Shaughnessy No.: 106001

Date Out of EFGWB: MAY 4 1989

TO: G. Werdig/B. Briscoe
Product Manager #50
Registration Division (H7505C)

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

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

Attached, please find the EFGWB review of:

Reg./File #(s): 106001

Common Name: Methazole

Chemical Name: 2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione

Type of Product: Herbicide

Product Name: PROBE

Company Name: Sandoz Crop Protection Corporation

Purpose: Review of photodegradation on soil study

Date Received: 1/27/89 Action Code: 495

EFGWB #(s): 90300

Total Reviewing Time: 2.0

Deferrals to: _____ Ecological Effects Branch/EFED

_____ Science Integration & Policy/EFED

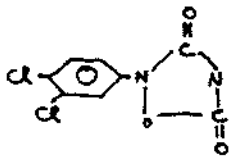
_____ Non-Dietary Exposure Branch/HED

_____ Dietary Exposure Branch/HED

_____ Toxicology Branch I/HED

_____ Toxicology Branch II/HED

1. CHEMICAL:
Common Name: Methazole
Chemical Name: 2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione
Type of Product: Herbicide
Trade Name: PROBE

Chemical Structure: 

2. TEST MATERIAL:
^{14}C labeled methazole (No label position or purity are given in the actual core of the study report. However, in the company's protocol for conducting the study provided as Appendix I, the test chemical is listed as phenyl labeled ^{14}C methazole of radiochemical purity > 98% and specific activity of 11.3 mCi/mmol.)

3. STUDY/ACTION TYPE:
Review of photodegradation on soil study.

4. STUDY IDENTIFICATION:
MRID #40943801
Yu CC, Ekdawi M, and Fostiak W. 1988. Photodegradation study of methazole on soil. Completed on December 16, 1988. Performed and submitted by Sandoz Crop Protection Corporation. Laboratory Project No. 480265.

5. REVIEWED BY:
Henry Nelson, Ph.D., Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Groundwater Branch/EFED
H Nelson
Date: 5/3/89

6. APPROVED BY:
Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Groundwater Branch/EFED
Date: MAY 4 1989

7. CONCLUSIONS:
The study is not acceptable in support of the photodegradation on soil (161-3) data requirement because the light source used does not emit radiation with wavelengths between 290 nm (the approximate minimum wavelength of solar irradiation at the earth's surface) and approximately 450 nm. In addition, some of the volatiles may have possibly been inadequately trapped.

8. RECOMMENDATIONS:
Please inform the registrant of the above conclusion and send them a copy of the review. The registrant must conduct a new photodegradation on soil study using natural sunlight or a different artificial light source (Of the artificial light sources reviewed by EFGWB to date, the irradiation output of the filtered (to remove wavelengths < 290 nm) xenon lamp appears to

be the closest to that of natural sunlight at the earth's surface). Ask the registrant to submit a protocol for approval prior to starting a new photodegradation on soil study.

9. BACKGROUND:

Sandoz Crop Corporation was issued a comprehensive data call-in for methazole on September 29, 1987. Methazole is the active ingredient in PROBE which is a wettable powder postemergence herbicide applied in aqueous solution to cotton to control weeds.

Based upon the terrestrial food crop use of methazole, the following environmental fate data requirements are applicable:

(1) Hydrolysis (161-1)
(2) Photodegradation in Water (161-2)
(3) Photodegradation on Soil (161-3)
(4) Aerobic Soil Metabolism (162-1)
(5) Anaerobic Soil Metabolism (162-2)
(6) Leaching and Adsorption/Desorption (163-1)
(7) Laboratory Volatility (163-2)
(8) Terrestrial Field Dissipation (164-1)
(9) Confined Accumulation in Rotational Crops (165-1)
(10) Laboratory Accumulation in Fish (165-4)

Based upon a review of EFGWB files, none of the above listed environmental fate data requirements have been satisfied. In addition to the data requirements listed above, the following environmental fate data requirements are being held in reserve:

(1) Photodegradation in Air (161-4) is held in reserve pending the results of the lab volatility study.

(2) Field Volatility (163-3) is held in reserve pending the results of the lab volatility study.

(3) Long Term Terrestrial Field Dissipation (164-5) is held in reserve pending the results of the terrestrial field dissipation study.

(4) Field Accumulation in Rotational Crops (165-2) is held in reserve pending the results of the confined accumulation in rotational crops study.

