Chemical Code: 129121

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To:

R. Kelgwin/A. Sibold

Registration Division (H7505)

From: Paul Mastradone, Section Chief

Chemistry Review Section 1

Environmental Fate & Ground Water Branch (EF

Thru:

Henry Jacoby, Chief

Environmental Fate & Ground

Attached, please find the EFGWB review of...

Insecticide	010/100//700	12 day		
Type Product:	Action Code: EFGWB #(\$):	Review Time:		
Purpose:	To review environmental fate studies (anaerobic aquat field dissipation, and fish accumulation) submitted to s registration of fipronii. In addition, a review of an EUP fipronii on turf in Southeastern United States			
iD #:	000264-EUP-RNN			
Company Name:	Rhone-Poulenc Ag. Company			
Common Name:	Fipronil Trade name:	Chipco Gauntlet		

STATUS OF STUDIES IN THIS PACKAGE: ADDRESSED IN THIS PACKAGE:

STATUS OF DATA REQUIREMENTS

Guideline #	MFGD	State:
162-3	43291704	Α
164-1	43291705	Α
.165-4	43291706 43291707	U
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White the same of		

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¹Study Status Codes:

A=Acceptable U=Upgradeable C=Ancillary I=Invalid.
2Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved W=Walved

1. CHEMICAL:

Chemical name: 5-Amino-3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl)-

4-[1R,S)-trifluoromethyl)sulfinyl]-1H-pyrazole-3-carboni-

trile

CAS no.:

120068-37-3

Common name:

Fipronil .

Trade name:

Chipco Gauntlet

Chemical structure:

Physical/Chemical properties of active ingredient fipronil:

Physical characteristics:

White powder with mouldy smell

Molecular formula:

C12H4F6N4C12OS

Molecular weight:

437.14

Melting point:

195.5-203°C

Vapor Pressure:

≈1 x 10⁻⁷ mm Hg

Solubility:

2.4 mg/L at 20°C

Octanol/water partition coefficient: 10,570

2: TEST MATERIAL:

See individual DERs.

3. STUDY/ACTION TYPE:

This study action is a review of environmental fate studies (anaerobic aquatic metabolism, terrestrial field dissipation, and fish accumulation) submitted to support the new chemical registration of fipronil on corn and turf. In addition, a review of an EUP application for use of Fipronil on turf in Southeastern United States is included.

STUDY IDENTIFICATION:

Waring, A.R. (14C)M & B 46.030: ANAEROBIC AQUATIC METABOLIAM. Sponsored and Submitted by Rhone-Poulenc Ag Company, Ongar, Essex, England;

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Performed by Hazleton UK, North Yorkshire, England under HUK Study No. 68/110; Completed 21 May 1993; Received by EPA 30 June 1994; MRID No. 43291704.

- Chancey, E.L. and Norris, F.A. A TERRESTRIAL FIELD SOIL DISSIPATION STUDY WITH FIPRONIL (MB 46030) A::OLIED INTO SLITS IN BARE SOIL AND SOIL WITH ESTABLISHED TURF. Sponsored and Submitted by Rhone-Poulenc Agriculture, Ongar, Essex, England; Performed by Rhone-Poulenc Ag. Company, Research Triangle Park NC under File No. 4424 and Study No. US93VO2R; Study completed on 23 May 1994; Received by EPA 30 June 1994; MRID No. 43291705.
- Chapleo, S. and Hall, B.E. (14C)M & B 46030; BIOACCUMULATION TEST IN BLUE-GILL SUNFISH. Sponsored and Submitted by Rhone-Poulenc Agriculture, Ongar, Essex, England; Performed by Inveresk Research International, Tranert, Scotland under IRI Project No. 381457; Study completed on 21 October 1992; Received by EPA 30 June 1994; MRID No. 43291706.
- Roohi, A., Coote, A. and Savage, E.A. (14C)M & B 46030: INVESTIGATION INTO THE NATURE AND POSSIBLE STRUCTURES OF METABOLITES IN FISH USED IN A BIOACCUMULATION STUDY AT INVERESK RESEARCH INTERNATIONAL. Sponsored and Performed by Rhone-Poulenc Agriculture, Ongar, Essex, England under Laboratory Project ID P 92/302; Study completed on 12 October 1992; Received by EPA 30 June 1994; MRID No. 43291707.

