US EPA ARCHIVE DOCUMENT

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PC Code No. : 099101,128872
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To: Jay Ellenberger
Product Manager PM #50
Registration Division (H7507C)

From: Akiva D. Abramovitch, Ph.D., Head
Environmental Chemistry Review Section #3
Environmental Fate & Ground Water Branch/EFED (H7507C)

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

Attached, please find the EFGWB review of...

Reg./File # :099101,128872

Common name :Benomyl, Methyl-1-(butylcarbamoyl)benzimidazol-2-yl carbamate

Type Product :Fungicide

Product Name :Benlate,Tersan 1991,Benex

Company Name :E.I. du Pont de Nemours and Company, Inc.

Purpose :Review of aerobic soil, and anaerobic and aerobic aquatic metabolism studies.

Action Code : 660 EFGWB #(s): 91-0949-50-51-62 Total Review Time: 4.0 days

EFGWB Guideline/MRID Summary Table: The review in this package contains...									
161-1		162-1	41255801	164-1		165-1		166-1	
161-2		162-2	41137701 40158401	164-2		165-2		166-2	
161-3		162-3	41137701	164-3		165-3		166-3	
161-4		162-4	41291501	164-4		165-4		167-1	
201-1		163-1		164-5		165-5		167-2	
202-1		163-3							

1. CHEMICAL: Common name:

Benomyl.

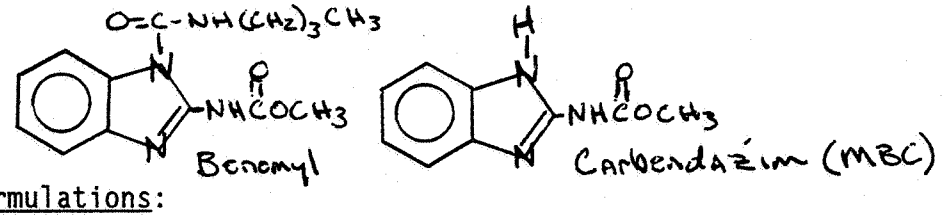
Chemical name:

Benomyl= Methyl-1-(butylcarbamoyl)benzimidazol-2-yl carbamate
Degradates include:
MBC = carbendazim, methyl-1H-benzimidazol-2-yl carbamate
STB = 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione
BUB = 2-(3-butylureido)benzimidazole
2-AB = 2-aminobenzimidazole

Trade name(s):

Benlate, Tersan 1991, Benex.

Structure:



Formulations:

Dry flowable, oil dispersible, wettable powder.

Physical/Chemical properties:

Benomyl

Molecular formula:	$C_{14}H_{18}N_4O_3$.
Molecular weight:	290.3.
Physical state:	Colorless, crystalline solid; on heating it decomposes (140C) without melting.
Vapor pressure (25 C):	Negligible.
Solubility (25 C):	c. 4 mg/kg water at pH 3 to 10; very soluble at pH 1, decomposes at pH 13; c. 18 g/kg acetone; c. 94 g/kg chloroform; c. 53 g/kg dimethylformamide; c. 4 g/kg ethanol; c. 400 g/kg heptane; c. 10 g/kg xylene.

2. TEST MATERIAL:

Studies 1-3: Active ingredient.

2

3. STUDY/ACTION TYPE:

Review of an aerobic soil metabolism, an anaerobic and aerobic aquatic metabolism study submitted in support of reregistration.

4. STUDY IDENTIFICATION:

MRID #41255801: Marsh, B.H., and M.F. Arthur. 1989. Aerobic metabolism of [phenyl(U)-^{14}C]benomyl in Keyport silt loam. Laboratory Project ID: Battelle Project No. N-0518-8200; du Pont Report No. AMR-1112-88. Unpublished study performed by Battelle Memorial Institute, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

MRID #40158401: Han, J. C-Y. 1986. Anaerobic soil metabolism of 2-^{14}C-benomyl and methyl 2-^{14}C-benzimidazolecarbamate. In Supplemental information and data related to the field monitoring study for benomyl residues in flooded rice fields. Unpublished study prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. PREVIOUSLY REVIEWED STUDY

MRID #41137701: Arthur, M.F., B.H. Marsh, L.C. Fadel, and T.C. Zwick. 1989. Anaerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in West Jefferson, Ohio, pond water and sediment. Laboratory Project ID: Battelle Project No. N0799-8800; du Pont Report No. AMR-770-87. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

MRID #41291501: Arthur, M.F., K.L. Schweitzer, L.C. Fadel, B.H. Marsh, and S.S. Marsh. 1989. Aerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in Greenville, Mississippi, water and sediment. Laboratory Project ID: Battelle Project No. N-0966-730; du Pont Report No. AMR-1452-89. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

5. REVIEWED BY:

Kevin Poff
Chemist
EFGWB/EFED/OPP
Review Section #3

Signature: Kevin Poff

Date: FEB 21 1992

6. APPROVED BY:

Akiva Abramovitch
Chief
EFGWB/EFED/OPP
Review Section #3

Signature: Akiva Abramovitch

Date: FEB 21 1992

3

7. CONCLUSION:

Aerobic Soil Metabolism (162-1) DER 1

1. Study MRID #41255801 does not satisfy the aerobic soil metabolism (162-1) data requirement for benomyl at this time for the following reasons:

a) Radioactivity present in the aqueous extracts present at up to 13.2% of the applied (0.92 ppm), and degradates present in the organic extracts at up to 2.3% of the applied (approximately 0.16 ppm), were not characterized.

2. Uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, du Pont) degraded with a registrant-calculated half-life of 19 hours in nonsterile silt loam soil incubated in the dark at 25 $\pm$ 1 C and 75% of field moisture capacity. The major degradate identified was methyl-1H-benzimidazol-2-yl carbamate (MBC), which degraded with a registrant-calculated half-life of >320 days. Two other nonvolatile degradates were identified: 2-aminobenzimidazole (2-AB) at 0.8-6.2% of the applied radioactivity in the nonsterile soil, and 2-(3-butylureido)benzimidazole (BUB) that reached a maximum of 4.6% of the applied radioactivity at 3 days posttreatment.

Anaerobic Aquatic Metabolism (162-3) DER 2

1. Study MRID #41137701 completely satisfies the anaerobic aquatic (162-3) data requirement for benomyl.

2. The registrant calculated half-life of carbendazim (MBC) (no benomyl was detected due to the rapid hydrolysis rate of benomyl to carbendazim) under anaerobic aquatic conditions was 743 days in a clay loam soil that was treated with 1 ppm (equivalent to 1 lb/ai/A) [^{14}C]Benomyl and incubated anaerobically for up to 365 days. In the sediment extracts, where the majority of the radioactivity was recovered, MBC was 83.4% of the recovered radioactivity (0.88 ppm) immediately posttreatment, 66.9% (0.83 ppm) at 60 days and 55.6% (0.70 ppm) at 365 days (Table V). The other degradate identified in the sediment extracts was 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione (STB), which was a maximum of 7.6% of the recovered radioactivity (0.10 ppm) at 365 days posttreatment. Unextracted radioactivity in the soil increased from 12% of the recovered immediately posttreatment to 36.2% at 365 days posttreatment.

Aerobic Aquatic Metabolism (162-4) DER 3

1. Study MRID #41291501 complete satisfies the aerobic aquatic metabolism (162-4) data requirement for benomyl.

2. The registrant calculated half-life of carbendazim (MBC) (no benomyl was detected due to the rapid hydrolysis rate of benomyl to carbendazim) under aerobic aquatic conditions was 61 days in a clay loam soil that was treated with 2 ppm (equivalent to 2 lb/ai/A) [^{14}C]Benomyl and incubated aerobically for 30 days. In the nonsterile floodwater, where the majority of the radioactivity was recovered, MBC was 57.2% of the recovered radioactivity

(1.14 ppm) immediately posttreatment, 37.4-37.8% (0.75-0.76 ppm) at 0.2-1 days, 12.5% (0.25 ppm) at 7 days, and was not detected (<0.01 ppm) at 30 days. 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H, 3H)dione (STB), was 28.8% of the recovered radioactivity (0.58 ppm) immediately posttreatment, increased to 40.4% (0.81 ppm) at 0.2 days posttreatment, declined to 1.97% (0.04 ppm) at 7 days, and was not detected (<0.01 ppm) at 14 days. 2-(3-butylureido)benzimidazole (BUB), was 1.54-2.30% of the recovered radioactivity (0.03-0.05 ppm) immediately posttreatment-1 day posttreatment, and was not detected (<0.01 ppm) at 7 days. 2-aminobenzimidazole (2-AB), was ≤0.083% of the recovered radioactivity (0.02 ppm) at all sampling intervals.

ENVIRONMENTAL FATE AND GROUND WATER ASSESSMENT

Due to the rapid conversion of benomyl to carbendazim (MBC), the following assessment is on the hydrolysis product (carbendazim, MBC)

Based upon data from acceptable studies, Carbendazim (MBC), has the following characteristics in common with those pesticides that are known to leach into ground water.

(a) Hydrolysis half-life of greater than 25 weeks. (carbendazim, MBC, is stable to hydrolysis at pH 5 and 7 and has a half-life of 54 days at pH 9)

(b) Photolysis half greater than 1 week. (carbendazim, MBC, appears to be stable to aqueous photodegradation, and photodegradation on soil)

(c) Soil half-life of greater than about 2 to 3 weeks. (carbendazim has an aerobic soil half-life of >320 days)

(d) Kd_{ads} less than 5.0. Kd_{ads} values established for benomyl and its degradates were 6.1, in a Woodston sandy loam 1.1% OM; 13, in a Cecil sandy loam 2.1% OM; 90 in a Flanagan silt loam 4.3% OM; and 50 in a Keyport silt loam with 7.5% OM. Kd_{des} values established for benomyl and its degradates (carbendazim {MBC}) were 2.5 in a Woodston sandy loam 1.1% OM; 2.5 in a Cecil sandy loam 2.1% OM; 2.5 in a Flanagan silt loam 4.3% OM; and 2.4 in a Keyport silt loam with 7.5% OM) See attached review.

(e) Water solubility greater than 30 ppm. (carbendazim has a solubility of 8.0 ppm at pH 7, 25 C)

The data indicate that carbendazim (MBC) may pose risks to ground water due mainly to its persistency. The above data also indicate that carbendazim is somewhat mobile in soils of relatively high organic matter, lowest Kd_{ads} reported was 6.1, in a Woodston sandy loam 1.1% OM. However, information submitted on soil column leaching indicate that carbendazim and other benomyl associated degradates (STB, 2-AB) are relatively immobile (>85% of applied remained in the upper 2 inches, > 95% in upper 4 inches) in columns (13-inch length) of two silt loam (Flanagan (4.3%OM) and Keyport (7.5% OM)) and two sandy loam (Cecil (2.1% OM) and sassafras (0.8% OM)) soils.

A more comprehensive assessment will be made after the review of the terrestrial field dissipation studies, although the current data indicate that benomyl has the propensity to leach to groundwater in soils of low organic matter.

8. RECOMMENDATIONS:

Inform the registrant that the anaerobic aquatic metabolism (162-3) and the aerobic aquatic metabolism (162-4) studies are completely satisfied and the aerobic soil metabolism (162-1) study may be made acceptable with the submission of supplemental data.