10. DISCUSSION:
See attached data evaluation record

11. COMPLETION OF ONE-LINER:
Not applicable

12. CBI INDEX:
Not applicable.

DATA EVALUATION RECORD

SHAUGHNESSY No. 106001
COMMON NAME: Methazole
CHEMICAL NAME: 2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione
FORMULATION: Active ingredient
DATA REQUIREMENT: Photodegradation on Soil (161-3)

MRID #40943800-1
Yu CC, Ekdawi M, and Fostiak W. 1988. Photodegradation study of methazole on soil. Completed on December 16, 1988. Performed and submitted by Sandoz Crop Protection Corporation. Laboratory Project No. 480265.

REVIEWED BY: Henry Nelson, Ph.D. Date: 5/3/89
TITLE: Chemist
ORGANIZATION: OPP/EPA
TELEPHONE: 557-2505

SIGNATURE: H' Nelson

CONCLUSIONS:

The study is not acceptable in support of the photodegradation on soil (161-3) data requirement because the light source used does not emit radiation with wavelengths between 290 nm (the approximate minimum wavelength of solar irradiation at the earth's surface) and approximately 450 nm. In addition, volatiles may have been inadequately trapped.

MATERIALS AND METHODS:

(1) Test Chemical:
^{14}C labeled methazole (No label position or purity are given in the actual core of the study report. However, in the company's protocol for conducting the study provided as Appendix I, the test chemical is listed as phenyl labeled ^{14}C methazole of radiochemical purity > 98% and specific activity of 11.3 mCi/mmol.)

(2) Test Soil:
A Greenville, Mississippi silt loam soil (pH 6.8, organic matter 0.52%)

(3) Analytical Standards:
methazole
3-(3,4-dichlorophenyl)-3-hydroxy-1-methylurea (DCPMUOH)
3-(3,4-dichlorophenyl)-1-methylurea (DCPMU)
3-(3,4-dichlorophenyl)-urea (DCPU)
3,4-dichloroaniline (DCA)

(4) Photolysis Cell/Exposure Chamber/Light Source:
The test soil was placed in a 30 cm diameter cylindrical glass photolysis cell possessing an outside jacket for the circulation of water bath cooling water. The photolysis cell was placed in a model M31-15 Environmental Growth Chamber equipped with two 400 W Optimarc high intensity super metal halide discharge lamps. The irradiation spectrum of one lamp is compared to the solar irradiation spectrum (white line) in Appendix 3. A vaccuum pump was used to draw air through the following in series: a wash bottle containing reagent grade water, the photolysis cell, a glasswool filter, a silica gel trap, an ethylene glycol trap, and a NaOH trap.

(5) Test Conditions:
The test soil with an initial mean methazole concentration of 562 ppm was maintained at 25-28°C and exposed to continuous irradiation from the artificial light source for a period of 30 days. The temperature for the dark control was not provided, but was presumably that of the water bath (25°C). Soil moisture was maintained by continuously drawing water vapor saturated air over the soil.

(6) Sampling:
Soil samples were collected from the irradiated soil at time 0 and after 0.42, 1.0, 2.0, 4.0, 10, 18, and 30 days irradiation. Only one soil sample was apparently collected from the dark control, presumably after 30 days incubation.

(7) Extraction of Soil Samples and Analysis of Extracts
Methazole and its degradates were extracted twice from 4 g aliquots of each soil sample by 25 mL of methanol. TLC was used to separate methazole and its degradates in the methanol extracts and to tentatively identify and quantify them. Normal and reverse phase HPLC were used to confirm the identities of methazole and its degradates. Some of the remaining methazole/degradates in soil were extracted twice by 25 mL of 0.5N NaOH. The pH of the NaOH extracts was lowered to 1 with concentrated HCl. The resulting precipitate was designated as the "humic acid fraction" and re-dissolved in 0.1 N NaOH for analysis for total radioactivity. The supernatant was designated as the "fulvic acid fraction" and also analyzed for total radioactivity.

(8) Analysis for Total Radioactivity
Liquid samples (methanol extracts, NaOH extracts, NaOH trapping solutions, and ethylene glycol trapping solutions) were analyzed for total radioactivity by liquid scintillation counting (LSC). Solid samples (soil, glass wool filter, and silica gel) were analyzed for total radioactivity by combustion, collection of the resulting $^{14}CO_2$ in NaOH trapping solutions, and the analysis of the trapping solutions for radioactivity by LSC.

RESULTS:

The results of the study are provided in Table II. Although no 0 time sample was collected from the dark control, a comparison of the 30 day dark control to the 0 time irradiated soil sample (which should be comparable to a 0 time dark control sample) indicates that methazole did not undergo any significant degradation in the dark control over the 30 day period. However, in the irradiated soil, methazole appears to have undergone slow photodegradation declining from 92.7% of applied (89.2% of recovered) at time 0 to 69.6% of applied (75.9% of recovered) after 30 days continuous irradiation with artificial light.

