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To: Product Manager Wilson (21)
TS-767

Through: Dr. Gunter Zweig, Chief
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Through: Mr. James Conlon, Acting Director
Hazard Evaluation Division, TS-769

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

Attached please find the environmental fate review of:

Reg./File No.: 618-7501, 8F2108

Chemical: *24*-(4-thiazolyl)benzimidazole

Type Product: Fungicide

Product Name: Mertect 340-F Fungicide

Company Name: Merck and Co., Inc.

Submission Purpose: New use on wheat

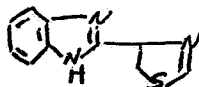
2BB Code 111B

Date in: 8/24/78

Date Completed: 3/15/79

1. Introduction

- 1.1 This is a resubmission for amendment of data requirements supporting registration of the fungicide MERTECT 340-F (EPA Registration No. 618-75AA), for new use on wheat to help control *Cercospora* foot rot.
- 1.2. MERTECT 340-F is a flowable formulation containing 42-28% (3-8 lb/gal) of the active ingredient 2-(4-thiazolyl)benzimidazole, and 57.72% of inert ingredients.
- 1.3. MERTECT is known by the name Thiabendazole (TBZ) which has the following configuration:



- 1.4. The environmental chemistry data^{is} submitted in response to data deficiencies identified in past reviews.

2. Direction for Use

The amended label provides the following for use on wheat.

- 2.1. Aerial Application - apply 16-24 fluid ounces of MERTECT 340-F in a minimum of 5 gallons water per acre.
- 2.2. Ground Application - apply 16-24 fl. oz. of MERTECT 340-F per acre in sufficient water for coverage.
- 2.3. Storage and Disposal - Do not store below 32° F (0° C). Do not contaminate water, food, or feed by storage or disposal. Open dumping is prohibited.

3. Discussion of Data

3.1. Leaching

The leaching investigation included comparative study of aerobically aged ¹⁴C-TBZ, photodegraded ¹⁴C-TBZ, ¹⁴C-DDT, and ¹⁴C-2,4-D for rapid and slow leaching in soils.

3.1.1 Rapid leaching

Mobility of Thiabendazole Aerobically Aged in Soil and Photodegraded Thiabendazole.
Collin Schroeder and John Steele, WARF Institute, Inc.

Procedure:

Four different soil types were used in the study: Elburn sandy loam, Plainfield sand, Troxel silty clay, loam, and Oatanogon clay. Soil characteristics were inadvertently omitted from report. Soils amended with 300.7 $\mu\text{g/ml}$ ^{14}C -TBZ were aged for 30 days aerobically at 70-100% field moisture capacity before placing in soil columns of 30 cm height.

Soils amended with 300 $\mu\text{g/ml}$ ^{14}C -ring labeled DDT, 298 $\mu\text{g/ml}$ ^{14}C -carboxyl labeled 2,4-D, and 60% photodegraded TBZ (9.26 μg TBZ) were placed in columns soon after solvents had evaporated. Deionized water was added to the columns at a rate equalling 1 inch hydrostatic pressure.

Analytical Methodology:

Columns eluates were analyzed for ^{14}C activity by combustion-scintillation counting technique. Soil columns segments were weighed, pulverized, mixed and combusted for 2 minutes using Packard Oxidizer. The resulting CO_2 was trapped and determined by liquid scintillation.

Conclusion:

Aerobically aged TBZ did not leach by water in the four soil types exhibiting very low mobility that was confined mostly to the top 1 inch segment.

There is no evidence to show that ^{14}C is still present as TBZ or formed any volatile products.

DDT exhibited same mobility as TBZ, while 2,4-D showed much higher mobility resulting in 98% leaching of the applied compound through the column.

Photolyzed TBZ had slightly greater mobility than TBZ in the four soils but remained in the top 1 inch segment.

3.1.2. Slow leaching

Soil Mobility of Thiabendazole Aerobically Aged in Soil and Photodegraded Thiabendazole.

Collin Schroeder and John Steele,
WARF Institute, Inc.

Procedure:

Only Elburn sand loam soil was used ~~to~~ carry out the slow leaching study on radiolabeled TBZ, 2,4 -D, DDT, and photodegraded TBZ. The same procedure in rapid leaching was followed, but water was applied at 0.5 inches (3.8 ml) per day for 45 days.

Conclusion:

Same conclusions as rapid leaching except for 2,4-D, where only 31.7% of the total activity was recovered and the loss is attributed to probable decarboxylation of 2,4-D and loss of ^{14}C as CO_2 .

- 3.1.3 Leaching of photodegraded TBZ Mobility of Thiabendazole Aerobically Aged in soil and Photodegraded Thiabendazole.

Procedure:

For the rapid and slow leaching investigation, photodegraded TBZ was prepared by exposing ^{14}C -TBZ solution containing 20.45 μg TBZ/ml and 1.759×10^5 dpm/ml to 300nm light in a Rayonet photochemical reactor for 2 hours. The resulting solution measured TBZ concentration of 9.26 μg /ml and 1.65×10^5 dpm ^{14}C /ml. ; i.e. about 60% of the TBZ is photodegraded.