The current status of environmental fate data requirements for registering benomyl and carbendazim end-use products for application to terrestrial food, nonfood and aquatic food crops are as follows:

MBC = carbendazim, methyl-1H-benzimidazol-2-yl carbamate
STB = 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione
BUB = 2-(3-butylureido)benzimidazole
2-AB = 2-aminobenzimidazole

(1) Satisfied

-161-1. Hydrolysis; EAB# 6080 (Dynamac review 2/26/86) at pH 5, the half-life of benomyl was 3.5 hr., major degradate was MBC. At pH 7, the half-life of benomyl was 1.5 hr., the major degradates were MBC (approx. 75% of total radioactivity) and (STB) at 25% of total radioactivity. At pH 9, the half-life of benomyl was less than 1 hr., the major degradate was (STB) at 80% of total radioactivity. MBC appeared to be stable to hydrolysis over the studies duration.

-161-2. Photodegradation in Water; EAB# 6080 (Dynamac review 2/26/86), Dupont AMR-420-85; Phenyl labeled [^{14}C]benomyl (radiochemical purity >99%), at 1 ppm, degraded with a half-life of < 4 hours in a sterile aqueous buffered solution (pH 5) maintained at 25 C, whether the solution was irradiated with natural sunlight or incubated in the dark. Under both conditions the major degradate (> 99% of applied) was MBC, STB was present at 1%. At the end of the 30 day study MBC represented 99% of the applied. (A PHOTODEGRADATION HALF-LIFE WAS NOT ESTABLISHED FOR MBC, HOWEVER, AVAILABLE DATA SUGGEST MBC APPEARS TO BE STABLE TO PHOTODEGRADATION)

-161-3. Photodegradation on Soil; EAB# 6080 (Dynamac review 2/26/86), Dupont AMR-423-85; Phenyl-labeled [^{14}C]benomyl (radiochemical purity >99%), at approx. 1 lb. ai/A, degraded with a half-life of < 4 days on nonsterile silt loam soil irradiated with natural sunlight at 25 C. [^{14}C]Benomyl degraded completely in < 15 days on silt loam soil, whether the soil was irradiated or maintained in darkness. Under both conditions, the major degradate (approx. 100% of applied) was MBC, 2-AB comprised <2.0% of the applied. At the end of the 32 day study MBC represented >99% of the applied. (A PHOTODEGRADATION HALF-LIFE WAS NOT ESTABLISHED FOR MBC, HOWEVER, AVAILABLE DATA SUGGEST MBC APPEARS TO BE STABLE TO PHOTODEGRADATION)

-162-2. Anaerobic Soil Metabolism; satisfied by the 162-3 submission.
-162-3. Anaerobic Aquatic Metabolism; this review, EFGWB #s: 91-0949,-50,-62. Benomyl's half-life was not established. The half-life of MBC was 743 days in a clay loam soil, pH 7.4, that was treated with 1 ppm (equivalent to 1 lb/ai/A) [^{14}C]Benomyl and incubated for up to 365 days. (STB), the only other degradate detected reached a maximum of 7.6% of the recovered radioactivity (0.10 ppm) at 365 days posttreatment.

-162-4. Aerobic Aquatic Metabolism; EFGWB #s: 91-0949,-50,-62. Benomyl's half-life was not established. The half-life of MBC was 61 days in a clay loam soil, pH 7.3, that was treated with 2 ppm (equivalent to 2 lb/ai/A) [^{14}C]Benomyl and incubated for 30 days. (STB) reached a maximum of 28.8% of the recovered radioactivity then dropped to non-detectable at day 14. (BUB) reached 1.54-2.30% of the recovered radioactivity (0.03-0.05 ppm) immediately posttreatment-1 day posttreatment, and was not detected (<0.01 ppm) at 7 days. (2-AB) was $\leq$0.083% of the recovered radioactivity (0.02 ppm) at all sampling intervals.

-163-1. Leaching and Adsorption/Desorption; EFGWB# 90-0276,EAB# 6080, (Dynamac review 2/26/86), Dupont AMR 426-85, Phenyl-labeled [^{14}C]benomyl and its degradates, including MBC, STB, and 2-AB were immobile (>85% of applied remained in the upper 2 inches, > 95% in upper 4 inches) in columns (13-inch length) of two silt loam (Flanagan and Seaport) and two sandy loam (Cecil and sassafras) soils. The columns were treated with <u>unaged</u> and <u>aged</u> residues at 1.2-1.6 lb ai/A and leached with 20 inches of water.

(EFGWB# 90-0276,EAB# 6080, (Dynamac review 2/26/86), Dupont AMR 425-85, Phenyl-labeled [^{14}C]benomyl and its degradates, including MBC, STB, and 2-AB were immobile in two silt loam and two sandy loam soils as measured by batch equilibrium and soil TLC studies. Freundlich Kd_{ads} values for benomyl and its degradates (carbendazim, {MBC}) in batch equilibrium studies ranged from 6.1 to 90 and 1/n values ranged from 0.80 to 0.89; R_f values for the soil TLC were 0.00-0.16. Kd_{des} values established for benomyl and its degradates (carbendazim {MBC}) were 2.5 in a Woodston sandy loam 1.1% OM; 2.5 in a Cecil sandy loam 2.1% OM; 2.5 in a Flanagan silt loam 4.3% OM; and 2.4 in a Keyport silt loam with 7.5% OM.

-164-2. Aquatic Field Dissipation; EFGWB #90-0276, <u>See attached review</u>, satisfied by unaged soil column leaching and field monitoring study 00146415 (previously rejected due to the fact that only the 0-2 inch layer of soil was sampled for analysis).

-165-1. Accumulation in confined rotational crops; EFGWB #90-0434, 6/6/90, the 165-1 was satisfied for carbendazim by the submission of additional data;in the 30 day soil aging study (application rate of 1 lb ai/acre) beets, beet foliage, and barley grain all had total ^{14}C-residue concentrations <0.01 ppm while barley straw and cabbage contained total ^{14}C-residues of 0.053 and 0.026 ppm, respectively.

-165-4. Accumulation in Fish (EAB# 6250, EAB# 70858; Acc. No. 260573, Hutton, Kasprzak and Priester (1985), Bluegill sunfish exposed to 2 concentrations of carbendazim, 0.018 mg/l and 0.17 mg/l for 4 wks. showed maximum BCF's in whole fish of 27 and 23 at the low and high exposures, respectively. Peak viscera

BCF's were 460 and 380 for low and high exposures, respectively. Little occurred in muscle tissue (<4 BCF) or the remaining carcass. After 14 days of depuration >94% decrease in whole fish, viscera, and muscle.

(2) The following study may be upgraded to acceptable if supplemental data is submitted:

-162-1. Aerobic Soil Metabolism; this review. EFGWB #s: 91-0949,-50,-62. The calc. half-life of benomyl was 19 hours in nonsterile silt loam soil, pH 6.5. The major degradate was (MBC), which degraded with a registrant-calculated half-life of >320 days. Two other nonvolatile degradates were (2-AB) and (BUB).

(3) Not Satisfied

-164-1 Terrestrial Field Dissipation

(4) Reserved

-164-5. Long Term Terrestrial Field Dissipation; EFGWB #80863,9/11/90, held in reserve pending review of results of aerobic soil metabolism and terrestrial field dissipation.

(5) Waived

-163-2. Laboratory Volatility; EFGWB # 80863, 9/11/90
-163-3. Field Volatility; EFGWB # 80863, 9/11/90
-165-3. Accumulation in Irrigated Crops; SEE MEMORANDUM FROM H. NELSON TO AMY RISPEN, 8/24/90.
-165-2. Accumulation in Field rotational crops; EFGWB #90-0434, 6/6/90 (See attached review.

9. BACKGROUND:

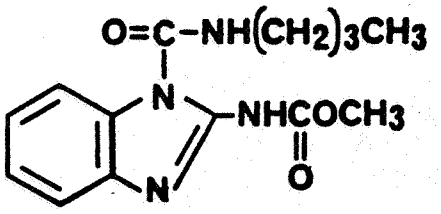
Benomyl is a protective and eradicant systemic fungicide registered for use to control a wide range of fungi affecting a variety of fruits and vegetables, nuts (almonds, peanuts, pistachios, pecans, watercress), field crops (barley, rape, wheat), turf, and ornamentals. It may also be used as a pre- and postharvest spray or dip for the control of storage rots of fruits and vegetables. Benomyl is also effective against mites, primarily as an ovicide. Single active ingredient formulations include dry flowable, oil dispersible, and wettable powder.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:
Refer to attached reviews.

11. COMPLETION OF ONE-LINER: Attached.

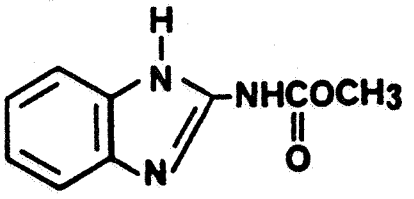
12. CBI APPENDIX:

All data reviewed here are considered "company confidential" by the registrant and must be treated as such.



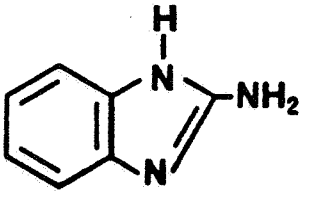
Methyl-1-(butylcarbamoyl)benzimidazol-2-ylcarbamate

(Benomyl)



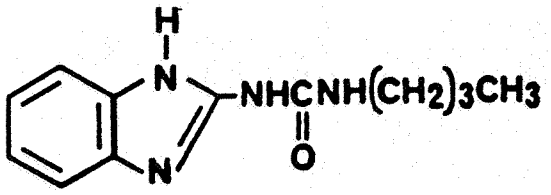
Methyl-1H-benzimidazol-2-yl carbamate

(MBC; Carbendazim)



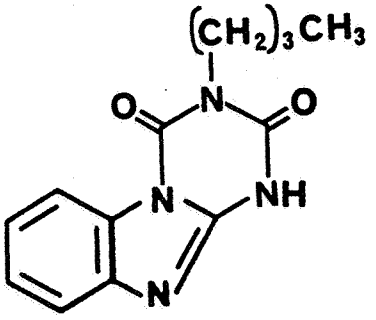
2-Aminobenzimidazole

(2-AB)



2-(3-Butylureido)benzimidazole

(BUB)



3-Butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione

(STB)

BENOMYL

TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES

February 4, 1992

Final Report

Contract No. 68D90058

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
2275 Research Boulevard
Rockville, MD 20850-3262

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BENOMYL

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References	4.1

DATA EVALUATION RECORD

STUDY 1

CHEM 099101 Benomyl §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41255801
Marsh, B.H., and M.F. Arthur. 1989. Aerobic metabolism of [phenyl(U)-^{14}C]benomyl in Keyport silt loam. Laboratory Project ID: Battelle Project No. N-0518-8200; du Pont Report No. AMR-1112-88. Unpublished study performed by Battelle Memorial Institute, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 16

REVIEWED BY: N. Shishkoff TITLE: Staff Scientist

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TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K. Poff

CONCLUSIONS:

Metabolism - Aerobic Soil

1. Study MRID #41255801 does not satisfy the aerobic soil metabolism (162-1) data requirement at this time for the following reasons:

a) Radioactivity present in the aqueous extracts present at up to 13.2% of the applied (0.92 ppm), and degradates present in the organic extracts at up to 2.3% of the applied (approximately 0.16 ppm), were not characterized.

2. Uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, du Pont) degraded with a registrant-calculated half-life of 19 hours in nonsterile silt loam soil incubated in the dark at 25 ± 1 C and 75% of field moisture capacity. The major degradate identified was methyl-1H-benzimidazol-2-yl carbamate (MBC), with a registrant-calculated half-life of >320 days. Two other nonvolatile degradates were identified: 2-aminobenzimidazole (2-AB) and 2-(3-butylureido)-benzimidazole (BUB).

METHODOLOGY:

Subsamples (50 g, dry weight basis) of sieved (2 mm) Keyport silt loam soil (17% sand, 63% silt, 20% clay, 2.3% organic matter, pH 6.5, CEC 4.5 meq/100 g) were added to 250-mL Erlenmeyer flasks and treated at 7 ppm with uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, specific activity 21.6 uCi/mg, du Pont), dissolved in acetone. The acetone was allowed to evaporate, the soil moisture was adjusted to 75% of field capacity, and the samples were mixed with a spatula. The treated soil was incubated in the dark at 25 ± 1 C for up to 12 months. Each flask was sealed with a rubber stopper and connected in series with rubber tubing. In order to trap volatiles, CO_2-free, humidified air was drawn through the system and exhausted through ethylene glycol and NaOH (two tubes) trapping solutions using a vacuum pump. Duplicate samples were removed for analysis immediately posttreatment, at 2 and 5 hours, at 1, 3, 7, and 14 days, and at 1, 2, 4, 9, and 12 months posttreatment. The trapping solutions were sampled and replaced at each sampling interval or sooner as necessary (indicated by a color change of the indicator in the NaOH solution).

Portions of the soil were refluxed with 1 N NaOH for 1 hour. The slurry was centrifuged, the supernatant was decanted, and the soil was washed with additional NaOH. The washes were combined with the reflux supernatant. This extract was partitioned three times with ethyl acetate; the aqueous phase was then adjusted to pH 3 (method not reported) and partitioned three additional times with ethyl acetate. All ethyl acetate phases were combined, concentrated, and filtered (methods not reported). Aliquots of the aqueous phases were analyzed by LSC. Additional portions of the soil were extracted with 1 M ammonium chloride (pH 7):acetone (1:1, v:v) for 20-24 hours. The slurries were centrifuged and the supernatants were decanted. After the supernatant was extracted with additional ammonium chloride:acetone, the two extracts were combined. The acetone was removed from the extracts by rotary evaporation, and the remaining aqueous phase was adjusted to pH >6.5 with 0.1 N NaOH. The aqueous phase was then partitioned six times with ethyl acetate; the extracted soil was also reextracted six times with ethyl acetate. All ethyl acetate extracts were combined, concentrated, and filtered (methods not reported). Aliquots of the aqueous phases were analyzed by LSC.

Aliquots of ethyl acetate and aqueous extracts were analyzed by one-dimensional TLC on silica gel plates developed with toluene:ethyl acetate:acetic acid (65:70:10, v:v:v). Radioactive areas were detected using a linear analyzer; nonlabeled reference standards cochromatographed with the extracts were located by UV fluorescence quenching. Additional aliquots of the ethyl acetate extracts were analyzed by HPLC on a Zorbax CN column eluted with a gradient of acetonitrile:water acidified with phosphoric acid (pH 2.5). Fractions were collected from the column and analyzed by LSC. The retention times of the degradates were compared to those of unlabeled standards (not identified) chromatographed in the same system. The ethyl acetate-extracted soil samples were then further extracted to isolate the humin, fulvic acid, and humic acid fractions. The detection limits for benomyl and its degradates were 0.021 ppm.

Duplicate aliquots of the volatile trapping solutions were analyzed by LSC. The presence of CO_2 in the trapping solutions was confirmed by barium chloride precipitation.

Additional flasks of Keyport silt loam soil were autoclaved (1 hour at 15 lbs/in^2 for 4 consecutive days) to serve as sterile controls. The sterilized soil samples were treated with uniformly phenyl ring-labeled [^{14}C]benomyl as described previously, except that the benomyl solution was filtered (0.2 um) and aseptically applied to sterile soil samples, and the acetone was removed by flushing flasks with filtered air. Sterile samples were capped and aerated at weekly intervals; the air was exhausted into ethylene glycol and NaOH trapping solutions. Samples of sterile treated soil were collected immediately posttreatment, at 14 days, and at 1, 4, 9, and 12 months posttreatment. The soil samples and trapping solutions were analyzed as described previously.

DATA SUMMARY:

Uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, Du Pont), at 7 ppm, degraded with a registrant-calculated half-life of 19 hours in nonsterile silt loam soil incubated in the dark at 25 $\pm$ 1 C and 75% of field moisture capacity for up to 12 months. The major nonvolatile degradate,

methyl-1H-benzimidazol-2-yl carbamate (MBC, carbendazim),

was 28.3-70.4% of the applied radioactivity during the study period in nonsterile soil, and 41.8-68.1% in the sterile soil. MBC degraded with a registrant-calculated half-life of 320 days in nonsterile soil and 1,000 days in sterile soil.

Two other nonvolatile degradates were identified:

2-aminobenzimidazole (2-AB),

at 4.6% of the applied radioactivity at 3 days posttreatment in the nonsterile soil; and,

2-(3-butylureido)benzimidazole (BUB),

at 0.8-6.2% of the applied radioactivity in the nonsterile soil, and 1.6-8.4% in the sterile soil.

Uncharacterized degradates in the organic extracts accounted for up to 2.3% of the applied radioactivity (approximately 0.16 ppm; Tables VI-VII). Unidentified residues were present in the aqueous extracts at up to 13.2% of the applied (0.92 ppm) at 270 days posttreatment (Table VI). Total carbon dioxide was 9.2% of the applied radioactivity in nonsterile soil and 0.1% in sterilized soil. Unextracted radioactivity increased from 4.4-5.1% of the applied immediately posttreatment to 41.8% at 30 days in the nonsterile soil and 26.2% at 270 days in the sterile soil.

The material balances were 81.2-99.0% for nonsterile samples and 75.6-100% for sterile samples, with no discernible pattern.

COMMENTS:

1. Radioactive residues were present in the aqueous phases of the extractions at up to 13.2% of the applied ("actual") radioactivity, which the registrant calculated to be equivalent to 0.92 ppm. Additionally, degradates present in the organic phases of the extracts at up to 2.3% of the applied (approximately 0.16 ppm) were not characterized. Subdivision N guidelines state that all degradates present at $\geq$0.01 ppm must be identified.

2. It is unclear when the immediate posttreatment samples were analyzed. In the nonsterile soil, the concentration of benomyl was lower immediately posttreatment than at the 2-hour sampling interval. The registrant should provide additional information as to when the samples were analyzed. The study authors stated that the test solution was used within 60 minutes of preparation. A previously reviewed hydrolysis study (Wheeler, 1985, Accession No. 259471, Dynamac document dated February 26, 1986) indicated a hydrolytic half-life of <2 hours for benomyl. Therefore, a delay in analysis could have had an impact on the initial concentration of benomyl in the soil.

3. The base hydrolysis extraction procedure converted benomyl into 2-(3-butylureido)benzimidazole (BUB) and methyl-1H-benzimidazol-2-yl carbamate (MBC) into 2-aminobenzimidazole (2-AB), and the organic extraction converted benomyl into methyl-1H-benzimidazol-2-yl carbamate. Therefore, the study authors calculated an "actual percent" of benomyl as the percent of 2-(3-butylureido)benzimidazole from the NaOH extraction, minus the percent of 2-(3-butylureido)-benzimidazole determined in the organic fraction. Likewise, the

"actual percent" of methyl-1H-benzimidazol-2-yl carbamate was calculated as the percent methyl-1H-benzimidazol-2-yl carbamate from the organic extraction, minus the actual percent benomyl. The amount of methyl-1H-benzimidazol-2-yl carbamate could have been confirmed by subtracting the amount of 2-aminobenzimidazole in the organic extraction from the 2-aminobenzimidazole in the base hydrolysis solution; however, the amount of 2-aminobenzimidazole was not quantified for organic extraction (Tables VI-VII). The base hydrolysis extraction of the soil samples was discontinued after 7 days when parent material was no longer present.

4. The data used to calculate the half-lives for methyl-1H-benzimidazol-2-yl carbamate in nonsterile and sterile soil do not differ appreciably, but the half-lives determined by the study authors were 320 days and 1,000 days in nonsterile and sterile soil, respectively.

   A half-life could not be calculated for sterilized soil samples since benomyl was only detected in samples collected immediately posttreatment.

5. Benomyl was not stable in acetone; the radiochemical purity was 76% at 6 hours after preparation. In order to determine the radiochemical purity of the benomyl, an acetone solution was packed in dry ice and stabilized with hydrogen chloride in anhydrous acetonitrile before HPLC analysis. Whether the radiochemical purity of the dosing solution was 97% was not reported.

6. Of the duplicate samples taken at each sampling interval, one was extracted immediately and the other was stored at -20 C (and apparently not analyzed). However, samples from days 1, 3, 14, and 30 days posttreatment were stored for 72-87 days prior to analysis. No storage stability data were presented.

7. The majority of the unextracted radioactivity in the soil was in the soluble and insoluble humin fractions.

Benomyl Sha# 099101

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Pages 18 through 27 are not included.

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____ Identity of product inert ingredients.

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____ 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.

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DATA EVALUATION RECORD

STUDY 2

CHEM 099101 Benomyl §162-3

FORMULATION--OO--ACTIVE INGREDIENT

STUDY ID 41137701
Arthur, M.F., B.H. Marsh, L.C. Fadel, and T.C. Zwick. 1989. Anaerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in West Jefferson, Ohio, pond water and sediment. Laboratory Project ID: Battelle Project No. N0799-8800; du Pont Report No. AMR-770-87. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 16

REVIEWED BY: N. Shishkoff TITLE: Staff Scientist

EDITED BY: M. Cairoli TITLE: Staff Scientist
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APPROVED BY: W. Spangler TITLE: Project Manager

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APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K. Poff

CONCLUSIONS:

Metabolism - Anaerobic Aquatic

1. Study MRID #41137701 completely satisfies the anaerobic aquatic (162-3) data requirement for benomyl.

2. The registrant calculated half-life of carbendazim (MBC) (no benomyl was detected due to the rapid hydrolysis rate of benomyl to carbendazim) under anaerobic aquatic conditions was 743 days in a clay loam soil that was treated with 1 ppm (equivalent to 1 lb/ai/A) [^{14}C]Benomyl and incubated anaerobically for up to 365 days. In the sediment extracts, where the majority of the radioactivity was

recovered, MBC was 83.4% of the recovered radioactivity (0.88 ppm) immediately posttreatment, 66.9% (0.83 ppm) at 60 days and 55.6% (0.70 ppm) at 365 days (Table V). The other degradate identified in the sediment extracts was 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione (STB), which was a maximum of 7.6% of the recovered radioactivity (0.10 ppm) at 365 days posttreatment. Unextracted radioactivity in the soil increased from 12% of the recovered immediately posttreatment to 36.2% at 365 days posttreatment.