Based upon an assumed first order decline of methazole in the irradiated soil, the study author computed a photodegradative half-life of 75.8 $\pm$ 16.7 days for methazole applied at 562 ppm to the silt loam test soil and exposed to artificial light with an average intensity (over all irradiation wavelengths) of 14,700 uW/cm^2 (Table III and Figure 15). According to the study author, that corresponds to a half-life of 139.5 days under continuous solar irradiation at noon in Cincinnati, Ohio (the computed half-life under artificial irradiation was multiplied by the ratio of the artificial light mean intensity to that of solar irradiation at noon in Cincinnati; the season is presumably summer, but is not specified). No major (eg., representing $\geq$ 10% of applied radioactivity) photodegradates were identified.

DISCUSSION:

(1) The study is not acceptable in support of the photodegradation on soil (161-3) data requirement because the light source used does not emit radiation with wavelengths between 290 nm (the approximate minimum wavelength of solar irradiation at the earth's surface) and approximately 450 nm. Solar irradiation with wavelengths between 290 and 400 nm is generally primarily responsible for the photodegradation of most chemicals because it is the most energetic part of the solar irradiation spectrum at the earth's surface. Therefore, the photodegradation of methazole under sunlight may be much more rapid and may result in additional photoproducts than indicated from the results of the photodegradation of methazole by the artificial light source used.

(2) The organic content of the test soil (0.52% organic matter) is substantially lower than for many soils. Therefore, the extent of any indirect photodegradation (via energy transfer from soil organics absorbing solar energy) may have been less than in soils with more typical organic contents.

(3) The study author identifies the following 3 minor "photoproducts": photoproduct C (structurally identified but not named), DCPMU, and DCPU (Figure 16). However, a comparison of the dark control to the irradiated soil after various irradiation

times (Table 1I) indicates that photoproduct C and DCPMU may not be photoproducts since they are present in the dark control at at least 50% of the levels in irradiated soil at 0 time and at all irradiation times. The presence of photoproduct C and DCPMU in irradiated soil at time 0 indicates that they may have been contaminants of the applied methazole. DCPU was not detected in the dark control or in irradiated soil samples at days 0, 1, or 2. However, it was detected in irradiated soil samples after 4 days exposure and there after. Therefore, DCPU may be formed from the photodegradation of DCPMU as shown in Figure 16.

(4) The total recovered radioactivity for the irradiated soil declines fairly uniformly from 103.9% of applied at time 0 to 91.7% of applied after 30 days irradiation (compared to 112% of applied in the dark control). That suggests that volatile photoproducts may have formed which were not adequately trapped.

Table II. Material balance and product distribution for methazole soil photolysis.

Fraction & Designation	% of applied ^{14}C at Indicated Sample Periods (Days)								Dark Control
	0	0.42	1.0	2.0	4.0	10.0	18.0	30.0	
A. Organic Extractables									
Spot 1	0.00	0.00	0.00	0.28	0.59	0.00	0.27	0.00	0.00
Spot 2 Methazole	92.64	94.04	85.45	88.42	79.07	82.19	72.73	69.64	99.62
Spot 3 Photoprod. C	0.66	0.40	1.55	0.86	1.43	1.25	1.30	1.46	0.87
Spot 3-A	0.64	0.49	1.06	0.47	0.80	0.48	0.49	0.56	0.82
Spot 4	0.82	0.28	1.26	0.52	0.78	0.54	0.48	0.58	0.85
Spot 5	0.47	0.30	0.71	0.29	0.59	0.29	0.10	0.57	0.00
Spot 5-C	0.00	0.00	0.59	0.21	0.46	0.24	0.15	0.00	0.00
Spot 5-D	0.47	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.92
Spot 6 DCPMU	2.54	1.54	4.35	2.17	4.47	3.91	4.12	5.09	3.48
Spot 7 DCPU	0.00	0.00	0.00	0.00	0.49	0.49	0.42	0.98	0.00
Spot 8	0.07	0.44	0.82	0.50	1.10	0.79	0.99	1.60	1.04
Sub total	98.93	97.71	96.10	93.71	89.79	90.18	81.05	80.48	107.59
B. Humic acid	3.28	3.21	3.07	3.22	3.39	4.52	3.90	3.81	2.95
C. Fulvic acid	0.24	0.37	0.32	0.42	0.36	0.60	0.56	0.34	0.38
D. Residual solids	1.45	1.37	1.88	1.86	1.27	1.85	2.28	2.72	2.19
E. NaOH Trap (CO_2)	0.00	0.00	0.00	0.03	0.09	0.37	0.81	1.23	0.00
F. Ethylene Glycol Trap	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.09	0.00
G. Glasswool & silica gel Traps	0.00	0.00	0.00	0.03	0.26	0.30	0.34	0.44	0.00
H. Acetone & methanol Container wash								2.53	
Total Recovery	103.90	102.66	101.37	99.27	95.17	97.83	88.98	91.66	110.50

Table III. Photolysis Rate and Half Life of Methazoleon soil[1/]

Photolysis Rate (± S.E.)	Half-Life (± S.E.)	Correlation Coefficient
0.0091 ± 0.0018 day	75.8 ± 16.7 days	0.90

1/ Under simulated sunlight at the intensity of 14,700 $\mu W/cm^2$.

