.5%.

COMMENTS:

1. Only one of the five metabolites was identified. The authors attributed this to their presence at low concentrations (0.01 to 0.191 ppm). EFGWB believes that the metabolites, ≥0.01 ppm, which the author stated could not be identified by GC/MS can be identified by LC/MS as used in the anaerobic aquatic metabolism study.

2. The radioactivity in the water layer steadily dropped from 92.8% to 10.0% of applied radioactivity by 30 days posttreatment. However, the radioactivity in the soil extracts increased from 6.5% to 84.7% of applied radioactivity by 30 days posttreatment.

3. Soil samples were extracted on the same day of sampling. The soil samples and extracts were then stored in a freezer at -20°C until further extractions HPLC analyses were completed. The soil extracts were determined to contained only parent. No significant quantity of metabolites were found in the soil extracts. The maximum storage period for the extracts was 35 days. Data was submitted which indicated that propiconazole is stable for up to 35 days at -20°C.

4. The calculated half-life value of 426.8 days reported in the study is of uncertain value. The test period was 30 days. Therefore, the half-life is known to be >>30 days.

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Pages 62 through 85 are not included.

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____ Identity of product inert ingredients.

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DATA EVALUATION RECORD

STUDY 5

CHEM 122101 PROPICONAZOLE §162-3

STUDY ID 42415702

Das, Y.T. METABOLISM OF [PHENYL(U)-^{14}C]PROPICONAZOLE UNDER ANAEROBIC AQUATIC SOIL CONDITIONS. Performed by Innovative Scientific Service, Inc., Piscataway, NJ under Laboratory Study No. 90071; Submitted by Ciba-Geigy Corporation, Greensboro, NC under Study No. 87-90; Study completed 22 June 1992; Received by EPA 10 June 1992.

DIRECT REVIEW TIME = 1.8 day

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OPP/EFED/EFGWB

Signature: Paul J. Mastradone

Date: [illegible] 1993

CONCLUSIONS:

The anaerobic aquatic metabolism study is scientifically valid. In addition, it can be used to fulfill the data requirement. No further anaerobic aquatic metabolism data for propiconazole are needed at this time.

Propiconazole had a calculated half-life of 363 days when applied to an aquatic sediment system and incubated under anaerobic conditions. However, degradation appeared to slow down after the first 30 days indicating a biphasic degradation of propiconazole. The half-life calculation reported was based on the linear (kinetic) phase of the study (0 to 30 days post-treatment period). In addition, propiconazole appears to readily bind to soil/sediment. As radioactivity in the water phase dropped from an initial concentration of 93.2% to 3.1% of applied at day 360 posttreatment, the radioactivity in the soil extracts increased form an initial concentration of 6.7% to 89.3% of applied at day 360 posttreatment.

There were no major metabolites. However, there were four minor metabolites; 1-[(2-phenyl-2-hydroxy)ethyl]-1H,1,2,4-triazole (Metabolite I), 1(2-phenyl-4-propyl-1,3-dioxalan-2-yl)-methyl alcohol (Metabolite II), 1-[(2-(4-chlorophenyl)-4-hydroxymethyl-1,3-dioxalan-2-yl]methyl-1H,1,2,4-triazole (Metabolite III), and 1[((2-(4-chlorophenyl)-4-propyl-1,3-dioxalan-2-yl)methyl]-1H,1,2,4-triazole (Metabolite IV). The maximum concentration of these metabolites ranged from ≈3.6% to ≈1.5% (≤0.38 ppm) of applied test material over the 360 day posttreatment testing period. The presence of mono-dechlorinated propiconazole indicates a dechlorination step is involved during metabolism.

MATERIALS AND METHODS:

Test Material: [Phenyl(U)-^{14}C]propiconazole with a reported specific activity of 40 μCi/mg was used. The radiochemical purity was reported to be 95.8%. The test substance was stored in a freezer at -20°C.

Reference Standards: See Figure 3.

The reference standards were stored in a freezer at -20°C. They appeared to be stable during the test period as evidenced by gas chromatography which was performed at termination of the test period.

Test Solution: A test solution of ^{14}C-propiconazole was prepared in acetonitrile. The solution was assayed by LSC and reported to be 3.8612 μg/μL (88,800 dpm = 1 μg) ^{14}C-propiconazole.

A 55 μL aliquot of the test solution was transferred to each of the test sample's water layer (10.6 μg/mL).

Soil and Water: See Table I and II.

The Sharkey Clay soil and natural water from a flooded rice field in Washington County, Mississippi were collected by Ciba-Geigy on 28 June 1990.

Sampling: Test samples were taken for analyses at 0, 1, 3, 7, 14, 21, 30, 60, 120, 180, 270, and 360 days posttreatment.

Trapping was performed at least once a week and at each sampling interval.

The anaerobicity and microbial viability of the soil was determined at the beginning and termination of the study.

Test System: See Figure 5

METHODOLOGY:

A Sharkey Clay soil and natural water was collected from a flooded rice field in Washington County, Mississippi. They were immediately stored in a refrigerator at 5°C. In addition, the physical characteristics of the soil and water were determined prior to use.

Prior to treatment with the test material the soil-water samples were acclimatized at 25°C in an incubator for 7 weeks. At termination of the acclimatized phase, the microbial viability was determined.

