6/13/94

Date Out: 13 JUN 1994

DP Barcode: D197449
Chemical Code: 129121

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: R. Brennis/D. Waldo PM #10
Registration Division (H7505C)

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

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C) 6/15/94

Attached, please find the EFGWB review of...

Common Name:	Fipronil	**Trade name**	
Company Name:	Rhone-Poulenc Ag Company		
ID #:	000264-EUP-OL		
Purpose:	Review of EUP for corn and environmental fate data submitted to support the food/feed use EUP.		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
Insecticide	710		12 days

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

Guideline #	MRID	Status[1]
161-1	42194701	A
161-2	42918661	A
161-3	42918662	A
162-1	42918663	A
163-1	42918664	A
163-1	43018801	A

STATUS OF DATA REQUIREMENTS

Guideline #	Status[2]
161-1	S
161-2	S
161-3	S
162-1	S
163-1	S

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

1. CHEMICAL:

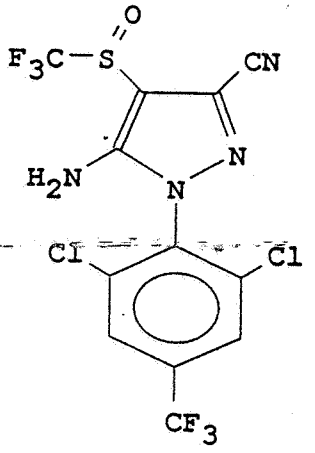
Chemical name: 5-Amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulphinyl pyrazole

CAS no.: 120068-37-3

Common name: Fipronil

Trade name: None

Chemical structure:



Molecular formula: $C_{12}H_4Cl_2F_6N_4OS$

Molecular weight: 437.14

FORMULATION: 1.5% Granular

Active Ingredient	1.5%
Inert Ingredients	98.5%

Physical/Chemical properties of active ingredient:

Physical characteristics: White powder with mouldy smell

Melting point: 195.5-203°C

Solubility: 2.4 mg/L @ 20°C

Octanol/water partition coefficient: 10,570

Vapor Pressure: $\approx 1 \times 10^{-7}$ mm Hg

2. TEST MATERIAL:

See individual DERs.

3. STUDY/ACTION TYPE:

Review of EUP for corn and environmental fate data submitted to support the food/feed use EUP.

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4. STUDY IDENTIFICATION:

Kwiatkowski, P.L. CORRESPONDENCE TO A. HEYWARD: EUP SUBMISSION AND PETITION FOR TEMPORARY TOLERANCES FOR FIPRONIL 1.5% GRANULAR SOIL INSECTICIDE FOR CONTROL OF CORN ROOTWORM IN FIELD CORN - A SUMMARY DOCUMENT. Submitted by Rhone-Poulenc Agriculture, Research Triangle Park, NC; 20 August 1993, Received by EPA 24 August 1993.

Corgier, M.M. and Plewa, A.P. ^{14}-MB 46030 HYDROLYSIS AT 25°c. Sponsored and Submitted by Rhone-Poulenc Secteur Agro; Lyon, France; Performed by Rhone-Poulenc under Study No. 91-25/File Ref.: AG/CRLD/AN?9215072; Study completed 16 March 1992; Received by EPA 24 August 1993; MRID 42194701.

Corgier, M.M. and Plewa, A.P. ^{14}C-MB 46030 AQUEOUS PHOTOLYSIS. Sponsored and Submitted by Rhone-Poulenc Secteur Agro; Lyon, France; Performed by Rhone-Poulenc under Study No. 91-55;File ref.: AG/CRLD/AN/9215873; Study Completed 15 May 1992; Received by EPA 24 August 1993; MRID 42918661.

Burr, C.M. and Austin, D.J. M&B 46030-^{14}C SOIL PHOTOLYSIS STUDY. Sponsored and Submitted by Rhone-Poulenc Rorer; Dagenham, Essex, England; Performed by Rhone-Poulenc under Laboratory Project ID P90/050; Study Completed 3 June 1992; Received by EPA 24 August 1993; MRID 42918662.

Waring, A.R. (^{14}C)M&B 46030: AEROBIC SOIL METABOLISM. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Hazleton UK, Harrogate, North Yorkshire, England under HUK Project No.: 68/109-1015; Study Completed 21 May 1993; Received by EPA 24 August 1993; MRID 42918663.

Godward, P.J. Quarmby, D.L. and Austin, D.J. (^{14}C)M&B 46030: LEACHING STUDY WITH FIVE SOILS. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Rhone-Poulenc Agriculture Ltd., Ongar, Essex, England under Laboratory Project No.: P91/089; Study Completed 8 June 1992; Received by EPA 24 August 1993; MRID 42918664.

Godward, P.J. Quarmby, D.L. and Austin, D.J. (^{14}C)M&B 46030: ADSORPTION/DESORPTION ON FIVE SOILS. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Rhone-Poulenc Agriculture Ltd., Ongar, Essex, England under Laboratory Project No.: P91/084; Study Completed 4 June 1992; Received by EPA 24 August 1993; MRID 43018801.

5. REVIEWED BY:

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

Signature: [signature]
Date: 13 JUN 1994

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6. APPROVED BY:

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

Signature: Paul J Mastradone
Date: 13 JUN 1991

7. CONCLUSIONS:

This is a request to review an EUP for fipronil, a new chemical, on corn. Since this is a new chemical, environmental fate data was submitted to support the EUP application. All the environmental fate data (hydrolysis, photodegradation in water, photodegradation on soil, aerobic soil metabolism, and mobility data) needed for the EUP were included and found acceptable to fulfill the data requirements. The review of these data are included in this action. However, a conditional data requirement, fish accumulation data, was not included in the EUP package. Based on the Kow (10570), fish accumulation data will be needed for terrestrial food and feed use pattern registration.

ENVIRONMENTAL FATE ASSESSMENT SUMMARY

This environmental fate assessment is based on a limited data base of acceptable laboratory data submitted for an EUP. Therefore, this enviromental fate assessment is tentative. Anaerobic metabolism, fish accumulation, and field dissipation data have not been submitted. However, available laboratory data indicate that below the soil surface fipronil dissipates by soil binding (Kds=26.2-148.6 for ads/des;Koc=2671 to 7818 followed by a slower biotic mediated processes ($t_{1/2}$=≈128 days for aerobic soil metabolism). However, on the soil surface the major route of dissipation may be abiotic photolysis ($t_{1/2}$=3.63 hours for aquatic, 34 days for soil) and/or soil binding followed by a slower biotic mediated processes. In addition, the laboratory data indicates that fipronil is not mobile in the five soils tested and degrades slowly under alkaline hydrolytic conditions ($t_{1/2}$=28 days at pH 9).

Review of request for Food/Feed use EUP on corn:

Given the relative low use/application rate and review of available laboratory data, there is sufficient data to support the EUP request for use of fipronil on corn. However, foreign soils were used in the laboratory data. The pH (7.8) and/or CEC (12.6-36.5) of these soils are not typical of most U.S. soils. Therefore, additional data on U.S. soils would provide a more complete quantitative environmental fate assessment. In addition, it would be more appropriate should a quantitative environmental fate assessment be necessary. A preliminary environmental fate assessment based only on these laboratory data indicate that fipronil is not mobile (Freundlich constant=26 to 148 in five soils) but may be persistent in soil ($t_{1/2}$=≈128 days for aerobic soil metabolism) below the soil surface. However, fipronil does appear to degrade by photolysis ($t_{1/2}$=3.63 hours for aquatic; 34 days in soil) on the soil surface.

See DISCUSSION for details.

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Review of Submitted Studies:

a. Hydrolysis (161-1)
MRID No. 42194701

The hydrolysis study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-1). No further hydrolysis data for fipronil are needed at this time.

Fipronil was reported to be stable (<3% degradated by day 30 posttreatment) in pH 5 and pH 7 buffered solutions. However, fipronil was reported to degrade with a half-life of 28 days in pH 9 buffered solution. A fipronil amide (for structure see attachment) was identified in the pH 9 buffered solution at a maximumm concentration of 51.70% of applied radioactivity. Only minor degradates were discernible in the pH 5 and pH 7 test samples. In addition, volatiles were not discernible in any pH buffered test solutions during the testing period.

b. Photodegradation in water (161-2)
MRID No. 42918661

The photodegradation in water study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-2). No further photodegradation in water data for fipronil are needed at this time.

Fipronil was reported to have a half-life of 3.63 hours when exposed to a xenon light source. There was no degradation reported in the dark controls. Two degradates, MB 46513 and RPA 104615 (for structures and chemical names of degradates see attachment), were identified in the light exposure test samples. Degradate MB 46513 in TLC and HPLC analysis reached a maximum concentration of ≈43% of applied radioactivity at 6 hours postexposure. Degradate RPA 104615 in HPLC analysis (not discernible in TLC analysis) reached a maximum concentration of ≈8% of applied radioactivity. One unidentified degradate (Rf= 0.37;RT=3.3 min) in TLC and HPLC analysis of the organic phase reached a maximum concentration of ≈5.5% of applied radioactivity. Further analysis of this unidentified compound by MS-^{19}F-NMR indicated it had a molecular weight of 410 a.m.u. However, no molecular structure could be assigned with certainly to this degradate product. In addition, one unidentified degradate was discernible in HPLC analysis of the aqueous phase, and reached a maximum concentration of ≈4% by termination (6 hours postexposure) of the testing period. Furthermore, there were practically no volatiles (<0.04% of applied radioactivity) in the ethylene glycol and NaOH traps at termination of the study.