Fig. 15. PLOT OF METHAZOLE PHOTOLYSIS ON SOIL

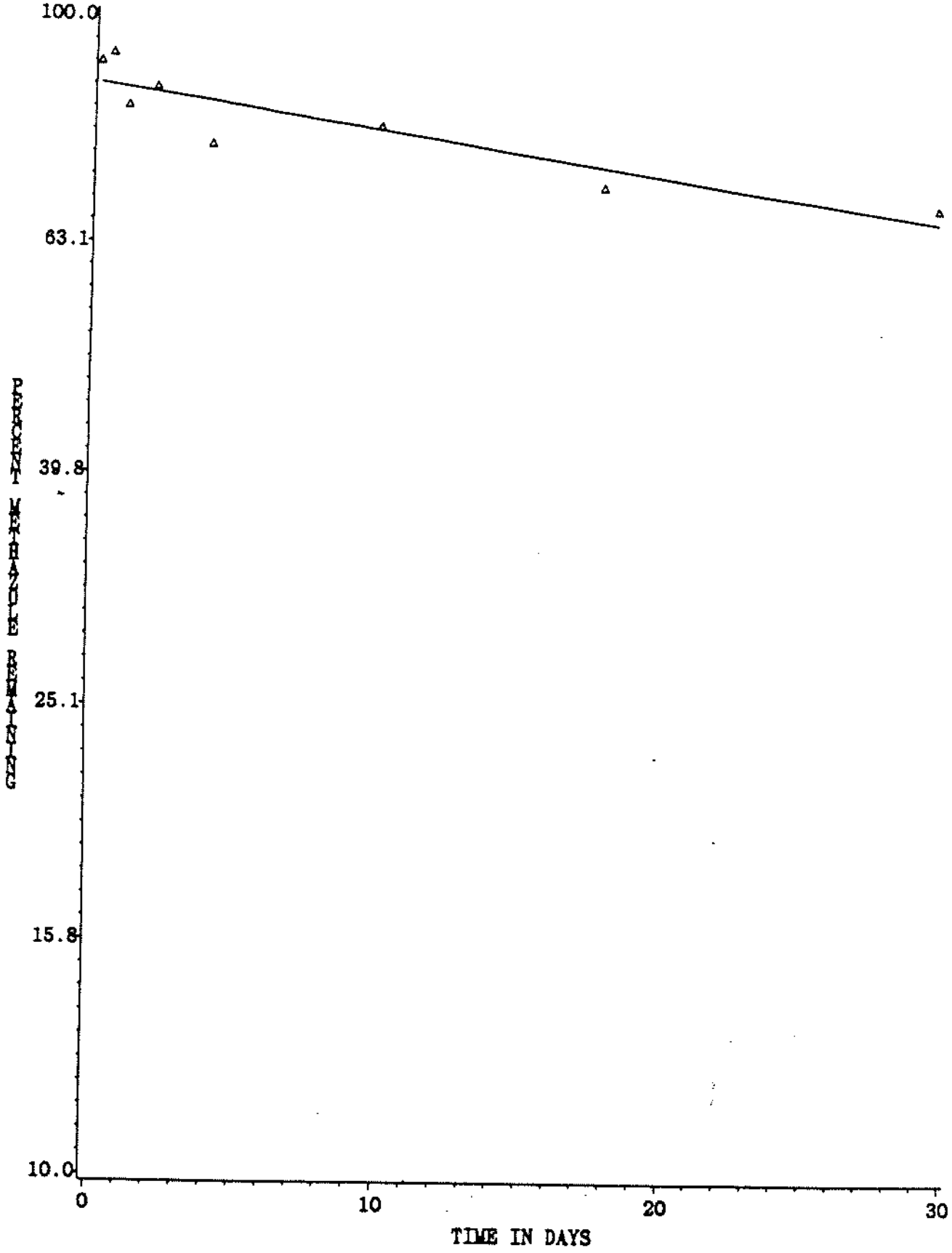


Fig. 16. Proposed photodegradation pathways for methazole on soil.