Conclusion:

This investigation did not identify the photolysis products that may have leached into soil. Photochemical degradation of TBZ in aqueous solution had been investigated and reviewed before, indicating that TBZ photodegrades very rapidly in deionized water ($t_{1/2} = 23.9$ mins.). The major photolysis products identified were Benzimidazole (28%) TBZ (14%), BIZ- CONH_2 (15%) and unknowns (18%), and no volatile products. Since in the rapid and slow leaching the photodegraded TBZ showed slightly greater mobility, it may be concluded that TBZ photodegradates are more mobile than TBZ and their bulk of activity is confined to top 1 inch soil.

3.2. Field Dissipation

Title: Supplement to Thiabendazole Field
Dissipation Studies
Collin Schroeder and John Steele
WARF Institute, Inc.

Procedure

This study supplements the original field dissipation study (report^e) reviewed on September 22, 1976, ^{and} providing data for a later date and down to depths of 6-12" and 12-18".

It involves the use of nonradioactive commercial TBZ formulation applied at rates of 3.3, 4.0, and 16.0 oz/A/Application, at four geographical locations; and use of radioactive TBZ incorporated in commercial formulation applied at a fifth location.

Soil characteristics of these areas are:

<u>Soil</u>	<u>Mineral Fraction</u>		<u>Clay</u> %	<u>Organic</u> <u>Carbon</u>	<u>pH</u>	<u>CEC</u> <u>Meg/100g</u>
	<u>Sand</u>	<u>Silt</u>				
Alabama SM	58	37	5	.51	5.6	3.4
Alabama WES	77	14	9	.56	5.1	4.5
Arkansas	3.2	78.0	18.8	.92	5.2	18.2
Louisiana 0-5"	12.5	81.5	6.0	.47	5.0	4.7
Louisiana 7-9"	9.5	74.5	16.0	.10	4.8	8.0
Wisconsin	53.6	29.2	17.2	1.65	6.7	21.4

Two field applications were made during the first season at 2 weeks interval on soybeans. And during the second season, application was made to plots planted in soybeans and rice. Crop residue were reincorporated into soils at end of first season. Radio-labeled ^{14}C -TBZ studies were carried out at WARF Institute applying TBZ at 1 and 4 times the recommended rate.

Analytical Methodology

The ^{14}C contents of whole soil samples prior to extraction, of extract solutions and extracted soils after extraction, were determined by methods validated in the previous report using HPLC and/or LSC.

Results:

Residues of TBZ found ≥ 0.1 ppm at 4 depths are summarized as follows:

<u>Sample Period</u>	<u>Thiabendazole ≥ 0.1 ppm at Depths of</u>			
	<u>0-3"</u>	<u>3-6"</u>	<u>6-12"</u>	<u>12-18"</u>
Prior to application	0/14 ⁽¹⁾	0/14	-(2)	-
24 hours post application	1/17	0/14	0/14	-
Prior to 2nd application	3/17	0/17	0/3	-
24 hours post 2nd application	4/17	0/17	-	-
1/3 season elapsed	2/17	0/17	-	-
2/3 season elapsed	3/17	1/17	-	-
First frost	1/12	1/12	0/2	0/2
Following spring	2/17	0/17	0/4	0/3
First frost 2nd year	5/17	5/17	2/17	1/17

(1) The entries tabulated are samples ≥ 0.1 ppm/total number of samples.

(2) A dash indicates no samples analyzed.

Conclusion:

1. The above data summary shows that TBZ > 0.1 ppm was found in less than 2% of the extracted soil samples at 0-3" depth, and in less than 1% at 3-6" depth.

In the 16-12" and 12-18" depths, TBZ in samples examined was hardly detectable.

2. Because of its low mobility, TBZ or its photodegradates hardly dissipated in soil under field conditions; and the movement ^{was} confined to 0-3" depth. And dissipation ~~took~~ place largely during the first season and diminishes by ~~the~~ the end of 2nd season.
3. Bound TBZ residues amounted to 90% or more.

3.3 Photodegradation

Title: Photodegradation in Soil
Collin Schroeder and John Steele
WARF Institute, Inc.

Procedure:

A methanol solution (7 ml) containing 774 μg of ^{14}C benzene ring labeled TBZ was incorporated into 150 gm of plainfield soil, mixed thoroughly and dried overnight to yield TBZ conc. of 4.51 ppm.

One hundred grams of this soil was placed in 1-liter quartz flask rotated at about 100 rpm and exposed to UV light (300nm peak.) Soil samples taken over 32 day exposure period.

Methodology:

Soil was analyzed for TBZ and extractable ^{14}C by HPLC and LSC.

Conclusion:

Measured TBZ concentration and recovered ^{14}C indicate very little degradation ($\leq 15\%$) to have taken place in soil during the 32 exposure period.