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c. Photodegradation on soil (161-3)
MRID No. 42918662

The photodegradation on soil study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-3). No further photodegradation on soil data for fipronil are needed at this time.

A half-life of 34 days was reported for fipronil when applied to a loam soil (USDA classification, called clay-loam in study) and exposed to an intermittent (8 hours on/16 hours off) artificial light source (xenon arc lamp). For the control samples, a half-life of 49 days was reported. Three degradates, RPA 200766, MB 46136, and MB 45950 (maximum concentrations reached 10.86%, 4.03%, and 1.91%, respectively; for structures and chemical names of degradates see attachment) and 2 unidentified degradates were discernible in the light exposed samples using TLC analysis. The two unidentified degradates were identified using HPLC analysis as MB 46513 and RPA 104615 at maximum concentrations of 8.65% and 8.87% of interest regions, respectively. There were differences in the metabolites discernible in the light exposed samples and in the control samples. RPA 104615 (could not be confirmed by GC-MS) and 46513 were found only in the light exposed samples. However, MB 45950 which was detected in small amounts in the light exposed samples (1.5% of nominal applied radioactivity), reached 12.7% of nominal applied radioactivity by day 30 posttreatment in the control samples. Volatiles were not detected at significant levels (<0.5%) in the light exposed or control traps except for CO_2 in light exposed samples (2.5% of applied radioactivity).

d. Aerobic soil metabolism (162-1)
MRID No. 42918663

The aerobic soil metabolism study is scientifically valid. In addition, it can be used to fulfill the data requirement (162-1). No further aerobic soil metabolism data for fipronil are needed at this time.

Fipronil appears to degrade slowly by biotic mediated processes. However, fipronil degraded faster in the sandy loam soil ($t_{½}$=128 days calculated from HPLC data;122 days calculated from TLC data) than sand soil ($t_{½}$=308 days calculated from HPLC data;342 days calculated from TLC data). Half-life valves calculated from HPLC analysis were considered more accurate than those calculated from TLC analysis. Unchanged parent material and the degradate labelled MB 45897 and degradates, RPA 200766 and RPA 105048 (for structures and chemical names see attachment) were difficult to separate by TLC linear analysis. However, two major degradates, RPA 200766 and MB 46136, were identified in sandy loam soil samples and the sand soil samples at maximum concentrations of 27-38% and 14-24% of applied radioactivity, respectively. Degradates MB 45950 and MB 46513 were identified in both soil types at maximum concentrations of <5% and <1% of applied radioactivity, respectively. Degradate, MB 45897, was discernible only in the sand soil samples at maximum concentrations <1%. Six unidentified degradates were detected by HPLC in the sandy loam soil samples and three in the sand soil samples. Each of these degradates comprised <4% of applied radioactivity. Degradate,

MB 46513, was found to be a photolysis product in photodegradation studies. Therefore, the authors indicated that its presence may be related to work up of certain samples for analysis. The data did show the amount of unextracted radioactivity increased from 1% to 15% and 1 to 6% in the sandy loam soil and the sand soil, respectively, during the testing period. Volatiles were not discernible at significant levels during the testing period.

e. Leaching mobility study (163-1)
MRID No. 42918664

Two mobility studies, column leaching study and adsorption/desorption study, were submitted, and are scientifically valid. In addition, they can be used to fulfill the data requirement (163-1). Therefore, no further mobility data for fipronil are needed at this time.

The column leaching study and the adsorption/desorption study each using five different soils (German loamy soil, Manningtree UK loamy-sand (called Manningtree sandy loam in study), Manningtree UK loam, French sandy-clay-loam (1), and French sandy-clay-loam (2)) indicated that unaged and aged fipronil is not mobile in soil. Most (>85%) of the applied radioactivity (unaged and aged fipronil residues) were detected in the top 0-8 cm segment of the soil columns except for the Manningtree UK loamy-sand soil in which most (>80%) of the applied radioactivity was detected in the top 0-14 cm segment. Approximately 1-8% of applied radioactivity was detected in the column leachate. The 8% recovery was from the Manningtree UK loamy sand soil columns. Degradate, RPA 200766 (see attachment for structures and chemical names), was discernible in all aged soil columns except one Manningtree UK loamy-sand column at maximum concentrations of 2 to 17% of recovered extracted radioactivity. In addition, degradates, MB 45950 and MB 46136, were discernible in some of the soil columns. Again the presence of degradate, RPA 104615, could not be confirmed by TLC and GC -MS. The above degradates were at concentrations of ≤4% Of applied radioactivity in the leachate.

The adsorption Koc values ranging from 2671 to 7818 indicate that fipronil is not mobile in the five soils tested. The Freundlich constants were reported to be 89.6, 26.2, 148.6, 58.1, and 67.2 for German loamy-sand, Manningtree UK loamy-sand, Manningtree UK loam, French sandy-clay-loam 1 and 2 soils, respectively. In addition, the results shows a negative correlation between adsorption and organic matter content. The lowest organic matter content soils had the highest Koc values while the high organic matter content soils had the lowest reported Koc values. Furthermore, the results did indicate a correlation between Kd values and soil pH and CEC (Cation Exchange Capacity). Soils with lowest pHs and CEC had the lowest Kds. The desorption K values indicate that, except for the Manningtree UK loamy-sand soil, the desorp-

It should be noted that these soils were from a foreign source. Therefore, this data may not totally reflect data from U.S. soils.

See individual DERs.

ENVIRONMENTAL FATE ASSESSMENT

This environmental fate assessment is based on a limited data base of acceptable laboratory data which was done on foreign soils not typical of U.S. soils and use areas. Anaerobic metabolism, fish accumulation, and field dissipation data have not been submitted. These data will be needed for registration to complete an environmental fate assessment of fipronil in aquatic and soil environments. Therefore, this environmental fate assesement is at best tentative.

Available laboratory data indicate that below the soil surface fiprnil dissipates by soil binding (Kds=26.2-148.6 for ads/des;Kd=35-253 for column;Koc=2671 to 7818) followed by a slower biotic mediated processes ($t_{1/2}$= ≈128 days for aerobic soil metabolism). However, on the soil surface the major route of dissipation may be abiotic photolysis ($t_{1/2}$=3.63 hours for aquatic, 34 days for soil) and/or soil binding followed by a slower biotic mediated processes. In addition, the laboratory data indicates that fipronil is not mobile in the five soils tested (kd=26.2-148;Koc=2671-7818) and degrades slowly under alkaline hydrolytic conditions ($t_{1/2}$=28 days at pH 9). There was a negative correlation between soil organic matter content and Kocs. However, there was a correlation beteween Kds and soil pH and CEC. Lower pH and CEC soils had lower Kds. Fipronil does appear to be stable to hydrolysis especially at pH 5 and pH 7.

Two major degradates, RPA 200766 and MB 46136, were identified in the aerobic metabolism study at maximum concentrations of 27-38% and 14-24% of applied radioactivity, respectively. The fipronil amide was the only degradate indentified in the hydrolysis study (pH 9) at a maximum concentration of 51.70% of applied radioactivity. In addition to the metabolites identified in the aerobic metabolism study, degradates, MB 46513, MB 45350 and RPA 104615, were identified in the photolysis studies. Other minor degradates in laboratory studies were discernible at concentrations of <5% of applied radioactivity. Due to the persistence of the parent material to hydrolysis at neutral pHs and to aerobic metabolism, there is limited data on the route of dissipation of degradates and their persistence and mobility. However, the limited data does indicate that the metabolites are not mobile in soil.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

a. The hydrolysis, photolysis in water and on soil, aerobic soil metabolism, and mobility studies can be used to fulfill the respective data requirements.

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b. There is sufficient data to support the fipronil food/feed EUP on corn. However, it should be noted that these laboratory studies were done on foreign soils which are not typical of U.S. use areas. Therefore, additional data on U.S. soils would provide a more complete quantitative environmental fate assessment.

c. The status of the Environmental Fate Data Requirements for the fipronil food/feed EUP use is as follows:[1]

Environmental Fate Data Requirement	Status of Data Requirement	MRID No.
Degradation Studies-Lab		
161-1 Hydrolysis	Fulfilled (WGM;	42194701
161-2 Photodegradation in water	Fulfilled (WGM; /94)	42918661
161-3 Photodegradation on soil	Fulfilled (WGM;	42918662
Metabolism Studies-Lab		
162-1 Aerobic (soil)	Fulfilled (WGM;	42918663
Mobility Studies		
163-1 Leaching, Adsorption Desorption	Fulfilled (WGM;	42918664 43018801
Accumulation Studies		
165-4 Fish	Not Submitted[2]	

[1] This Table is the status of the data requirements for the food/feed corn EUP use of fipronil. It does not reflect the status of the data requirements for registration of fipronil for food and feed use pattern.

[2] The conditional fish accumulation data requirement was not submitted. Based on the octanol water partition coefficient (Kow=10,570), EFGWB needs an accumulate in fish study for registration of Fipronil for use on terrestrial food/feed use sites.

9. BACKGROUND:

Fipronil is a phenylpyrazole insecticide used to control rootworm and/or wireworm in corn. Fipronil affects the gamma-aminobutyric acid neurotransmission system by interfering with the passage of chloride. Therefore, the CNS actively is disrupted resulting in death of the insect.

The application rate for the is 0.13 lb a.i./A. Fipronil is applied by ground equipment directly into the seed furrow behind the planter shoe. The application rate for fipronil is approximately one-tenth of that of previous used insecticides, terbufos and chlorpyrifos.