METHODOLOGY:

Portions (50 g, dry weight basis) of clay loam sediment (45% silt, 30% clay, 25% sand, 6.8% organic matter, pH 7.4, CEC 31.0 meq/100 g) from a pond and 100 mL of pond water (not characterized) were added to 250-mL Erlenmeyer flasks. The flasks were purged with nitrogen, sealed with rubber stoppers, and incubated for 20 days (conditions not specified). After 20 days of anaerobic incubation, the samples were treated at 1 ppm with uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, specific activity 21.6 uCi/mg, du Pont) dissolved in acetone. The flasks were purged with nitrogen, resealed, and the samples were incubated in the dark at 25 $\pm$ 1 C. Duplicate flasks were removed for analysis immediately posttreatment, at 7 and 14 days, and at 1, 3, 4, 9, and 12 months posttreatment. At each sampling interval, all of the flasks were connected in series to ethylene glycol and NaOH trapping solutions, and the flasks were flushed with nitrogen. The trapping solutions were sampled following the nitrogen purging. After sampling, the contents of the flasks were filtered, and the water and sediment fractions were stored at -25 C for up to 244 days prior to analysis.

The water samples were concentrated by rotary evaporation (at 40 C) and filtered (0.2 um). Aliquots of the water samples were analyzed by LSC "and stored at less than 6 C".

The sediment samples were air-dried for 1-2 days, weighed, and subsamples were extracted with 1 M aqueous ammonium chloride (pH 7):acetone (1:1, v:v) for 20-24 hours, followed by centrifugation. The soil was reextracted with the same solvent; extracts were combined, concentrated to the aqueous phase, and adjusted to pH >6.5 with 0.1 N NaOH. The extract was partitioned six times with ethyl acetate and the extracted soil was reextracted six times with ethyl acetate. All organic extracts were combined and concentrated. Aliquots of the concentrated ethyl acetate and aqueous extracts were analyzed by TLC on silica gel plates developed with toluene:ethyl acetate:acetic acid (65:70:10, v:v:v). Radioactive areas were quantified with a linear analyzer; unlabeled reference standards cochromatographed with the extracts were located by UV fluorescence quenching. Additional aliquots of the extracts were analyzed by HPLC on a Zorbax CN column eluted with a gradient of acetonitrile:water adjusted to pH 2.5 with phosphoric acid. Fractions were collected

from the column and analyzed by LSC. Retention times were compared to those of unlabeled standards chromatographed in the same system. The ethyl acetate-extracted soil samples were further analyzed to quantify radioactivity in the humus, fulvic acid, hymatomelanic acid, and soluble and insoluble humin fractions. Additional subsamples of the air-dried soil were analyzed by LSC following combustion.

Aliquots of the trapping solutions were analyzed by LSC. Additional aliquots of NaOH solutions were treated with barium chloride to confirm the presence of CO_2.

DATA SUMMARY:

[^{14}C]Benomyl was not found in any sample at any sampling interval in clay loam sediment that was initially incubated anaerobically for 20 days in the dark, then treated at 1 ppm with uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%), and subsequently anaerobically incubated for up to 365 days. The major degradate was

methyl-1H-benzimidazol-2-yl carbamate (MBC, carbendazim),

which degraded with a registrant-calculated half-life of 743 days in this system.

In the sediment extracts, MBC was 83.4% of the recovered radioactivity (0.88 ppm) immediately posttreatment, 66.9% (0.83 ppm) at 60 days and 55.6% (0.70 ppm) at 365 days (Table V). The other degradate identified in the sediment extracts was

3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H, 3H)dione (STB),

which was a maximum of 7.6% of the recovered radioactivity (0.10 ppm) at 365 days posttreatment. Uncharacterized radioactivity in the sediment was a maximum of 2.6% of the recovered (0.04 ppm) at 120-270 days posttreatment. Unextracted radioactivity in the soil increased from 12% of the recovered immediately posttreatment to 36.2% at 365 days posttreatment (Table III).

In the floodwater, uncharacterized radioactivity was 3% of the recovered immediately posttreatment and decreased to <1% at 270-365 days posttreatment (Table III).

Carbon dioxide was <0.1% of the recovered radioactivity throughout the study.

The material balances were 105-139% of nominal applied radioactivity.

COMMENTS:

1. Despite the rapid hydrolysis of benomyl [half-life <2 hours (Wheeler, 1985, Accession No. 259471,) the sediment was air-dried for 1-2 days and the soil was extracted in an aqueous solution for up to 24 hours. The study authors of the aerobic soil metabolism study (Study 1, MRID 41255801) indicated that benomyl is degraded to MBC under these extraction conditions. Benomyl was degraded by the analytical method; it is impossible to distinguish between the test substance and its major degradate.

2. The pond water was not characterized.

3. The methods description was incomplete. For example, it was unclear if the volatile trapping solutions were changed at each sampling interval or if aliquots were removed for analysis. It was also unclear if the water samples were stored at <6 C or if the aliquots analyzed by LSC were stored at <6 C.

4. In the Results section, it was unclear how the study authors calculated the total radioactivity in unextracted sediment and pond water.

5. Benomyl was not stable in acetone; the purity was 66% at 48 hours after preparation. In order to determine the radiochemical purity of the benomyl, an acetone solution was packed in dry ice and stabilized with hydrogen chloride in anhydrous acetonitrile before HPLC analysis. Whether the radiochemical purity of the dosing solution was the 97% obtained by this method was not reported. In this study, the test solution was used within 15 minutes of preparation.

6. The study author stated that the application rate, 1 ppm, was approximately equivalent to the expected soil residues in the 10-cm topsoil at an application rate of 1 lb ai/A. In the aerobic soil metabolism study (Study 1, MRID 41255801), the maximum application rate was reported to be 7 lb ai/A. The use of a lower application rate may have prevented the identification of some degradates.

7. In this study, the majority of the radioactivity was recovered from the sediment. In the aerobic aquatic metabolism study (Study 3, MRID 41291501), most of the radioactivity was recovered from the floodwater.

8. Most of the radioactivity bound to the soil was in the soluble and insoluble humin fractions.

9. The test systems remained anaerobic throughout the study; the dissolved oxygen ranged from 0.3 to 1.6 mg/L.

Benomyl Sha# 099101

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Pages 32 through 41 are not included.

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.

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DATA EVALUATION RECORD

STUDY 3

CHEM 099101 Benomyl §162-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41291501
Arthur, M.F., K.L. Schweitzer, L.C. Fadel, B.H. Marsh, and S.S. Marsh. 1989. Aerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in Greenville, Mississippi, water and sediment. Laboratory Project ID: Battelle Project No. N-0966-730; du Pont Report No. AMR-1452-89. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 16

REVIEWED BY: N. Shishkoff TITLE: Staff Scientist

EDITED BY: M. Cairoli TITLE: Staff Scientist
W. Martin Staff Scientist

APPROVED BY: W. Spangler TITLE: Project Manager

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Rockville, MD
TEL: 301-417-9800

APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Aquatic

1. Study MRID #41291501 complete satisfies the aerobic aquatic metabolism (162-4) data requirement for benomyl.

2. The registrant calcualted half-life of carbendazim (MBC) (no benomyl was detected due to the rapid hydrolysis rate of benomyl to carbendazim) under aerobic aquatic conditions was 61 days in a clay loam soil that was treated with 2 ppm (equivalent to 2 lb/ai/A) [^{14}C]Benomyl and incubated aerobically for 30 days. In the nonsterile floodwater, where the majority of the radioactivity was

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recovered, MBC was 57.2% of the recovered radioactivity (1.14 ppm) immediately posttreatment, 37.4-37.8% (0.75-0.76 ppm) at 0.2-1 days, 12.5% (0.25 ppm) at 7 days, and was not detected (<0.01 ppm) at 30 days. 3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H, 3H)dione (STB), was 28.8% of the recovered radioactivity (0.58 ppm) immediately posttreatment, increased to 40.4% (0.81 ppm) at 0.2 days posttreatment, declined to 1.97% (0.04 ppm) at 7 days, and was not detected (<0.01 ppm) at 14 days. 2-(3-butylureido)benzimidazole (BUB), was 1.54-2.30% of the recovered radioactivity (0.03-0.05 ppm) immediately posttreatment-1 day posttreatment, and was not detected (<0.01 ppm) at 7 days. 2-aminobenzimidazole (2-AB), was ≤0.083% of the recovered radioactivity (0.02 ppm) at all sampling intervals.

METHODOLOGY:

Subsamples (50 g, dry weight basis) of sieved (2 mm) silty clay loam sediment (14.4% sand, 54.8% silt, 30.8% clay, 0.9% organic matter, pH 7.3, CEC 18.3 meq/100 g) collected from a rice paddy, were added to 250-mL Erlenmeyer flasks, flooded with paddy water (100 mL, not characterized), and treated at approximately 2 ppm with uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%, specific activity 21.6 uCi/mg, du Pont), dissolved in acetone. The soil:water slurries were incubated in the dark at 25 ± 1 C for up to 30 days. The flasks were connected in series with rubber tubing. In order to trap volatiles, CO_2-free, humidified air was drawn through the system and exhausted through ethylene glycol and NaOH (three tubes) trapping solutions using a vacuum pump. Duplicate samples were removed for analysis immediately posttreatment, at 2 and 5 hours, and at 1, 3, 7, 14, 21, and 30 days posttreatment. The trapping solutions were sampled and replaced at each sampling interval.

The soil and water were separated by centrifugation. Portions of the soil were refluxed with 1 N NaOH for 1 hour. The slurry was centrifuged, the supernatant was decanted, and the soil was washed with additional NaOH. The washes were combined with the reflux supernatant. This extract was partitioned three times with ethyl acetate; the aqueous phase was then adjusted to pH <3 (method not reported) and partitioned three additional times with ethyl acetate. All ethyl acetate phases were combined, concentrated, and filtered (methods not reported). Aliquots of the aqueous phases were analyzed by LSC. Additional portions of the soil were extracted with 1 M ammonium chloride (pH 7):acetone (1:1, v:v) for 20-24 hours. The slurries were centrifuged and the supernatants were decanted. After the supernatant was extracted with additional ammonium chloride:acetone, the two extracts were combined. The acetone was removed from the extracts by rotary evaporation, and the remaining aqueous phase was adjusted to pH >6.5 with 0.1 N NaOH. The aqueous phase was then partitioned six times with ethyl acetate; the extracted soil was also reextracted six times with ethyl acetate. All ethyl acetate extracts were combined, concentrated, and filtered

(methods not reported). Aliquots of the aqueous phase were analyzed by LSC.

Aliquots of the ethyl acetate and aqueous extracts were analyzed by one-dimensional TLC on silica gel plates developed with toluene:ethyl acetate:acetic acid (50:80:15 or 50:80:10, v:v:v). Radioactive areas were detected using a linear analyzer; nonlabeled reference standards cochromatographed with the extracts were located by UV fluorescence quenching. Additional aliquots of the ethyl acetate extracts were analyzed by HPLC on a Zorbax CN column eluted with a gradient of acetonitrile:water acidified with phosphoric acid (pH 2.5). Fractions were collected from the column and analyzed by LSC. The retention times of the degradates were compared to those of unlabeled standards (not identified) chromatographed in the same system. The ethyl acetate-extracted soil samples were then further extracted to isolate the humin, fulvic acid, and humic acid fractions. The detection limits for benomyl and its degradates were 0.01 ppm.

Duplicate aliquots of the volatile trapping solutions were analyzed by LSC. The presence of CO_2 in the trapping solutions was confirmed by barium chloride precipitation.

Additional flasks of flooded silty clay loam sediment were autoclaved (1 hour at 15 lbs/in^2 for 3 consecutive days) to serve as sterile controls. The sterilized samples were treated with uniformly phenyl ring-labeled [^{14}C]benomyl as described previously, except the benomyl solution was filtered (0.2 um) and aseptically applied to sterile soil samples. Sterile samples were capped and independently aerated with filter-sterilized air at harvest times, except at 0 and 2 hours, when the air was exhausted into ethylene glycol and NaOH trapping solutions. Samples of sterile treated flooded sediment were collected at the same intervals as the nonsterile samples. The sediment samples and trapping solutions were analyzed as described previously.

