

MAR 31 1980

Date Out EFB: MAR 31 1980

TO: Product Manager Jacoby (21)
TS-767

Through: Dr. Gunter Zweig, Chief /
Environmental Fate Branch

From: Review Section No. 1 *McCabe*
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 618-75, 9F2216

Chemical: 2-(4-Thiazolyl)benzimidazole

Type Product: Fungicide

Product Name: Mertect 340-F Fungicide

Company Name: Merck Sharp & Dohme

Submission Purpose: Rice

EFB #240 + #259

Action Code - None

ZBB Code: Sec. 3

Date in: 8/6/79 + 9/20/79

Date Completed: MAR 31 1980

Deferrals To:

Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

I. Introduction

Submission No. 618-75, 9F2216, is reviewed for the conditional registration of MERTECT 340-F for use on rice.

MERTECT[®] 340-F is a flowable fungicide (water dispersal suspension) contains 3.8 lb/gal (42.28%) the active ingredient 2-(4-thiazolyl) benzimidazole*.

The product is identical to the registered products used for similar uses; none of which, however, used for aquatic food-crop use.

Submission includes some of the environmental chemistry studies required for the proposed use.

II. Directions for Use

The proposed label indicates the following amendment.

Rice:

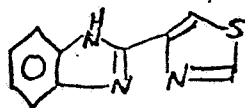
Apply MERTECT 340-F at 6.0-12.0 fl. oz. per acre per application, in sufficient water to cover, minimum 15 gallons of water per acre for aerial application. Make 2 applications per season; the first application at boot initiation followed by a second application 14-21 days later.

Do not use in California.

III. Discussion of Data

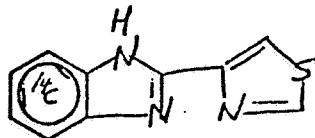
3.1 Thiabendazole Anaerobic Aquatic Metabolism (Interim Report C), Vol. 1, July 26, 1979 by Raltech Scientific Services, Inc. for Merck and Co.

* Structure:



Procedure

Four flask metabolism chambers (2 sterile and 2 non-sterile), each containing a layer of California rice paddy soil (sandy loam - clay loam; CEC estim. 24; pH=4.9; OM=30%) covered with rice paddy water, were exposed to anaerobic conditions for 15 days prior to addition of ^{14}C -TBZ (labeled in the benzene ring, as shown below), at the field use rate (i.e. 8 oz/Ac).



Soil and water were sampled after 2, 7, 14, 30, and 60 days. (Noted in the report that additional samples will be taken after 3, 4, 6, 9, and 12 months).

Analytical Method

Duplicates of water samples were assayed for TBZ contents by specific HPLC after extraction with routine solvent systems; and for ^{14}C contents by LSC at ambient temperature. Duplicates of soil samples were assayed for TBZ by fortification prior to extraction and analyzed by HPLC; ^{14}C contents were assayed, following combustion, using LSC.

Traps were also assayed for $^{14}\text{CO}_2$ and ^{14}C volatiles.

Results:

Through the first two months of 12-month study - Data Summary:

Summary - Aquatic Anaerobic Metabolism of ^{14}C -Thiabendazole^{1/}

Time (Days)	Soil			Water		Volatiles	
	Extractable ^{14}C ^{2/} (%)	Thiabendazole- ^{14}C (% of Extract ^{14}C)	Carbon-14 ^{14}C ^{3/} (% of Initial ^{14}C)	Thiabendazole (% of ^{14}C)	$^{14}\text{CO}_2$ and Organic ^{14}C (% of Added ^{14}C)		
<u>Sterile</u>							
2	86	77	25	104	0.0012		
7	74	91	7.6	106	0.0038		
14	68	83	3.8	78	0		
30	70	99	1.8	74	0		
60	73	92	1.0	56	0		
<u>Non-Sterile</u>							
2	44	88	41	88	0.0029		
7	44	97	15	99	0.0028		
14	44	101	4.1	93	0.0027		
30	47	93	1.6	60	0.0062		
60	62	90	0.8	107	0.0068		

1/ - Values are averages of duplicate analyses from each of duplicate chambers.
 - Comparison of Extract ^{14}C and ^{14}C found in soil by oxidation.
 - 9.33 x 10³ dpm ^{14}C -thiabendazole was added to each flask.