10. DISCUSSION:

Food/Feed EUP on Corn

A total of 1000 acres is to be treated with fipronil for this EUP. This 1000 acres will be divided into fifty test among eight states, Iowa, Illinios, Indiana, Minnesota, Nebraska, Ohio, South Dakota, and Wisconsin, in the Northern-Midwestern area. Each test will be up to 20 acres in size to which 0.13 lb a.i./acre of fipronil is applied at planting directly into the seed furrow behind the planter shoe. Therefore, a total of 130 lbs of fipronil will be used in the EUP to control corn rootworm and/or wireworm. The duration of this EUP is one year.

This EUP is to obtain data on the application rate, crop stand, root ratings, and crop phytotoxicity data (% injury). In addition, the study will be used to obtain performance data over the environmental conditions in the northern-midwestern to control the corn rootworm and/or wireworm, and the products strengths and weaknesses will be assessed in comparison to current products on the market.

Environmental Fate Studies Submitted

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
FIPRONIL
Last Update on April 18, 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 #:

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: $C_{12}H_4Cl_2F_6N_4OS$
Molecular Wgt.: 437.14 Vapor Pressure: E -7 Torr
Melting Point : 195-203 C °C Boiling Point: °C
Log Kow : 4 pKa: @ °C
Henry's : E Atm. M3/Mol (Measured)

Solubility in ...				Comments
Water	2.40E	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
[V] pH 7.0:STABLE
[V] pH 9.0:28 DAYS
[ ] pH :
[ ] pH :
[ ] pH :

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Environmental Fate & Effects Division
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Photolysis (161-2, -3, -4)
[V] Water:3.63 HOURS OR 0.33 DAYS FLORIDA SUNLIGHT
[ ] :
[ ] :
[ ] :

[V] Soil :34 DAYS
[ ] Air :

Aerobic Soil Metabolism (162-1)
[V] 122-128 DAYS
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Anaerobic Soil Metabolism (162-2)
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Anaerobic Aquatic Metabolism (162-3)
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Aerobic Aquatic Metabolism (162-4)
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Soil Partition Coefficient (Kd) (163-1)
[V] 26.2 - 35 FOR MANNINGTREE UK LOAMY SAND SOIL
[V] 58-128 FOR FRENCH SANDY-CLAY-LOAM SOIL
[V] 89.6-253 FOR GERMAN LOAMY SAND SOIL
[V] 148.6-222 FOR MANNINGTREE UK LOAM SOIL
[V] Koc FOR SAME SOILS = 2671 TO 7818
[ ]

Soil Rf Factors (163-1)
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Laboratory Volatility (163-2)
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Field Volatility (163-3)
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Terrestrial Field Dissipation (164-1)
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Aquatic Dissipation (164-2)
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Forestry Dissipation (164-3)
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Long-Term Soil Dissipation (164-5)
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Accumulation in Rotational Crops, Confined (165-1)
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Accumulation in Rotational Crops, Field (165-2)
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Accumulation in Irrigated Crops (165-3)
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Bioaccumulation in Fish (165-4)
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Bioaccumulation in Non-Target Organisms (165-5)
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Ground Water Monitoring, Prospective (166-1)
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Ground Water Monitoring, Small Scale Retrospective (166-2)
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Ground Water Monitoring, Large Scale Retrospective (166-3)
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Ground Water Monitoring, Miscellaneous Data (158.75)
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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
FIPRONIL
Last Update on April 18, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Field Runoff (167-1)
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Surface Water Monitoring (167-2)
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Spray Drift, Droplet Spectrum (201-1)
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Spray Drift, Field Evaluation (202-1)
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Degradation Products

FIPRONIL AMIDE FOR HYDROLYSIS
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
Last Update on April 18, 1994
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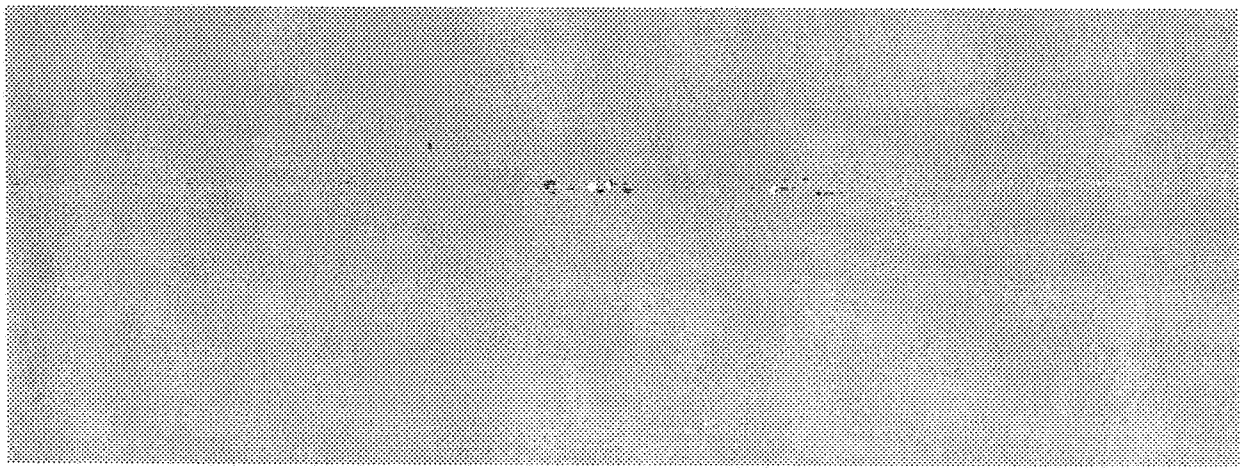
Comments



References: ENVIRONMENNTAL FATE STUDIES, FARM CHEMICAL HANDBOOK
Writer : GML

Fipronil, revised

Page _____ is not included in this copy.

Pages 18 through 27 are not included in this copy.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of 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.

✓ FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

_____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

FILE COPY

STUDY 1

CHEM 129121 FIPRONIL §161-1

STUDY ID 42194701

Corgier, M.M. and Plewa, A.P. ^{14}-MB 46030 HYDROLYSIS AT 25°c. Sponsored and Submitted by Rhone-Poulenc Secteur Agro; Lyon, France; Performed by Rhone-Poulenc under Study No. 91-25/File Ref.: AG/CRLD/AN?9215072; Study completed 16 March 1992; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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CONCLUSIONS:

The hydrolysis study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-1). No further hydrolysis data for fipronil are needed at this time.

Fipronil was reported to be stable (parent material=≈97.6% of applied during testing period) in pH 5 and pH 7 buffered solutions. However, fipronil was reported to degrade with a half-life of 28 days in pH 9 buffered solution. A fipronil amide was identified in the pH 9 buffered solution at a maximum concentration of 51.70% of applied radioactivity. Only minor degradates were discernible in the pH 5 and pH 7 test samples. In addition, volatiles were not discernible in any pH buffered test solutions during the testing period.

MATERIALS AND METHODS:

Test Material: [^{14}C]phenyl radiolabelled fipronil with a reported radiochemical purity of ≥98% and specific activity of 730 MBq/mmol was used for the test material (See Appendix A).

Reference Standards: Unlabeled standards of fipronil and RPA 200766, the hydrolyzed amide, with chemical purity of 99.3 and 96.5%, respectively, were obtained.

Treatment Solution: A 90 μg/mL ^{14}C-fipronil in acetonitrile was made up for dosing testing samples.

Buffered Solution: pH 5--Citric acid (8.4 g) was dissolved in ≈1950 mL of water and adjusted to pH 5 with 2N NaOH. The flask was brought to volume (2000 mL) with water.

pH 7--Imidazole (2.72 g) was dissolved in ≈1950 mL of water and adjusted to pH 7 with N HCL. The flask was brought to volume (2000 mL) with water.

pH 9--Dinatrium tetraborate (8.0 g) was dissolved in ≈1950 mL of water and adjusted to pH 9 with N HCL. The flask was brought to volume (2000 mL) with water.

All pHs were rechecked after the final dilution.

Sampling: Each test solution was sampled in duplicate at 0, 5, 9, 14, 20, 26, and 30 days posttreatment.

METHODOLOGY:

Prior to treatment with ^{14}C-fipronil, the buffer solutions, test bottles, and other glassware and equipment were sterilized. In a sterile system fourteen test bottles and two bottles with volatile traps (for each pH) were filled with 99 mL of the respective sterile pH buffer solution. To each test bottle 1 mL of the treatment solution was added. The sample bottles were then placed in a dark incubator at 25°C ± 1°C.

During the testing period (30 days) the temperature and pH of the testing solutions were monitored. In addition, volatile compounds formed during the testing period were trapped for in ethylene glycol monomethyl ether and 2N NaOH.

The test samples were extracted twice with 50 mL of dichloromethane. The aqueous and solvent phases were analyzed for radioactivity by LSC. In addition, the solvent phase (dichloromethane phase) was analyzed by TLC and HPLC analysis of the day 0 and day 30 test samples. Dichloromethane/ethyl acetate (85/15;v/v) and water/acetonitrile/methanol (36/34/30; v/v/v) were used for the eluent in the TLC and HPLC analysis, respectively.

NMR (nuclear magnetic resonance) was used to analyze pH 9 test samples (solvent phase) and a reference compound mixture. The signal assignment of test samples was determined by comparison of the detected signal to those of the reference compound mixture.

DATA SUMMARY:

Fipronil was reported to be hydrolytically stable at pHs 5 and 7. However, fipronil appeared to hydrolyzed to form an amide degradate at pH 9 (See Tables X-XIX). A linear regression half-life of 28 days and a rate constant of -0.0243 day^{-1} were calculated for fipronil at pH 9.

A fipronil amide (For structure see Appendix C) was reported to be discernible only in pH 9 buffered test samples. It was believed to be formed by the hydrolysis of the nitrile function of fipronil. During the testing period of 30 days it reached a maximum concentration of ≈51%.