5. REVIEWED BY:

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

6. APPROVED BY:

Paul Mastradone, Chief Review section #1 OPP/EFED/EFGWB Date: 95

Signature: faul

Date: 18 SEP 1995

7. <u>CONCLUSIONS</u>:

This action is a request to review three environmental fate studies (anaerobic aquatic metabolism, terrestrial field dissipation, and fish accumulation) submitted by Rhone-Poulenc to support an Experimental Use Permit (EUP) and Section 3 registration of fipronil for terrestrial non-food and terrestrial food and feed uses. A review of the EUP application for use of Fipronil on turf in Southeastern United States (Alabama, Florida, Georgia, Mississippi, North Carolina, South Carolina) is included, as well. Other environmental fate studies (not reviewed in this action) needed to support the EUP and Section 3 registrations were submitted with an EUP application for use of fipronil on corn. Those studies were reviewed in June 1994 (WGM;06/13/94). In addition, the environmental fate of fipronil in aquatic and soil environments is assessed.

ENVIRONMENTAL FATE ASSESSMENT SUMMARY

Based on acceptable laboratory and terrestrial field data submitted to support registration and EUP, fipronil appears to dissipates below the soil surface by soil binding (kds=26.2-148.6 for ads; Kocs=2671 to 7818) followed by slower biotic mediated processes (aerobic soil half-life=128 days; anaerobic aquatic half-lives=116-130 days). However, on the soil surface (or

turf foliage) the major route of degradation may be photolysis (aquatic photolysis half-life=3.63 hours, soil photolysis half-life=34 days) and/or laboratory data indicate that fipronil is not mobile in soils tested and degrades slowly under alkaline hydrolytic conditions (hydrolysis half-life and pH 9=28 days). Fipronil does appear to be stable to hydrolysis at pH 5 tory data. Half-lives of 1.1 to 1.5 months for bare soil and 0.4 to 0.5 ronil residues were discernible only in the 0-6 inch soil depth. Therefore, appear to be associated with sediment contained in surface water and runsidered low.

Review of EUP Application for use of Fipronil on Turf:

Based on the EFGWB files, there is sufficient data to support the EUP for use of fipronil on turf in the Southeastern United States. Except for the fish accumulation data requirement which is conditionally required, all the environmental fate data requirements for Section 3 registration of fipronil for terrestrial food and feed crop and terrestrial non-food crop uses (corn and turf uses) are fulfilled for applications rates of ≤ 0.05 lb a.i./ these data are not expected to significantly change the environmental fate assessment of fipronil.

Review of Section 3 Registration for Terrestrial Non-Food Crop. Uses:

There is sufficient data to support Section 3 registration of terrestrial non-food crop uses of fipronil. The environmental fate data requirements (laboratory and field) for terrestrial non-food crop uses are fulfilled for application rates of ≤ 0.05 lb a.i./A.

Review of Section 3 Registration for Terrestrial Food and Feed Crop Uses:

All environmental fate laboratory data requirements for Section 3 registration of fipronil for terrestrial food and feed crop uses are fulfilled. However, additional field data are needed for Section 3 registration of terrestrial food and feed crop uses at application rates ≥0.05 lb a.i./A. Therefore, additional terrestrial field dissipation rate of 0.13 lb a.i./A. port the higher application rate for corn. However, these field dissipation data for the higher application rate are not expected to significantly change the environmental fate assessment of fipronil.

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Review of Submitted Environmental Fate Studies to Support Registration:

a. Anaerobic Aquatic Metabolism (162-3): MRID No. 43291704/

This anaerobic aquatic metabolism study is scientifically valid and can be used to fulfill the data requirement (162-3). No further anaerobic metabolism data for fipronil are needed at this time.