- Based on the initial concentration, the concentration of ^{14}C and TBZ in water depleted rapidly in both sterile and non-sterile chambers to <5% in 14 days and <2% in 30 days; presumably due to the quick adsorption of TBZ on the soil surface in this aqueous anaerobic system.
- In soil, percent of extractable radiolabeled residue amounted to 44-62% in the non-sterile flasks and remained constant during first 60 days; while it was constant after the 7th day in the sterile flask and amounted to 68-86%. Of these extracts, TBZ accounted for 82-112% in the non-sterile, and for 71-112% in the sterile.
- Very little $^{14}\text{CO}_2$ detected in the nonsterile chambers (and none was produced in the sterile ones) amounting to 0.02% of the initial ^{14}C quantity during the 60 days. Negligible quantities (<0.002%) of ^{14}C volatiles were detected.

Conclusion

- Study is acceptable for ~~an~~ interim reporting.
- Results for the 12-months study should be reported as soon as they are available in order to establish ^{the} rate of decline of TBZ in aquatic anaerobic environment.
- Apparent from this report, that TBZ is not metabolized in California soil type rice paddies.
- Radiolabel balance in the water-soil system couldn't be established because of lack of homogeneity of the water soil system. However, it is shown that ^{14}C concentration in water dropped rapidly to <5% of the initial level within 14 days, and the extractable TBZ from the soil amounts to 77% or more of the extractable ^{14}C .

3.2 Partition of Thiabendazole between water and soils (Report B), Vol. II, by Raltech Scientific Services, Inc., for Merck and Co., July 9, 1979.

Procedure

Low and high resolutions investigations were employed to determine TBZ concentration at equilibrium in water-rice paddy soils. In the low resolution investigation, soil samples from rice paddies from

California and Louisiana were prepared and their moisture content adjusted to 0.7% for CA-soil, and 6% for LA-soil; then mixed with ^{14}C -TBZ aqueous solution to give final concentration of 0.0, 0.01, 1, 10, and 100 ppm. The soil TBZ mixtures were then air dried for 7 days and equilibrated by shaking for 48 hrs, at 25°C, centrifuged and then submitted to analysis of TBZ and ^{14}C contents. Based on the low resolution investigation, a high resolution study was carried out in the same manner utilizing final concentration of TBZ of 0.078, 0.312, 1.25, 5, 20, and 80 ppm in soil.

Analytical Method

TBZ concentration in the aqueous phase was determined by HPLC. In the solid phase, TBZ concentration was determined by LSC following combustion.

Results

1. Desorption of TBZ from soil into water in the Low Resolution Investigation

Nominal TBZ in Soil	0 ppm	0.01 ppm	0.10 ppm	1.00 ppm	10.0 ppm	100 ppm
Free TBZ in CA Soil	ND	ND	0.0009 ppm	0.002 ppm	0.011 ppm	≈ 0.27 ppm
Free TBZ in in LA Soil	ND	ND	ND	0.0018 ppm	0.0035 ppm	0.037 ppm

2. Desorption of TBZ in the High Resolution Investigation

Nominal TBZ loaded on soil	0.078 ppm	0.313 ppm	1.25 ppm	5.00 ppm	20.0 ppm	80 ppm
Free TBZ (ppm) in LA Soil	0.00007	0.0001	0.0001	0.0011	0.0098	0.051
% TBZ Desorbed in LA Soil	0.9	0.03	0.075	0.02	0.05	0.07
Free TBZ (ppm) in CA Soil	0.00009	0.00005	0.00004	0.00012	0.0014	0.019
% TBZ desorbed in CA Soil	0.12	0.02	0.004	0.003	0.008	0.03

3. Freundlich* Constants for Desorption

LA Soil $K = 490 \text{ ppm}$ $1/n = 1.5$
CA Soil $K = 700 \text{ ppm}$ $1/n = 1.8$

* equation used $\ln(x/m) = \ln K + 1/n \ln C$

x = amt. of test substance adsorbed on mass (m) of soil, c = concentration of test substance.