Only minor degradate peaks were discernible in the pH 5 and pH 7 test samples during the study period when analyzed by TLC. Parent material made up 97.6% of the applied radioactivity in the pH 5 and pH 7 buffered solutions at all sampling intervals.

During the testing period the temperature of the incubation chamber ranged from 23.8 to 25.4°C with a mean range of 24.6 to 25.2°C (See Table 1).

The pH for the individual buffer solutions after sterilization ranged from 5.05 to 5.07 for the pH 5 buffer solution, 7.03 to 7.14 for the pH 7 buffered solu-

tion, and 9.03 to 9.08 for the pH 9 buffered solution for the testing period (See Table 2).

The total radioactivity recovered for each individual sample (all pHs included) ranged from 96.4 to 101.6% of the initial radioactivity (See Tables III-IX).

The TLC analysis was confirmed by analyzing the day 0 and day 30 test samples by HPLC.

NMR confirmed the pH 9 TLC and HPLC analysis, as well.

COMMENTS:

1. Sterility of test solutions was not monitored during the study. Since fipronil was stable to hydrolysis in the test pH 5 and pH 7 buffered and relatively stable at pH 9 ($t_{½}$=28), the testing method is acceptable for this pesticide. Fipronil has a half-life of 28 days at pH 9. EFGWB believes additional information on sterility during one study would not change our interpretation of the data. In future studies, the registrant should evaluate the sterility of the test samples at the initiation and termination of hydrolysis studies.

2. Even though the stock solutions were prepared using a solvent, acetronitrile, the final concentration of that cosolvent was ≤1% of the test sample.

Fipronil Review

Page _____ is not included in this copy.

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_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

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DATA EVALUATION RECORD

STUDY 2

CHEM 129121 FIPRONIL §161-2

STUDY ID 42918661

Corgier, M.M. and Plewa, A.P. ^{14}C-MB 46030 AQUEOUS PHOTOLYSIS. Sponsored and Submitted by Rhone-Poulenc Secteur Agro; Lyon, France; Performed by Rhone-Poulenc under Study No. 91-55;File ref.: AG/CRLD/AN/9215873; Study Completed 15 May 1992; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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APPROVED BY: Paul Mastradone, Chief
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Signature: Paul Mastradone
Date: 13 JUN 1994

CONCLUSIONS:

The photodegradation in water study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-2). No further photodegradation in water data for fipronil are needed at this time.

Fipronil was reported to have a half-life of 3.63 hours when exposed to a xenon light source. At 6 hours postexposure ^{14}C-fipronil made up ≈33% of applied radioactivity. There was no degradation reported in the dark controls (<2.0% of applied radioactivity). Two degradates, MB 46513 and RPA 104615 (Appendix B), were identified in the light exposure test samples. Degradate MB 46513 in TLC and HPLC analysis reached a maximum concentration of ≈43% of applied radioactivity at 6 hours postexposure. Degradate RPA 104615 in HPLC analysis (not discernible in TLC analysis) reached a maximum concentration of ≈8% of applied radioactivity. One unidentified degradate (Rf= 0.37;RT=3.3 min) in TLC and HPLC analysis of the organic phase reached a maximum concentration of ≈5.5% of applied radioactivity. Further analysis of this unidentified compound by MS and ^{19}F-NMR indicated it had a molecular weight of 410 a.m.u.. However, no molecular structure could be assigned with certainly to this degradation product. In addition, one unidentified degradate was discernible in HPLC analysis of the aqueous phase, and reached a maximum concentration of ≈4% by termination (6 hours postexposure) of the testing period. Furthermore, there were practically no volatilies (<0.04% of applied radioactivity) in the ethylene glycol and NaOH traps at termination of the study.

MATERIALS AND METHODS:

Test Material: [^{14}C]phenyl radiolabelled fipronil was obtained from Rhone-Poulenc LTD, Dagenham, U.K. A specific activity of 730 MBq/mmole and radiochemical purity of >97.5% was reported.

Reference Standards: See Appendix B.

Treatment Solution: A 90 μg/mL ^{14}C-fipronil in acetonitrile was made up for dosing testing samples.

Buffered Solution: pH 5--Citric acid (8.4 g) was dissolved in ≈1950 mL of water and adjusted to pH 5 with 2N NaOH. The flask was brought to volume (2000 mL) with water.

Light Source: A Xenon arc lamp with a ultra-violet glass to filter UV output below 290 nm was used. See Appendix C.

Sampling: The test samples were sample at the following sample intervals: 0, 1, 2, 4, and 6 hours postexposure. Whereas, the dark control sample was only sampled at one time interval (6 hours posttreatment).

Test System: See Figure 1 & 2.

METHODOLOGY:

Based on the hydrolytic stability of fipronil at pH 5, a 20 mM pH 5 buffer solution was made using citric acid. The 2000 mL buffered solution was adjusted to pH 5 with 2N NaOH and sterilized along with all necessary glassware and equipment. To 99 mL of sterile buffer solution 1 mL of the treatment solution (90 μg/mL) was added. Therefore, the final test samples contain 0.9 μg/mL fipronil and 1% acetonitrile co-solvent.

One mL of the above buffer solution and one mL of the test solution was diluted to 100 mL with acetonitrile in a flask and analyzed by LSC in duplicate for radioactivity content.

The treated test samples were placed in the light exposure apparatus (See Figures 1 & 2). The light exposure apparatus was maintained at 25 ± 1°C with a humidified, CO_2-free air, system pump which draw any volatile compounds eventually formed into the traps (1 ethylene glycol mono methyl ether, 2 x 2 N NaOH, and 1 H_2O). The light of the artificial light source, xenon arc lamp, was filtered through a ultra-violet glass to remove radiation below 290 nm. Wavelength distribution/light intensity and UV-visible absorption spectrum are shown in Appendix C_2 and C_3, respectively.

In addition, two dark control samples were placed in an incubator at 25 ± 1°C in the dark without any trapping system.

For the light exposed test solutions, the sampling intervals were at 0, 1, 2, 4, and 6 hours post-light exposure. The dark control solutions were sampled only at the termination of the test (6 hours).

During the testing period, the air flow, pH, temperature, and light intensity of the xenon lamp were monitored. The flow rate was measured and reported to be 233 mL/min. The pH data, temperature data, and light intensity data are reported in Table II, I, and III, respectively.

The test sample was transferred to a 250 mL separator and extracted twice with dichloromethane. Both extracts were mixed and a 0.2 mL aliquot was analyzed for radioactivity content by LSC. The samples were the stored at -20°C until TLC and HPLC analyses. For TLC and HPLC analyses, approximately 25 mL of the extract was evaporated to dryness under vacuum and redissolved in 1 mL of acetonitrile.

Ten μL of the concentrated test solution was applied to the TLC plate and eluted with dichloromethane/ethyl acetate (95/2,v/v). Standards of MB 46030, MB 46513, MB 46136, and MB 45950 were simultaneously chromatographed with the test samples.

The distribution of the radioactivity was quantified using a TLC analyzer and spots were also visualized by autoradiography.

Twenty-five μL of the same concentrated test solution was also analyzed by reverse phase HPLC. Each sample injected in duplicate. The mobile phase used was acetonitrile/0.05 M ammonium acetate in water (36/64,v/v).

The aqueous phases were analyzed by HPLC. For determination of the aqueous phases, the whole aqueous phases was evaporated to dryness and redissolved in 1 to 2 mL of water. An aliquot (100 μL) was injected into the HPLC column along with analytical standards of RPS 104615 and RPA 200761. The mobile phase used was the same (acetonitrile/0.05 M ammonium acetate in water (36/64,v/v) as that used for the extract phase analyses.

To purify the Rf-0.37 degradate, the dichloromethane extracts of the 6 hour samples were mixed and evaporated to dryness. The residue was then redissolved in 5 mL of dichloromethane and evaporated to ≈300 μL. An aliquot was then analyzed by MA-^{19}F-NMR. The 4 hour samples were used to confirm the presence of parent material and MB46513, as well.

The organic extracts from the 4 hour post light exposed samples were concentrated and analyzed by MS-^{19}F-NMR for confirmation of TLC and HPLC analysis.

DATA SUMMARY:

Fipronil was reported to have a half-life of 3.63 hours (0.33 days of Florida summer sunlight) when exposed to a xenon light source. At 6 hours postexposure ^{14}C-fipronil made up ≈33% of applied radioactivity. There was no degradation reported in the dark controls. Two degradates, MB46513 and RPA 104615 (See Table IA), were identified in the light exposure test samples. Degradate MB 46513 in TLC and HPLC analysis (See Tables V - XVI) reached a maximum concentration of ≈43% of applied radioactivity at 6 hours postexposure. Degradate RPA 104615 in HPLC analysis (not discernible in TLC analysis) reached a maximum concentration of ≈8% of applied radioactivity. One unidentified degradate (Rf= 0.37;RT=3.3 min) in TLC and HPLC analysis of the organic phase reached a maximum concentration of ≈5.5% of applied radioactivity. Further analysis of this unidentified compound by MS-^{19}F-NMR indicated it had a molecular weight of 410 a.m.u.. However, no molecular structure could be assigned with certainly to this degradate product. In addition, one unidentified degradate was discernible in HPLC analysis of the aqueous phase, and reached a maximum concentration of ≈4% by termination (6 hours postexposure) of the testing period. There was no apparent degradation (<2.0%) of ^{14}C-fipronil in the control test samples. Furthermore, there were practically no volatilies (<0.04% of applied radioactivity) in the ethylene glycol and NaOH traps at termination of the study.

