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From: Samuel M. Creeger, Chief
Environmental Chemistry Review Section 1
Hazard Evaluation Division TS-769C

Attached, please find the EAB review of:

Reg./File No.: 3125-283

Chemical: Fenamiphos

Type Product: Nematicide

Product Name: Nemacur

Company Name: Mobay

Submission Purpose: response to data gap -- photolysis

ZBB Code: other

Date In: 12/14/83

Date Completed: 2/28/84

Deferrals To:

________ Ecological Effects Branch

________ Residue Chemistry Branch

________ Toxicology Branch

Action Code: 400

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TAIS (Level II)	Days
63	3.0

16 pages

1.0 INTRODUCTION

Mobay Chemical Corporation has submitted a new photolysis study for fenamiphos (ethyl 3-methyl-4-(methylthio) phenyl-(1-methylethyl) phosphoramidate) in response to the EAB review of 9/18/84 which noted the photolysis data gap.

2.0 STRUCTURE AND DIRECTIONS FOR USE

See previous reviews for structure.

There is no use pattern for this submission.

3.0 DISCUSSION OF DATA

3.1 Merry-Go-Round Reactor (MGRR) for Photodecomposition Studies. R.A. Dime. November 15, 1983. Notebook Reference: 82-R-202. Acc. No. 251891.

This report describes a merry-go-round photoreactor for use in photodecomposition studies in solution or coated onto the the surface of soil. A 450 watt medium pressure mercury arc lamp in a borosilicate glass immersion well (to remove wavelengths of light below 290 nm) is placed in the center of the apparatus and cooled with cold water from a constant-temperature circulating water bath. Borosilicate tubes containing solutions, or microscope slides coated with soil, are secured to a cylinder 12 cm from the light source. Light intensity in the 300-400 nm range is measured with a Black-Ray Ultraviolet Meter by placing the photocell within the maximum output of the lamp. The cylinder is rotated around the light source at 17 rpm on a turntable. A cardboard shield is placed in front of the unit to minimize exposure to high intensity light during sampling. Table I on page 1A and Figure 1 on page 1B show the energy and wavelength distributions of the mercury arc lamp and Figure 2 on page 1C shows the apparatus.

3.2 Photodecomposition of NEMACUR in Aqueous Solution and on Soil. R.A. Dime, C.A. Leslie, and R.J. Puhl. November 3, 1983. Notebook Reference: 82-R-202, 82-R-240. Acc. No. 251891.

Procedure:

<u>Aqueous Photolysis</u>

A 12 ppm solution of NEMACUR-ring-1-^{14}C was prepared in pH 7.0 buffer. Aliquots placed in borosilicate vials and sealed with parafilm. Samples were placed in the Merry-Go-Round Reactor described in 3.1 above and the intensity of the light measured (average intensity ca. 5200 $\mu W/cm^2$). The temperature in the vicinity of the samples was 27-28^{o}C. Duplicate samples were taken for analysis at 0, 1, 2, 4, 6, 12, and 24 hours of constant irradiation. Dark controls were taken for analysis at the same time.

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Pages 3 through 5 are not included. The pages include data submitted by Mobay Corporation and are stamped confidential.

Aliquots were extracted with chloroform twice and the organic extracts combined. Triplicate samples of both phases were taken for LSC. Aliquots were also taken for TLC analysis on silica gel. The organic extracts were developed in diethyl ether/acetone (1/1) and diethyl ether. Aqueous extracts were developed in acetonitrile/water/acetic acid (90/8/2), chloroform/methanol (3/1) and dichloromethane/methanol/ammonium hydroxide (70/25/1). Samples were applied and developed in the dark to minimize the oxidation of NEMACUR to the sulfoxide. Radioactive zones were detected by autoradiography.

Non-labeled standards were developed along with the radioactive samples and visualized under uv light. Polar products were isolated by evaporating the aqueous samples to dryness in vacuo and dissolving the residue in methanol. This solution was applied to a TLC plate and developed in chloroform/methanol (3/1). The ^{14}C-zones were scraped and eluted with methanol.

Soil Photolysis

A sandy loam soil (74% sand, 14% silt, 13% clay, 2.8% O.M., pH 6.6, CEC = 12.6 meq/100 gms) was sieved on a 420 μ sieve and slurried with water. Microscope slides were dipped in the slurry, dried in an oven at 100°C and scraped so that a 40 X 25 mm section of soil (approximately 0.5 gm) remained on the plate. A 0.5 ug/ul standard solution of NEMACUR-^{14}C in acetonitrile was prepared and 10 ug were applied to the soil. Solvent was allowed to evaporate prior to placing the slide into the photoreactor.

Soil was scraped from the plate and extracted twice with an acetone/water (10/1, v/v) solution. The extracts were combined and analyzed by LSC in triplicate. TLC analyses were performed as in the aqueous study.

Results:

The recovery and distribution of radioactivity in the photolysis studies are shown in Tables III-VIII on pages 2A-2F. The disappearance of ^{14}C-fenamiphos during the studies is shown graphically in Figures 4 and 6 on pages 2G and 2H. A proposed aqueous photodegradation pathway is shown in figure 5 on page 2I.

Under the conditions of this study the aqueous photolytic half-life of fenamiphos was calculated to be 3.6 hr with a first order rate constant of 0.19 hr^{-1}. Assuming the rate of reaction is directly proportional to the intensity of light, the half-life of fenamiphos on a July day in Kansas City, Mo. would be 6.8 hr since the intensity of light is ca. 2745 $\mu W/cm^3$. In the absence of light, fenamiphos was found to be stable.

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The major degradation product was fenamiphos sulfoxide which comprised 17.3% of the radioactivity at 24 hr. Other components comprised less than 5% of the radioactivity. These other components were determined to be fenamiphos phenol sulfonic acid, fenaimphos sulfonic acid and fenamiphos phenol sulfoxide.

The half-life of the sulfoxide could not be determined from this study. In a previous study, however, linear regression analysis of the fenamiphos sulfoxide indicated a half-life of 188 days at a lower temperature (19^{o}C) and intensity (1020 uW/cm^{3}).

The soil photolytic half-life of femamiphos was calculated to be 1.6 hr with a first order rate constant of 0.42 hr^{-1}. This first order condition was true through 2 half-lives, however, the semilog plot of concentration vs time then deviates from a straight line and the rate of degradation slows. Fenamiphos is stable in soil under similar conditions in the dark.

Fenamiphos was rapidly oxidized to the sulfoxide which was slowly oxidized to the sulfone. No other major degradation products were detected. The half-life for the sulfoxide was not calculated in soil.

Conclusions:

Fenamiphos is rapidly photodegraded in both soil and water. The major degradate is fenamiphos sulfoxide. However, the spectrum of the radiation (as measured thru the borosilicate glass water jacket) does not simulate natural sunlight. Presence of other wavelengths could cause formation of different photolysis products.

4.0 CONCLUSIONS/RECOMMENDATIONS

The fenamiphos photolysis requirement for both water and soil is not satisfied by the submitted data. We cannot determine if other photoproducts would be formed if the full spectrum of wavelengths for sunlight was used for irradiation. However, if the company can show from the previous photolysis study* that other degradates are not formed when fenamiphos is irradiated with the full spectrum of wavelengths in soil and water, then we could conclude that the photolysis data requirement had been met.

* previous photolyis study submitted in 1976 and initially reviewed on 12/16/76.

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February 28, 1984
Review Section No. 1
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