Anaerobic conditions were established and maintained by flushing the test samples with nitrogen for 30 min/day for 7 weeks prior to treatment. Anaerobic condi-

tions were maintained posttreatment by continuing to flush the test samples once a week until termination of test. Anaerobic conditions were monitored by measuring the redox potential prior to initiation of test and at the termination of the test period.

Individual 40 mL test vessels were used to contain the soil and water. Each test vessel contained 20 g of soil (dry weight) and a total of 20 mL of water. Fifty-five mL of test solution was into each individual test vessel which resulted in a 10.6 ppm propiconazole concentration.

There was a total of 38 test vessels: 2 for each 13 scheduled sampling intervals, 4 for the microbiological assays and aerobically measurements, and 8 for structural analysis of propiconazole and its metabolites by GC/MS.

The test vessels were individually wrapped in aluminum foil to exclude light. The wrapped test vessels were placed in a biological incubator. The incubator was maintained at 25 ± 1°C under dark conditions. The temperature was measured with an electronic thermometer and recorded every 10 minutes using data acquisition (Table IV). In addition, the temperature data was recorded manually every day (Table III).

The test vessels were collected at 0, 1, 3, 7, 14, 21, 30, 60, 120, 180, 270, and 360 days posttreatment. Analyses were performed immediately after collection of sample. Therefore, samples were not stored prior to analyses.

LSC was used to determine radioactivity. Aliquots of soil extracts or volatile trapping solutions were mixed with liquid scintillation cocktail and counted for 5 minutes. A minimum amount of 0.34 ng of [^{14}C]propiconazole, or 0.0032% of the applied test material (0.00034 ppm) could be detected using this LSC methodology.

The headspace of each test vessel was flushed out into a series of traps comprised of ethylene glycol, 1.0N sulfuric acid and 1.0N potassium hydroxide, alternating with an empty trap (Figure 5). Traps were sampled at least once a week and at each sampling interval. Traps were sampled for 10 minutes under negative pressure with air. The radioactivity in each trap was measured by counting triplicate 1 mL aliquots with LSC.

After the headspace analysis, the test vessel was centrifuged. The water layer was decanted into a glass tube and assayed for [^{14}C]propiconazole with LSC.

The soil layer in the test vessel was extracted. Fifteen mL of methanol-water mixture (90:10;v/v) was added to the soil and agitated. The vessel was again centrifuged. The solvent/water layer was decanted into another tube. The soil was subjected to 2 more identical extractions using fresh 15 mL and 10 mL aliquots of methanol-water mixtures, respectively. The 3 extracts were combined and assayed for radioactivity by LSC.

Following the above extraction, the soil was transferred into a longer vessel and extracted with 100 mL of methanol. After centrifugation, the solvent/ water was decanted into a separate vessel. The soil was then finally extracted with 60 mL of acetonitrile-water mixture (80:20;v/v). These two extracts were combined and assayed by LSC for radioactivity.

After the above extractions, the sediment portion was allowed to dry at room temperature. The unextractable radioactivity was then measured by combustion analysis on triplicate samples. After oxidation for 4 minutes, the $^{14}CO_2$ trapped in the cocktail was assayed by LSC. The BMO efficiency was determined to be 98.4%.

Separation of [^{14}C]residues found in the water layer and sediment extracts of each sample was done by a reversed phase column HPLC. In addition, a mobile phase solvent was used. A solvent of 50% acetonitrile in water to 100% acetonitrile provided separation of parent and degradates of interest. An aliquot of 100 μL of water layer or sediment extract was injected into the system. The separated ^{14}C-residues were identified by retention times of ^{14}C-propiconazole and reference standards. Individual residues were quantitated by integration of area under the peak.

A detection limit of 0.01% of applied was reported by the author.

Confirmation of the identity of compounds of interest (parent and degradates) was carried out by LC/MS. Identification of compounds of interest were based on unlabeled reference standards of propiconazole and expected degradates, retention time, presence of nitrogen and chlorine, and selected ions in the spectra.

The anaerobicity of the test sediment was measured with by redox potential. Measurements were made at the initiation and termination of the study.

The microbial population was determined by using suitable dilutions in sterile pH 7.4 buffer for lacing the culture media. Measurements were made at the initiation and termination of the study.

DATA SUMMARY:

Propiconazole had a calculated half-life of 363 days when applied to an aquatic sediment system and incubated under anaerobic conditions. The presence of monodechlorinated propiconazole indicates a dechlorination step is involved during metabolism. There were no major metabolites. However, there were four minor metabolites; 1-[(2-phenyl-2-hydroxy)ethyl]-1H,1,2,4-triazole (Metabolite I), 1(2-phenyl-4-propyl-1,3-dioxalan-2-yl)-methyl alcohol (Metabolite II), 1-[(2-(4-chlorophenyl)-4-hydroxymethyl-1,3-dioxalan-2-yl]methyl-1H,1,2,4-triazole (Metabolite III), and 1[((2-(4-chlorophenyl)-4-propyl-1,3-dioxalan-2-yl) methyl]-1H,1,2,4-triazole (Metabolite IV). The maximum concentration of these metabolites ranged from ≈3.6% to ≈1.5% (≤0.38 ppm) of applied test material over the 360 day posttreatment testing period.