There was no significant pH change observed after sterilization and during photolysis (pHs ranged from 5.02 to 5.04) (See Table II).

The temperature ranged from 24.2 to 25.5 for the test (light source) samples and 25.1 to 25.3 for the dark control samples (See Table I).

The maximum amount of radioactivity recovered in the aqueous phases was 13.3% of applied radioactivity which was at 6 hours postexposure. At 0 hours postexposure practically all the radioactivity was found in the extract phases. Therefore, fipronil was completely extracted using the test procedures extraction method. The total radioactivity recovery of for each individual sample ranged form 99.1 to 103.5% of applied radioactivity (See Table IV).

COMMENTS:

1. The conversion for light source hours to summer sunlight in Florida was based on an incident light intensity of 464 W/m^2.

2. An UV spectrum of the buffered solution and the buffered test solution was not furnished.

Fipanil Sulfone

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Pages 59 through 86 are not included in this copy.

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_____ Description of quality control procedures.

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DATA EVALUATION RECORD

STUDY 3

CHEM 129121 FIPRONIL §161-3

STUDY ID 42918662

Burr, C.M. and Austin, D.J. M&B 46030-^{14}C SOIL PHOTOLYSIS STUDY. Sponsored and Submitted by Rhone-Poulenc Rorer; Dagenham, Essex, England; Performed by Rhone-Poulenc under Laboratory Project ID P90/050; Study Completed 3 June 1992; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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APPROVED BY: Paul Mastradone, Chief
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OPP/EFED/EFGWB

Signature: Paul J Mastradone

Date: 13 JUN 1994

CONCLUSIONS:

The photodegradation on soil study is scientifically valid. In addition, it can be used to fulfill the data requirement (161-3). No further photodegradation on soil data for fipronil are needed at this time.

Fipronil appears to degrade slowly with a half-life of 34 days reported for fipronil when applied to a loam soil (USDA classification, called clay-loam in study) and exposed to an intermittent (8 hours on/16 hours off) artificial light source (xenon arc lamp). For the control samples, a half-life of 49 days was reported. The percentage of ^{14}C determined in the solvent extracts of the control samples decreased only slightly (<5% of nominal radioactivity applied) during the 30 days testing period, whereas the radioactivity found in the solvent extracts of the light exposed samples decreased to 79% of the nominal radioactivity applied during the 30 day testing period. There was a corresponding increase in bound resi-dues in both the light exposed and control samples. Three degradates, RPA 200766, MB 46136, and MB 45950 (See Figure 1) (maximum concentrations=10.86% 4.03%, and 1.91% of interest regions, respectively) and 2 unidentified degradates were discernible in the light exposed samples using TLC analysis. The two unidentified degradates were identified using HPLC analysis as MB 46513 and RPA 104615 (See Figure 1) at maximum concentrations of 8.65% and 8.87% of interest regions, respectively. There were differences in the metabolites discernible in the light exposed samples and in the control samples. RPA 104615 (could not be confirmed by GC-MS) and 46513 were found only in the light exposed samples. However, MB 45950 which was detected in small amounts in the light exposed samples (≈1.5% of nominal applied radioactivity), reached 12.7% of nominal applied radioactivity by day 30 posttreatment in the control samples. The amount of CO_2 in the light exposed samples reached 2.50% of nominal radioactivity applied. CO_2 was discernible in the control samples trap at 0.29% of nominal radioactivity applied. Other volatilies were not detected at significant levels (<0.5%) in the light exposed or control traps.

MATERIALS AND METHODS:

Test Material: [^{14}C]radiolabelled fipronil, labelled at position 5 of the pyrazole ring, was obtained from Rhone-Poulenc Rorer LTD, Dagenham, Essex, England. A specific activity of 9.4 mCi mmole was reported. In addition, it was reported to be free of significant radiochemical impurities.

Reference Standards: See Figure 1. Non-radioalabelled standards of MB 46030, MR 45950, MB 45897, MB 46136, RPA 200766, RPA 105048, and RPA 104615 were obtained for analytical purposes. No chemical purities were reported.

Test Solution: Fipronil-^{14}C was dissolved in acetone and the radioactivity was measured for the stock solution. By calculating the amount present a dosing solution with a nominal concentration of 224 $\mu g/mL^{-1}$ was prepared from the stock solution.

Soil: See Table 1. The author refer to the soil as a clay-loam. However, according to the USDA classification triangle, it is a loam. Therefore, the soil in this study is referred to as a loam soil.

Light Source: A Xenon arc lamp with a ultra-violet glass to filter UV output below 290 nm was used. See Appendix IV.

Sampling: The test samples were sample at the following sample intervals: 0, 1, 3, 7, 14, 21, and 30 days samples were taken from the light exposed and control test vials. In addition, the polyurethane foam plugs, ethylene glycol, and ethanolamine/2 ethoxyethanol trap solutions were sampled for analysis and fresh replaced.

Test System: Not furnished.

METHODOLOGY:

Approximately 50 grams of 2 mm sieved, oven-dried loam soil was transferred to a test metal tray. The test tray had a surface area of 44.895 cm and an approximate soil depth of 1 cm. The test soil was then adjusted to 75% of ⅓ bar moisture holding capacity. An 0.5 mL aliquot of the test solution was applied evenly to the test soil surface. The test solution was analyzed by LSC prior to and immediately following treatment of soil. It was calculated that this procedure gave an application rate equivalent to 0.258 kg a.i. ha^{-1}.

Six prepared test trays were placed in a photolysis test chamber. The test chamber was covered with a quartz glass plate and made air-tight. Attached to the lower surface of the test chamber was an water jacket connected to a circulating cooling system in which water/ethylene glycol was pumped to maintain a soil temperature throughout the testing period of 25 ± 2°C. This allowed moist air to be drawn over the surface of the test samples and through the traps so that volatile metabolites and carbon dioxide evolved could be trapped and determined during the testing period.

These test samples were exposed to a xenon arc lamp at a intermittent light interval of 8 hours (light)/16 hours (dark) which resemble natural sunlight. The spectral energy distribution of the xenon light source and its comparison to natural sunlight are given in Appendix IV.

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All the test samples (light exposed and control) were weighed daily and any weight loss compensated for by the addition of water to keep the soil moisture at 75% of ⅓ bar moisture holding capacity. The soil in the dish used for temperature monitoring was maintained at 75% of ⅓ bar moisture capacity, as well.

In addition, six separate test trays were placed inside another photolysis chamber and sealed for control test samples. The quartz glass lid for these was covered with black polyurethane to exclude extraneous light and no light source was applied.

Samples were taken for analysis at 0, 1, 3, 7, 14, 21, and 30 days posttreatment. In addition, at the same sampling intervals the polyurethane foam plugs, ethylene glycol, and ethanolamine/2-ethoxyethanol trap solutions were taken for analysis and replaced with fresh.

The soil samples taken for analysis were extracted with acetonitrile for 3 hours and an aliquot then radioassayed by LSC. The extracts were concentrated by evaporation and the residues dissolved in 2 mL of acetone and analyzed by TLC together with reference standards of possible metabolites. Two solvent systems, dichloromethane/acetic (19:1;v/v) and dichloromethane/ethylacetate (9:1;v/v) were used for metabolite identification. Following development of the TLC plates, the plates were radioscanned and non-radiolabelled standards visualized using UV light.

In addition, to the TLC analysis described, HPLC analysis was performed. The initial HPLC method did not separate all the metabolites. Therefore, a modified HPLC method was used to reanalyze the test samples. To confirm that the samples had not deteriorated during the interval between the original chromatographic work and repeat analysis a validation exercise was undertaken.

Furthermore, the day 30 solvent extracts were submitted for GC-MS analysis for confirmation of parent and degradate analysis.

The polyurethane foam plugs, ethylene glycol trap, ethanolamine/ethoxyethanol trap, and paper tissues were extracted by acetone and analyzed by LSC.

DATA SUMMARY:

A half-life of 34 days was reported for fipronil when applied to a loam soil (USDA classification, called clay-loam in study) and exposed to an intermittent artificial light source (xenon arc lamp). For the control samples, a half-life of 49 days was reported. The percentage of ^{14}C determined in the solvent extracts of the control samples decreased only slightly (<5% of nominal radioactivity applied) during the 30 days testing period, whereas the radioactivity found in the solvent extracts of the light exposed samples decreased to 79% of the nominal radioactivity applied during the 30 day testing period. There was a corresponding increase in bound residues in both the light exposed and control samples. The amount of CO_2 in the light exposed samples reached 2.50% of nominal radioactivity applied. CO_2 was discernible in the control samples trap at 0.29% of nominal radioactivity applied. Other volatilies were not detected at significant levels (<0.5%) in the light exposed or control traps.

Three degradates, RPA 200766, MB 46136, and MB 45950 (See Figure 1) (maximum concentrations=10.86% 4.03%, and 1.91% of interest regions, respectively) and 2 unidentified degradates were discernible in the light exposed samples using TLC analysis. The two unidentified degradates were identified using HPLC analysis as MB 46513 and RPA 104615 (See Figure 1) at maximum concentrations of 8.65% and 8.87% of interest regions, respectively. There were differences in the metabolites discernible in the light exposed samples and in the control samples. RPA 104615 and 46513 were found only in the flight exposed samples. However, MB 45950 which was detected in small amounts in the light exposed

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samples (≈1.5% of nominal applied radioactivity), reached 12.7% of nominal applied radioactivity by day 30 posttreatment in the control samples.

Day 30 samples from both control and light exposed test were analyzed by GC-MS, as well. MB 46030, MB 45950, RPA 200766, and MB 46146 were confirmed in the control samples. These compounds in addition to 46513 were also confirmed in the light exposed sample. However, RPA 104615 could not be confirmed by GC-MS in the light exposed sample.

