Date Out: MAR 15 1994

Chemical Code:121301
DP Barcode:D199290

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: Phillip Hutton, PM # 18
Special Review and Reregistration Division (H7508W)

From: Elizabeth Behl, Section Head
Ground Water Technology Section
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C) Henry Jacoby 3/14/94

Attached, please find the EFGWB review of...

Common Name:	Cyromazine	Trade name:	Trigard
Company Name:	Ciba		
ID #:	000100-00654		
Purpose:	Review addendum to Final Report for Small-Scale Ground-Water Monitoring Report of Cyromazine on Tomatoes in Florida.		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
insecticide	331	DP Barcode 199290	3 days

STATUS OF STUDIES IN THIS PACKAGE:

Guideline #	MRID	Status[1]
166-1	430612-00 to 03	A

STATUS OF DATA REQUIREMENTS ADDRESSED IN THIS PACKAGE:

Guideline #	Status[2]
166-1	S*

2021002

* Additional ground-water studies have been required.

[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.

DP BARCODE: D199290

CASE: 003141
SUBMISSION: S456384

DATA PACKAGE RECORD
BEAN SHEET

DATE: 03/10/94
Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REGISTRATION ACTION: 331 RESUBMISSION
RANKING : 15 POINTS (K)
CHEMICALS: 121301 Cyromazine 75.0000%

ID#: 000100-00654 TRIGARD 75W
COMPANY: 000100 CIBA-GEIGY CORP.
PRODUCT MANAGER: 18 PHILLIP HUTTON 703-305-7690 ROOM: CM2 213
PM TEAM REVIEWER: MICHAEL MENDELSOHN 703-305-5409 ROOM: CM2 203
RECEIVED DATE: 12/22/93 DUE OUT DATE: 06/30/94

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 199290 EXPEDITE: Y DATE SENT: 02/10/94 DATE RET.: / /
CHEMICAL: 121301 Cyromazine
DP TYPE: 001 Submission Related Data Package

	CSF:	LABEL:	
ASSIGNED TO	DATE IN	DATE OUT	ADMIN DUE DATE: 06/10/94
DIV : EFED	02/14/94	/ /	NEGOT DATE: / /
BRAN: EFGB	02/15/94	/ /	PROJ DATE: 03/10/94
SECT: GTS	02/15/94	03/10/94	
REVR : JWOLF	03/02/94	03/08/94	
CONTR:	/ /	/ /	

* * * DATA REVIEW INSTRUCTIONS * * *

Attention Betsy Behl/David Wells/Jim Wolf:

Subsequent to our 9/9/93 meeting with Ciba, minutes attached FYI, they have submitted additional sampling data and requested to terminate the cyromazine prospective groundwater study. Please review the attached letter and data and determine whether the study can be terminated. Thanks.

* * * DATA PACKAGE EVALUATION * * *

No evaluation is written for this data package

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

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RESPONSE TO REVIEW OF SMALL-SCALE PROSPECTIVE GROUND-WATER MONITORING STUDY FOR CYROMAZINE FINAL REPORT AND REQUEST TO TERMINATE STUDY.

1. CHEMICAL:
Chemical name: N-Cyclopropyl-1,3,5-Triazine-2,4,6-Triamine
Common name: Cyromazine
Trade name: Trigard® 75W, Larvadex®, Citation®
Structure: Not Applicable

Physical/Chemical Properties:

Chemical Formula	$C_6H_{10}N_6$
Molecular Weight	166.19
Water Solubility	1100 mg/L @20 °C (pH7.5)¶
	136000 mg/L§
	13600 mg/L¶
K_d	0.52 to 3.87
Vapor Pressure	3.36×10^{-9} torr
$\log K_{ow}$	--
Field dissipation half-lives	75 to 284 days¶§
Aerobic soil metabolism	150 days¶
Anaerobic soil metabolism	--

¶Wauchope et al., 1992
§One-Liner Database, USEPA, 1992

2. TEST MATERIAL:
Not Applicable.

3. STUDY/ACTION TYPE:
331 RESUBMISSION/REGISTRATION Review of Responses to Final Report for Small-scale prospective ground-water monitoring study and request to terminate study.