- Graphic illustration of aqueous TBZ concentration and initial TBZ content of the soils, indicates that after 48 hrs. of equilibration Free and Bound TBZ in LA soil are of equal concentration but in CA soil bound TBZ is double the Free TBZ concentration.

Conclusion

The study protocol is acceptable; however, the report failed to provide the soils characteristics which are valuable in establishing TBZ desorption/adsorption characteristics in relation to the soil various parameters such as pH, CEC, etc.

- The reported results suggests that TBZ applied at 12 oz/Acre could result in soil concentrations of about 1 ppm TBZ - assuming uniform distribution in 0-3" soil layer - would yield TBZ concentration in water at equilibrium equal to 0.05 ppb. And at 80 ppm TBZ, concentration in water at equilibrium is $2 \times 10^{-2} \text{ to } 5 \times 10^{-3} \text{ ppm}$ (i.e. 5 ppb).
- Hence, it may be concluded from these observations that TBZ is rendered immobile once it is adsorbed onto soil.

3.3 Thiabendazole - Combined Field Dissipation and Water Dispersal from Rice Paddies (Report A), By Raltech Scientific Services, Inc. for Merck and Co., July 6, 1979.

Procedure

Five sites in five states (California, Texas, Louisiana, Mississippi, and Arkansas) were selected for the study of the movement and loss of TBZ applied at recommended rates to rice. Field site characteristics are as follows:

Summary of Field Site Characteristics

Location	Size (m x m)	Number of Plots	Rate of formulated product (fl. oz/acre)	Number of Applications	Water System	Growth Stages at Application
Rice Experiment Station Biggs, California Stockton Clay Adobe	85 x 14.5	8	24	1 or 2 ^a 2 applications 14 days apart	Flowthrough	1. Mid tiller 2. 14 days later
Wamba, Texas Clayloam soil	39 x 8.23	1	12	2 ^a 21 days apart	Impounded 3" flood on field at 1st appli- cation	1. Pre boot 2. Late boot
Mississippi	2.44 x 3.05	4	12	2 ^a 14 days apart	Flowthrough	1. - 2. -
Prevot Plantation Monroe, Louisiana Loam Soil	22.8 x 12.2	1	12	2 ^a 21 days apart	Flowthrough 4-5" flood on field	1. Boot 2. Heading
Sprit Lake Corporation Lewisville, Arkansas	401 x 10.6	1	12	2 ^b 21 days apart	Impounded 3" flood on field	1. Internode elongation 2. Early heading

a) Applied by CO₂-powered back pack sprayer.

b) Aerial application.

Sampling schedule included: prior to first application, 24 hrs. post application, prior to second application, 24 hrs. post second application, one-third season elapsed, and two-thirds season elapsed, maturity, and just before first frost. Water samples were taken from the paddies, the associated holding ponds and adjacent irrigation canals. Water effluent, when released from ponds, were also sampled and analyzed. Soil samples were taken at 0-3" and 3-6" layers from rice paddies, holding ponds, and connecting canal.

Mature rice was sampled and separated into straw and grain for analysis.

Results

1. Arkansas site (Spirit Lake Corp., Lewisville). Two applications of TBZ at equivalent of 6 fl. oz. TBZ/A/application. No egress water samples; i.e. water maintained without drain. Maximum levels of TBZ encountered measured 0.175 and 0.119 ppm^a found in the 3-6" soil layer immediately after second application and 7 days after it. The remaining detectable TBZ levels ranged from 0.006-0.009 ppm for water and a 0.028-0.093 ppm for soil. Two positive measurements of TBZ prior to first application are attributed to drift problems from a cross wind.
2. California Site (The Rice Experimental Station, Biggs). TBZ applied only to the downstream half of each plot. Half of the plots received one application at rate of 24 fl. oz. Mertect/A, and the other half received 2 such applications 14 days apart.