A radiochemical balance of 90-110% of nominal ^{14}C applied was reported for all samples during the testing period.

COMMENTS:

1. In this study the ^{14}C-fipronil labelled position was the 5th position of the pyrazole ring. In other laboratory studies the benzene ring was uniformly labelled. However, the material balance was satisfactory at all sampling intervals. Therefore, the label position for this study would not appear to significantly change the results.

2. Due to the low recovery of radioactivity obtained for the day 3 posttreatment light exposed test sample, a second experiment was set up with samples taken at day 0 and day 3 only. This time excess condensation was wiped off the quartz glass with paper tissue and applied to the extraction procedure. The data did provide the necessary information to validate the study.

3. The stock solutions were prepared using a solvent, acetone. The exact concentration of that cosolvent applied to the test sample could not determined from the data furnished. However, acetone is a very volatile compound, and since the half-life was determined to be 34 days, acetone present in the test solution is not expected to change the results.

4. All data was reported as percent of nominal applied radioactivity instead of ppm. In addition, the application rate was reported as kg a.i. ha. Since degradates were identified in the light exposed and control samples, no further data is needed at this time.

5. The source of the test soil was not furnished. However, the soil characterization was furnished. Therefore, the USDA classification of the soil texture could be determined.

6. The test soil, loam soil, used in this photodegradation on soil study was not the same as the test soil, sandy loam and sand, used in the aerobic soil metabolism study. EFGWB prefers that the same texture soil and from the same location be used for the test soil which allows for correlation of the laboratory data.

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Figural Device

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_____ Identity of product impurities.

_____ Description of the product manufacturing process.

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_____ Sales or other commercial/financial information.

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DATA EVALUATION RECORD

STUDY 4

CHEM 129121 FIPRONIL §162-1

STUDY ID 42918663

Waring, A.R. (^{14}C)M&B 46030: AEROBIC SOIL METABOLISM. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Hazleton UK, Harrogate, North Yorkshire, England under HUK Project No.: 68/109-1015; Study Completed 21 May 1993; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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CONCLUSIONS:

The aerobic soil metabolism study is scientifically valid. In addition, it can be used to fulfill the data requirement (162-1). No further aerobic soil metabolism data for fipronil are needed at this time. However, foreign soil with a pH of 7.8 was used for this study which is not typical of most U.S. soils. Therefore, it should be noted that this aerobic soil metabolism data may not be typical for U.S. soils.

Fipronil appears to degrade slowly by biotic mediated processes. In addition, Fipronil was reported to degrade faster in the sandy loam soil ($t_{½}$=128 days calculated from HPLC data;122 days calculated from TLC data) than sand soil ($t_{½}$=308 days calculated from HPLC data;342 days calculated from TLC data) which had a lower organic matter content and higher CEC. Half-life valves calculated from HPLC analysis were considered more accurate than those calculated from TLC analysis. Unchanged parent material and the degradate labelled MB 45897 and degradates, RPA 200766 and RPA 105048 were difficult to separate by TLC linear analysis.

Two major degradates, RPA 200766 and MB 46136 (See Appendix B2 thru Appendix B10), were identified in sandy loam soil samples and the sand soil samples at maximum concentrations of 27-38% and 14-24% of applied radioactivity, respectively. Degradates MB 45950 and MB 46513 were identified in both soil types at maximum concentrations of <5% and <1% of applied radioactivity, respectively. Degradate, MB 45897, was discernible only in the sand soil samples at maximum concentrations <1%. Six unidentified degradates were detected by HPLC in the sandy loam soil samples and three in the sand soil samples. Each of these degradates comprised <4% of applied radioactivity. Degradate, MB 46513, was found to be a photolysis product in photodegradation studies. Therefore, the authors indicated that its presence may be related to work up of certain samples for analysis. The data did show the amount of unextracted radioactivity increased from 1% to 15% and 1 to 6% in the sandy loam soil and the sand soil, respectively, during the testing period. There was no radioactivity discernible in

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the ethanedion traps and only small quantities (<3% of applied radioactivity) discernible in the ethanolamine and 2% liquid paraffin traps. Therefore, formation of volatilies is considered insignificant in the aerobic metabolism of fipronil.

MATERIALS AND METHODS:

Test Material: [^{14}C]radiolabelled fipronil, uniformly labelled in the benzene ring, was obtained from Rhone-Poulenc Agriculture. A specific activity of 44.81 μCi/mg and radiochemical purity of 99.5% was reported. Hazleton Laboratory repurified the radiolabelled fipronil and had a reported specific radioactivity of 45.06 μCi/mg. The radiochemical purity determined by Hazleton Laboratory using HPLC was reported to be 98.6%. The radiolabelled material was stored at approximately -20°C in the dark when not in use.

Reference Standards: Non-radiolabelled standards of MB 46030, MB 45950, MB 45897, MB 46136, MB 46513, RPA 200766, RPA 105048, and RPA 104615 were obtained from Rhone-Poulenc Agriculture for analytical purposes. No chemical purities were reported.

Test Solution: Fipronil-^{14}C was dissolved in acetone and the radioactivity was measured for the stock solution. By calculating the amount present a dosing solution with a nominal concentration of 224 μg/mL^{-1} was prepared from the stock solution.

Soil: Manningtree sandy loam soil was obtained from Rhone-Poulenc Agriculture, and Speyer 2.2 soil was obtained from Landwirtchaftliche und Forschungsanstalt, Speyer, Germany. The soils were sieved through a 2 mm mesh screen. See Appendix 9.5 for test soils characterization.

Sampling: Test samples were taken at the following sample intervals: 0, 1, 3, 7, 14, 30, 41, 80, 149, 252, and 336 days post-treatment. Duplicate samples were taken from each soil type at each sampling interval.

Test System: Not furnished.

METHODOLOGY:

After repurification of the test material, a 16 μg/mL fipronil solution was prepared in acetonitrile and stored for two days at 0-4°C. The radiochemical purity ws then determined by HPLC using two different solvent systems, acetonitrile:water (65:35;v/v) and acetonitrile:water:methanol (34:36:30;v/v/v). The radiochemical purity was reported to be >98%.

To 50 g aliquots of a soil in an incubation dish, 200 gm a.i./ha (0.01 mg in 525 μL acetonitrile) of fipronil was applied dropwise onto the soil surface. This was repeated forty-four times (22/soil type). Sixteen (8/soil type) separate soil dishes containing 50 g of soil were treated with fipronil at ten times the normal field application rate (0.1 mg in 500 μL of acetonitrile). In addition, non-radiolabelled fipronil was applied to six units of each soil type for biomass and microbial activity monitoring at the termination of the testing period. The treated test soil samples were then mixed separately, adjusted to 75% of ⅓ bar moisture capacity, and placed in their respective (soil type and treatment level) dark incubation chamber at 25 ± 1°C.

During the testing period, the moisture content was monitored weekly, and moist CO_2-free air was pass through the incubation chambers to collect volatilies in the systems five traps (one security trap, two polar and non-polar traps containing ethanediol/2% liquid paraffin in xylene, and two CO_2 traps containing ethanolamine).

Samples were taken in duplicate of each soil type and treatment level at 0, 1, 3, 7, 14, 30, 41, 80, 149, 252, and 336 days posttreatment. Each soil sample was extracted with acetonitrile and analyzed by LSC to determine radioactivity concentration. To identify residues the acetonitrile extract was concentrated and analyzed by HPLC. The HPLC mobile phases used were acetonitrile:water (1:1; v/v) and acetonitrile:water:methanol (34:36:30;v/v/v) along with the reference standards for parent fipronil and its degradates (MB 46136, MB 45950, MB 45897, MB 46513, RPA 200766, RPA 105048). Reference standard for RPA 104615 was included with samples taken after day 149 posttreatment and analyzed by HPLC. In addition, each test sample extract along with reference standards were analyzed by TLC using dichloromethane:glacial acetic acid (19:1;v/v) for the solvent system. Selected soil sample extracts were analyzed by GC/MS, as well.

The volatile trap solutions were analyzed by LSC to determine the radioactivity concentration. Traps solutions were replaced with fresh reagent at each sampling interval except between days 149-202 posttreatment.

DATA SUMMARY:

Fipronil degraded faster in the sandy loam soil ($t_{½}$=128 by HPLC;122 days by TLC) than sand soil ($t_{½}$=308 by HPLC;342 by TLC). Over the testing period the amount of parent compound detected declined to 12-22% of applied radioactivity in sandy loam soil and 44-46% in sand soil. Half-life valves calculated from HPLC analysis were considered more accurate than those calculated from TLC analysis due to the difficulty in separating unchanged parent material and the degradate labelled MB 45897. In addition, degradates, RPA 200766 and RPA 105048 were difficult to separate by TLC linear analysis (See Tables 7.1-7.6; See Figures 8.1-8.4).

Two major degradates, RPA 200766 and MB 46136, were identified in sandy loam soil samples and the sand soil samples at maximum concentrations of 27-38% and 14-24% of applied radioactivity, respectively. Degradates MB 45950 and MB 46513 were identified in both soil types at maximum concentrations of <5% and <1% of applied radioactivity, respectively. Degradate, MB 45897, was discernible only in the sand soil samples at maximum concentrations <1%. Six unidentified degradates were detected by HPLC in the sandy loam soil samples and three in the sand soil samples. Each of these degradates comprised <4% of applied radioactivity. Degradate, MB 46513, was found to be a photolysis product in photodegradation studies. Therefore, the authors indicated that its presence may be related to work up of certain samples for analysis.