4. STUDY IDENTIFICATION:

MRID #	TITLE
430612-00	Transmittal Document
430612-01	Authors: B. Gold/K. Balu. Response to EPA Review of Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine (MRID 422835-03)
430612-02	Authors: B. Gold/K. Balu. Response to EPA Review of Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine (MRID 422835-03)
430612-03	Author: Andrew M. Hiscock. Response to EPA Review of Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine (MRID 422835-03)

Regulatory Classification

MRID	STUDY	DATA REQUIREMENT
430612-01(2 of 4)	N/A	166-1
430612-02(3 of 4)	N/A	Supportive Information
430612-03(4 of 4)	N/A	Supportive Information

Identifying No: ID# 000100-00654
Case: 003141
Submission: S456384
DP Barcode: 199290
Action Code: 331 Resubmission
Date Sent to EFED: 2/14/94
Date Received by EFED: 3/02/94

5. Reviewed by:
James K. Wolf
Soil Scientist
OPP/EFED/EFGWB/GWTS

Signature: James K. Wolf
Date: 3/8/94

6. Approved by:
Elizabeth Behl
Section Head
OPP/EFED/EFGWB/GWTS

Signature: EBehl
Date: 3/9/94

7. CONCLUSIONS:

Cyromazine and melamine are quite persistent under certain conditions and can reach ground water. Additional soil and water samples were requested by the Branch in the previous review (DP 178192, 1993). No further cyromazine residues were detected in soil samples 456 and 484 days after treatment (DAT) with a detection limit of 10 ng/g (ppb). Melamine was present in two (10.1 and 12.6 ng/g) of three 0 to 6 inch soil samples 456 DAT and one (19.3 ng/g) of three 0 to 6 inch soil samples 484 DAT. In summary, melamine may remain in soil at low levels for some time after application.

Additional ground-water samples were collected 334, 370, 407, and 429 DAT and analyzed for cyromazine and melamine. There continued to be no detections of cyromazine in ground-water samples with a detection limit of 0.10 µg/L (ppb). There was one melamine detection (0.11 µg/L) out of four samples collected in the shallow control (up-gradient) monitoring well. There were no detections of melamine in any of the other nine monitor wells (36 samples). The source of the melamine in the control well was unknown. The registrant speculated that it was due to analytical interference or from another source (e.g., fertilizer or plastic).

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The study is acceptable to meet the requirements of a small-scale prospective ground-water monitoring (166-1) study, as the registrant conducted the study more or less using *draft* Guidance for Ground-Water Monitoring Studies (Eiden, Lorber, Holden, and DeBuchananne, 1988). The overall study results and conclusions are limited, due to the fact that the study was conducted at one site and reflects only the conditions of the one site.

8. RECOMMENDATIONS:

a). It is recommended that Ciba's request for the decommissioning of the Florida study site be approved.

b). The (2), (5) and (6) recommendations from the earlier review still are required and repeated below.

(2) Because this study indicated that cyromazine residues can leach in a worst-case environment, it is recommended that the registrant conduct one or more well-water monitoring surveys in a cyromazine use area, such as lettuce and celery rather than retrospective studies as previously stated in earlier reviews (memos C. Eiden, 7/26/89; Hutton, 1/4/90). The registrant could also consider conducting a prospective study in a use area in AZ, CA, or TX.

(5) A label advisory should be developed indicating that a potential exist for ground-water contamination. The label advisory should state:

> "Residues of cyromazine have been found in ground water as a result of agricultural use. Use of this product in areas where soils are permeable and water tables are shallow could result in contamination of ground water. The utilization of irrigation water in these areas will increase the likelihood of contamination".

Based upon the results of the additional analyses from the prospective ground-water monitoring study conducted in Florida, well monitoring studies in cyromazine use areas, and the results of the environmental and human risk assessment, use restrictions may be required under certain conditions.

