

US EPA ARCHIVE DOCUMENT

CONFIDENTIAL

Shaughnessy #: 090301

EAB Logout

Date: 03 JUL 1984

Init:

To: Ellenberger/Edwards

Product Manager # 12
Registration Division (TS-767)

From:

Lionel A. Richardson Chief,
Environmental Chemistry Review Section # 3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769c)

Attached please find the EAB review of...

Reg./File No.: 352-370

Chemical: Methomyl

Type Product: I

Product Name: Methomyl

Company Name: E. I. duPont

Submission Purpose: Review of data submitted in response to

Registration Standard

(Mobility / Leaching)

ZBB Code:

ACTION CODE: 606

Date In: 4-10-84

EAB # 4290

Date Completed: 7/2/84

TAIS (level II)

DAYS

42

15

Deferrals To:

Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

Completion delayed by lateness
(6/26/84) of receipt of data
from registrant clarifying
statements made in their report.

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ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY

INCORPORATED

WILMINGTON, DELAWARE 19898

1-20-82

119532
119533

LEGAL DEPARTMENT

March 28, 1984

Mr. J. S. Ellenberger (PM-12)
U.S. Environmental Protection Agency
1921 Jefferson Davis Highway
Arlington, VA 22202

Subject: Methomyl Registration Standard

Dear Mr. Ellenberger:

Attached in partial fulfillment of the requirements of the Methomyl Registration Standard as clarified in our meeting with EPA of 5/26/83, are three sets of Toxicology and Environmental fate data. These reports complete requirements of the standard in these areas. Prior submissions were made in January, 1983 (Product Chemistry) and September, 1983 (Product Chemistry, Residue Chemistry, Toxicology and Environmental Fate, including a discussion of methomyl reentry interval data).

Those requirements still outstanding are all in the area of supplemental residue chemistry. These studies will be completed during the coming growing season and will be submitted to the Agency in a single volume after the final reports become available.

Sincerely,

James J. Trexel

JJT
Attachment

RECEIVED

APR 02 1984

Registration Division (TS-767)

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REQUIREMENTS OF THE
METHOMYL REGISTRATION STANDARD
DATA INCLUDED IN THIS SUBMISSION (3/26/84)

Environmental Fate

- o Leaching Study - Adsorption/Desorption. AMR-174-84
- o Photolysis of Technical Methomyl. AMR-121-83
- o Avian Single-Dose Oral LD50 - Bobwhite Quail. HLO-464-83

Toxicology

- o Mammalian In-Vivo Cytogenetics. HLO-63-84
- o Mammalian In-Vitro Point Mutation. HLR 556-83

ADDITIONAL DATA TO BE SUBMITTED - FALL '84

Residue Chemistry

- o Corn-cannery Waste
- o Grain Crops - Data Supporting Aerial Application
- o Peaches - Additional data 1-8 lb/acre, geographical distribution, and 4- day phi
- o Orchard Cover Crop - Residue Data
- o Greenhouse Tomatoes - Additional Data
- o Grapes - Data East of the Rockies
- o Small Grains - Aerial Application Data
- o Tobacco - Residues in Smoke. Raw data and experimental procedures

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APR 02 1984

Registration Division (LS-767)

DU PONT RESPONSE TO THE METHOMYL

REGISTRATION STANDARD

MARCH, 1984

PART I - ENVIRONMENTAL FATE

EXHIBIT

- 1 Batch Equilibrium (Adsorption/Desorption) and Soil Thin-Layer Chromatography Studies with Methomyl, AMR 174-84

Methomyl has intermediate to moderate mobility on the soils studied. It tends to be slightly more mobile than the herbicide terbacil. Its adsorption and desorption properties are very similar to this standard and are very much a function of the soils' organic matter content.

- 2 Photolysis of ¹⁴C-Methomyl in Water, AMR 121-83

The subject study was conducted in pH5 water at 25°C and the following observations were made:

- o Under fluorescent UV irradiation the first half-life is approximately 2 days at an initial concentration of 100 ppm and 5.5 days at an initial concentration of 10 ppm.
- o Acetonitrile was identified by gas chromatography mass spectrometry as the major, radiolabeled photo product.
- o Methomyl does not photolyze to S-methyl-N-hydroxythioacetimidate, one of the major hydrolysis products.

- 3 Acute Oral LD50 Bobwhite Quail (HLO-464-83)

LD50 is 24.2 mg/kg.

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CASE 090301

PM

CHEM Methomyl

BRANCH EAB DISC 30 TOPIC 050515 GUIDELINE 163-1

FORMULATION DC - ACTIVE INGREDIENT

FICHE/MASTER ID No Fisch CONTENT CAT 01

Priester, T.M. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with methomyl. Doc. No. AMR-174-84. An unpublished confidential study submitted by E.I. duPont de Nemours and Co., Inc., in support of registration standard.

SUBST, CLASS

OTHER SUBJECT DESCRIPTORS

PRIM:
SEC:

DIRECT RVM TIME (MM) START-DATE END DATE

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TITLE: Chemist
ORG: EAB
LOC/TEL: Room 807-I 557-0267

SIGNATURE:

DATE:

APPROVED BY: *H. L. Boyd*
TITLE: *Chemist*
ORG: *EAB*
LOC/TEL: *Room 807-I*

SIGNATURE:

DATE: 7-2-84

CONCLUSION:

Mobility - leaching -

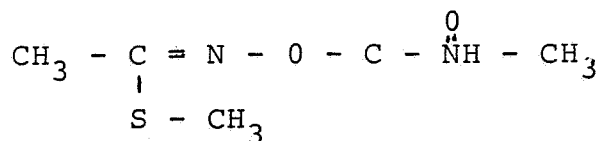
1. This study is scientifically valid.
2. Methomyl is moderately mobile to mobile (class 3-4) in silt loam and sandy loam soils.
3. Adsorption is directly related to the organic matter content of the soil. With $r = 0.85$ methomyl is bound to the organic matter rather than to the clay or other soil constituents.
4. Adsorption of methomyl to organic matter is similar to that of terbacil.
5. Desorption of methomyl is related to soil organic matter content but to a lesser degree than is adsorption ($r = 0.85$ vs 0.95).
6. Mobility and adsorption characteristics of methomyl are similar to those of terbacil. However, desorption of methomyl is less o.m. dependent than that of terbacil.

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7. Data from this study satisfy EPA's 1982 proposed data requirements for registering pesticides: Sec. 158.130, Guidelines Reference 163-1, leaching (adsorption/desorption) data.

