

RH-3866

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

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**Submitted to:** Environmental Protection Agency Arlington, VA 22202

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# RH-3866

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## INTRODUCTION

The following is a reassessment of the environmental fate and exposure data submitted by Rohm and Haas in support of the proposed EUP use of RH-3866 40% WP (Systhane) as a fungicide on apples, grapes, and turf grass. The registrant has withdrawn the use on wheat and the 2 lb/gal EC formulation. This reassessment is based on two additional studies (Study 1 and 2), and on additional data and comments submitted by Rohm and Haas (Accession No. 073601 and 256773) in response to the initial review of RH-3866 data (Dynamac Corp., March 19, 1985). The initial review contains a complete description of the procedures and results from each study and that information is not fully repeated here. The effect of this recent information on the satisfaction of registration requirements is indicated in the recommendations section.

#### STUDY 1

Ackermann, I.B. Dec., 1984. Aqueous photolysis of RH-3866. Technical Report No. 310-84-33. Rohm and Haas Company, Philadelphia, Pennsylvania. Acc. No. 256773. Reference 3.

## Introduction

This study investigates the rate of photodegradation of RH-3866 in natural pond water.

# Procedure

Samples (400 ml) of pre-filtered pond water (pH 7.72, Horsham, Pennsylvania) were treated with triazole-ring-labeled [ $^{14}$ C]RH-3866 or chlorophenyl-ring-labeled [ $^{14}$ C]RH-3866 (specific activity 10.98 mCi/g and 10.28 mCi/g, respectively; radiochemical purity >99%) at ~8 ppm. A third solution was prepared by treating a 400-ml sample of milli-Q-water (deionized) with chlorophenyl-labeled [ $^{14}$ C]RH-3866 at ~8 ppm. The pond water samples were placed in a photoreactor equipped with chromosorb and CO2 traps, and were irradiated continuously with a fluorescent sunlamp (Westinghouse FS20 W SunLamp, intensity 2.8 W/m², wavelength distribution between 250 and 500 nm). The deionized water sample was maintained in darkness. Aliquots (10 ml) of the test and trapping solutions were removed for analysis at intervals from 0 to 384 hours of irradiation.

# Methodology

Radioactivity in a portion of each test solution and trapping solution was quantified directly by LSC. Separate portions of the test solutions were eluted through a Sep-Pak cartridge with methanol and deionized water, and the water eluate was assayed for <sup>14</sup>C activity by LSC. The methanol was evaporated, and the residue redissolved in methanol for TLC analysis. Silica gel TLC plates were developed in ethyl acetate: isopropanol:water (65:25:10) or butanol:water: acetic acid (65:25:10). Radioactive zones, located by autoradiography, were scraped from the plates and quantified by LSC.

## Results

RH-3866 degraded in irradiated pond water with half-lives of 485.2 hours (chlorophenyl-labeled,  $r^2$  = 0.97) and 253.5 hours (triazole-labeled,  $r^2$  = 0.99), based on first-order kinetics (Table 1). The half-life for RH-3866 in deionized water maintained in darkness was 3229.5 hours ( $r^2$  = 0.33). Radioactivity evolved as CO<sub>2</sub> and volatiles was <2% of the applied at any sampling interval for the triazole-labeled [ $^{14}$ C]RH-3866, and increased to a maximum of 17% of the applied for the chlorophenyl-labeled compound at 384 hours of irradiation (Table 2). TLC characterization data are shown in Tables 3 and 4. Final photoproducts were free triazole, CO<sub>2</sub>, and minor amounts of volatile compounds.

Table 1. Concentrations of RH-3866 (% of applied) in methanol eluate.

Sampling interval (hours)	Chlorophenyl- labeled (dark) <sup>a</sup>	Chlorophenyl- labeled (light) <sup>b</sup>	Triazole- labeled (light) <sup>b</sup>	
0		99	98	
2	81	97	98	
2 6 9.5	82	97	98	
9.5		<b>9</b> 8	98	
24	85	94	95	
48	82	93 .	90	
72	87	90	85	
	89	87	74	
96	94	74	62	
168	83	67	55	
216	88	65	52	
264	86	61	38	
336 384	93	60	36	

a Deionized water.