(6) The potential for surface water contamination should be addressed by the registrant.

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9. BACKGROUND:

Cyromazine is stable to hydrolysis and photolysis, and is also quite persistent since the aerobic soil metabolism half-life ($T_{½}$) is around 150 days. Field dissipation values are quite variable, ranging from 75 days to more than 250 days. Soil adsorption coefficients are generally quite low. Freundlich adsorption coefficients (K_{ads}) were less than 5 for three mineral soils (sand, silty clay loam, and silt loam). The K_{ads} values are not equal to K_d, because the slope (1/n) in the adsorption isotherm was less than 1 (0.77 to 0.85). A primary degradate of cyromazine is melamine. At least two other degradates have also been identified. The registrant has indicated that certain plastics and fertilizers are potential sources of melamine in addition to cyromazine degradation. A comparison of environmental fate data of cyromazine is compared to environmental fate data of pesticides know to leach (Table 1).

Environmental fate data, submitted by the registrant, indicated that under certain conditions (sandy soils) cyromazine is both mobile and persistent, and will leach in soil.

Environmental fate data and monitoring data also indicate that the melamine degradate is both mobile and persistent, and will leach in soil. The persistence ($T_{½}$), adsorption (K_d), and dissipation rate of melamine has not been addressed. Aerobic metabolism studies indicated that melamine levels could be as much 33 percent of the parent. Melamine residues were detected at levels ranging from 0.10 to 0.21 µg/L in shallow ground water at the study site in Florida.

No detections of cyromazine residues were reported in the Pesticides in Ground Water Data Base (Hoheisel et al., 1992). This maybe because very few ground-water samples have been analyzed for cyromazine (and melamine) residues in the United States and because it has limited use areas and crops. Cyromazine (and melamine) was not included in the suite of analyses conducted in the USEPA's National Survey of Pesticides in Drinking Water Wells (USEPA, 1990a).

Currently, the only registered uses of cyromazine (Trigard® 75WP) are on celery and head lettuce to control leafminers; on chrysanthemums (Citation® 75W) grown in greenhouses; and to control flies in chicken houses (Larvadex). Cyromazine is typically applied in multiple applications to foliage by aerial or ground equipment. Cyromazine is applied up to six times per year with application rates range between 0.125 and 0.25 lbs ai/acre

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(0.167 to 0.333 lb per acre) for a total of 0.75 lbs ai/acre (1 lb/acre). The registrant is proposing to register cyromazine for use on peppers, tomatoes, carrots, cucurbits, leaf lettuce, spinach, and mushrooms. EFGWB has previously recommended that Section 18 requests for cyromazine in Florida, New York, and Texas not be granted.

Health Advisory (HA) levels have not been established for cyromazine or cyromazine degradates.

Table 1. Physical and Chemical Characteristics[1] of CYROMAZINE Relative to EPA Leaching Criteria.

CHARACTERISTIC	LEACHING CRITERIA	CYROMAZINE PARAMETERS
Water Solubility	> 30 mg/L	1.35×10^5
Henry's Law Constant	$<10^{-2}$ atm-m^3/mol	5.83×10^{-7} atm-m^3/mol
Hydrolysis half-life	> 25 weeks	pH5 - stable pH7 - stable pH9 - stable
Photolysis half-life	> 1 week (water)	stable
Soil adsorption: K_d	< 5 (usually <1-2) [listed as K not K_d]	kads 1/n clay %OM 0.52 0.83 2.8 2.2 2.37 0.85 22.6 5.6 3.87 0.77 12.6 3.6 17.0 0.81 - 22.9
Soil adsorption: K_{oc}	<300-500	81,208, 970, 1800
Aerobic soil metabolism half-life	> 2-3 weeks	150 days (21 wks)
Field dissipation half-life	> 2-3 weeks	83-284 days
Depth of leaching in field dissipation study	> 75-90 cm	46-91[2] cm

[1] USEPA One-liner Database, 1992.