The applied test material appeared to migrate rapidly from the water phase to the soil phase during the first 30 days posttreatment. Only 9.1% of the applied material remained in the water phase at 30 days posttreatment (See Table VIII). The soil-bound radioactive material was extracted using extensive extraction methods. The necessity of extensive extraction methods indicated a tight binding of propiconazole to the soil clay minerals. Furthermore, the breakdown of propiconazole was linear only for days 0-30 posttreatment. De-

gradation appeared to slow down after the first 30 days indicating a biphasic degradation of propiconazole. The half-life calculation reported was based on the linear (kinetic phase) of the study (0 to 30 days posttreatment period).

There were five peaks found by HPLC radiochromatograms of the water and sediment extract phases which were designated as components 1, 2, 3, 4, and 5. In an attempt to identify these metabolites in the combined extracts, the extracts were concentrated using nitrogen air flow and subjected to HPLC fraction collection. The fractions representing the 5 metabolites and parent were then analyzed by isobutane-DCI-MS. However, only the parent fraction could be structurally confirmed based on the MS. No meaningful MS were obtained from the metabolite fractions, presumably due to their low concentration in the fractions. They were identified by LC-MS using the same analytical column and chromatographic conditions as employed for HPLC. Therefore, the metabolites confirmation was based on their retention time and their MS. Metabolite IV was determined to an isomer of Component 4 and 5.

There was no significant radioactivity (<0.01% of applied dose) in the volatile traps at any time during the study.

The test samples were anaerobic throughout the study. The redox potential of the test samples at the initiation and termination of the study were -274 and -275, respectively.

The material balance was 99.6 ± 1.4% (Table VIII). This represented a drop from 93.2% to 3.1% of applied material in the water phase which corresponded to an increase from 6.7% to 89.3% in the sediment phase from days 0-360, respectively.

COMMENTS:

1. Only the parent could be confirmed by GC/MS. The authors attributed this to the presence of metabolites at low concentrations 90.06 to 0.382 ppm). However, structural confirmation was obtained by LC/MS.

2. The radioactivity in the water layer steadily dropped from 93.2% to 3.1% of applied radioactivity by 360 days posttreatment. However, the radioactivity in the sediment extracts increased from 6.7% to 89.3% of applied radioactivity by 30 days posttreatment.

3. Soil samples were extracted on the same day of sampling. The soil samples and extracts were then stored in a freezer at -20°C until further extractions HPLC analyses were completed. The maximum storage period for the extracts was 35 days. Data was submitted which indicated that propiconazole is stable for up to 35 days at -20°C. The data indicated that propiconazole is stable under anaerobic aquatic conditions for up to 1 year.

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Pages 92 through 121 are not included.

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____ Description of the product manufacturing process.

____ Description of 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.

____ Information about a pending registration action.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 6

CHEM 122101 Propiconazole §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41727001
Saxena, A.M. THE ADSORPTION AND DESORPTION OF ^{14}C-PROPICONAZOLE ON REPRESENTATIVE AGRICULTURAL SOILS. Performed by Hazleton Laboratories America, Inc., Madison, WI under Laboratory Project ID: HLA 6117-140; Submitted by Ciba-Geigy Corporation, Greensboro, NC; Study completed 27 July 1988; Received by EPA 12 December 1990.

STUDY ID 93194056
Hochman, J. 1990b. Phase 3 Summary of MRID 41727001. Propiconazole - Adsorption/desorption study: Project HLA 6117-140. Summary report prepared by Quality Associates, Inc., Ellicott City, MD, for Hazleton Laboratories America, Inc., Madison, WI.

DIRECT REVIEW TIME = 12

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SIGNATURE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study can be used to partially fulfill the mobility data requirement at this time.

2. Propiconazole appears to be mobile (Kd = <5) in soils (mostly sands) with an organic matter content of <1.0%. In other soils propiconazole appears to be moderately mobile to relatively immobile with Kds values for silt loam, sandy loam, silty clay loam, and clay loam soils ranging from 2.81-9.34. However, propiconazole appears to adsorb to glass (4.4 to 8.0% of applied). This condition may actually decrease the Kd which could make the pesticide appear to be more mobile. Previous adsorption/desorption data (Kds ranged from 8.40 to 59.03) and column leaching data (most of unaged and aged material found in top 8 cm (≈80% of applied) of column) appear to suggest that propiconazole is moderately mobile to relatively immobile in most soils.

3. This study is scientifically valid and provides data on the mobility of unaged propiconazole. Based on the following understanding of propiconazole's environmental fate, the study can be used to fulfill the unaged mobility data requirement (163-1):

   a. The reported stability of propiconazole to hydrolysis, photolysis, and microbial degradation indicates that the radioactivity residue detected was unchanged parent material.

   b. Previous adsorption/desorption and column leaching data (HTA; 06/17/81) suggest that propiconazole is moderately mobile to relatively immobile in most soils, as well.

4. Data are needed on the mobility of aged propiconazole residues.

METHODOLOGY:

Sand, silt loam, sandy loam, silty clay loam (Arizona), and clay loam (Hagerstown) soils (Table A) were air-dried and sieved (2 mm). Based on the results of a preliminary study, a 1:5 soil:solution ratio and a 24-hour equilibration period were selected for use in the definitive study. In a separate experiment, it was determined that propiconazole adsorbed slightly to glass.