Table 2. Distribution of radioactivity (% of applied) in pond water samples during exposure to artificial sunlight.

		Triazole-la	beled	<u> </u>	Chlorophenyl-labeled					
Sampling interval (hours)	Methanol eluate	Water eluate	co <sub>2</sub>	Volatiles	Methanol eluate	Water eluate	co <sub>2</sub>	Volatiles		
0	100				100	***				
9	100				100					
, <u>C</u>	100				100					
6 9 <b>.</b> 5	100				100					
	99	1			99	1				
24	97	1			99	ī		-,-		
48		,2			98	2				
72	95	10		1	96	3		1		
96	89	10	1	1	92	4	2	2		
168	78	20	1	ń	85	Ġ	5	4		
216	73	26	1		82	7	7	Á		
264	69	29	1	1		,	á	6		
336	57	41	1		76	10	11	6		
384	54	43	2		73	10	.11	,		

b Pond water.

Table 3. Distribution of radioactivity (% of recovered) on TLC plates (triazole-labeled  $[1^4\mathrm{C}]\mathrm{RH}$ -3866).

TLC	Sampling interval (hours)													
zone	0	2	6	9.5	24	48	72	. 96 .	168	216	264	336	384	
Origin	0	0	0	0	0	0	0	2	2	4	4	5	6	
0.5-5.0 cm	.0	0	0	0	1	2	2	4	7	7.	7	9	11	
5.0-11.3 cm	2	2	,2	2	3	5	8	12	14	15	15	20	19	
11.3-12.5 cm (RH-3866)	<b>9</b> 8	98	98	98	96	93	89	82	77	74	74	66	64	

Table 4. Distribution of radioactivity (% of recovered) on TLC plates (chlorophenyl-labeled  $[^{14}\text{C}]\text{RH-3866}$ ).

TLC	Sampling interval (hours)												
zone	0 2	2	6	9.5	24	48	72	96	168	216	264	336	384
Origin	0	0	0	0	0	1	1	1	. 2	2	2	2	2
0.5-5.0 cm	0	0	,0	0	1	1	1	2	6	7	8	9	9
5.0-11.3 cm	2	3	3	3	.4	4	6	7	14	18	19	20	20
11.3-12.5 cm (RH-3866)	98	97	97	97	95	94	92	90	78	72	71	<b>6</b> 8	68

## Conclusions

This study is scientifically invalid because an inappropriate test solution was used (distilled or deionized water is required), and it could not be determined whether any of the test solutions were sterile. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because wavelengths <290 nm were not filtered out, the incubation temperature was not reported, and degradates separated during TLC analysis were not identified.

#### STUDY 2

Deakyne, R.O. and C.K. Brackett. Nov., 1984. Analytical report on the decline of RH-3866 residues in soil. Rohm and Haas Company, Philadelphia, Pennsylvania. Acc. No. 256773. Reference 7.

# Introduction

This study describes the dissipation of RH-3866 from field plots located in Pennsylvania and Mississippi.

# Procedure

RH-3866 (Systhane, 2 lb/gal EC) was applied twice to field plots in Cleveland, Mississippi (loam soil) and Newtown, Pennsylvania (silt loam soil) at 0.25 lb ai/A. Both field plots were planted (crop unspecified) in October, 1983. The Mississippi field plot was treated with RH-3866 on March 9 and April 12, 1984; the Pennsylvania plot was treated for the second time on May 18, 1984 (first application date unspecified). Soil samples (0- to 3-, 3- to 6-, and 6- to 12-inch depths) were taken from treated and control plots at intervals up to 160 days after the second application.

# Methodology

Soil samples were analyzed for the parent compound according to method TR-31084-13 (method not available for review). Recovery of RH-3866 from spiked soil samples averaged  $105\pm7.4\%$  (Mississippi study) and  $99.9\pm7.3\%$  (Pennsylvania study). The detection limit was 0.005 ppm.