MATERIALS AND METHODS

METHOMYL, LANNATE, NUDRIN



S-Methyl-N-[(methylcarbamoyl)oxy]thioacetimidate

Radiolabeled [1-¹⁴C] methomyl, synthesized at New England Nuclear (Boston, MA) with a specific activity of 28.3 uCi/mg (6.28 x 10⁴ dpm/ug) and 98.2% purity was used in the adsorption and the soil TLC tests; the sample used in the desorption test (same source) had a specific activity of 19.3 uCi/mg (4.28 x 10⁴ dpm/ug) and a purity of 98%.

Terbacil [2-¹⁴C] 19.12 u Ci/mg = 2.02 x 10⁴ dpm/ug 99% purity and diuron [¹⁴C - carbonyl] (4.11 u Ci/mg 9.12 x 10³ dpm/ug, 95.2% purity were used as standards for hydrophilic and hydrophobic properties, respectively.

Four different soils (Cecil sandy loam, Flanagan silt loam, Keyport silt loam, Woodstown sandy loam - sources not given - characterized in Table 1) were used in these studies.

Adsorption Study

Aqueous solutions of the radiolabeled test compounds were prepared at concentrations of 0.2, 0.5, 1.0, 2.5, and 6.0 ppm. Concentrations were verified by liquid scintillation counting (LSC). Twenty-ml aliquots of each standard solution (C₁) were mixed with

20 g oven-dry equivalent of soil for 24 hours at 25°C and then centrifuged at 1000G for 10 minutes. Concentration of radioactivity (C_2) was determined by LSC in triplicate and expressed as ug/ml or ug/g for the supernatant from each test sample.

Desorption Study

From a test sample having the highest radioactive concentration (C_2) a known volume of the supernatant was discarded and replaced by distilled water to reestablish the original 1:1 (w/w) water/soil ratio. Bottles of the soil suspension were shaken in a constant temperature shaker bath at 25°C for 24 hours and the concentration of radioactivity in the resultant supernatant determined again (C_2). This procedure was repeated five more times, fresh distilled water being added each time.

Soil Thin-Layer Chromatography (TLC) Study

A study of methomyl mobility in each soil was made by soil thin-layer chromatography. Duplicate 20 x 20 cm glass plates were coated with a 400 um layer of soil which had previously been hammer-milled to a 1-5 um particle size. Test compounds (methomyl, terbacil, and diuron - individually) were dissolved in acetone (1 mg/ml) and one microliter of each sample solution was spotted 3 cm from the bottom of individual TLC plates. The lower 0.5 cm of each plate was submerged in water and the water allowed to rise to a height of 10 cm, after which the plates were air dried for 24 hours and then exposed to Kodak X-ray film (SB-5) for two weeks.

Calculations

C_s = concentration of radioactivity in soil after equilibration
in ug/g soil.

C_2 = concentration of radioactivity in aqueous solution at equilibrium in ug/ml

C_1 = initial concentration in standard solution in ug/ml

$C_5 = C_1 - C_2$

C_2 and C_5 values plotted on log-log paper to generate Freundlich isotherms are shown in Figures 1, 3 and 5.

The adsorption distribution constant (K_a) of each compound on each soil was calculated as the C_5 value corresponding to C_2 at 1 ppm.

Coefficient of adsorption per unit of organic matter (K_a, OM) was calculated from each K_a value from the equation

$$K_{a, OM} = \frac{(K_a) (100\%)}{(\% OM)}$$

and the slope of each line ($1/n_a$) was calculated using a least squares regression curve fitting program.

Adsorption (K_a) and desorption ($1/n_d$) vs soil organics are shown in Figures 7 and 8.

In desorption studies, the initial radioactivity concentration in the aqueous phase (C_1) and the soil (C_5) prior to the first desorption equilibrium was taken from the adsorption study. The concentration of pesticide removed from the soil (C_{2a}) was determined at subsequent periods (Days 1-5) by subtracting the value for C_1 (aqueous concentration at the beginning of the day) from the concentration at the end of the day (C_2); soil concentration (C_5) was determined by subtracting the C_{2a} value from the previous day's C_5 value. Desorption data are plotted and shown in Figures 2, 4, and 6. Desorption distribution coefficients (K_d) and (K_d, OM) and slopes

of the isotherms ($1/n_d$) were determined in a manner analogous to that for adsorption. Theoretical desorption distribution coefficients (K'_d) were calculated from the experimental adsorption distribution coefficient values using the equation:

$$K'_d = K_a (n_a/n_d) \times S_m (1 - n_a/n_d)$$

where S_m = maximum concentration of test compound on soil .

The R_f value of each test compound on each soil TLC was calculated from the equation

$$R_f = \frac{d}{s}$$

where d = the average distance traveled by the test compound at the end of the test and S = the distance between the point where the test compound was applied and the end of the solvent front after development.

RESULTS

As previously mentioned, the experimentally measured and calculated concentration data from the adsorption and desorption studies are plotted in Figures 1-6. A summary of the calculated adsorption/desorption distribution coefficients (K_a , K_d) is given in Tables 2 and 3. K'_d = the theoretical desorption coefficient calculated as $K'_d = K_a (n_a/n_d) \times S_m (1 - n_a/n_d)$. Keyport silt loam with 7.5% organic matter weakly adsorbed methomyl ($K_a = 1.4$) but the other three soils showed poor adsorption of the chemical (K_a ranged from 1.0 to 0.23). Desorption (K_d) values of methomyl from these soils were similar to those for terbacil, and K_d , OM, $1/n_d$, and % O.M. values indicated that desorption of methomyl was directly related

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to the organic matter level. Once adsorbed, methomyl did not appear to be readily desorbed from the soils used.