For the definitive study, portions (approximately 2 g) of the sieved, air-dried soils were weighed into duplicate glass culture tubes. Aliquots (10 mL) of aqueous 0.01 M calcium nitrate solution containing uniformly triazole ring-labeled [^{14}C]propiconazole (radiochemical purity 97.7%, specific activity 52.1 uCi/mg, Ciba-Geigy) plus nonlabeled propiconazole (purity not reported) at 0.496, 1.01, 5.01, or 10.0 ug/mL were added to the tubes. The tubes were sealed with Teflon-lined screw-caps, and placed on a shaker for 24 hours at "approximately" 25 C. Following equilibration, the samples were centrifuged and an aliquot (7 mL) of the supernatant was removed; duplicate aliquots (1 mL) were analyzed by LSC.

To measure desorption, pesticide-free calcium nitrate solution (7 mL) was added to the tubes. The tubes were capped, and the samples were

equilibrated for 24 hours at "approximately" 25 C. Following equilibration, the samples were centrifuged. Duplicate aliquots (1 mL) of the supernatant were analyzed by LSC.

DATA SUMMARY:

Based on batch equilibrium studies, uniformly triazole ring-labeled [^{14}C]propiconazole (radiochemical purity 97.7%) was determined to be mobile (in soil with O.M. = <1.0%) to relative immobile (in soils with >1.0% O.M.) in sand, silt loam, sandy loam, silty clay loam, and clay loam soil:solution slurries (1:5) that were equilibrated for 24 hours at 25 C. Freundlich K_{ads} values were 1.20 for the sand soil, 2.81 for the silt loam soil, 4.49 for the sandy loam soil, 8.88 for the clay loam soil (Hagerstown), and 9.34 for the silty clay loam soil (Arizona); respective K_{oc} values were 685, 436, 382, 604, and 1134 (Table 6).

Following desorption, 40.8-45.3% of the radioactivity that had been adsorbed to the soils was desorbed from the sand soil, 38.2-42.2% was desorbed from the silt loam soil, 23.4-32.0% from the sandy loam soil, 14.5-22.7% from the clay loam soil (Hagerstown), and 16.5-24.3% from the silty clay loam soil (Arizona; Table 5). Freundlich K_{des} values were 1.57 for the sand soil, 3.00 for the silt loam soil, 5.35 for the sandy loam soil, 10.3 for the clay loam soil (Hagerstown), and 10.1 for the silty clay loam soil (Arizona); respective K_{oc} values were 893, 464, 455, 703, and 1229 (Table 6).

COMMENTS:

1. EFGWB prefers that [^{14}]residues in samples be separated by chromatoraphic methods (such as TLC, HPLC, and GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

   In this study, only LSC analysis was performed.

   Based on the reported stability of propiconazole to hydrolysis, photolysis, and microbial degradation, EFGWB believes the radioactivity found was unchanged parent material.

2. Material balances were not reported; the author of the Phase 3 Summary (MRID 93194056) stated that the material balance information was not received at the time of submission.

3. A preliminary study was conducted to determine the adsorption of propiconazole to glass. In the preliminary study, adsorption was 4.4-8.0%; in the definitive study, adsorption ranged from 4.7% to 7.0%. The study author stated that the adsorption to glass was

independent of the concentration of test material used. It was unclear if the results from the definitive experiment were corrected for adsorption to the glass. This adsorption to glass could result in lower Kds which would make the pesticide appear to be more mobile.

4. The soil classified by the study author as a Hagerstown silty clay soil (Table A) should be classified as a clay loam soil according to the USDA Soil Textural Analysis System; therefore, the soil is referred to as a clay loam in this review. This is consistent with the other soil texture classifications used in this study. However, it should be noted that soil texture classification does not indicate texture of surface soil.

5. The detection limit for the LSC analyses was not reported.

6. The solubility of propiconazole in water was reported to be 110 mg/L at 20 C.

7. The purity of nonlabeled propiconazole was not reported.

8. The silty clay loam soil (Arizona) was not available for the preliminary studies.

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Pages 127 through 135 are not included.

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____ Identity of product inert ingredients.

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DATA EVALUATION RECORD

STUDY 7

CHEM 128834 PROPICONAZOLE §164-2

STUDY ID 42560501

Krueger, H.O., Hosmer, A.J., and McIninch, S.P. DISSIPATION OF TILT IN TWO ARKANSAS RICE FIELDS. Sponsored and Submitted by Ciba-Geigy Corporation, Greensboro, NC; Performed by Wildlife International Ltd., Easton, MD and EN-CAS Analytical Laboratories, Winston-Salem, NC under Project ID 108-261; Study completed on 9 November 1992; Received by EPA 18 November 1992.

DIRECT REVIEW TIME = 2.5 days

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CONCLUSIONS:

The aquatic dissipation study is scientifically valid and provides supplemental data at this time. However, the study may be upgraded to acceptable if the registrant provides information on the identification and concentration of significant degradates (≥10% of applied and/or ≥0.01 ppm) present. These data are needed to fully understand the dissipation of propiconazole in aquatic systems.