### Results

RH-3866 dissipated with a half-life of  $\sim$ 62 days from the 0- to 3-inch depth of the Mississippi field plot (calculated by reviewer assuming first-order kinetics,  $r^2=1.00$ ), and a half-life of  $\sim$ 45 days from the Pennsylvania field plot ( $r^2=0.79$ ). Movement of RH-3866 into lower soil depths was minimal (Tables 5 and 6). No RH-3866 was detected (<0.005 ppm) in soil samples from control plots. Although the regression coefficient indicated perfect correlation, there were only three data points. If more samples had been taken the correlation would have been much lower.

Table 5. RH-3866 concentrations (ppm) in loam soil (Cleveland, MS) treated twice with RH-3866 at 0.25 lb ai/A.

Sampling interval (days)	Sampling depth (inches)	מון מסככם
(uays)	(mcnes)	RH-3866 <sup>a</sup>
0p	0-3	0.041
0c	0-3	0.110
	3-6 6-12	0.014 0.007
47	0-3	0.088
	3-6 6-12	0.016 0.002
160	0-3	0.025
	3 <b>-</b> 6 6 <b>-</b> 12	0.003 NDd

a Average of 3-4 replicate samples.

 $<sup>^{\</sup>rm b}$  Immediately after the first treatment (3/29/84).

 $<sup>^{\</sup>rm C}$  Immediately after the second treatment (4/12/84).

 $<sup>^{</sup>m d}$  Not detected in any sample; detection limit is 0.005 ppm.

Table 6. RH-3866 concentrations (ppm) in silt loam soil (Newtown, PA) treated twice with RH-3866 at 0.25 lb ai/A.

Sampling interval (days)	Sampling depth (inches)	RH-3866 <sup>a</sup>
Ор	0-3 3-6 6-12	0.891 NDC 0.002
24	0-3 3-6 6-12	0.126 0.010 0.013
49	0-3 3-6 6-12	0.033 ND ND
80	0-3 3-6 6-12	0.032 0.013 0.004
115	0-3 3-6 6-12	0.021 0.008 0.003
132	0-3 3-6 6-12	0.018 0.003 ND

a Average of 2-4 replicate samples.

 $<sup>^{\</sup>rm b}$  Immediately after the second treatment (5/18/84). Date of first treatment not reported.

 $<sup>^{\</sup>rm c}$  Not detected in any sample; detection limit is 0.005 ppm.

## Conclusions

RH-3866 (2 lb/gal EC) dissipated from field plots of loam (Mississippi) and silt loam (Pennsylvania) soils with half-lives of ~62 and 45 days, respectively. This study provides information on the dissipation of the parent compound only; degradates were not identified or quantified. In addition, the analytical method was referenced but was not available for review. Final conclusions regarding this study are tentative pending receipt of the method.

Numerous additional deficiencies were noted. Soil characteristics (i.e., textural analyses, pH, organic matter content, and CEC) were not provided. Field test data, including rainfall and irrigation amounts, depth to water table, slope and size of test plot, and soil and air temperatures, were not reported. The date of the first application of RH-3866 to the Pennsylvania test plot was not provided. In addition, no explanation was provided for the difference in day-0 concentrations (following the second application) for the two test plots (0.110 ppm for Mississippi vs. 0.891 ppm for Pennsylvania).

## Response to Additional Data and Comments

In response to comments made in a review of environmental data for RH-3866 (Dynamac Corp., March 19, 1985) the registrant raised several points for clarification by the reviewer. Questions will be addressed in the same sequence as set forth in the registrant's response of 5/15/85.

1. Registrant: EPA states that further information on the mobility of soil metabolites will be required for full registration.

What metabolites are they referring to?

Reviewer: Mobility data are required for the parent compound and

for aged residues of the test substance (parent plus metabolites). For full registration, a study is needed providing information on the mobility of the test substance and its metabolites, after being aged in a sandy loam soil under aerobic conditions for 30 days or one

half-life (whichever is shorter).

2. Registrant: In the aged leach study, exactly where are the "apparent discrepancies" the reviewer cites in data between tables in the text and appendix and also in the body of the text?

Reviewer: Raw data presented in the appendix showed different

recovery values from table summaries. An explanation for this apparent discrepancy is discussed in item No. 8

below.