DISCUSSION

1. A prior study in which soil was treated with polyvinyl alcohol and then equilibrated with saturated CaSO_4 (not 0.01M Ca ion soln. as specified in guidelines) was invalidated and the registrant was asked to repeat the test, using distilled H_2O but otherwise adhering to guideline test procedures. The present study was an outgrowth of that request.
 2. Equations were not given for slope n_a or n_d , nor for K_a .
 3. K_a was calculated as the C_s value corresponding to C_2 value of 1 ppm - probably just plotted.
 4. Conclusions of this reviewer sometimes differed from those of the researcher. Statement was made that methomyl was weakly held by Keyport soil ($K_a = 1.4\%$, O.M. = 7.5%) but poorly adsorbed on the other three soils is not entirely true. Methomyl was poorly adsorbed on all three soils
 5. In soils with organic matter levels greater than 1% methomyl will not likely leach as readily as terbacil although the research concluded that methomyl would be slightly more mobile.
-

TABLE 1

SOIL CHARACTERIZATION*

<u>Parameter</u>	<u>Soil Sample</u>			
	<u>Cecil</u>	<u>Flanagan</u>	<u>Keyport</u>	<u>Woodstown</u>
% Sand (0.05-2.0 mm)	61	2	12	60
% Silt (0.002-0.05 mm)	21	81	83	33
% Clay (<0.002 mm)	18	17	5	7
% Organic Matter	2.1	4.3	7.5	1.1
pH	6.5	5.4	5.2	6.6
Cation exchange capacity, meq/100 g	6.6	21.1	15.5	5.3
Origin	Cecil, MD	Rochelle, IL	Newark, DE	Dover, DE
Type	Sandy-loam	Silt-loam	Silt-loam	Sandy-loam

*Soil analyses were performed at the Soils Testing Laboratory, College of Agricultural Sciences, University of Delaware, Newark, DE. Mechanical analysis, to determine the sand, silt, and clay content, was conducted after removal of the organic matter by wet oxidation.

TABLE 2

ADSORPTION CHARACTERISTICS OF METHOMYL, TERBACIL, AND DIURON ON FOUR SOILS

Soil*	K _a ** (μg/g)			K _a , OM*** (μg/g)			1/n _a ****
	Methomyl	Terbacil	Diuron	Methomyl	Terbacil	Diuron	
Cecil Sandy Loam	0.72	0.96	8.8	34	46	419	0.86 0.85 0.80
Woodstown Sandy Loam	0.23	0.38	4.0	21	35	364	0.90 0.95 0.79
Keyport Silt Loam	1.4	1.9	12	19	25	160	0.86 0.92 0.79
Flanagan Silt Loam	1.0	1.3	18	23	30	419	0.88 0.88 0.82

* Soil properties are summarized in Table 1.
 ** Freundlich adsorption distribution coefficient.
 *** Coefficient of adsorption per unit organic matter.
 **** Slope of Freundlich adsorption isotherm.

TABLE 3

DESORPTION CHARACTERISTICS OF METHOMYL, TERBACIL, AND DIURON ON FOUR SOILS

Soil*	K _d ** (µg/g)		K _{d,OM} *** (µg/g)			1/n _d ****			
	Methomyl	Terbacil	Diuron	Methomyl	Terbacil		Diuron		
Cecil Sandy Loam	1.0 (1.1)	1.2 (1.4)	6.1 (6.5)	48	57	290	0.55	0.54	0.31
Woodstown Sandy Loam	0.50(0.50)	0.71(0.76)	4.1 (4.2)	45	65	370	0.46	0.51	0.56
Keyport Silt Loam	2.8 (2.8)	2.4 (2.4)	6.6 (6.4)	37	32	88	0.093	0.63	0.12
Flanagan Silt Loam	1.6 (1.6)	1.9 (1.8)	6.5 (6.8)	37	44	150	0.50	0.58	0.11

* Soil Properties are summarized in Table 1.

** Freundlich desorption distribution coefficient. Values in parentheses were calculated from the K_a values using the Hornsby equation.