Propiconazole was reported to dissipate from paddy water and paddy soil (≤2.4 ppb and ≤0.13 ppm by Day 28 posttreatment of second application, respectively) when aerially applied to rice paddy field plots at Walnut Ridge and Lonoke, Arkansas (AR). However, it appears that only propiconazole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at Walnut Ridge, AR were reported to be 3.4 and 6.1 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at Lonoke, AR were reported to be 5.4 and 16.1 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil. Therefore, it appears that propiconazole, which is persistent in laboratory and terrestrial field studies and is soluble in water (110 ppm in water at 20°C), may be photodegrading in the presents of a sensitizer (HTA;06/17/81). Furthermore, propiconazole does not appear to leach through paddy soil. The concentration in most paddy soil samples was <0.01 ppm at 8" during the testing period.

Propiconazole detected in storm drainage from the Walnut Ridge and Lonoke plots reached a maximum level of 57 and 97 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤0.01 ppb and ≤14 ppb for Walnut Ridge and Lonoke sites, respectively. Propiconazole levels in the 4-8" segment of paddy soil was ≤0.02 ppm (except for two detections, 0.17 ppm at T1 + 14 and 0.05 ppm at T2 +250 days, at the Lonoke site) at both sites. However, propiconazole was detected at slightly higher concentrations (≤0.07 and ≤0.34 ppm for Walnut Ridge and Lonoke sites, respectively) in the 0-4" soil paddy segment.

MATERIALS AND METHODS:

Test Material: Tilt 3.6E (end-product)

Reference Standards: Unlabeled propiconazole

Soil: See Table 1

Water: DO ranged from 3.0 to 15.0 ppm for the Walnut Ridge site
DO ranged from 1.6 to 12.6 ppm for Lonoke site

Temperature ranged from 21.5°C to 33.5°C for the WR site
Temperature ranged from 16.0°C to 32.0°C for the LO site

pH averaged 7.69 for the WR site
pH averaged 7.07 for the LO site

METHODOLOGY:

Two sites, Walnut Ridge and Lonoke, were chosen in Arkansas for this aquatic dissipation study. The static irrigation system, the silt (48%) content, and the elevation (≈220 ft.) of the sites made it different from the sites chosen for the Texas study (MRID 42560502). Both the Walnut Ridge and Lonoke site where considered level low-lands by the authors.

The Walnut Ridge test site was ≈26 acres which was subdivided by 7 levees. The soil texture of the site ranged from loam to clay loam to silt loam with bedrock at 72 ft. In order to avoid dilution of test material and contamination of untreated areas, water flow was restricted as much as possible. Typical Arkansas basin irrigation was used with the water being supplied from a 25' well. The site was situated so that fluctuation in water level were minimized and discharge of treated water could be monitored in the drainage ditch.

In the treated levee was established a grid of sampling stations, as well. Sixty soil and water sampling stations were established in three rows of twenty. There was ≈25 ft. between stations and ≈50 ft. between rows. These grids were arranged in such a way to minimized variability of pesticide residues between sampling locations. During the testing period, each location was sampled one time only.

The Lonoke test site was ≈80 acres which was subdivided by 7 levees. The soil texture of the site was determined to be loam throughout the entire 48" sampling core. Again, in order to minimize dilution of test material and contamination of untreated areas, water flow was restricted as much as possible. Irrigation water was supplied from five 150-250 ft ground wells and water pumped from the White Oak Branch of two Prairie Bayou. However, a well located in the field near the treated plot served as the primary water source.

In the treated levee was established a grid of sampling stations, as well. Sixty soil and water sampling stations were established with ≈25 ft. between stations in a row and between rows. However, the number of stations in a row varied due to plot shape and limitations of application of test material. In addition, grids were arranged in such a way to minimized variability of pesticide residues between sampling locations.

Four sampling stations were established at each testing site for monitoring of dissolved oxygen, pH, and temperature of the water phase at each testing site. In addition, three soil and water sampling stations were established for monitoring the discharge ditch.

Control plots for the Walnut Ridge and Lonoke sites were located in a separated area than the treated plot. In addition, the control plots had separate water drainage from their corresponding treatment plot. There were fifteen soil/water sampling stations established on each control plot.

Propiconazole was aerially applied twice to the Walnut Ridge site. Each application was half the maximum labelled application rate per season for rice (0.169 lb ai/acre). The Lonoke site was treated twice at 2X the maximum labelled application rate per season (0.675 lb ai/acre) using aerially application. The 2X application rate was used to ensure that discernible residue levels were present.

Samples of the undiluted Tilt (propiconazole formulation used) were collected for analysis prior to each application. In addition, samples of the tank mixture were collected for analysis prior to and at termination of application of the Tilt formulation. Furthermore, spray deposition was monitored during each application using mounted disposition cards. Sixteen sampling stations were established at the Walnut Ridge site, whereas, twenty sampling stations were established at the Lonoke site.

Soil samples were collected at random from among the 60 stations. At each station ten cores were taken in 46 cm x 5 cm cellulose acetate tubes. Two methods of collecting the soil cores were used depending on water and soil content. From 0-day posttreatment to approximately 180 days posttreatment (second application), soil cores were taken to a depth of 25 cm. The ten cores samples at a given station were collected in roughly a 5 foot radius circle around the station. If there was water in the tube, the water was drained from the tubes through punctured holes.