Indicates exceeds leaching criteria (environmental fate data are not complete).

[2] Depth of leaching may in some instances may have been deeper than sampling depth.

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10. DISCUSSION:

a. Background

The registrant submitted a protocol for a small-scale prospective ground-water monitoring study which was reviewed and found to be deficient (USEPA, 1990b). The registrant also met with EFGWB several times and submitted responses to the EFGWB review (EFGWB #s 91-0222, 91-0569). The prospective study was initiated and completed prior to the registrant receiving EFGWB approval and acceptance of the protocol. The registrant submitted a Final Report for this prospective study which was received on April 16, 1992. The report was reviewed by the Environmental Fate and Ground Water Branch (EFGWB) and found to be incomplete (EFGWB, USEPA; 1/11/1993; DP Barcode 178192; EFGWB # 92-0891).

Two primary issues were identified in the previous review of the cyromazine prospective ground-water monitoring study. The first issue dealt with the impact of cyromazine use on tomatoes on ground-water quality in Florida. The second issue was whether the Florida study could be used to support additional uses (vegetables, cucurbits, and carrots) of cyromazine and in other states (Arizona, California, Florida, and Texas) to control leafminers.

The purpose of this review is to evaluate Ciba's responses to the EFGWB Branches review (DP Barcode 178192; EFGWB # 92-0891) of the Final Report for the Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine use on tomatoes in Florida; and to evaluate Ciba's request to terminate the Florida ground-water monitoring study. This review does not address the survey of wells in cyromazine use areas and the mitigation measures (paragraph 1 and 2 of the Transmittal Document, MRID# 430612-00).

b. Discussion to Response to EPA Review of Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine (MRID# 430612-01).

Note: page numbers refer to the stamped page number at the top of each page and thus are consecutive page numbers.

1. Data Requirement

The title page indicates that the study addresses data requirement 164-1. This would appear to be incorrect as this study address data requirement 166-1 (Prospective Ground-Water Monitoring).

2. Additional Analyses of Soil and Ground Water, page 9. (October 7, 1991 to March 5, 1992).

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The Branch required Ciba to sample and/or analyze additional ground-water samples and to collect additional soil samples (0 to 6 inches, because melamine residues were detected in four monitoring wells after the last cyromazine application and melamine and cyromazine in soil were shown to be quite persistent.

Ciba collected three additional (reps A, B, C) soil samples at their intervals 34 and 35 (446 and 484 days after treatment (DAT)). Two depth increments (0-6 and 6-12 inches) were collected at interval 34; three intervals (0-6, 6-12, and 12-18 inches) were collected at interval 35. The results are summarized by Table II (page 24 of Ciba report). There were no cyromazine detections with a detection limit of 10 ng/g in any sample. Melamine was detect in three of the 0 to 6 inch samples: two for interval 34 (10.1 and 12.6 ng/g) and one for interval 35 (19.3 ng/g). The results are summarized by the attached Table III (Table II, page 24 of Ciba report). Procedural recoveries were also shown and appear to adequate.

The monitor wells were sampled at interval 30, 31, 32, and 33 (334, 370, 407, and 429 DAT). There were no detections of cyromazine with a detection limit of 0.1 µg/L, which corresponded to earlier results. There was one detection (0.11 µg/L) in the shallow control well at sampling interval 31. Results summarized in Table III (Table I, page 23 of Ciba report). These results more or less conform with the earlier results, in that there were in frequent detections of low levels of melamine and no detections of cyromazine.

The cause of the melamine in the up-gradient (control well) was not known. Ciba speculates that it could be due to the analytical method or "from field sources". The exact context of "from field sources" is not known, but is assumed to mean from another source other than the cyromazine. Both these are possible, as is perhaps a change in the direction of ground-water flow. Soil and ground-water samples show that melamine can be quite persistent under certain conditions, as it is still present in low levels in a few samples.

3. Analytical Methods, page 5 to 7; and Response to EPA Review of Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine (Volume 3 of 4, MRID 430612-02).