During the testing period the amount of unextracted radioactivity increased from 1% to 15% and 6% in the sandy loam soil and the sand soil, respectively, during the testing period. In addition, there was no radioactivity discernible in the ethanedion traps and only small quantities (<3% of applied radioactivity) discernible in the ethanolamine and 2% liquid paraffin traps. Therefore, formation of volatilies is considered insignificant in the aerobic metabolism of fipronil.

In addition, the material balances ranged from 92-103% of applied radioactivity during the testing period.

COMMENTS:

1. Foreign soils were used for the study. However, the USDA soil characteriza

tions were given and the soil texture could be determined. Based on the OM/CEC coctent, these soils may not reflect US soils, and some differences may be noted in US soils.

2. The stock solutions were prepared using a solvent, acetonitrile. This use of a acetonitrile instead of water for the solvent in the test solution should not significantly affect the results of this study.

3. All data was reported as percent of nominal applied radioactivity instead of ppm. In addition, the application rate was reported as kg a.i. ha. Since degradates were identified in the light exposed and control samples and the material balance was acceptable, no further data is needed at this time.

Appendix 9.5

Final Review

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DATA EVALUATION RECORD

STUDY 5

CHEM 129121 FIPRONIL §163-1

STUDY ID 42918664

Godward, P.J. Quarmby, D.L. and Austin, D.J. (^{14}C)M&B 46030: LEACHING STUDY WITH FIVE SOILS. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Rhone-Poulenc Agriculture Ltd., Ongar, Essex, England under Laboratory Project No.: P91/089; Study Completed 8 June 1992; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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Date:_____

CONCLUSIONS:

The mobility study is scientifically valid. In addition, it can be used to fulfill the data requirement (163-1). Based on the acceptability of the adsorption/desorption study (MRID 43018801) and this column mobility study, no further mobility data for fipronil are needed at this time.

The column leaching studies using five different soils (German loamy soil, Manningtree UK loamy-sand (called Manningtree sandy loam in study), Manningtree UK loam, French sandy-clay-loam (1), and French sandy-clay-loam (2)) indicate that unaged and aged fipronil have low mobility. Most (>85%) of the applied radioactivity (unaged and aged fipronil residues) were detected in the top 0-8 cm segment of the soil columns except for the Manningtree UK loamy-sand soil in which most (>80%) of the applied radioactivity was detected in the top 0-14 cm segment. Approximately 1-8% of applied radioactivity was detected in the column leachate. The 8% recovery was from the Manningtree UK loamy sand soil columns. Two degradates, MB 46136 and MB 45950 (See Appendix B2-B10) were discernible in test samples. The degradate, RPA 200766, was discernible in the Manningtree UK loam, Manningtree UK loamy-sand, and the French sandy-clay-loam soil test samples, as well. Another degradate, RPA 104615, discernible by HPLC could not be confirmed by TLC or GC-MS. No half-life was reported for the aged fipronil since no degradation of the parent compound was observed in the French sandy-clay-loam, German loamy-sand, and Manningtree UK loam soils. The above degradates were at concentrations of ≤4% of applied in the leachate.

The adsorption/desorption study, which used the same soils as the column mobility study, indicated that fipronil was not mobile in soil, as well. These data is reviewed an attached DER.

MATERIALS AND METHODS:

Test Material: [^{14}C]radiolabelled fipronil, uniformly labelled in the benzene ring, was obtained from Rhone-Poulenc Agriculture. A specific activity of 19.62 mCi/mmole and radiochemical purity of 95.5% was reported.

Reference Standards: Non-radiolabelled standards of MB 46030, MB 45950, MB 45897, MB 46136, MB 46513, RPA 200766, RPA 105048, and RPA 104615 were obtained from Rhone-Poulenc Agriculture for analytical purposes. No chemical purities were reported for potential degradates. However, the non-radioactive fipronil had a reported chemical purity of 99.3%.

Test Solution: Fipronil-^{14}C was dissolved in acetone at a concentration of 0.157 mg/mL, and the radioactivity was measured for the solution. By calculating the amount present a dosing solution with a treatment aliquot of 250 µL was applied per column.

Soil: A total of five soils were used in the study. Two of the soils were obtained form Manningtree, UK, two from France, and one from Germany. See Table 1 and Table 2 for soil characterization. It should be noted that the soil with soil reference number 91/8 by USDA classification is a loamy-sand soil.

Test System: Column leaching study.

METHODOLOGY:

This leaching study was carried out using unaged ^{14}C-fipronil and aged ^{14}C-fipronil on five soils. Each column test was carried out in duplicate.

A 250 µL aliquot of the test solution was applied evenly to the top of the soil column and the soil surface covered. This resulted in an application rate of 197.7 g a.i./ha for fipronil. Columns were leached with 0.005M calcium chloride solution (997.5 mL) at a rate which did not exceed the infiltration capacity of the soil and kept in the dark. Following leaching, the columns were separated into six segments, extracted, and appropriate samples were analyzed by HPLC, TLC, and GC-MS. The volume of leachate was recorded from each column and analyzed by LSC.

For the aged fipronil testing, samples of the test soils, German loamy sand and UK loamy sand, were adjusted to 75% of ⅓ bar moisture holding capacity and weight into test dishes. Each test dish was treated with 250 µL of test solution and placed in a dark incubator at 22 ± 2°C. Moist CO_2-free air was passed over the soil surface through 2-ethoxyethanol/ethanolamine and ethylene glycol traps to collect volatilies and any CO_2 evolved during the aerobic incubation process. The moisture content was monitored throughout the incubation period and samples taken at 0, 2, 7, 14, 21, and 35 days posttreatment. Each test sample was extracted and analyzed to follow aerobic metabolism during the aging process prior to preparing the aged leaching columns. Aliquots of the aged soil (equivalent to 20 grams of oven-dried) was placed on the top of the column. The amount of previously aged pesticide on each column was equivalent to that used for the unaged fipronil columns. These columns were leached, extracted, and analyzed in the same manner as the unaged discussed above.

The soil segments were extracted using 280 mL of acetonitrile for three hours. Following solvent extraction, the soil residues were air-dried, weighed and

ground. Triplicate portions were weighed into combustion dishes and analyzed for bound residues by LSC.

For HPLC analysis twenty-five mL of the acetonitrile extract from each section was concentrated by evaporation to 1 mL. An aliquots of the concentrated extract was analyzed using two mobile phases. The parent and some aged extract samples were analyzed using a binary gradient system methanol/water in 1% ammonium acetate (60:40;v/v) and methanol. Some aged extract samples and preliminary samples were analyzed using acetonitrile:water (60:40) and acetonitrile:water:methanol (10:40:50) for the mobile phase.

In addition, aliquots of the extracts analyzed by HPLC were assayed by TLC using dichloromethane/acetone/ethyl acetate (95:2:3;v/v/v) for development. Plates indicating the presence of radioactivity were redeveloped with pure methanol to determine the presence of and identify metabolites.

Aliquots of solvent extracts with sufficient concentrations of parent fipronil and/or metabolites were again concentrated by evaporation. These concentrated extracts were analyzed by GC-MS for confirmation analyses.

DATA SUMMARY:

Leaching of Unaged Fipronil

Unaged fipronil appears to be slightly mobile to immobile in the five soils tested (Manningtree UK loamy-sand, German loamy-sand, Manningtree UK loam, and two French sandy-clay-loam soils. Radioactivity detected in leachates from the test column varied from <1% of applied radioactivity for the German loamy-sand and French sandy-clay-loam 1 soils to 8% of applied radioactivity in the Manningtree UK loamy-sand soil (See Table 2-4). Approximately 73-98.8% of the applied radioactivity remained in the top 0-6 cm segment of the test column, except for the Manningtree UK loamy sand columns in which most of the applied radioactivity remained in the top 0-12 cm (82-89%) segment of the test columns (see Table 3). Most of the applied radioactivity was extractable, with the exception of the French sandy-clay-loam 1 soil columns which 25-36% of the total radioactivity was unextractable. The calculated Kds (coefficient of distribution) were 35, 67, 128, 222, and 253 (See Appendix V) for the Manningtree UK loamy-sand, French sandy-clay-loam 1, German loamy-sand, Manningtree UK loam, and French sandy-clay-loam 2 soils.

The degradate RPA 200766 was discernible at concentrations of <1 to 13% of recovered extracted radioactivity in the Manningtree UK loam, Manningtree UK loamy-sand, and the French sandy-clay-loam soils. In addition, two degradates, MB 46136 and MB 45950 were discernible at levels ≤20% of recovered extracted radioactivity (See Table 6). Another degradate, RPA 104615, discernible by HPLC could not be confirmed by TLC or GC-MS.

Leaching of Aged Fipronil

Aged fipronil appears to be slightly mobile to immobile in the five soils tested (Manningtree UK loamy-sand, German loamy-sand, Manningtree UK loam, and two French sandy-clay-loam soils. Radioactivity detected in leachates from the test column varied from <1% of applied radioactivity for the French sandy-clay-loam 2 soil to 3% of applied radioactivity in the Manningtree UK loamy-sand soil (See Table 5&7). Approximately 81-94% of the applied radioactivity remained in the top 0-8 cm segment of the test column, except for the Manningtree UK loamy sand columns in which most of the applied radioactivity remained in the top 0-14 cm (≈82-84%) segment of the test columns (see Table 5).