For discharge ditch, five cores were taken at each sampled station for analysis. These cores were taken in roughly a 5 foot radius circle of the drainage ditch station, as well.

Ten soil cores were collected from each treated site to a depth of 75 cm at ≈200 day posttreatment (second application) to termination of study. These samples did not require water drainage since they were collected after paddy drainage.

Water samples were collected similarly to the soil samples at both treated sites. Three stations were samples at random at each sampling interval. Water samples were taken prior to soil sample collection in order to avoid sediment in water samples. Approximately 1.3 liters of water were collected at each sampling station. The final water samples were collected at 28 days posttreatment (second application) on each site.

One liter water samples were collected from discharge ditch. Four sample bottles were used at each sampling interval.

Water temperature, dissolved oxygen, and pH were measured in the treated site and discharge ditch at each sampling interval. Four stations were established around each treated site. Samples from the discharge ditch were taken at the 0 yard, 50 yard, and 100 yard of sapling stations. However, additional samples were collected at the discharge stations during field drainage.

Samples were stored and shipped frozen until analysis. Water samples were analyzed by reversed phase GC analysis. Analysis of spray card were performed by solvent extraction followed by GC analysis. However soil/sediment samples were analyzed by GC and HPLC. The detection limits were 1 ppb in water and 10 ppb in soil/sediment samples.

In addition, to the other monitoring during the testing period, flow monitoring and weather monitoring were reported for the testing period.

DATA SUMMARY:

Propiconazole was reported to dissipate from paddy water and paddy soil (≤32.0 ppb and ≤0.15 ppm by Day 28 posttreatment of second application, respectively) when aerially applied to rice paddy field plots at Walnut Ridge and Lonoke, Arkansas (AK). However, it appear that only propiconazole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at Walnut Ridge, AK were reported to be 3.4 and 6.1 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at Lonoke, AK were reported to be 5.4 and 16.1 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil.

Propiconazole detected in storm drainage from the Walnut Ridge and Lonoke plots reached a maximum level of 57 and 97 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤0.01 ppb and ≤14 ppb for Walnut Ridge and Lonoke sites, respectively. Propiconazole levels in the 4-8" segment of paddy soil was ≤0.02 ppm (except for two detections, 0.17 ppm at T1 + 14 and 0.05 ppm at T2 +250 days, at the Lonoke site) at both sites. However, propiconazole was detected at slightly higher concentrations (≤0.07 and ≤0.34 ppm for Walnut Ridge and Lonoke sites, respectively) in the 0-4" soil paddy segment.

Water residue values and discharge values reached ≈200 ppb on day 1 posttreatment (first application) at the Lonoke site. However, by day 13 posttreatment, the propiconazole residues had declined to 1.5 ppb. Residues reached 122 ppb at day 1 posttreatment (second application). By day 28 posttreatment (second application), they had declined to 32 ppb. The Walnut Ridge site had similar results reported in comparison to application rates. Residues levels of 61 ppb and 45 ppb for Day 1 and 2.4 ppb and 1.9 ppb for Day 13 and Day 28 posttreatment for first and second application, respectively.

For the eleven on-site sediment fortifications from the Walnut Ridge site the recoveries were 75% ± 6.7%. These fortified samples were stored for 575 days prior to analysis. For two on-site water fortifications from the Walnut Ridge site the recoveries were 81% ± 6.7% when stored for 245 days. Water fortifications from the Lonoke site had recoveries of 75% when stored for ≈240 days.

COMMENTS:

1. The chromatographies and Tables furnished by the analytical laboratory indicate that only parent propiconazole was analyzed for all the samples. However, tables furnished by the authors reported the results as propiconazole residues for all samples. Even though at the Lonoke site a 2X application rate was used to obtain discernible propiconazole residues, degradates were not address at either site.

   In order to fully understand the degradation and dissipation of propiconazole in an aquatic system, propiconazole degradates discernible (if discernible at concentrations ≥0.01 ppb) in paddy water, paddy soil/sediment, and discharge drainage systems should be determined. Propiconazole residues were determined and identified in the anaerobic aquatic study using LC/MS.

2. EFGWB prefers that [^{14}]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

   In this study, the samples were analyzed using GC and/or HPLC.

3. No sediment fortification samples were collected from the Lonoke to determine the storage stability of those samples. The authors believed that the Walnut Ridge storage stability data was sufficient. Data indicates that all samples were analyzed within 575 days for soil/sediment samples and ≈240 days for water samples.

4. The analytical laboratory stated that the formulation and tank mix samples were not analyzed.

TILT

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____ Identity of product impurities.

____ Description of the product manufacturing process.

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DATA EVALUATION RECORD

STUDY 8

CHEM 128834 PROPICONAZOLE §164-2

STUDY ID 42560502

Krueger, H.O., Hosmer, A.J., and McIninch, S.P. DISSIPATION OF TILT IN TWO TEXAS RICE FIELDS. Sponsored and Submitted by Ciba-Geigy Corporation, Greensboro, NC; Preformed by Wildlife International Ltd., Easton, MD and EN-CAS Analytical Laboratories, Winston-Salem, NC under Project ID 108-262; Study completed on 6 November 1992; Received by EPA 18 November 1992.