Ciba provided information on analytical procedures used for cyromazine, melamine, and bromide analysis. Methods for soil characterization were also provided.

c. Vol 3 of 4, Table 2 - Recovery Data for Well Water Fortified with cyromazine and melamine, page 17 and Table II - Recovery Data for Soil Fortified with cyromazine and melamine, page 34.

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i) Recoveries of cyromazine and melamine appear to fairly good for water. The recoveries in water ranged from 81 to 92% for cyromazine at levels from 0.1 to 10.0 µg/L, and 86 to 104% for melamine at levels from 0.1 to 10.0 µg/L.

ii) Recoveries of cyromazine and melamine in soil were not quite as good. In soils fortified with 10 ng/g of cyromazine recoveries ranged from 70 to 83 percent. The sample fortified with 100 ng/g was off scale, and therefore not determined (note no replication). Recoveries were better (84 and 92%) for melamine fortified with 10 ng/g melamine. Recovery of melamine in a soil sample fortified with 100 ng/g was only 16% (again note no replication).

The lack of adequate replication, especially for the soils, provide limited information about how reproducible the methods are and lowers the confidence in the values reported.

b. The methods of bromide determination in water and soil was also provided (Vol 3 of 4, pages 40 to 66). Tables I (page 56), II (page 57), and Table III (page 58) show that overall recoveries of bromide in soil and water were good, ranging typically between 90 and 110 percent (extremes were 74 to 150 %) for water and between 85 and 100 percent for soil.

4. Ciba's responses to questions from EPA review.

The responses and additional information and clarifications for these questions are acceptable.

d. Discussion to Small-Scale Prospective Ground-Water Monitoring Study for Cyromazine, Addendum to EPA Report (MRID# 430612-03). Volume 4 of 4.

This volume is the addendum to the final report which addresses the additional sampling from October 7, 1991 through March 5, 1992 (sampling intervals 30 to 35) and provides a detailed discussion on the additional monitoring data, which are summarized in part b of this document.

The results of this study which were reported in the earlier final report and this addendum to the final report do not entirely agree with the last paragraph of the Summary and Conclusions (Vol. 4 of 4, page 16 of 49). The last paragraph is as follows:

"The lack of detection of the test substance in the monitoring wells indicates that cyromazine and the degradate melamine, under worst case conditions, do not pose a threat to ground water. Therefore, normal use of Trigard® insecticide (active ingredient cyromazine) following typical agronomic practices for tomato

production results in no potential impact on ground water resources".

The cyromazine degradate melamine was detected in ground water at the Florida study site, so the use of cyromazine did impact ground water quality. There were melamine detections in several wells, thus the statement "lack of detection" is not correct. The levels of melamine were, however, quite low and tended to vary greatly both spatially and temporally. Thus, there is a demonstrated impact to ground water quality from the use of the cyromazine. Based upon the limited data which were obtained from the Florida study site, the levels of melamine detected in ground water would probably not have a detrimental impact to water quality.

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REFERENCES

Hoheisel, C., J. Karrie, S. Lees, L. Davies-Hilliard, P. Hannon, R. Bingham, E. Behl, D. Wells, and E. Waldman. 1992. Pesticides in Ground Water Database. A compilation of monitoring studies: 1971 - 1991 National Summary. EPA 734-12-92-001. U. S. Environmental Protection Agency: Arlington, VA.

USEPA. 1990a. National Survey of Pesticides in Drinking Water Wells. OW/OPTS Washington, DC

USEPA. 1990b. Review of protocol for small-scale prospective ground-water study. Dated: 12/10/90. EFGWB #(s) 90-0604, 90-0721. USEPA OPP/EFED/EFGWB Washington, DC

USEPA. 1992. Pesticide Environmental Fate One-liner Database. Date: 3/17/92 OPP/EFGWB. Washington, DC

Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, and J.P. Burt. 1992. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. Reviews of Environ. Contam. and Tox. 123:1-164.

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