*** Coefficient of desorption per unit organic matter.

**** Slope of Freundlich desorption isotherm.

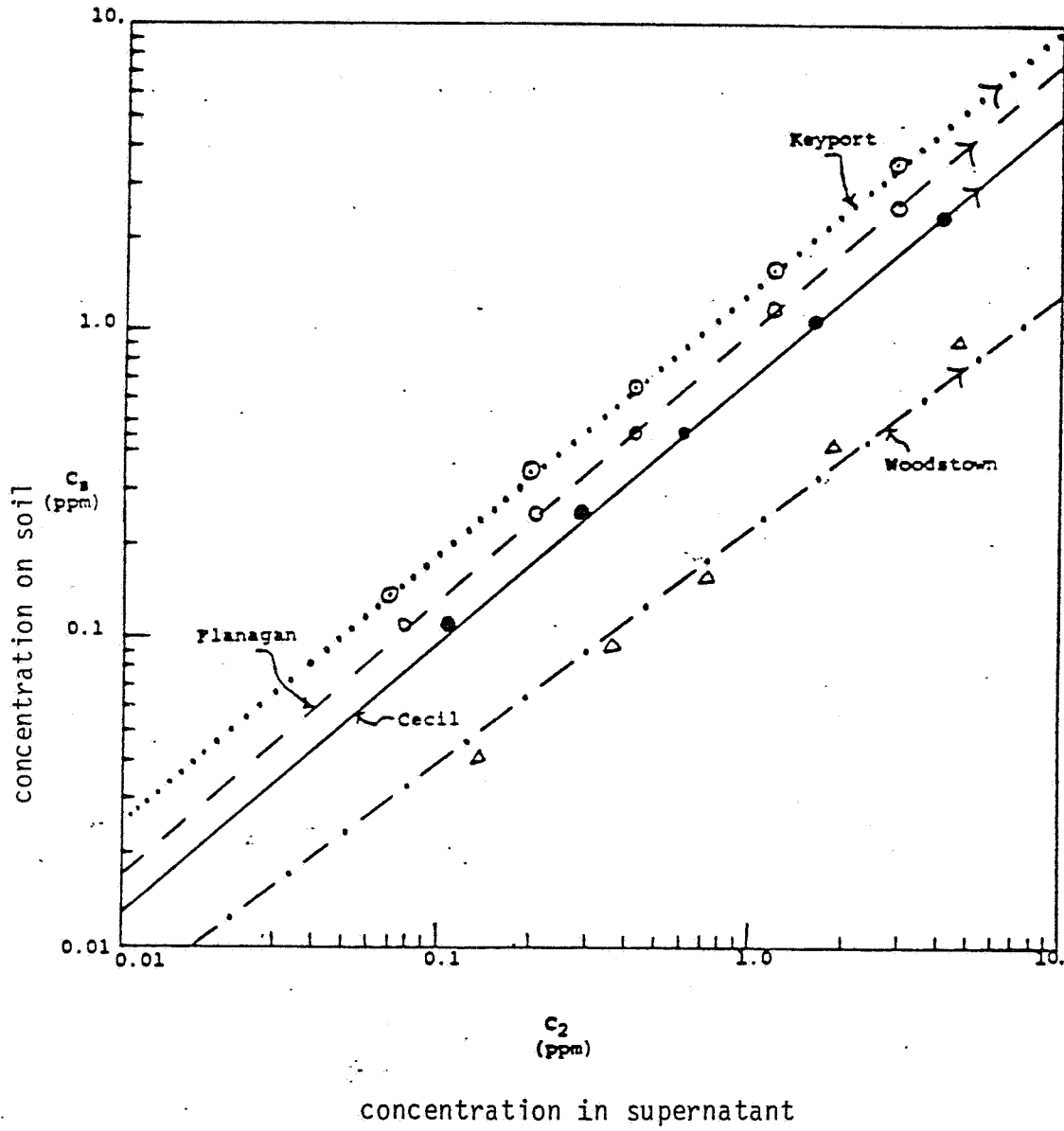
TABLE 4

SOIL THIN-LAYER CHROMATOGRAPHY R_f VALUE OF METHOMYL,
TERBACIL, AND DIURON ON FOUR SOILS

Soil	R _f Value		
	Methomyl	Terbacil	Diuron
Cecil Sandy Loam	0.53	0.44	0.10
Woodstown Sandy Loam	0.82	0.64	0.21
Keyport Silt Loam	0.52	0.28	0.05
Flanagan Silt Loam	0.46	0.36	0.08