DIRECT REVIEW TIME = 2.5 days

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CONCLUSIONS:

The aquatic dissipation study is scientifically valid and provides supplemental data at this time. However, the study may be upgraded to acceptable if the registrant provides information on the identification and concentration of significant degradates (≥10% of applied and/or 0.01 ppm). These data are needed to fully understand the dissipation of propiconazole in an aquatic system.

Propiconazole was reported to dissipate from paddy water and paddy soil (≤13.0 ppb and ≤0.02 ppm, respectively) when aerially applied to two rice paddy field plots (B.C. and M.O. plot) in Bay City, TX. However, it appear that only propicona-zole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at the B.C. site were reported to be 3.04 and 2.40 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at the M.O. site were reported to be 4.58 and 3.22 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil. Therefore, it appears that propiconazole, which is persistent in laboratory and terrestrial field studies and is soluble in water (110 ppm at 20°C in water), may be photodegrading in the presents of sensitizers (HTA;06/17/81). Furthermore, propiconazole does not appear to leach through paddy soil. The concentration in most paddy soil samples was <0.01 ppm at 8" depth.

Propiconazole detected in drainage water from the B.C. and M.O. sites reached a maximum level of 26 and 149 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤2.0 ppb and ≤9.2 ppb for B.C. and M.O. sites, respectively. Propiconazole reached maximum levels of ≤0.03 ppm in the 4-8" segment of paddy soil at both sites during the testing period. However, propiconazole was detected at slightly higher concentrations (≤0.06 and ≤0.19 ppm for B.C. and M.O. sites, respectively) in the 0-4" soil paddy segment.

MATERIALS AND METHODS:

Test Material: Tilt 3.6E (end-product)

Reference Standards: Unlabeled propiconazole

Soil: See Table 1

Water: DO ranged from 1.2 to 8.4 ppm for the B.C. site
DO ranged from 1.4 to 10.2 ppm for M.O. site

Temperature ranged from 27.0°C to 33.5°C for the B.C. site
Temperature ranged from 27.0°C to 35.0°C for the M.O. site

pH averaged 7.27 for the WR site
pH averaged 7.42 for the LO site

METHODOLOGY:

Two sites, B.C. and M.O., were chosen near Bay City, Texas for this aquatic dissipation study. The flow-through irrigation system, the clay (45%) content, and the low elevation (≈≤15 ft.) of the sites made it different from the sites chosen for the Arkansas study (MRID 42560501). Poor drainage, very slow runoff, and slow permeability were typical of both test sites.

The B.C. test site was located at the eastern edge of the testing farm and subdivided by 3 levees. The soil texture of the site was reported as clay to a depth of 46 inches. In order to avoid dilution of test material and contamination of untreated areas, water flow was restricted as much as possible. The irrigation water from the lateral canal flowed through several untreated levees and discharged into a drainage ditch.

The site was situated so that fluctuation in water level were minimized and discharge of treated water could be monitored in the drainage ditch. In the treated levee was established a grid of sampling stations, as well. Sixty soil and water sampling stations were established in three rows. There was ≈25 ft. between stations and ≈50 ft. between rows. These grids were arranged in such a way to minimized variability of pesticide residues between sampling locations. During the testing period, each location was sampled one time only.

The M.O. test site was located at the southern corner of the testing farm and subdivided by 7 levees. The soil texture of the site was reported to range from clay to clay loam throughout the 45" sampling core. Again, in order to minimize dilution of test material and contamination of untreated areas, water flow was restricted as much as possible. Lateral canal water was used for the M.O. site, as well. Irrigation water flowed through several untreated levees and drained into a drainage ditch.

In this treated levee was established a grid of sampling stations, as well. Sixty soil and water sampling stations in five rows were established with ≈25 ft. between stations in a row and ≈50 ft. between rows. However, the number of stations in a row varied due to plot shape and limitations of application of test material. In addition, grids were arranged in such a way to minimized variability of pesticide residues between sampling locations.

Four sampling stations were established at each testing site for monitoring of dissolved oxygen, pH, and temperature of the water phase at each testing site. In addition, three soil and water sampling stations were established for monitoring the discharge ditch.

Control plots for the B.C. and M.O. sites were located in a separated area than

the treated plot. In addition, the control plots had separate water drainage from their corresponding treatment plot. There were fifteen soil/water sampling stations established on each control plot.

Propiconazole was aerially applied twice to the B.C. site. Each application was half the maximum labelled application rate per season for rice (0.169 lb ai/acre). The M.O. site was treated twice at 2X the maximum labelled application rate per season (0.675 lb ai/acre) using aerially application. The 2X application rate was used to ensure that discernible residue levels were present.

Samples of the undiluted Tilt (propiconazole formulation used) were collected for analysis prior to each application. In addition, samples of the tank mixture were collected for analysis prior to and at termination of application of the Tilt formulation. Furthermore, spray deposition was monitored during each application using mounted disposition cards. Twenty-four sampling stations were established at the B.C. site, whereas, thirty-eight sampling stations were established at the M.O. site.

Soil samples were collected at random from among the 60 stations. At each station five cores were taken in 46 cm x 5 cm cellulose acetate tubes. Two methods of collecting the soil cores were used depending on water and soil content. From 0-day posttreatment to approximately 180 days posttreatment (second application), soil cores were taken to a depth of 25 cm. The five cores samples at a given station were collected in roughly a 5 foot radius circle around the station. If there was water in the tube, the water was drained from the tubes through punctured holes.