Degradate, RPA 200766, was discernible in all soil columns except one Manningtree UK loamy-sand column at maximum concentrations of 2 to 17% of recovered

extracted radioactivity. In addition, degradates, MB 45950 and MB 46136, were discernible in some of the soil columns (See Table 7). Again the presence of degradate, RPA 104615, could not be confirmed by TLC and GC-MS. However, all other residues identified using TLC and HPLC analyses were confirmed by GC-MS. Even though the distribution of radioactivity in the soil columns and extractable and unextracted radioactivity was similar to that observed with the unaged test columns, the degradates were present at higher concentrations than in the unaged test columns. Potential degradates RPA 105048 and MB 45897 and MB 46513 were not discernible in any of the test samples by the analytical methods (TLC, HPLC, and GC-MS).

The material balances ranged from 94 to 103% for the unaged test columns, except for one French sandy-clay-loam-1 test column which had a material balance of 87%. The aged test columns had a reported material balance of 95 to 102% except for the two French sandy-clay-loam test columns which had material balances of 91%.

COMMENTS:

1. Foreign soils were used for the study. However, the USDA soil characterizations were given and the soil texture could be determined. The authors provided the USDA classification for all five soils used. However the Manningtree UK sandy loam soil is a loamy-sand soil by USDA classification. Therefore, the soil was referred to as a Manningtree UK loamy-sand in this DER. Furthermore, based on OM/CED content, these soils may not reflect US soils, and there may be some differences in the test results when using US soils.

2. Soil segments below 14 cm were found to have residues below the detection limits (<0.018 mostly <0.01 ppm). Therefore, those soil segments below 14 cm were not analyzed by HPLC, TLC, and GC-MS. This should not significantly change the results of this study since the material balances for all test columns was satisfactory.

3. All data was reported as percent of nominal applied radioactivity instead of ppm. In addition, the application rate was reported as kg a.i. ha. However, it appears that all residues <0.02 ppm (mostly 0.01 ppm) were identified. The corrected data was calculated, as well.

4. Because soil column by their nature are not in equilibrium and hence reliable and/or reproducible, partition coefficient can not be determined/calculated. Therefore, EFGWB does not except soil column Kds and were not included in this DER.

Final Review

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Pages 123 through 131 are not included in this copy.

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_____ Identity of product inert ingredients.

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DATA EVALUATION RECORD

STUDY 6

CHEM 129121 FIPRONIL §163-1

STUDY ID 43018801

Godward, P.J. Quarmby, D.L. and Austin, D.J. (^{14}C)M&B 46030: ADSORPTION/DESORPTION ON FIVE SOILS. Sponsored and Submitted by Rhone-Poulenc Agriculture Ltd.; Ongar, Essex, England; Performed by Rhone-Poulenc Agriculture Ltd., Ongar, Essex, England under Laboratory Project No.: P91/084; Study Completed 4 June 1992; Received by EPA 24 August 1993.

DIRECT REVIEW TIME = 1.8 day

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APPROVED BY: Paul Mastradone, Chief
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OPP/EFED/EFGWB

Signature:

Date: 13 JUN 1994

CONCLUSIONS:

The mobility study is scientifically valid. In addition, it can be used to fulfill the data requirement (163-1). Based on the acceptability of this adsorption/desorption study (MRID 43018801) and the column leaching study (MRID 42918664), no further mobility data for fipronil are needed for this EUP.

This study had reported adsorption Koc values ranging from 2671 to 7818 which indicate that fipronil is not mobile in the five foreign soils tested. The Freundlich constants were reported to be 89.6, 26.2, 148.6, 58.1, and 67.2 for German loamy-sand, Manningtree UK loamy-sand, Manningtree UK loam, French sandy-clay-loam 1 and 2 soils, respectively. In addition the results shows a negative correlation between adsorption and organic matter content. The lowest organic matter content soils had the highest Koc values while the high organic matter content soils had the lowest reported Koc values. Furthermore, the results did indicate a correlation between Kd values and soil pH and Cation Exchange Capacity (CEC). The isotherms obtained for the adsorption of fipronil from aqueous solutions at concentrations of 0.01 to 1.0 μg/mL fipronil were linear. The correlation coefficients (R^2) obtained using linear regression analysis were in the range of 0.947 to 0.969 for the adsorption phase and 0.88-1.003 for the desorption phases. The desorption K values indicate that, except for the Manningtree UK loamy-sand soil, the desorption K values were of the same order as those for adsorption. There was a slow increase in desorption for most soil at each desorption cycle.

The column leaching study used the same five soils as the adsorption/desorption study. The results of the column leaching study indicated that fipronil is not mobile in the five soils tested, as well. This data is reviewed an attached DER.

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MATERIALS AND METHODS:

Test Material: [^{14}C]radiolabelled fipronil, uniformly labelled in the benzene ring, was obtained from Rhone-Poulenc Agriculture. A specific activity of 19.62 mCi/mmole and radiochemical purity of 95.5% was reported.

Reference Standards: Non-radiolabelled standards of MB 46030, MB 45950, MB 45897, MB 46136, MB 46513, RPA 200766, RPA 105048, and RPA 104615 were obtained from Rhone-Poulenc Agriculture for analytical purposes. No chemical purities were reported for potential degradates. However, the non-radioactive fipronil had a reported chemical purity of 99.3%. Another non-radiolabelled MB 46030 standard was obtained from Rhone-Poulenc Agrochimie, St. Fons, Lyon, France which had a reported chemical purity of 95.4%.

Test Solutions: Stock solution was diluted with 0.005 M aqueous calcium chloride to obtain test solutions containing 1, 0.2, 0.05, and 0.01 µg/mL MB 45030 and concentrations determined by LSC.

Soil: A total of five soils were used in the study. Two of the soils were obtained form Manningtree, UK, two from France, and one from Germany. See Table 1 and Table 2 for soil characterization. It should be noted that the soil with soil reference number 91/8 by USDA classification is a loamy-sand soil. Each soil was air-dried to constant weight and sieved through a 2 mm sieve.

Test System: Adsorption/desorption test method.

METHODOLOGY:

After each test solutions was analyzed by LSC, a 10 mL 0.005 M calcium chloride + test solution aliquot (See Table 3) of the appropriate test solution was applied to duplicate 2.5 gram aliquots of each air dried test soil in separate test tubes. The test tubes were stoppered, reweighed, and wrapped in aluminum foil to avoid photolysis during the testing period. These prepared test tubes were then shaken vigorously for 24 hours to ensure complete suspension of the test soils and centrifuged. Supernatants were decanted into separate vials and taken in triplicate aliquots (0.05, 0.25, or 1.0 mL) for LSC analysis.

The desorption phase was carried out by adding 10 mL of 0.005 M aqueous calcium chloride to each of the test tubes after the supernatants were removed. The test tubes were again stoppered, shaken for 1 hour, and centrifuged. After centrifugation the supernatants were decanted and triplicate aliquots (0.05 to 3.0 mL) submitted for LSC analysis. This entire desorption phase was repeated more four times.

After completion of the desorption phase, the each test soil residue was extracted with acetonitrile. The acetonitrile phases from each test soil was decanted and triplicate aliquots of the acetonitrile extracts (0.05, 0.25, or 1.0 mL) were submitted for LSC analysis. The extracted soil residues were then weighed, mixed, and ground prior to being submitted to combustion for radioactivity analysis.

To determine the stability of fipronil adsorption phase extracts were concentrated by freeze drying and redissolved in methanol for TLC analysis. TLC was

performed on the concentrated adsorption and first desorption extracts from the test soils treated at the 1.0 μg/mL level. The TLC mobile phase used was dichloromethane/acetone/ethyl acetate (95:2:3;v/v/v). In addition, one TLC plate was redeveloped with methanol to determine if degradate, RPA 104615, was present in the radioactive material remaining at the origin. Reference standard, MB 46030-parent fipronil, was applied along side of the test samples for comparison. These samples were analyzed by HPLC and GC-MS, as well. The mobile phases used for the HPLC was methanol/water (40:60 + 1% ammonium acetate) and pure methanol.

DATA SUMMARY:

Reported K (Freundlich constant) and Koc (organic carbon basis) values of 89.6 and 2671 for German loamy-sand soil, 26.2 and 818 for Manningtree UK soil, 148.6 and 3493 for Manningtree UK loam soil, 58.1 and 4991 for French sandy-clay-loam 1 soil, and 67.2 and 4214 for French sandy-clay-loam 2 soil, respectively, indicate that fipronil is immobile to very slightly mobile. There appears to be a negative correlation between Koc values and organic matter content since the soils high in organic matter (German loamy-sand and Manningtree UK loam soils) had low Koc values. In addition there does not appear to be a correlation between K and Koc values and soil types. The two loamy-sand soils had very different Koc values (2671 and 7818) while the other test soils had relative similar Koc values (3493 to 4991). The slopes (1/n) values for the adsorption phase ranged from 0.947-0.969.

The desorption values from the desorption phases were of similar order to the adsorption values. The desorption values slowly increased if at all with each of the five desorption phases. Therefore, the study authors indicated that the forces involved in the adsorption phase were similar to those involved in the desorption phases for most of the test soils.

The material balances for the treated fipronil test soils at all concentrations ranged from 91.85 to 99.21 of applied radioactivity.

COMMENTS:

1. Foreign soils were used for the study. However, the USDA soil characterizations were given and the soil texture could be determined. The authors provided the USDA classification for all five soils used. However the Manningtree UK sandy loam soil is a loamy-sand soil by USDA classification. Therefore, the soil was referred to as a Manningtree UK loamy-sand in this DER. Furthermore, based on OM/CED content, these soils may not reflect US soils, and there may be some differences in the test results when using US soils.

2. All data was reported as percent of nominal applied radioactivity instead of ppm. In addition, the application rate was reported as kg a.i. ha. However, it appears that all residues <0.01 ppm and/or 10% of applied were identified.

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