Fipronil was reported to degrade with half-lives of 116 days (by HPLC analyses) and 130 days (by TLC analyses) under anaerobic conditions. Two major degradates, MB 45,950 (5-amino-1-(2,6-dichloro-4-trifluoro-thylphenyl)-3-cyano-4-trifluoromethyl-thio-pyrazole) and RPA 200766, the amide (5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethanesulfinylpyrazole), were discernible at maximum

concentrations of \approx 47% and \approx 18% of applied radioactivity, respectively, at 365 days posttreatment. MB 45,950 was predominantly detected in the soil extracts. However, RPA 200766 was detected in both water and soil extracts. One other major component, unextractable soil residue, reached a maximum concentration of \approx 18% of applied radioactivity during the testing period. There were ten unidentified minor degradates (\leq 6% applied radioactivity) discernible in soil and water extracts by TLC analyses. However, there were four and three minor unidentified minor degradates (\leq 7% of applied radioactivity) discernible in soil and water extracts, respectively, by HPLC analyses.

See DER for details.

b. Terrestrial field dissipation (164-1): MRID No. 43291705

This terrestrial field dissipation study is scientifically valid and can be used to fulfill the data requirement (164-1). No further terrestrial field dissipation data for fipronil are needed for applications of ≤ 0.044 ppm at this time.

Fipronil was reported to dissipate with half-lives of 1.1, 0.4, 1.5, and 0.5 months when applied to Florida bare sand soil, Florida turfed sand soil, North Carolina bare loamy sand soil, and North Carolina turfed sandy loam soil, respectively. Of the six degradation products identified in soil metabolism and photolysis studies, two were discernible in field soil samples at >2 ug/kg (limit of detection). These were the oxidation product, MB 46136 (5-amino-1-(2,6-dichloro-4-trifluoro-methylphenyl)-3-cyano-4-trifluoromethyl-sulphonyl-pyrazole, and the carbonitrile hydrolysis product, RPA 200766, the amide (5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethanesulfinylpyrazole). MB 46136 was detected in both bare soil and turfed soil samples at maximum concentrations ranging from 5.6 to 8.9 ug/kg at 2-3 months postapplication during the 4 month testing period. RPA 200766 was detected in the bare soil test samples at both test sites reaching a maximum concentration of 3.7 ug/kg at 3 months postapplication for each test site. Despite excess rainfall/irrigation levels, the fipronil residues remained in the upper 6 inch soil segment (no residue detected in the 0.15-0.30 meter soil depth) at each location during the 4 month testing period. Therefore, fipronil appears to demonstrate a low potential for leaching to ground-water.

See DER for details.

c. Fish Accumulation (165-4): MRID No. 43291706 & 43291707

This fish accumulation study is scientifically valid and can be used as supplemental data. However, it can not be used to fulfill the data requirement (165-4) at this time. Storage stability data for tissue samples and the length of storage of tissue samples were not reported. These data are needed to validate the tissue characterization data.

Fipronil appears to bioaccumulate in Bluegill Sunfish when exposed to treated water at a concentration of ≈900 ng equiv.1⁻¹ for 35 days. Bioconcentration factors (BCFs) of 321, 164, and 575 were reported for whole fish, edible tissue, and non-edible tissue, respectively. These BCFs were determined for the apparent steady-state phase, days 14 and 35 post-exposture, of the testing period. The depuration phase indicates that accumulated fipronil residues are almost completely eliminated (>96%) after 14 days depuration. By day 7 of the depuration period