For discharge ditch, five cores were taken at each sampled station for analysis. These cores were taken in roughly a 5 foot radius circle of the drainage ditch station, as well.

Ten soil cores were collected from each treated site to a depth of 75 cm at ≈220 day posttreatment (second application) to termination of study. These samples did not require water drainage since they were collected after paddy drainage.

Water samples were collected similarly to the soil samples at both treated sites. Three stations were samples at random at each sampling interval. Water samples were taken prior to soil sample collection in order to avoid sediment in water samples. Approximately 1.3 liters of water were collected at each sampling station. The final water samples were collected at 28 days posttreatment (second application) on each site.

One liter water samples were collected from discharge ditch. Four sample bottles were used at each sampling interval.

Water temperature, dissolved oxygen, and pH were measured in the treated site and discharge ditch at each sampling interval. Four stations were established around each treated site. Samples from the discharge ditch were taken at the 0 yard, 50 yard, and 100 yard of sapling stations. However, additional samples were collected at the discharge stations during field drainage.

Samples were stored and shipped frozen until analysis. Water samples were analyzed by reversed phase GC analysis. However, after acetone/hexane and hexane/ethyl acetate extractions of samples spray cards and soil/sediment were analyzed by GC. The detection limits were 1 ppb in water and 10 ppb in soil/sediment samples.

In addition, to the other monitoring during the testing period, flow monitoring and weather monitoring were reported for the testing period.

DATA SUMMARY:

Propiconazole was reported to dissipate from paddy water and paddy soil (≤13.0 ppb and ≤0.02 ppm, respectively) when aerially applied to rice paddy field plots (B.C. and M.O. plot) in Bay City, TX. However, it appear that only propiconazole was determined in paddy water, paddy soil, and drainage waters. The half-lives for propiconazole in paddy water at the B.C. site were reported to be 3.04 and 2.40 days for the first and second application, respectively. The half-lives for propiconazole in paddy water at the M.O. site were reported to be 4.58 and 3.22 days for first and second application, respectively. Since propiconazole levels were variable and near the detection limit in paddy soil, the study authors did not report half-lives for propiconazole in paddy soil. Therefore, it appears that propiconazole, which appears to be persistent in laboratory and terrestrial field studies and is soluble in water (110 ppm at 20°C in water), may be dissipating through drainage water. Propiconazole does not appear to leach through paddy soil (most samples <0.01 ppm at 8" depth).

Propiconazole detected in drainage water from the B.C. and M.O. sites reached a maximum level of 26 and 149 ppb, respectively. However, at harvest time the drainage water was reported to contain propiconazole at levels of ≤2.0 ppb and ≤9.2 ppb for B.C. and M.O. sites, respectively. Propiconazole reached maximum levels of ≤0.03 ppm in the 4-8" segment of paddy soil at both sites during the testing period. However, propiconazole was detected at slightly higher concentrations (≤0.06 and ≤0.19 ppm for B.C. and M.O. sites, respectively) in the 0-4" soil paddy segment.

Water residue values and discharge values reached 29.0 ppb and 47.5 ppb on day 1 posttreatment (first application) at the B.C. and M.O. sites, respectively. However, the propiconazole residues at the B.C. site had declined to 9.7 ppb and 13 ppb by Day 13 and Day 11 posttreatment of first and second application, respectively . Discharge water residues levels reached 16 and 26 ppb at day 1 posttreatment of first and second application, respectively. However, by Day + 1 and Day + 7 posttreatment of first and second application, they had declined to 10 ppb. The M.O. site had similar results reported in comparison to application rates. Residue levels were highest on the day of the second application reaching a maximum value of 143.0 ppb. The residue levels declined to 10 ppb by Day T2 + 13 posttreatment.

For three on-site sediment fortifications the recoveries were 96% ± 6.9%. These fortified samples were stored for 546 days prior to analysis. However, for four on-site water fortifications the recoveries were 78% ± 15% when stored for 218 days. These were shorter intervals than those for the between sampling and analysis of sediment and water test samples.

COMMENTS:

1. The chromatographies and Tables furnished by the analytical laboratory indicate that only parent propiconazole was analyzed for all the samples. However, tables furnished by the authors reported the results as propiconazole residues for all samples. Even though at the M.O. site a 2X application rate was used to obtain discernible propiconazole residues, degradates were not address at either site.

   In order to fully understand the degradation and dissipation of propiconazole in an aquatic system, propiconazole degradates discernible (if discernible at concentrations ≥0.01 ppb) in paddy water, paddy soil/sediment, and discharge drainage systems should be determined. Propiconazole residues were determined and identified in the anaerobic aquatic study using LC/MS.

2. EFGWB prefers that [^{14}]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) with at least three solvent systems

of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

In this study, the samples were analyzed using GC.

3. No sediment fortification samples were collected from the M.O. to determine the storage stability of those samples. The authors believed that the B.C. storage stability data was sufficient. Data indicates that all samples were analyzed within 546 days for soil/sediment samples and 218 days for water samples.

4. The analytical laboratory stated that the formulation and tank mix samples were not analyzed.

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____ A draft product label.

____ The product confidential statement of formula.

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