DATA SUMMARY:

[^{14}C]Benomyl was not found in any sample at any sampling interval in nonsterile clay loam sediment treated at approximately 2 ppm with uniformly phenyl ring-labeled [^{14}C]benomyl (radiochemical purity 97%) and incubated aerobically in the dark at 25 $\pm$ 1 C. The major degradate of benomyl was

methyl-1H-benzimidazol-2-yl carbamate (MBC, carbendazim),

which degraded with a registrant-calculated half-life of approximately 61 days in this system, and 303 days in a similar sterilized system. The other degradates identified were

3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H, 3H)dione (STB),

2-aminobenzimidazole (2-AB), and

2-(3-butylureido)benzimidazole (BUB).

In the nonsterile floodwater, MBC was 57.2% of the recovered radioactivity (1.14 ppm) immediately posttreatment, 37.4-37.8% (0.75-0.76 ppm) at 0.2-1 days, 12.5% (0.25 ppm) at 7 days, and was not detected (<0.01 ppm) at 30 days (Table VI). STB was 28.8% of the recovered radioactivity (0.58 ppm) immediately posttreatment, increased to 40.4% (0.81 ppm) at 0.2 days posttreatment, declined to 1.97% (0.04 ppm) at 7 days, and was not detected (<0.01 ppm) at 14 days. BUB was 1.54-2.30% of the recovered radioactivity (0.03-0.05 ppm) immediately posttreatment-1 day posttreatment, and was not detected (<0.01 ppm) at 7 days. 2-AB was ≤0.083% of the recovered radioactivity (0.02 ppm) at all sampling intervals. Total uncharacterized radioactivity in the floodwater was a maximum of 2.85% of the recovered (0.06 ppm) immediately posttreatment.

In the nonsterile sediment extracts, MBC was 1.78-6.02% of the recovered radioactivity (0.04-0.12 ppm) immediately posttreatment, 54.1% (1.08 ppm) at 14 days and 42.3-46.1% (0.85-0.93 ppm) at 21-30 days (Table VI). STB increased to 18.6-21.5% of the recovered radioactivity (0.37-0.43 ppm) at 7-30 days posttreatment; BUB was a maximum of 2.59-2.63% of the recovered radioactivity (0.05 ppm) at 3-7 days posttreatment. 2-AB was ≤1.21% of the recovered radioactivity (0.02 ppm) at all sampling intervals. Total uncharacterized radioactivity in the sediment extracts was a maximum of 5.04% of the recovered (0.10 ppm) at 14 days posttreatment. Unextracted radioactivity in the soil increased from 0.49-0.89% of the recovered immediately posttreatment to 22.3% at 30 days posttreatment (Table II).

In the nonsterile system, CO_2 was <0.1% of the recovered radioactivity throughout the study.

The material balances were 92.5 ± 8.5% for nonsterile samples, and 92.2 ± 6.5% for sterile samples.

COMMENTS:

1. It is unclear when the immediate posttreatment samples were analyzed.

2. The time between sampling and analysis was not reported. The study authors stated that aliquots of water samples were "stored at 4 C ± 1 C until extraction and analysis".

3. The extraction method for the water was not provided.

4. The base hydrolysis extraction procedure converted benomyl into 2-(3-butylureido)benzimidazole (BUB) and methyl 1H-benzimidazol-2-ylcarbamate (MBC) into 2-aminobenzimidazole (2-AB), and the organic

extraction converted benomyl into methyl 1H-benzimidazol-2-yl carbamate. Therefore, the study author calculated an "actual percent" of benomyl as the percent of 2-(3-butylureido)benzimidazole from the NaOH extraction minus the percent of 2-(3-butylureido)-benzimidazole determined in the organic fraction. Likewise, the "actual percent" of methyl 1H-benzimidazol-2-yl carbamate was calculated as the percent methyl 1H-benzimidazol-2-yl carbamate from the organic extraction minus the actual percent benomyl. The amount of methyl 1H-benzimidazol-2-yl carbamate could have been confirmed by subtracting the amount of 2-aminobenzimidazole in the organic extraction from the 2-aminobenzimidazole in the base hydrolysis solution; however, the amount of 2-aminobenzimidazole was not quantified for organic extraction (Tables VI-VII). The base hydrolysis extraction of the soil samples was discontinued after 7 days when parent material was no longer present.

5. Benomyl was not stable in acetone; the radiochemical purity was 76% at 6 hours after preparation. In order to determine the radiochemical purity of the benomyl, an acetone solution was packed in dry ice and stabilized with hydrogen chloride in anhydrous acetonitrile before HPLC analysis. Whether the radiochemical purity of the dosing solution was 97% was not reported. The study authors stated that the test solution was used within 90 minutes of preparation.

6. The field water was not characterized. It was not stated that the water was sterilized prior to being added to the flasks of sterile soil.

7. Of the duplicate samples taken at each sampling interval, one was extracted immediately and the other was stored at -20 C (and apparently not analyzed).

8. Initially, most of the recovered radioactivity was found in the floodwater layer. In the anaerobic aquatic metabolism study (Study 2, MRID 41137701), most of the radioactivity was recovered from the sediment.

9. Most of the radioactivity bound to soil was in the soluble and insoluble humin fractions.

Benomyl Sha# 099101

Page_____ is not included in this copy.

Pages 47 through 59 are not included.

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.

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____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

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REFERENCES

The following studies were reviewed:

Arthur, M.F., B.H. Marsh, L.C. Fadel, and T.C. Zwick. 1989. Anaerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in West Jefferson, Ohio, pond water and sediment. Laboratory Project ID: Battelle Project No. N0799-8800; du Pont Report No. AMR-770-87. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. (41137701)

Arthur, M.F., K.L. Schweitzer, L.C. Fadel, B.H. Marsh, and S.S. Marsh. 1989. Aerobic aquatic metabolism of [phenyl(U)-^{14}C]benomyl in Greenville, Mississippi, water and sediment. Laboratory Project ID: Battelle Project No. N-0966-730; du Pont Report No. AMR-1452-89. Unpublished study performed by Battelle Columbus Division, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. (41291501)

Marsh, B.H., and M.F. Arthur. 1989. Aerobic metabolism of [phenyl(U)-^{14}C]benomyl in Keyport silt loam. Laboratory Project ID: Battelle Project No. N-0518-8200; du Pont Report No. AMR-1112-88. Unpublished study performed by Battelle Memorial Institute, Columbus, OH, and submitted by E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. (41255801)

The following study was not reviewed because it has been previously reviewed by Dynamac in a Benomyl Addendum Report submitted October, 1987:

Han, J. C-Y. 1986. Anaerobic soil metabolism of 2-^{14}C-benomyl and methyl 2-^{14}C-benzimidazolecarbamate. In Supplemental information and data related to the field monitoring study for benomyl residues in flooded rice fields. Unpublished study prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. (40158401)

Shaughnessy No.: 099101

Date Out of EFGWB: FEB 23 1990

TO: P. Hundemann
Product Manager #74
Registration Division (H7505C)

FROM: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review #2
Environmental Fate and Groundwater Branch/EFED (H7507C)

THRU: Hank Jacoby, Chief
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Attached, please find the EFGWB review of:

Reg./File #(s): 257428

Common Name: Benomyl

Chemical Name: Methyl-1-(butylcarbamoyl)-2-benzimidazole

Type of Product: Fungicide

Product Name: Benelate, Tersan 1991, Benex

Company Name: E.I. duPont de Nemours & Co.

Purpose: Review of soil column leaching and rice paddy infiltration rate data in support of the aquatic field dissipation data requirement. Review of soil characteristics information in support of the mobility in soil data requirement.

Date Received: 1/5/90 Action Code: 660

EFGWB #(s): 90-0276

Total Reviewing Time: 3.0

Deferrals to: _____ Ecological Effects Branch/EFED

_____ Science Integration & Policy/EFED

_____ Non-Dietary Exposure Branch/HED

_____ Dietary Exposure Branch/HED

_____ Toxicology Branch I/HED

_____ Toxicology Branch II/HED

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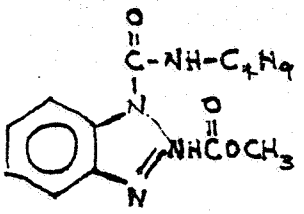
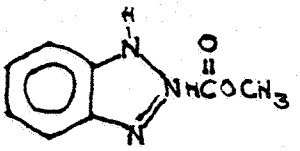
1. CHEMICAL:
Common Name: Benomyl
Chemical Name: Methyl-1-(butylcarbamoyl)-2-benzimidole
Type of Product: Fungicide
Trade Name: Benelate, Tersan 1991, Benex

Chemical Structures: Benomyl, carbendizam (the major degradate)





2. TEST MATERIAL:
See DER.

3. STUDY/ACTION TYPE:
Soil column leaching study and flooded rice growing soil infiltration rates in support of the aquatic field dissipation (164-2) data requirement. Characteristics of typical rice growing soils in support of the adsorption/desorption (163-1) data requirement.

4. STUDY IDENTIFICATION:

(1) Letter dated 11/7/89 from R. Hamlen of Du Pont to P. Hundemann of RD/OPP.

(2) MRID #41274801
Ryan D. 1989. Soil column leaching of [phenyl(U)-^{14}C]benomyl in a rice paddy soil. Completed on October 9, 1989. Performed and submitted by E.I. du Pont de Nemours and Company, Wilmington, DE. (included in a package with the 11/7/89 letter referenced above).

(3) Internal du Pont memo dated 10/11/89 from K. Monson to R. Hamlen. Attached to the memo were infiltration rate data for various rice fields (memo and attachment were included in a package with the 11/7/89 letter referenced above).

(4) Letter dated 8/11/89 from R. Hamlen of du Pont to J. Mitchell of RD/OPP. Attached to the letter are summaries of the characteristics of 7 typical rice growing soils (letter and attachment were included in a package with the 11/7/89 letter referenced above).

5. REVIEWED BY:
Henry Nelson, Ph.D., Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Groundwater Branch/EFED

H. Nelson
Date: 2/22/90

6. APPROVED BY:
Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Groundwater Branch/EFED

Date: FEB 23 1990

7. CONCLUSIONS:

(1) The supplemental unaged soil column leaching study (41274801, see attached DER) and infiltration rate data for flooded rice fields (see discussion) are acceptable for supplemental information. Along with previously reviewed (see EAB #6080 dated 4/4/86) soil column leaching (00151421, see attached Tables 1, 2, and 3) and batch equilibrium/soil TLC (00151422, see attached Tables 4, 5, and 6) studies, the supplemental information indicates that benomyl and its major degradate (carbendizam) are unlikely to be susceptible to leaching from flooded rice growing soils. Therefore, EFGWB concludes that study 00146415 satisfies the aquatic field dissipation data requirement for benomyl use on rice even though only the top 2 inches of soil were sampled.