3. Registrant: Will the adsorption/desorption study submitted fulfill the requirement for parent mobility studies?

Reviewer: Not for full registration. Adsorption of RH-3866 by the soils tested (Study 4) appeared to be independent of organic matter content and Freundlich K values were questionable.

4. Registrant: Temperatures are needed for the hydrolysis, aerobic soil metabolism, and anaerobic soil metabolism studies. All three were conducted at ambient temperature.

Reviewer: Hydrolysis reaction temperatures must be  $25 \pm 1^{\circ}\text{C}$  for the results to be valid. Aerobic and anaerobic soils must be maintained at a constant temperature between 18 and  $30^{\circ}\text{C}$  during aging with the test compound to yield reproducible results. "Ambient" temperature is too vague.

5. Registrant: An explanation was offered for the discrepancy between the two triazole label leaching columns based on "denser soil packing" leading to water remaining at the top of the column and consequently more <sup>14</sup>C in the upper 10 cm, and less in the leachate.

Reviewer: The registrant's comments appear valid.

6. Registrant: The mobility of RH-3866 has been adequately determined from results of the three other soil columns.

Reviewer: Reviewer disagrees because of other discrepancies mentioned in Study 4 such as questionable K values. In addition, only a single soil (four are required) was tested.

7. Registrant: Two weeks air drying of leached soil samples had no effect on results since recovery values were high (93-110%).

Reviewer: Aerobic aging of RH-3866 (Study 1) will support these comments by the registrant.

8. Registrant: Discrepancies between the appendix and the report in regards to % recovery values was explained: Recovery values listed in the Appendix represented  $^{14}\mathrm{C}$  residues present in the organic extract only and was not total recovery since leachate and water atop the soil column  $^{14}\mathrm{C}$  activity was not included.

Reviewer: Registrant's point appears valid.

9. Registrant: Confined accumulation rotational crop data are included in the addendum.

Reviewer: Data have not been received.

10. Registrant: Fish bioaccumulation data is not required since the octanol/water partition coefficient of RH-3866 is

<1000.

Reviewer: Registrant's point is supported by EPA's Pesticide As-

sessment Guidelines - Subdivision N.

# **EXECUTIVE SUMMARY**

Only additions to or alterations of the conclusions in the initial review (Dynamac Corp., March 19, 1985) of the environmental fate and exposure assessment data on RH-3866 are discussed here. Neither of the following two studies fulfill data requirements.

Tentative results indicate that RH-3866 degrades more rapidly in pond water exposed to artificial sunlight than in deionized water maintained in darkness. An inappropriate test solution was used (natural pond water vs. deionized water), and it was not stated that the test solutions were sterile.

RH-3866 (2 lb/gal EC, parent compound only) dissipated with half-lives of ~62 and 45 days from field plots of loam (Mississippi) and silt loam (Pennsylvania) soils, respectively. Final conclusions regarding this study are tentative pending receipt of the analytical method.

# Recommendations

Available data are insufficient to fully assess the environmental fate of RH-3866. The submission of data relative to EUP requirements (Subdivision N) is summarized below:

<u>Hydrolysis studies</u>: One study (Allen, 1984, Acc. No. 072909) was submitted and reviewed. This study is scientifically valid. However, in order to satisfy Guideline Requirements the experiment should be conducted at  $25 \pm 1^{\circ}C$ .

Photodegradation studies in water: One study (Ackermann, 1984, Acc. No.  $\overline{256773}$ ) was submitted and reviewed. This study is scientifically invalid because an inappropriate test solution was used, and sterility was not addressed.

Aerobic soil metabolism: One study (Ackermann, 1984, Acc. No. 072907) was submitted and reviewed. This study does not fulfill data requirements because the incubation temperature was not constant and between 18 and 30°C. In addition, for full registration, data from a longer sampling period will be required (Guideline Requirements are for up to 12 months posttreatment), degradates identified, and residue decline curves constructed.

Anaerobic soil metabolism: One study (Ackermann, 1984, Acc. No. 072907) was submitted, reviewed and found to be scientifically valid for an EUP. However, in order to satisfy Guideline Requirements the incubation temperature must be constant and between 18 and 30°C and degradates identified.