FIGURE 1

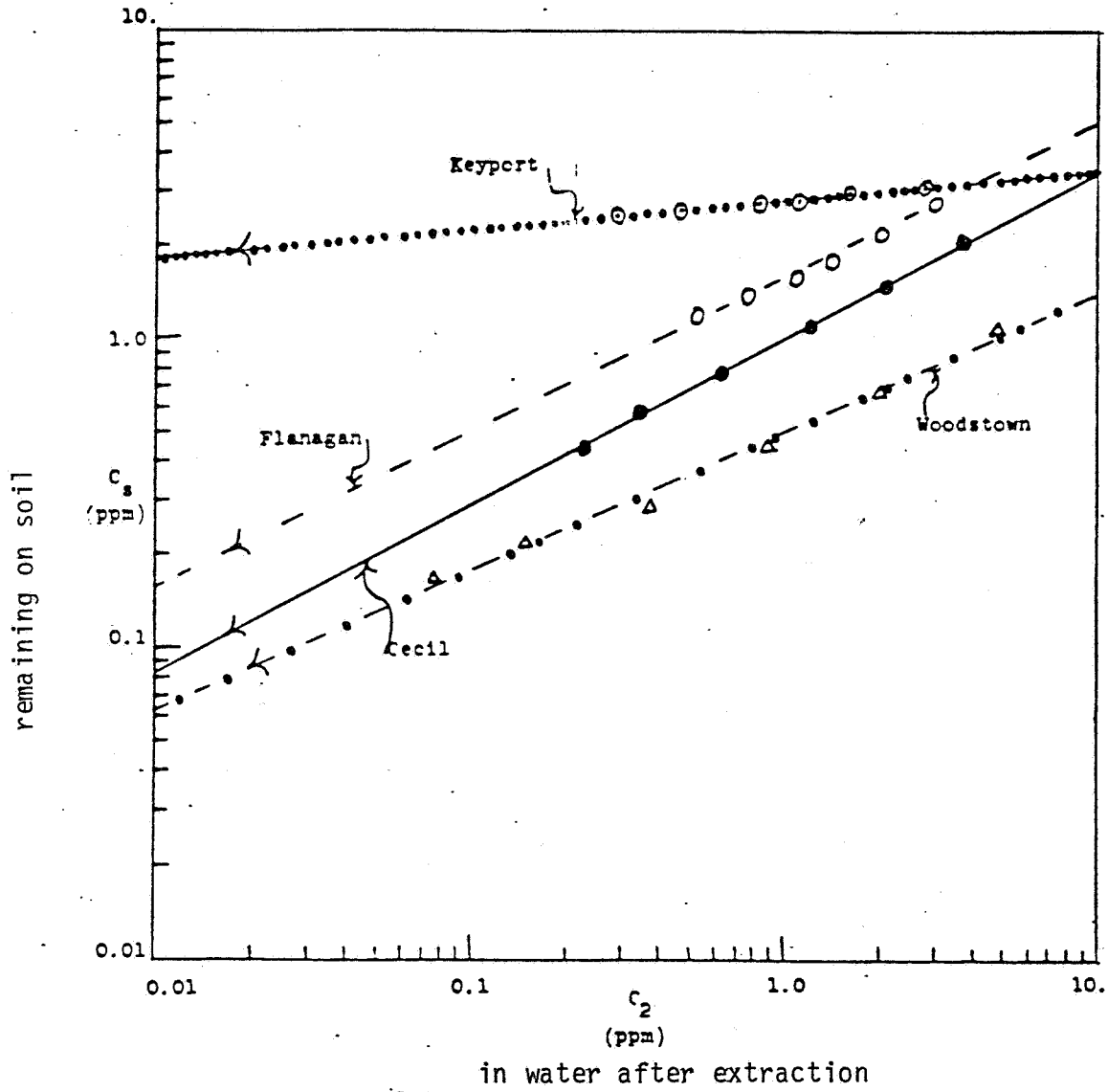
ADSORPTION OF METHOMYL



From AMR-1-174-84

FIGURE 2

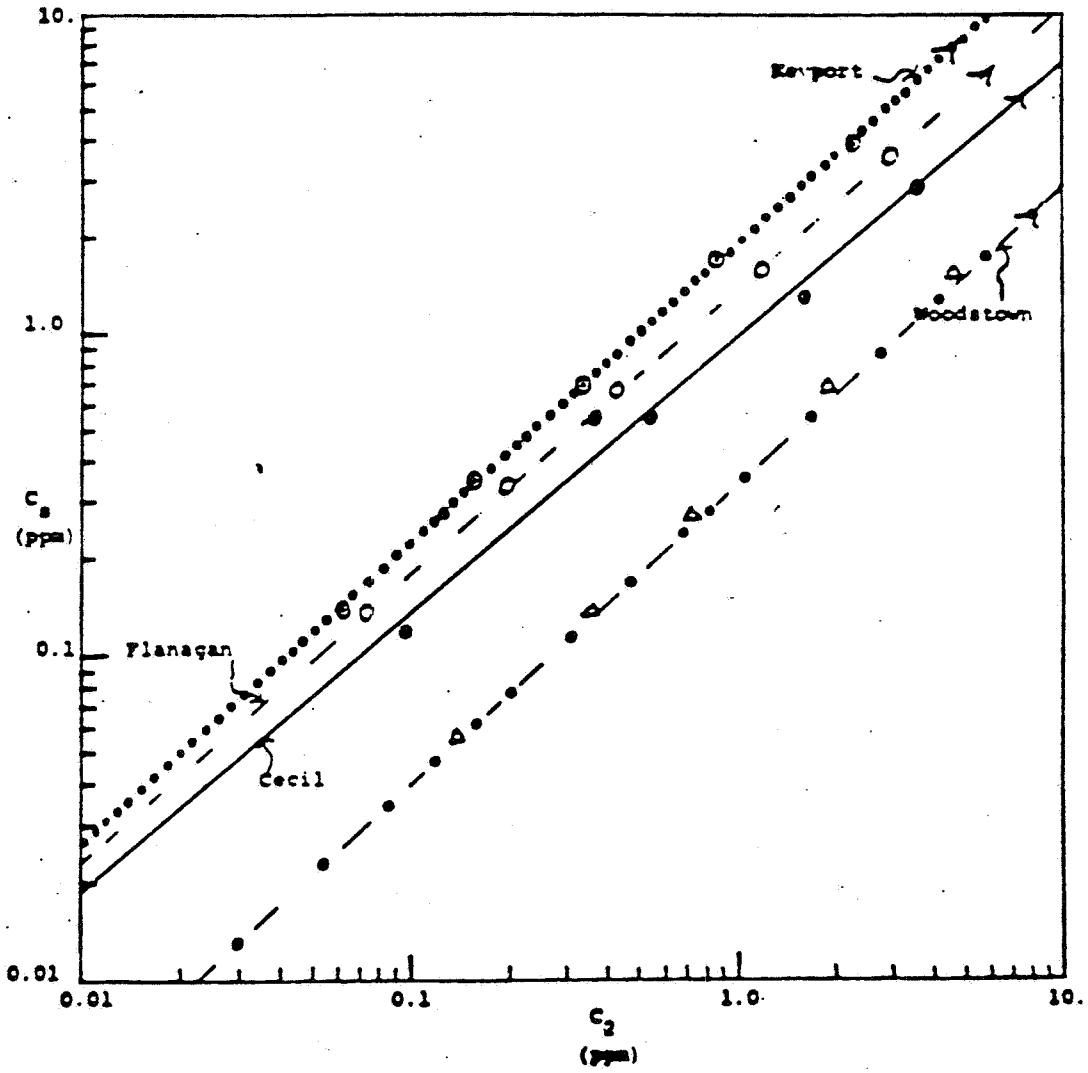
DESORPTION OF METHOMYL



From AMR-1-174-84

FIGURE 3

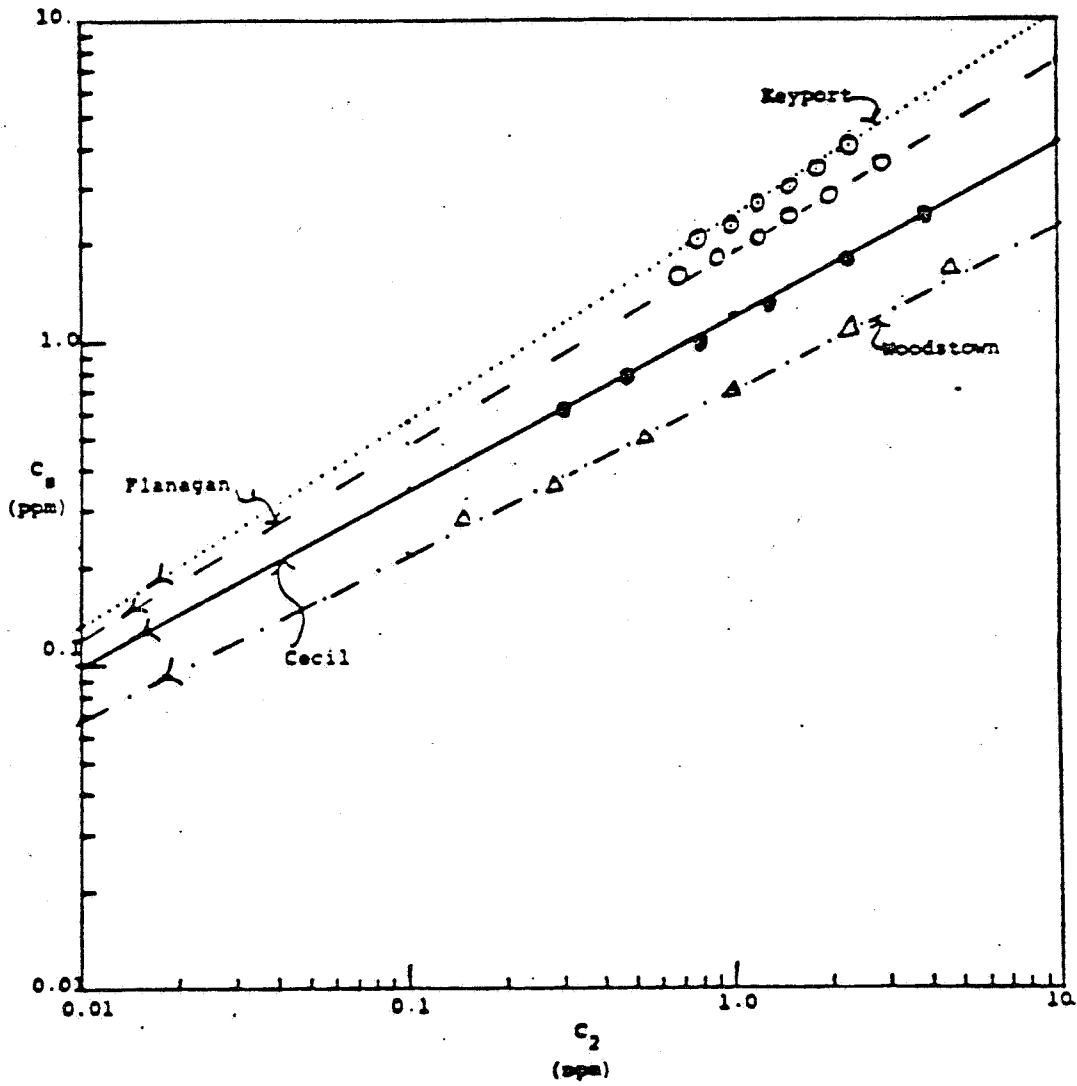
ADSORPTION OF TERBACIL



From AMR-1-174-84

FIGURE 4

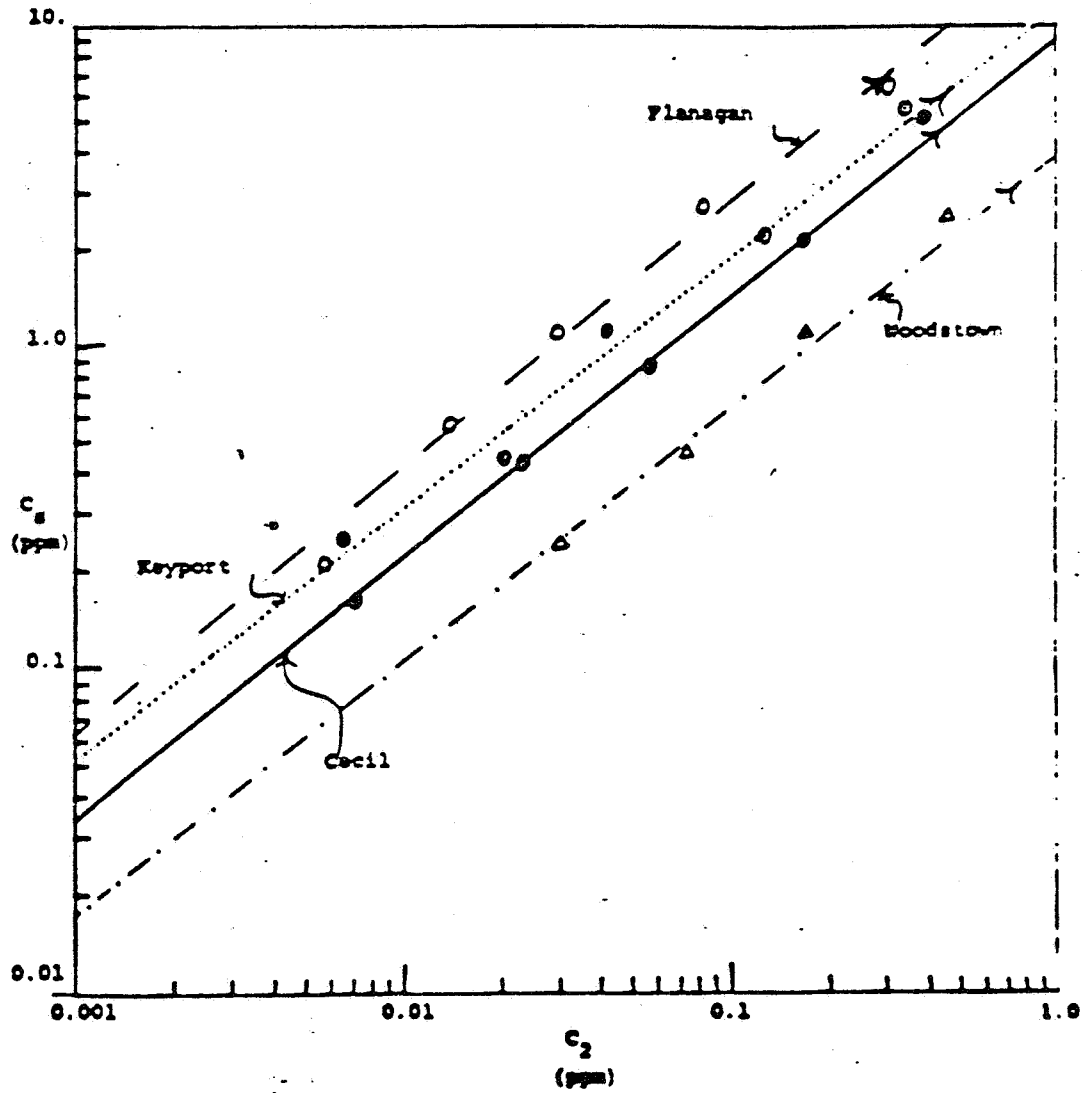
DESORPTION OF TERBACIL



From AMR-1-174-84

FIGURE 5

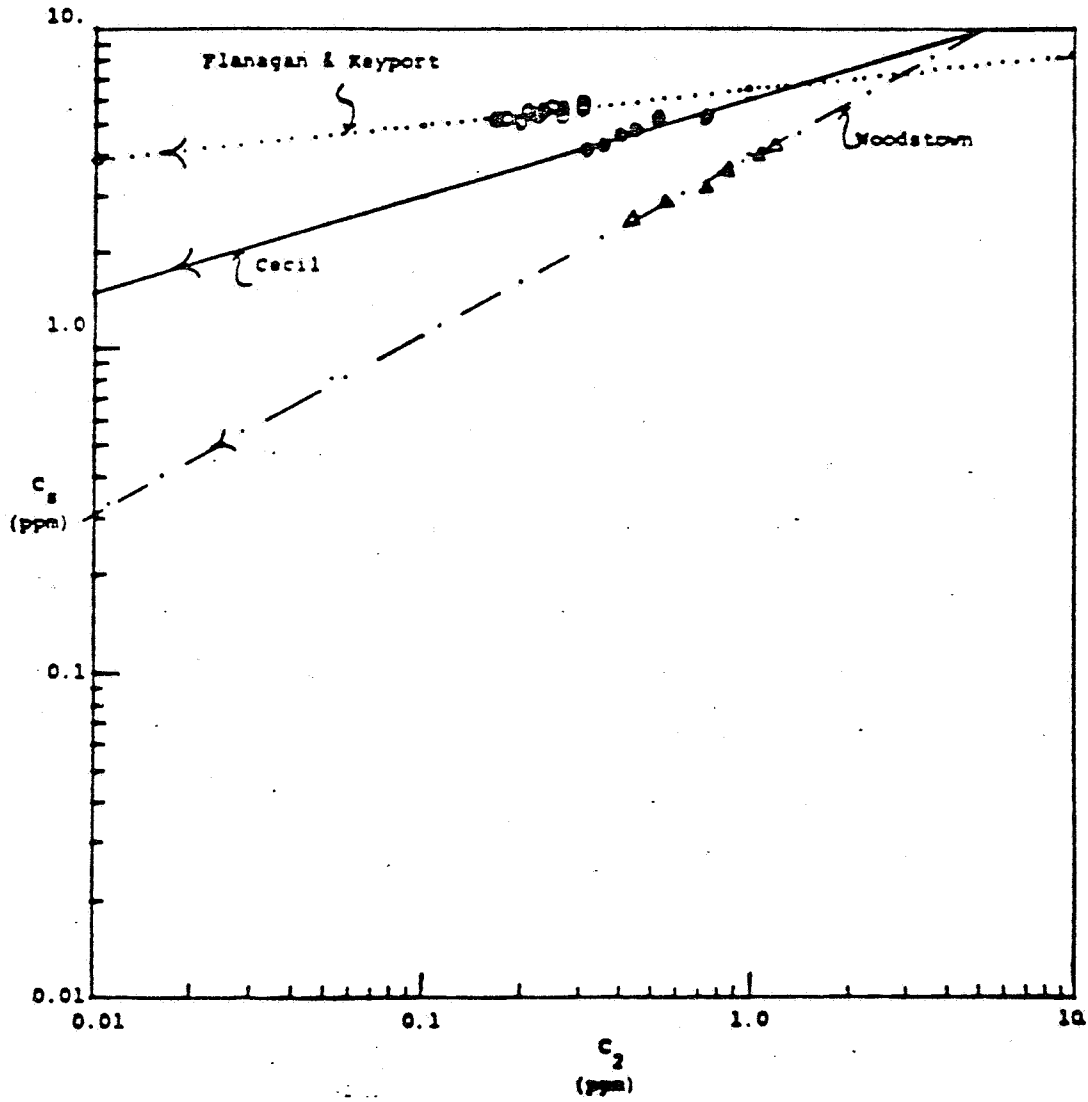
ADSORPTION OF DIURON



From AMR-1-174-84

FIGURE 6

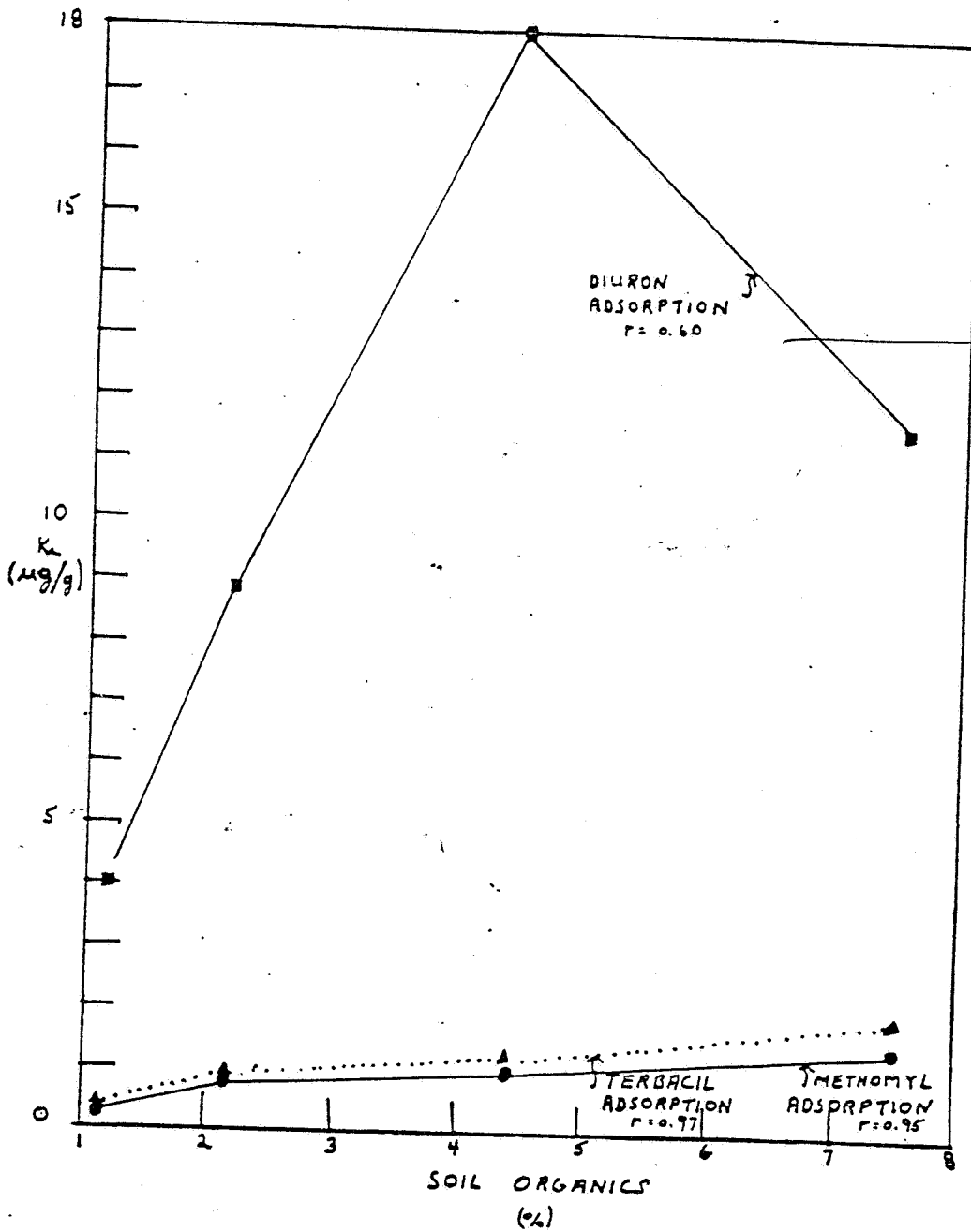
DESORPTION OF DIURON



From AMR-1-174-84

FIGURE 7

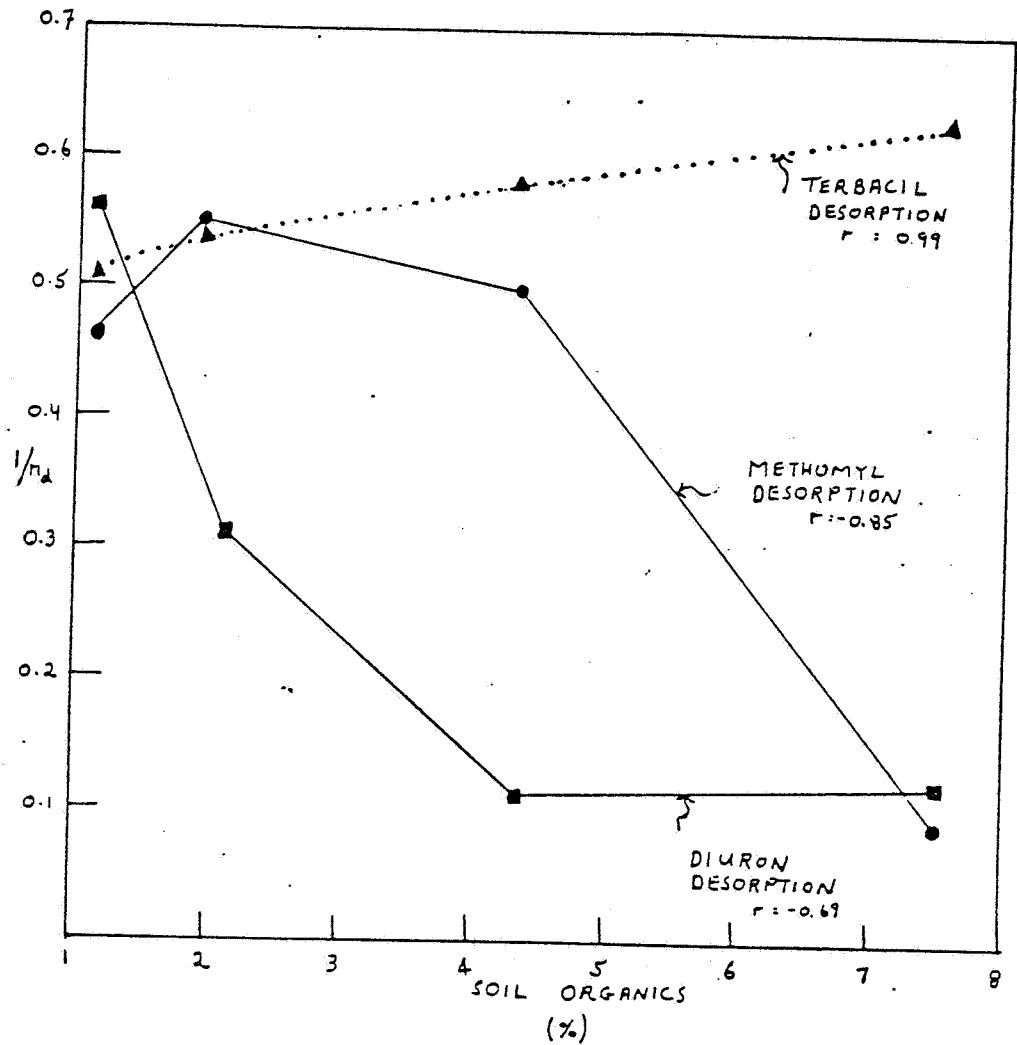
Adsorption (K_a) versus % Soil Organics



This suggests adsorption diuron dependent on factors other than just % organic matter i.e. pH, chemical composition of organic & inorganic matter

FIGURE 8

Desorption ($1/n_d$) versus % Soil Organics



Addendum to AMR-1-174-84 submitted 6-26-84

CASE 090301

PM

CHEM Methomyl

BRANCH EAB DISC 30 TOPIC 050515 GUIDELINE 161-2