(2) The comparison of the characteristics of the 4 test soils used in the batch equilibrium adsorption/desorption study to characteristics of 7 typical rice growing soils (Table 1) is acceptable for supplemental information. The comparison shows that from the standpoint of combined characteristics (texture, pH, and %OM together), the test soils do not represent typical rice growing soils very well. However, for unionized organics such as benomyl and its major degradate (carbendizam), the percentage organic matter is generally the most important factor affecting adsorption to soil. The range of organic matter for the test soils (1.1-7.5%) is comparable to that of the surface layers of 7 typical rice growing soils (0.9-6.0%). Furthermore, flooded rice growing soils are not really aquatic sediments. Therefore, the requirement for batch equilibrium data on the adsorption/desorption of benomyl to a rice growing soil/sediment is waived.

8. RECOMMENDATIONS:

Please inform the registrant that study 00146415 satisfies the aquatic field dissipation (164-2) data requirement for the use of benomyl on rice and that the requirement for batch equilibrium data on the adsorption/desorption of benomyl to a rice growing sediment is waived.

9. BACKGROUND:

Benomyl is a fungicide registered for use on a variety of food crops including rice, soybeans, apples, oranges, peaches, and pecans. Application rates range from 0.063 to 1.5 lbs ai/acre.

In a review dated 9/14/88, EFGWB (see EFGWB #80863) concluded that study 001464415 did not satisfy the aquatic field dissipation (164-2) data requirement because soil was sampled to a depth of only 2 inches. The registrant's argument that sampling below 2 inches was unnecessary because "data from the two silt loam soils (typical of Louisiana and Arkansas silt loam soils) studied in the submitted soil column leaching study (EPA Accession No. 259471) indicated that 98% and 93% of all residues were contained in the upper 2" of the soil column" was rejected by EFGWB for the following reason: The percent organic matter for the 2 silt loam soils cited in the cited leaching study (4.3 and 7.5%) were much higher than those studied in the aquatic field dissipation study (1.1 and 1.4%). In response the registrant has submitted an additional soil column leaching study (41274801) on a low organic rice growing soil and infiltration rate data for flooded rice fields to support their argument.

In the same review dated 9/14/88, EFGWB (see EFGWB #80863) rejected a waiver request for data on the adsorption/desorption of benomyl to a soil representative of rice growing areas for the following reason: The registrant did not submit soil characteristic information to support their claim that the characteristics of the 4 test soils used in the batch equilibrium adsorption/desorption study (00151422) were within the range of characteristics exhibited by typical rice growing soils. In response, the registrant has submitted a comparison of the characteristics of the 4 test soils to characteristics of 7 typical rice growing soils.

10. <u>DISCUSSION:</u>

(1) A comparison of the characteristics of 7 typical rice growing soils to those used in the adsorption/desorption study is presented in Table 7. The registrant's contention that the characteristics of soils used in the adsorption/desorption study are within the wide range of characteristics exhibited by typical rice growing soils is generally but not completely correct as can be seen from Table 7. The percentage organic matter of the Keyport silt loam test soil (7.5%) is greater than the maximum percentage organic matter (0.9-6.0%) for the 7 typical rice growing soils listed in Table 1. The range of pHs represented by the test soils (5.2-6.6) is substantially less than the range exhibited by the rice growing soils (4.5-8.4). In addition, in looking at combinations of characteristics, the 4 test soils do not appear to represent typical rice growing soils very well.

(2) It is unclear how the submitted infiltration rate data for various flooded rice paddies in Texas were derived. Table 22 provides evapotranspiration plus infiltration (column 4), evapotranspiration (column 5), and infiltration (column 6) data

for several flooded rice growing soils in Texas. The infiltration numbers in column 6 are generally not equal to the evapotranspiration plus infiltration numbers in column 4 minus the evapotranspiration numbers in column 5. Based upon the numbers in column 6, mean infiltration rates for various rice growing soils in Texas under flooded conditions ranged from 0.02 to 0.24 in./day averaging 0.093 in./day over 8 soils. Over a 90 day flood period, the corresponding total infiltration would range from 1.8 to 21.6 inches averaging 8.4 inches which is less than the 20 inches used in the soil column leaching studies.

(3) See the attached DER for a discussion on the supplemental soil column leaching study (41274801).

11. COMPLETION OF ONE LINER:
Not applicable.

12. CBI INDEX:
Not applicable.

Benomyl Sha# 099101

Page_____ is not included in this copy.

Pages 66 through 73 are not included.

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

SHAUGNESSY No. 99101
COMMON NAME: Benomyl
CHEMICAL NAME: Methyl-1-(butylcarbamoyl)-2-benzimidazole
FORMULATION: Active Ingredient
DATA REQUIREMENT: Soil Column Leaching (163-1)

MRID # 41274801
Ryan D. 1989. Soil column leaching of [phenyl(U)-^{14}C]benomyl in a rice paddy soil. Completed on October 9, 1989. Performed and submitted by E.I. du Pont de Nemours and Company, Wilmington, DE.

REVIEWED BY: Henry Nelson, Ph.D. Date: 2/22/90
TITLE: Chemist
ORGANIZATION: OPP
TELEPHONE: 557-2505

SIGNATURE: H Nelson

CONCLUSIONS:

(1) This supplemental unaged soil column leaching study (41274801) was submitted in support of the aquatic field dissipation data requirement, and is acceptable for that purpose.

(2) The equivalent of 2.2 lb ai/acre of ^{14}C-benomyl was applied to the top of a 12 inch soil column packed with a silty clay loam (pH = 7.3, OM = 0.9%). After elution with 20 inches of water under a constant head, the distribution of applied radioactivity was as follows: total soil column plus eluate (103.4%), 0-2 inch (93.9%), 2-4 inch (8.7%), 4-12 inches combined (< 1.0%), and eluate (0.34%). Based upon the results of hydrolysis, soil metabolism, and other soil column leaching studies, the study author postulated that most of the applied ^{14}C-benomyl had been hydrolyzed to ^{14}-carbendazim during the > 20 hour duration of the study. The results indicate that benomyl/carbendazim residues had extremely low mobility in the test soil. The test soil is reportedly typical of rice growing soils in Mississippi.

MATERIALS AND METHODS:

(1) Test Chemical:
[Phenyl(U)-^{14}C] benomyl (21.6 uCi/mg, radiochemical purity = 97%)

(2) Stock Solution:
Nominal 0.91 mg ^{14}C-benomyl/ml acetone (At the time of application to the soil column, 23% of the applied was accounted for by carbendazim).

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(3) Test Soil:
Greenville, MS silty clay loam (pH = 7.3, OM = 0.9%). Other reported characteristics of the test soil are listed in Table I. Soil particles passing through a 2 mm sieve, but excluded from a 0.84 mm sieve were used in the study. Therefore, since the clay, silt, and fine sand fractions can pass through a 0.84 mm sieve, it is probable that the actual characteristics of the test soil are different than those listed in Table 1 (see discussion).

(4) Experimental Conditions:
The equivalent of 2.2 lbs ai/acre of ^{14}C-benomyl was applied to the top of a 12 inch soil column packed with sieved silty clay loam soil. The column was eluted with 20 inches of water under a constant head. Due to the low draining characteristics of the study soil, a microperistatic pump was used to draw water from the column at 50 mL/hr.

(5) Sampling and Analysis:
After the soil column was eluted with 20 inches of water, the soil within the 12 inch column was cut into 2 inch segments. Triplicate aliquots of each soil segment were analyzed for total radioactivity by combustion followed by LSC. Eluate fractions were analyzed for total radioactivity by LSC. Neither the soil segments nor the eluate were analyzed specifically for benomyl or its degradates such as carbendazim.

RESULTS:

The distribution of radioactivity between the eluate and soil column is presented in Table II. The distribution of radioactivity remaining in the soil column is presented in Table III.

Approximately 103.4% of the applied radioactivity was recovered. After elution of the soil column with 20 inches of water under a constant head, the distribution of applied radioactivity was as follows: total soil column plus eluate (103.4%), 0-2 inch (93.9%), 2-4 inch (8.7%), 4-12 inches combined (< 1.0%), and eluate (0.34%). Based upon the results of hydrolysis, soil metabolism, and other soil column leaching studies, the study author postulated that most of the applied ^{14}C-benomyl had been hydrolyzed to ^{14}-carbendazim during the > 20 hour duration of the study. The results indicate that benomyl/carbendazim residues had extremely low mobility in the test soil. The test soil is reportedly typical of rice growing soils in Mississippi.

DISCUSSION:

(1) The study would not partially satisfy the mobility in soil (163-1) data requirement because radiolabeled residues were not

analyzed specifically for benomyl and its degradates. In addition, soil particles passing through a 2 mm sieve, but excluded from a 0.84 mm sieve were used in the study. Therefore, the clay, silt, and fine sand fractions of the soil were removed from the soil prior to packing the column. However, the study was submitted to support the aquatic field dissipation (164-2) data requirement, not the mobility in soil data requirement.

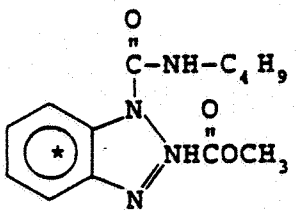
(2) Although the failure to analyze radiolabeled residues specifically for benomyl and its degradates is a serious deficiency, the results of soil column leaching studies on 4 other soils (see EAB No. 6080 dated 4/4/86) support the study author's assumption that most of the applied radioactivity at the termination of the study was probably accounted for by carbendazim.

(3) The study author did not explain why the clay, silt, and fine sand fractions were removed from the soil. It was probably an attempt to present a worst case estimate of mobility in an aquatic sediment. Due to the greater settling velocities of larger particles and the typical formation of suspended clay colloids in surface waters, sediments typically have much higher percentages of course sand and much lower percentages of clay, silt, and fine sand then do the soils from which they originate. However, a flooded rice growing soil is not an aquatic sediment. Nevertheless, the removal of the clay, silt, and fine sand fractions probably reduced the adsorption capacity of the soil due to a decrease in surface area and a probable decrease in the percentage of soil accounted for by humic materials (humic materials are typically preferentially bound by the smaller soil fractions). Therefore, even though the removal of the clay, silt, and fine sand fractions from the test soil probably does not simulate flooded rice growing soil, it probably does provide a worst case estimate of leaching potential.

(4) The test soil used in the soil column leaching study (a Mississippi silty clay loam with pH = 7.3 and OM = 0.9%) was submitted to support an aquatic field dissipation study on a Louisiana silt loam (pH = 6.6, OM = 1.0%) and an Arkansas silt loam (pH = 6.2, OM = 1.4%). No explanation was provided on the use of a different soil for the soil column leaching study. In addition, the characteristics provided for the Mississippi silt clay in Table I are not those of the test soil since the clay, silt, and fine sand fractions were removed prior to packing the column.

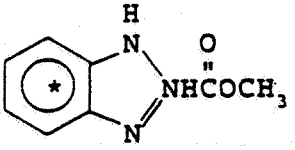
FIGURE 1

CHEMICAL STRUCTURES OF BENOMYL AND CARBENDAZIM



Benomyl

Methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate



Carbendazim

Methyl 2-benzimidazole carbamate

* denotes location of ^{14}C-label

TABLE I

SOIL CHARACTERIZATION*

Parameter	Greenville, Mississippi
% Sand (0.05 mm to 2.0 mm)	14.4
% Silt (0.002 mm to 0.05 mm)	54.8
% Clay (<0.002 mm)	30.8
Textural Class	Silty Clay Loam
% Organic Matter	0.9
pH	7.3
Cation Exchange Capacity (meq/100 g)	18.3

* Analyses were performed at Harris Laboratories, Inc., Lincoln, Nebraska.