It may be included that TBZ in soil is not subject to extensive photodegradation. This conclusion contrasts sharply with its rapid photodegradation in a aqueous solution.

3.4. Microbial Metabolism

Effects of Soil Microflora and Algae on
Thiabendazole.

Collin Schroeder and John Steele
WARF Institute, Inc.

Procedure:

Sterile and non-sterile soil samples of Elburn sandy loam and Troxel silty clay soils were adjusted to 50 and 100% field moisture capacity, amended with 0.5 ppm ¹⁴C-TBZ, inoculated with eight different bacterial species and incubated at 20° and 30° for 30 days. In addition, 2 algal species were grown in Allen medium for 2 weeks and mixed with solutions containing 0.5 and 0.1 ppm TBZ and maintained under fluorescent lighting at room temperature until sampled.

Soil Properties

		%			
	% organic matter	Silt	Sand	Clay	pH
Elburn	3.33	30.0	54.0	16.0	6.4
Troxel	3.50	73.0	1.0	26.0	5.2

Microbial Species and Media

<u>Aspergillusniger</u>	Potato Dextrose Agar (Difco)
<u>Penicillium chrysogenus</u>	Potato Dextrose Agar (Difco)
<u>Trichoderma viride</u>	Potato Dextrose Agar (Difco)
<u>Streptomyces albus</u>	Potato Dextrose Agar (Difco)
<u>Arthrobacter globiformis</u>	Nutrient Agar (Difco)
<u>Azotobacter beijerinckii</u>	Azotobacter Medium
<u>Bacillus subtilis</u>	Nutrient Agar (Difco)
<u>Pseudomonas fluorescens</u>	Nutrient Agar (Difco)
<u>Xanthomonas alfalfae</u>	Nutrient Agar (Difco)

Algae Species

Chlorocuccum Hypnosporum
Chlorella Pyrenoidosa

At the end of ^{the} incubation period, bacterial and algal ^{the} cultures were treated and analyzed for TBZ and ^{the} ¹⁴C contents.

Analytical Methodology

Soil ^{14}C contents were measured by $^{14}\text{CO}_2$ evolved upon oxidation of samples. TBZ extracts from soil samples were treated with methanol and water solvent system and analyzed by HPLC.

Algal cultures filtrates were treated with water: aceto-nitrile solvent system and analyzed by HPLC.

Results:

The microbial metabolism was assessed by comparing the TBZ content of sample extracts analyzed by HPLC with their ^{14}C contents.

In a set of 152 ratio determinations of bacterial cultures, only 2 measured TBZ reduction in excess of 20% of the applied amounts at the 14th day of incubation. No metabolic products were identified. Algal cultures showed decrease in TBZ with no corresponding reduction in ^{14}C contents at 30 day. This reduction was assumed to be due to abiotic processes including photodegradation (of-TBZ in ^{medium} med.) or chemical reaction with the culture medium. Such reduction was accounted for by normalization. On this basis, $^{14}\text{C}/\text{TBZ}$ ratios obtained were within the 20% reduction limit attributed to metabolism.

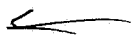
It is noted, however, that the extractable TBZ and ^{14}C concentrations were in excess of the amended TBZ conc. This phenomenon may be interpreted to be due to bioaccumulation of the compound by algal cells, and not metabolism as claimed by the author.

Conclusion:

Bacterial organisms are capable of metabolizing TBZ in soil up 20% over 30 day period. It is questionable, however, ^{whether} the reduction of TBZ in soil up to that limit is achievable by metabolism or bioaccumulation in algal cells.

4. Conclusion:

1. All the studies reviewed here have been carried out in accordance with the guidelines protocols.
2. The aerobically aged TBZ in soil does not leach beyond the 0-3" soil segment. The bound residues have very low mobility (practically immobile) and hence constitute no hazards to non target organisms.
3. The photodegraded TBZ and its photolytic products do not leach in soil below 3" depth, but slightly more mobile than aged TBZ.
4. Under field conditions, TBZ dissipates ^{in soil} via binding and undergoes less than 10% degradation. Dissipation of TBZ residues is confined to the top 3" segment during the first season, and occasionally reaches 6" depth by the end of second season.
5. In contrast to its rapid photodegradation in aqueous solution, TBZ in soil does not photodegrade beyond the 10% maximum during 32 day exposure period.
6. Bacterial organisms flourish in presence of TBZ in soil metabolising up to 20% of the compound.

No difference in ^{microbial} activity noted between sterile and non-sterile soil. 

Agal species, on the other hand, act on TBZ either by metabolism or bioaccumulation process.

5. Recommendation

As established here, and supported by past reviews, the fate of TBZ in the environment investigated (assumed soil pH values ≤ 7.0) is known. And the conclusions support the proposed use.

Ronald E. Ney, Jr.
Madeline Nawar,
Review Section 1
March 15, 1979

Madeline Nawar 7/21/79