≈90% of the accumulate fipronil residues were eliminated. These results are considered by the study authors to be in agreement with the octanol/water coefficient (kw-10,570). Residues for both the uptake and depuration phase were characterized. The major metabolites identified in fish tissues were MB 46,136 (5-amino-1-(2,6-dichloro-4-trifluoro-methylphenyl)-3-cyano-4-trifluoromethyl-sulphonyl-pyrazole) with reported concentrations of 54.90%, 59.07%, and 27.98% of accumulated residue in pooled uptake edible, inedible, and whole fish tissue fractions, respectively, and MB 45,897 (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoro-methylphenyl) pyrazole) with reported concentrations of 14.16%, 22,92%, and 24.28% of accumulated residue in pooled uptake edible, inedible, and whole fish tissue fractions, respectively, and MB 45950 (5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethyl-thio-pyrazole) with reported concentrations of 9.04%, 9.03%, and 8.55% of accumulated residue in pooled uptake edible, inedible, and whole fish tissue fractions, respectively. The study authors stated that another metabolite, RPA 200766 (the amide), was discernible in test samples at much smaller quantities (amount not reported).

See DER for details.

ENVIRONMENTAL FATE ASSESSMENT

Available laboratory data indicate that below the soil surface fipronil dissipates by soil binding (kds=26.2-148.6 for ads; Kocs=2671 to 7818) followed by slower biotic mediated processes (aerobic soil half-life=128 days; anaerobic aquatic half-lives=116-130 days). However, on the soil surface (or turf foliage) the major route of degradation may be photolysis (aquatic photolysis half-life=3.63 hours, soil photolysis half-life=14 days) and/or soil binding followed by slower biotic mediated processes. In addition, laboratory data indicate that fipronil is not mobile in soils sis half-life at pH 9=28 days). Fipronil does appear to be stable to hydrolysis at pH 5 and pH 7 (half-life=stable). The field data appears to soil and 0.4 to 0.5 months for turfed soil are reported in field data. In soil depth. Therefore, since fipronil appears to bind to soil matter, movement off-target would appear to be associated with sediment contained water contamination is considered low.

There is limited data on the persistence and mobility of degradates. Howsoil. There were two major degradates, RPA 200766 (the amide) and MB
46136 (5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluat maximum concentrations of 27-38% and 14-24% of applied radioactivity,
at maximum concentrations of 27-38% and 14-24% of applied radioactivity,
MB 45,950 (5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4trifluoromethyl-thio-pyrazole) and RPA 200766 which were discernible at
tively. In addition to the metabolites identified in the metabolism stutrifluoromethylphenyl)-4-trifluoromethylphenyl)-3-cyano-1-(2,6-dichloro-4dies, degradation products MB 46513 (5-amino-3-cyano-1-(2,6-dichloro-4104615 (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl))-yrazoledies. Other minor metabolites were identified in the photolysis stuconcentrations of <6% each.

Supplemental fish accumulation indicate that fipronil does absorb in fish tissues. Bioconcentration factors (BCFs) of 321, 164, and 575 for whole fish, edible tissues, and non-edible tissues, respectively, are reported for the steady-state phase. However, the depuration data indicate that these fipronil residues are almost completely eliminated (>96%) after 14 days of non-exposure. These data appear to be in agreement with the octonal/water coefficient (10,570). Storage stability data on tissue samples are needed to validate the analytical data for the fish accumulation study to be upgraded to acceptable.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

- a. There is sufficient environmental fate data to support the EUP and Section 3 registration of fipronil on Turf at application rates of ≤ 0.05 lb a.i./A.
- b. There is insufficient environmental fate data to support Section-3 registration for use of fipronil on corn at an application rate of 0.13 lb a.i./A due to lack of field dissipation data at this higher application rate.
- c. The anaerobic aquatic metabolism and terrestrial field dissipation (for application rates ≤0.05 lb a.i./A) studies are acceptable to fulfill the respective data requirements.
- d. The fish accumulation study is not acceptable at this time to fulfill the data requirement. Storage stability data for tissue samples are needed to validate the tisue characterization data.
- e. The current status of environmental fate data requirements to support the registration of fipronil on terrestrial food and feed and terrestrial non-food crops (including turf) is as follows:

Environmental Fate <u>Data Requirements</u>	Status of Data Requirement	MRID No.	
Degradation Studies-lab	•	<u> </u>	
161-1 Hydrolysis 161-2 Photodegradation in water 161-3 Photodegradation on soil 161-1 Photodegradation in air ¹	Fulfilled (WGM;06/15/94) Fulfilled (WGM;06/15/94) Fulfilled (WGM;06/15/94)	42194701 42918661 42918862	
Metabolism Studies-lab			
162-1 Aerobic soil 162-2 Anaerobic soil ² 162-3 Anaerobic aquatic	Fulfilled (WGM;06/15/94) Fulfilled	42918663 43291706	
Mobility Studies	(WGM;09/18/95)	43291707-	
163-1 Leaching, Adsorption/ Desorption	Fulfilled (WGM;06/15/94)	42918664 43018801 (00137544	

Con't-- Environmental Fate
Data Requirements

Status of Data Requirement

MRID No.

163-2 Volatility-Lab¹ 163-2 Volatility-Field¹

Dissipation Studies-field

164-1 Soil

Fulfilled³ (WGM:09/18/95)

43291705

Accumulation Studies

165-4 in Fish

Not Fulfilled⁴ (WGM;09/18/95)

43291706 43291707

- Based on the low vapor pressure ($\approx 1 \times 10^{-7}$ mm Hg), volatility data is not needed at this time.
- An acceptable anaerobic aquatic metabolism study will fulfill the anaerobic metabolism data requirement.
- The terrestrial field dissipation data requirement is fulfilled for applications rates of ≤0.05 lb a.i./A. The suggested application rate of fipronil on corn is 0.13 lb a.i./A. Additional terrestrial field dissipation data are needed to support the higher application rate and to make a complete environmental fate assessment of the higher application rate.
- Additional storage stability data are needed for tissue samples.

9. BACKGROUND:

Fipronil is a phenylpyrazole insecticide at present used to control rootworms and/or wireworms in corn and to control mole crickets in turf. According to the manufacture's data, fipronil affects the gamma-aminobutyric acid neurotransmission system by interfering with the passage of chloride. In addition, research data indicate that fipronil displays a higher potency in insect GABA chloride channel than in vertebrate GABA chloride channel which may indicate selective toxicity.

The application rate for fipronil is 0.13 lb a.i./A for control of rootworms and wireworms in corn and 0.0125 lb a.i./A to 0.025 lb a.i./A for
control of mole crickets in turf. For corn fields fipronil is applied by
ground equipment directly into the seed furrow behind the planter shoe.
Slit-placement equipment is used for application of fipronil on infected
turf. The application rate for fipronil is approximately one-tenth of
that of previous used insecticides, terbufos, and chlorpyrifos.

10. <u>DISCUSSION:</u>

See individual DERs for details of reviewed studies.

11. COMPLETION OF ONE-LINER:

See attached one-liners.

12: CBI APPENDIX:

N/A

ONE-LINER

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY

FIPRONIL

Last Update on October 24, 1994 [V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT Reviewer: Section Head: Date:

Common Name: FIPRONIL

Smiles Code:

PC Code # :129121

CAS #:120068-37-3

Caswell #:

Comments

Chem. Name: 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl-4-

trifluoromethylsulphinyl pyrazole

Action Type:insecticide

Trade Names:

(Formul'tn): 1.5% granular Physical State: white powder

Use :: control of rootworm and wireworm in corn

Patterns :terrestrial food and feed (% Usage) :approximately 0.13 lb a.i./A

Empirical Form: $C_{12}H_4Cl_2F_6N_{40}S$ Molecular Wgt.: Vapor Pressure: E -7 Torr Melting Point: 195-203 C °C Boiling Point: · °C Log Kow > pKa: Henry's Atm. M3/Mol (Measured) E

Solubility in ... Water 2.40E ppm 620.0 °C Acetone E ppm 6 °C Acetonitrile E ppm °C Benzene E ppm Chloroform É ppm @ Ethanol E ppm @ Methanol E ppm @ Toluene E ppm @ Xylene

ppm 0 ppm @ *C ppm 0 °c

Hydrolysis (161-1)