TABLE II

DISTRIBUTION OF RADIOACTIVITY RECOVERED FROM GREENVILLE, MISSISSIPPI SOIL COLUMN

Percent of Applied Radioactivity		
^{14}C Recovered in Eluate	^{14}C Retained in Soil	^{36}Cl Recovered in Eluate
0.34	103.4	94.5

TABLE III

DISTRIBUTION OF [^{14}C] RADIOACTIVITY REMAINING ON SOIL COLUMN

Column Segment	% of Applied Radioactivity
0-2 inch	93.9
2-4 inch	8.7
4-6 inch	0.4
6-8 inch	0.2
8-10 inch	0.1
10-12 inch	<0.1
top sand layer	0.1
bottom sand layer	<0.1
Total	103.4

Shaughnessy No.: 128872

Date Out of EFGWB: JUN 6 1990

To: P. Hundemann
Review Manager PM #74
Reregistration Division (H7508C)

From: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate & Ground Water Branch/EFED (H7507C)

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

Attached, please find the EFGWB review of...

Reg./File # : 352-LER

Chemical Name : Carbendazim

Type Product : Fungicide

Product Name : DELSENE

Company Name : E.I. du Pont de Nemours

Purpose : Additional data submitted in response to the 8/8/88 EFGWB review of a Confined Accumulation in Rotational Crops study.

Action Code : 660

EFGWB #(s) : 90-0434

Date Received : 3/8/90

Total Review Time: 2 days

Deferrals to:

___ Ecological Effects Branch

___ Dietary Exposure Branch

___ Non-Dietary Exposure Branch

___ Toxicology Branch I

___ Toxicology Branch II

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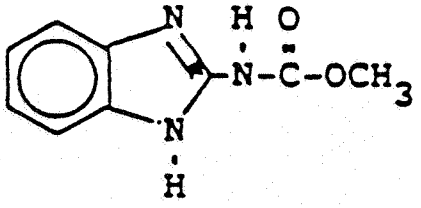
CHEMICAL:

chemical name: Methyl 2-benzimidazole carbamate (MBC)

common name: Carbendazim

structure:



2. TEST MATERIAL:

Not applicable. No studies were submitted.

3. STUDY/ACTION TYPE:

Review additional data submitted in response to the August 8, 1988 EFGWB review of a Confined Accumulation in Rotational Crops study (Rhodes, B.C.; study number AMR-495-86).

4. STUDY IDENTIFICATION:

Letter with additional data attached from Ronald Hamlen of E.I. du Pont to Jane Mitchell (EPA) dated August 9, 1989. Subject: Response to EAB 80753, Review of Confined Crop Rotation Study with Carbendazim (AMR 495-86), as Satisfying Data Requirement 165-1 for Re-registration of Benomyl, RS-119. Received by EFED on March 8, 1990.

5. REVIEWED BY:

Dana Spatz
Chemist, ECRS #2
EFGWB/EFED/OPP

Date: JUN 4 1990

6. APPROVED BY:

Emil Regelman
Supervisory Chemist, ECRS #2
EFGWB/EFED/OPP

Date: JUN 6 1990

7. CONCLUSIONS:

In the August 8, 1988 review of the "Greenhouse Crop Rotation Study with [2-^{14}C]Carbendazim", EFGWB stated that the study was unacceptable for a number of reasons including incomplete soil residue characterization, and failure to identify crop residues. However, EFGWB also concluded that if certain additional data were submitted and found acceptable, then the study

would support a 30-day rotational crop interval at an application rate of 1 lb ai/acre for small grains and root crops. The following specific information was required:

a. Data/calculations for confirming the application rate.

b. Data on how the ppm values were obtained from the LSC quantitative measurements.

c. Detection limits.

E.I. du Pont has submitted the required additional information and this data has been found to be acceptable. The additional information is attached.

Of the crops grown in the 30-day soil aging study (application rate of 1 lb ai/acre); beets, beet foliage, and barley grain all had total ^{14}C-residue concentrations <0.01 ppm while barley straw and cabbage contained total ^{14}C-residues of 0.053 and 0.026 ppm, respectively. The crops grown in the 120-day or 145-day soil aging study (application rate of 3 lb ai/acre); beets, beet foliage, cabbage plants, barley grain, and barley straw, contained total ^{14}C-residues of 0.012, 0.013, 0.053, 0.025, and 0.129 ppm, respectively.

Although residues were detected in all crop samples at each treatment-to-planting interval, the levels found were significantly less than the tolerances set for crops treated with Benomyl (Carbendazim is a hydrolysis product of benomyl which is known to hydrolyze almost totally to carbendazim and other minor degradates shortly after its application). The tolerances established for benomyl include the combined residues of the parent compound and its metabolites containing the benzimidazole moiety. These tolerances would, therefore, include carbendazim and all of its significant metabolites/degradates.

8. RECOMMENDATIONS:

The additional information submitted in response to EFGWB's review of the Confined Accumulation in Rotational Crops study is acceptable. Although there was no identification of accumulated residues, the study is now considered acceptable in fulfilling the Confined Accumulation in Rotational Crops data requirement because of the crop tolerances already established for benomyl. The total accumulated residue levels in the crops tested were significantly below the established crop tolerances for benomyl. These tolerances include the combined residues of the parent compound and its metabolites containing the benzimidazole moiety and would, therefore, include carbendazim and all of its significant metabolites/ degradates. Consequently, EFGWB can concur with the proposed 30-day rotational crop interval at a maximum application rate of 1 lb ai/acre for small grains, root crops, and leafy vegetables.

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STATUS OF DATA REQUIREMENTS FOR REGISTRATION ON WHEAT

SATISFIED

Hydrolysis
Leaching-Adsorption/Desorption
Confined Accumulation in Rotational Crops
Fish Accumulation

NOT SATISFIED

Photodegradation in Water
Photodegradation on Soil
Aerobic Soil Metabolism
Anaerobic Soil Metabolism
Soil Field Dissipation

RESERVED

Long-Term Soil Field Dissipation

9. BACKGROUND:

E.I. du Pont has applied for registration of a new fungicide, Carbendazim, for use on wheat. On December 10, 1987 E.I. du Pont requested that a tolerance for residues of carbendazim be granted as follows:

wheat grain	0.2 ppm
wheat straw	10.0 ppm

According to 40 CFR Part 180 (7-1-89 Edition), no tolerances for residues of carbendazim have yet been established.

Carbendazim is a hydrolysis product of benomyl which is known to hydrolyze almost totally to carbendazim and other minor degradates shortly after its application.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Not applicable. No studies were submitted.

11. COMPLETION OF ONE-LINER:

The data from this Confined Accumulation in Rotational Crops study should be entered into the Carbendazim one-liner summary.

12. CBI APPENDIX:

Not applicable.

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§ 180.294 Benomyl; tolerances for residues.

(a) Tolerances are established for the combined residues of the fungicide benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate) and its metabolites containing the benzimidazole moiety (calculated as benomyl) in or on the following raw agricultural commodities:

Commodities	Parts per million
Almond hulls	1.0
Apples (pre- and post-H)	7.0
Apricots (pre- and post-H)	15.0
Avocados	3.0
Bananas (pre- and post-H) (NMT 0.2 ppm (N) shall be present in the pulp after peel is removed and discarded)	1.0
Barley, grain	0.2
Barley, straw	0.2
Beans	2.0
Bean vine forage	50.0
Beets, sugar, roots	0.2
Beets, sugar, tops	15.0
Blackberries	7.0
Blueberries	7.0
Boysenberries	7.0
Broccoli	0.2
Brussels sprouts	15.0
Cabbage	0.2
Carrots	0.2
Cattle, fat	0.1
Cattle, meat	0.1
Cattle, mbyp	0.1
Cauliflower	0.2
Celery	3.0
Cherries (pre- and post-H)	15.0
Chinese cabbage	10.0
Citrus fruit (pre-and post-H)	10.0
Collards	0.2
Corn, fresh (inc. sweet K+CWHR)	0.2
Corn, sweet, fodder and forage	0.2
Cucumbers	1.0
Currants	7.0
Dandelions	10.0
Dewberries	7.0
Eggplants	0.2
Eggs	0.1
Garlic	0.2
Goats, fat	0.1
Goats, meat	0.1
Goats, mybp	0.1
Grapes	10.0
Hogs, fat	0.1
Hogs, meat	0.1
Hogs, mbyp	0.1
Horses, fat	0.1
Horses, meat	0.1
Horses, mbyp	0.1
Kale	0.2
Kohlrabi	0.2
Loganberries	7.0
Mangoes	3.0
Melons	1.0
Milk	0.1
Mushrooms (pre-and post-H)	10.0
Mustard greens	0.2
Nectarines (pre- and post-H)	15.0
Nuts	0.2 (N)
Oats, grain	0.2
Oats, straw	0.2
Papayas	3.0
Peaches (pre- and post-H)	15.0
Peanuts	0.2
Peanut forage	15.0
Peanut hay	15.0
Peanut hulls	2.0
Pears (pre-and post-H)	7.0
Peppers	0.2
Pineapples (post-H)	35.0
Pistachios	0.2
Plums (including fresh prunes) (pre- and post-H)	15.0
Poultry, fat	0.1
Poultry, liver	0.2
Poultry, meat	0.1
Poultry, mbyp	0.1
Pumpkins	1.0
Raspberries	7.0
Rice	5.0
Rice straw	15.0
Rutabagas	0.2
Rye, grain	0.2
Rye, straw	0.2
Sheep, fat	0.1
Sheep, meat	0.1
Sheep, mbyp	0.1
Soybeans	0.2
Spinach	0.2
Squash, summer	1.0
Squash, winter	1.0
Strawberries	5.0
Sweet potatoes	0.2
Tomatoes	5.0
Turnips, roots	0.2
Wheat, grain	0.2
Wheat, straw	15.0

(b) Tolerances with regional registration, as defined in § 180.1(n), are established for residues of the fungicide benomyl (methyl 1-[butylcarbamoyl]-2-benzimidazolecarbamate) and its metabolites containing the benzimidazole moiety (calculated as benomyl) in or on the raw agricultural commodities.

Commodities	Parts per million
Pistachios	0.2
Turnip greens	6.0
Watercress	10.0

[52 FR 58536, Dec. 23, 1987, as amended at 52 FR 58538, Dec. 23, 2987; 53 FR 9024, Mar. 18, 1988]

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ATTACHMENT I

Response to EPA Review of Data Requirement 165-1:

Greenhouse Crop Rotation Study with [2-^{14}C] Carbendazim

(Du Pont Agricultural Products Department Document No. AMR-495-86)

prepared by

B. C. Rhodes, Study Director

In accord with recommendations made by the reviewer in EAB No. 80753 dated 8/8/88, the following supplemental data, specific to Conclusions d,f,and h, are supplied in anticipation of EAB's concurrence with a 30-day rotational crop interval for small grains and root crops at the proposed maximum application rate of 1 lb a.i./A.

Response to Item d: Calculations confirming application rate

30-day study: 1 lb a.i./A

a. 1 lb a.i./A x 454 g a.i./lb a.i. x 1A/43560 ft^2 x 1.22 ft^2/pot = **0.013 g a.i./pot**

b. 0.051 g a.i./1000 mL test soln x 250 mL test soln/pot = **0.013 g a.i./pot**.

120-day study: 3 lb a.i./A

a. 3 lb a.i./A x 454 g a.i./lb a.i. x 1 A/43560 ft^2 x 1.22 ft^2/pot = **0.038 g a.i./pot**

b. 0.152 g a.i./1000 mL test soln x 250 mL test soln/pot = **0.038 g a.i./pot**.