Following each application the TBZ levels in paddy waters rose within an hour to 0.144 ppm at first application and to 0.227 ppm following second application; followed by gradual decline to 0.003-0.01 ppm.

The TBZ levels in 0-3" soil layer rose to ^a maximum of 0.371-0.656 ppm at 7-14 days following first application and then declined. In the 3-6" layer, TBZ concentration followed a similar pattern at somewhat lower values. Reported final equilibrium concentration in soil is in the order of 0.05-0.25 ppm.

3. Louisiana Site (Prevot Plantation, Monroe) two applications at rate equivalent to 6 fl. oz. TBZ/A. In water samples, TBZ was found at very low levels (0.002-0.014 ppm), and in soil, it was also detected in very low levels with only one sample in 0-3" layer measuring 0.111 ppm. The remaining soil samples measured <0.002 ppm; i.e. detection limit.

4. Mississippi Site (Site's location is not identified). Two applications at a rate equivalent to 6 fl. oz. TBZ/A

In effluent water, TBZ was found one day following application in effluent water in concentration of <0.002-0.013 ppm, and in water over plots measured 0.003-0.006 ppm. In soil, TBZ levels were more higher and uniform, measuring 0.03-0.061 ppm in 0-3" soil layer and 0.034-0.043 ppm in 3-6". Following second application, TBZ in effluent water measured 0.003-0.006 ppm and in soil samples 0.020-0.068 ppm in 0-3" and 0.026-0.05 ppm in 3-6" soil segments.

5. Texas Site (Wamba). Two applications at rate equivalent 6 fl. oz. TBZ/A. Immediately following first application TBZ found sporadically in the 3-6" soil segment measuring 0.042 and 0.035 ppm. Following second application TBZ levels in soil 0-3" segment measured 0.027 and 0.021 ppm, and .029 and 0.136 ppm in 3-6" segment, showing variability that may have resulted from run-off of local TBZ concentrations into the test paddy.

After reflooding, only 2 soil samples registered 2 measurement in the 0-3" soil segment at 0.049 and 0.035 ppm.

Conclusion

1. The protocol of this study is acceptable for determining TBZ dissipation and mobility applied at field use rate.
2. In general, TBZ first appeared in paddy waters with a consequent increase in soil concentration in 0-3" and 3-6" layers, and followed by a gradual residue decline over 1-2 weeks after application. In the flowthrough water systems (such as in the California and Mississippi sites) effluent water (i.e. water leaving treated area) rarely had TBZ concentration above 0.01 ppm.
3. Paddy sediment rapidly adsorbs TBZ within two weeks of application in most soil types, rendering immobile once adsorbed, resulting in a final soil residue concentration of <0.02 ppm-0.146 ppm; over 2-3 months sampling period.
4. It appears that only a small fraction (10-20%) of the TBZ applied reached the water surface.

IV. Executive Summary

The studies reviewed here provide a preliminary profile of TBZ anaerobic metabolism, desorption, and field dissipation in aquatic environment used for growing rice.

Under anaerobic conditions, TBZ is minutely metabolized in soil and is rapidly depleted in water to <5% of the initial concentration in 14 days and <2% in 30 days. Of the soil extractable residue, TBZ accounts for 77% or more.

Under actual field use conditions, the discernible pattern and rate of dissipation in various soil types indicate that TBZ first appear in paddy waters following application and then decrease with a consequent increase in soil residue concentration in the 0-3" and 3-6" soil layer. At the desorption equilibrium, TBZ (applied at field rate) may result in about 1 ppm residue concentration in soil; and it is expected to reach the 0.05 ppb level in water.

TBZ adsorbs rapidly to paddy sediments within 2 weeks and is rendered immobile once adsorbed.

V. Recommendation

The environmental chemistry studies submitted in support of the conditional registration of TBZ on rice suffice in providing a preliminary assessment of TBZ fate in the environment, with the following conditional: The final report of the anaerobic aquatic metabolism is submitted for evaluation and is judged satisfactory.

M. Nawar

3/11/80

M. Nawar
3/20/80