FORMULATION UC = ACTIVE INGREDIENT

FICHE/MASTER ID No Fisch CONTENT CAT 01

Harvey, John, Jr. Photolysis of [1-14C] Methomyl. Doc. No. AMR-121-83.
An unpublished confidential study submitted by E.I. duPont de Nemours and Co., Inc.,
in support of registration standard.

SUBST. CLASS

OTHER SUBJECT DESCRIPTORS

PRIM:
SECI

DIRECT RVM TIME (MM) START-DATE END DATE

REVIEWED BY: H.L. Boyd
TITLE: Chemist
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SIGNATURE: *Andrew L Boyd*

DATE:

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: *Andrew L Boyd*

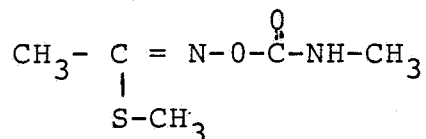
DATE: 6-7-84

Conclusion:

1. This study is scientifically valid.
2. At pH 5.0 and a concentration of 100 ppm the halflife of methomyl would be expected to be 2-3 days; at 10 ppm the halflife would be approximately two weeks. (in sunlight)
3. The photolytic product of methomyl is acetonitrile.
4. Data from this study satisfy EPA's 1982 proposed data requirements for registering pesticides: Sec. 158.130, Guidelines Reference 161-2, photodegradation in water.