Response to Item f: Calculations showing how ppm values were derived from LSC data

Example: Determine total ppm ^{14}C-MBC equivalents in final harvest cabbage - 120 day study

a. specific activity - 120-day study:

$$\frac{602.55\ \mu Ci}{(11.7\ mg\ ^{14}C\text{-}MBC + 140.3\ mg\ MBC)} \times \frac{2.22 \times 10^6\ dpm}{\mu Ci} \times \frac{1\ mg}{1.0 \times 10^5\ \mu g} = \frac{8800\ dpm}{\mu g\ MBC}$$

b.

Combustion aliquot #	Aliquot Wt. (g)	Raw dpm	Net dpm	Net dpm/g dry
1	0.163	673	625	3834
2	0.137	573	525	3832
3	0.191	810	762	3990
		Mean Bkg =48		Mean = 3885

c. [Mean dpm/g dry x sample dry wt. (g)]/[sample fresh wt. (g) x spec. act. MBC] = µg MBC/g fresh sample = **ppm MBC**.

(3885 dpm/g dry x 14.22 g dry)/(118 g fresh x 1 µg MBC/8800 dpm) = 0.053 µg MBC/g fresh sample = **0.053 ppm MBC**.

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Response to Item h: Calculation of detection limits

a. LSC of extract from 50-g sample of dried plant material

Given: Mean background = 25 dpm
Lower limit of detection (LLD) = 2 x mean bkg = 50 dpm

Limit calculation:
[LLD (dpm)/specific activity of MBC (dpm/µg MBC)] ÷ dried sample wt. (g)
= µg MBC/g dried sample = **ppm MBC**

30-day study
(50 dpm/2.66 x 10^7 dpm/mg MBC) ÷ 50 g dry
= 3.8 x 10^{-8} mg MBC/g dry
= **0.04 ppb MBC.**

120-day study
(50 dpm/8.79 x 10^6 dpm/mg MBC) ÷ 50 g dry
= 1.14 x 10^{-7} mg MBC/g dry
= **0.11 ppb MBC.**

b. Combustion/LSC of plant tissue residue from extraction of 50-g sample of dried plant material

Given: Mean background = 48 dpm
Lower Limit of detection = 2 x mean bkg = 96 dpm

Limit calculation:
[LLD (dpm)/specific activity of MBC (dpm/µg MBC)] ÷ sample wt. (g)

30-day study
(96 dpm/2.66 x 10^7 dpm/mg MBC) ÷ 50 g dry
=7.23 x 10^{-8} mg MBC/g dry
= **0.07 ppb MBC.**

120-day study
(96 dpm/8.79 x 10^6 dpm/mg MBC) ÷ 50 g dry
= 2.18 x 10^{-7} mg MBC/g dry
= **0.22 ppb MBC.**

c. TLC/Radiometry of extract from 50-g soil sample

Given: smallest nonbackground peak detected = 51.9µV = 136 dpm.

Limit calculation:

[LLD (dpm)/spec. act. (dpm/mg MBC)] ÷ sample size (g)

= mg MBC/g soil = ppm MBC

30-day study

(136 dpm/2.66×10^7 dpm/mg MBC) ÷ 50 g soil

= 1.02×10^{-7} mg MBC/g soil

= **0.10 ppb MBC.**

120-day study

(136 dpm/8.79×10^6 dpm/mg MBC) ÷ 50 g soil

= 3.09×10^{-7} mg MBC/g soil

= **0.31 ppb MBC.**

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TABLE 2

CONCENTRATION OF RADIOACTIVITY
IN MATURE CROPS GROWN IN SOILS TREATED WITH ^{14}C-CARBENDAZIM

Crop Sample	Total Concentration of Radioactivity, ppm*
30-Day Soil Aging	
Beets	
Foliage	0.008
Roots	0.005
Cabbage	0.026
Barley	
Straw	0.053
Grain	0.009
120-Day Soil Aging	
Beets	
Foliage	0.013
Roots	0.012
Cabbage	0.053
145-Day Soil Aging	
Barley	
Straw	0.129
Grain	0.025

* Calculated as ^{14}C-carbendazim equivalents on fresh weight basis, based on combustion/liquid scintillation counting analyses.

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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
BENOMYL
Last Update on March 4, 1992
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer:	Section Head:	Date:

Common Name: BENOMYL
PC Code # : 99101 CAS #: 17804-35-2 Caswell #:

Chem. Name : METHYL-1-(BUTYLCARBAMOYL)-2-BENZIMIDAZOLECARBAMATE

Action Type: Fungicide

Trade Names: BENEX; BENLATE; TERSAN
(Formul'tn): G, 50% WP, FLC, SC/L, OIL DISPERSIBLE
Physical State: COLORLESS CRYSTALS

Use : FRUIT TREES/NUT CROPS/FIELD CROPS/VEGETABLES
Patterns :
(% Usage) :
:

Empirical Form: $C_{14}H_{18}N_4O_3$
Molecular Wgt.: 290.32 Vapor Pressure: 3.70E -8 Torr
Melting Point : DEC 140C °C Boiling Point: N/A °C
Log Kow : 1.38 atpH 5 pKa: @ °C
Henry's : 4.20E -9 Atm. M3/Mol (Measured) 7.07E -9 (calc'd)

Solubility in ...					Comments
Water	2.00E	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	
Water	3.60E	ppm	@25.0	°C	at pH 5
Water	2.90E	ppm	@25.0	°C	at pH 7

Hydrolysis (161-1)
[V] pH 5.0: <2 HOURS
[V] pH 7.0: <2 HOURS
[V] pH 9.0: <2 HOURS
[ ] pH :
[ ] pH :
[ ] pH :

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TABLE 3

TOTAL RADIOACTIVITY IN SOILS AT INDICATED SAMPLING TIME*

Soil	Number of Days Post-Treatment at Sampling	Total Concentration of Radioactivity, ppm
30-Day Soil Aging		
Treatment	0	0.779
Planting	30	0.236
Beet Harvest	122	0.192
Barley Harvest	128	0.059
Cabbage Harvest	135	0.123
120-Day Soil Aging		
Treatment	0	1.779
Planting	120	0.652
Beet Harvest	212	0.361
Cabbage Harvest	225	0.333
145-Day Soil Aging		
Planting	145	0.222
Barley Harvest	266	0.112

* Calculated as ppm ^{14}C-carbendazim equivalents on dry weight basis, based on combustion/liquid scintillation counting analyses.

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Photolysis (161-2, -3, -4)
[V] Water:<4 HOURS EITHER IN SUN OR
[ ] :IN DARKNESS
[ ] :
[ ] :

[V] Soil :<4 DAYS ON SiLm
[ ] Air :

Aerobic Soil Metabolism (162-1)
[S] Benomyl degraded with a calc.t1/2= 19 hours. silt loam soil pH6.5
[ ] MBC(major degradate) degraded with a calc.t1/2= 320 days. 2-AB +
[ ] BUB were 2 other non-volatile degradates.
[ ]
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[V] satisfied with the submission of 162-3
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Aquatic Metabolism (162-3)
[V] (no benomyl was detected due to rapid hydrolysis), carbendazim
[ ] degraded with a calc. half-life of 743 days in a clay loam soil
[ ] treated w/ 1ppm and incubated for 365 days. In sediment extracts
[ ] where most of the radioact. was recovered MBC was 55.6% at 365day
[ ] STB was 7.6% at 365 days. Unextracted radioactivity increased
[ ] from 12% immediately post-treat. to 36.2% at 365 days.
[ ]

Aerobic Aquatic Metabolism (162-4)
[V] Half-life of MBC was 61 days in a clay loam soil treated w/2ppm,
[ ] STB reached a max. of 28.8% then dropped to non-detect. at 14 day
[ ] BUB reached 1-2.3% immed. post-treat. then dropped to non-detect.
[ ] at 7 days. 2-AB was < .083% of recovered radioactivity at all
[ ] sampling intervals.
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
BENOMYL
Last Update on March 4, 1992
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)
[V] Kads FOR SiLm AND SdLm SOILS
[ ] RANGED FROM 6.1 TO 90
[ ]
[ ]
[ ]
[ ]

Soil Rf Factors (163-1)
[V] IN 13" COLUMNS OF SiLm OR
[ ] SdLm, WASHED WITH 20" WATER,
[ ] >85% REMAINED IN UPPER 2".
[ ] DEGRADATES WERE ALSO IMMOBILE
[V] 0.19 IN HAGERSTOWN SiClLm
[ ]

Laboratory Volatility (163-2)
[ ] waived
[ ]

Field Volatility (163-3)
[ ] waived
[ ]

Terrestrial Field Dissipation (164-1)
[S] C14 RESIDUES DISSIPATE SLOWLY WITH 54% OF THE APPLIED
[ ] REMAINING 12 MONTHS IN SOILS CONFINED IN CYLINDERS. AFTER
[ ] 1 MONTH IN SiLm OR FINE SAND, NO PARENT BENOMYL DETECTED.
[S] RESIDUES DISSIP. FROM SiClLm (0-4" DEPTH) WITH T1/2=<3 MOS;
[ ] RESIDUES DETECTED AT 4-8"DEPTH ONLY AT 3 MOS AFTER TREATMENT
[ ]
[ ]
[ ]
[ ]
[ ]

Aquatic Dissipation (164-2)
[V] satisfied by soil column leaching + dissipation study.
[ ] benomyl/carbendazim in the silty clay loam OM 0.9%,pH=7.3 had
[ ] extremely low mobility, applied at 2.2 lbs./ai/A.
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

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Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[V] In 30 day soil aging study (1 lb/ai/A) beets, beet foliage, barly
[ ] grain <0.01ppm,(while barleystraw+cabbage 0.053+0.026 ppm)

Accumulation in Rotational Crops, Field (165-2)
[ ] waived
[ ]

Accumulation in Irrigated Crops (165-3)
[ ] waived
[ ]

Bioaccumulation in Fish (165-4)
[V] sunfish exposed to 2 conc.0.018mg/l+0.17mg/l showed max BCF's of
[ ] 27+23 respectively in wholfis. Pk.vis.460+380 res.low+high conc.

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

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)
[ ]
[ ]
[ ]

Field Runoff (167-1)
[ ]
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[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
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Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

Methyl-2-benzimidazolecarbamate (T1/2 = 3-6 mos anaerobically in SdLm and SiLm; after 6 months, 41-54% of the applied was this compound which is known as MBC or carbendazim).
3-butyl-2,4-dioxo [1,2-a]-S-triazinobenzimidazole (= 90% of the parent compound in alkaline hydrolysis).
2-amino-benzimidazole
Koc = 1900 (U)
MBC=carbendazim
STB=3-butyl-1,3,5-triazolinol[1,2a]-benzimidazole-2,4(1H,3H)dione
BUB=2-(3-butylureido)benzimidazole
2-AB=2-aminobenzimidazole

Comments

MBC residues are relatively immobile in runoff water and leachate from keyport SiLm soil at a 5 degree slope.
MBC and 2-aminobenzimidazole represented 86-90% of extracted C14 after 6 wks aerobic soil incubation.
Summary: Benomyl is degraded in the soil in about 6 weeks under aerobic conditions, but fungicidal residues are fairly persistent in soil with a half-life of >60 days.

Soil Koc = 2100.

References: FARM CHEM. HDBK.
Writer : PJH,KLP