[V] pH 5.0:STABLE

[V] pH 7.0:STABLE

[V] pH 9.0:28 DAYS

. •

[] Hq

[] pH

[] pH

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY FIPRONIL

Last Update on October 24, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Photolysis (161-2, -3, [V] Water: 3.63 HOURS (-4) DR 0.33	DAYS FI	ORIDA :	SUNLIGHT
[V] Soil :34 DAYS [] Air :	•		•	
Aerobic Soil Metabolism [V] 122-128 DAYS []	(162-1	L)		
				-
Anaerobic Soil Metabolis	cm (162	-21		•
[] [] [] []		-	-	
Anaerobic Aquatic Metabo [V] tl=116 days by HPI [] tl=130 days by TIA	LC	162-3)		
[] [] [] []				
Aerobic Aquatic Metaboli	sm (16:	2-4)	oj "Kr	
	, 200			

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY **FIPRONIL**

Iast Update on October 24, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

[V] [V] [V]	26.2 - 3 58-128 I 89.6-253 148.6-22 Koc FOR	COEFFICI FOR MAN FOR FRENCH FOR GERM FOR MAN SAME SOIL	NINGTREE SANDY-CI AN LOAMY NINGTREE	UK LOAMY LAY-LOAM S SAND SOII UK LOAM S	
Soil [] [] [] []	Rf Factor	rs (163–1)			
Labor [] []	atory Vol	atility (163-2)		
[] [] !erre [V]	strial Fi tl=1.1 t	ty (163-3 eld Dissi o 1.5 mon	oation (1 ths for h	are coil	
quat: [] [] [] [] []	ic Dissipa	ation (164	i−2)		
orest []	ry Dissip	oation (16	54-3)		1

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY FIPRONIL

Iast Update on October 24, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Long-Term Soil Diss [] []	ipation (164-5)		
Accumulation in Rota	ational Crops, Co	onfined (165-1)	
Accumulation in Rota	ational Crops, Fi	ield (165-2)	
Accumulation in Irr	igated Crops (165	i – 3)	
Bioaccumulation in I [S] BCF= 321, 164, [] tissue, respec	, 575 for whole f	ish, edible tissue	, and non-edible
Bioaccumulation in N [] [-]	Mon-Target Organi	sms (165-5)	
Ground Water Monitor	ing, Prospective	(166–1)	
[] Ground Water Monitor	ing, Small Scale	Retrospective (166	:
		merrobective (100) - 2)
Ground Water Monitor [] []	ing, Large Scale	Retrospective (166	i–3)
[] Fround Water Monitor	ing, Miscellaneon	us Data (158 75)	
	J,	~ Juliu (200,75)	

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY FIPRONIL

Last Update on October 24, 1994

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Fie [[[ld]]]	Runoff	(167-	1)	
Sur [[[fac]]]	æ Wate	r Moni	toring (16	7-2)
Spr [[[ay]]]	Drift,	Drople	et Spectru	n (201-1)
Spra [[[ay]]]	Drift,	Field	Evaluation	n (202-1).

Degradation Products

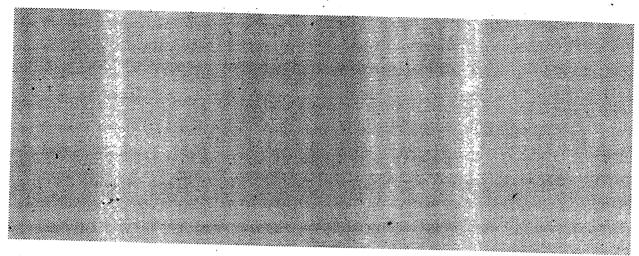
MB 46513 FOR PHOTOLYSIS
MB 45897, RPA 200766, RPA 105048, MB 46136, RPA 104615, MB45950,
MB 46058 FOR AEROBIC METABOLISM

SEE ATTACHED FOR CONFIGURATIONS

Environmental Fate & Effects Division PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY FIPRONIL

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Comments



References:

ENVIRONMENNTAL FATE STUDIES, FARM CHEMICAL HANDBOOK

Writer