MATERIALS AND METHODS

Methomyl, Lannate, Nudrin



S-methyl-N-[(methylcarbamoyl)oxy] thioacetimidate

[1-¹⁴C] methomyl (New England Nuclear), with a specific activity of 14.1 u Ci/mg, 95% methomyl, 3% oximino compound and 2% unidentified materials and analytical grade (du Pont) methomyl and the related oximino compound were used in this experiment. Common chemicals were of analytical grade or better; solvents were HPLC grade.

Buffer solution at pH 5.0 was prepared from 0.1M potassium hydrogen phthalate, distilled water and 0.1M sodium hydroxide.

Glassware, buffer solution, and distilled water were sterilized under 15 psi steam for 1-hr on each of 3 consecutive days. A 100 ppm solution of methomyl was prepared by adding 2.0 mg [1-¹⁴C] methomyl and 48.0 mg non-radioactive methomyl in 500 ml of sterilized buffer; a 10 ppm solution was prepared with 80 ml of 100 ppm solution and 720 ml of sterilized pH 5 buffer.

One aliquot of the 100 ppm solution and two aliquots of the 10 ppm solution were placed in separate jacketed beakers, covered with quartz lids, and placed in a 25° water bath. These solutions were stirred constantly with magnetic stirrers while being exposed to ultraviolet light from a combination

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of fluorescent sunlamps and fluorescent black lamps that provided a calculated light intensity equivalent to half that of a typical summer day at noon (average intensity of 300-400 nm, 1000 $\mu\text{W}/\text{cm}^2$ in, from the solutions' surface).

One of the beakers containing 10 ppm methomyl solution was modified by the addition of a side-arm to accommodate the passage of a slow stream of air through the head-space and its washing through 100 ml of 1N NaOH.

Stoppered volumetric flasks of 100 ppm and 10 ppm methomyl in pH 5 buffer were kept in a dark incubator at 25° to serve as controls.

One 20 ml sample was removed from each solution on Day 0 and after exposure periods of 1, 2, 3, 4, 7, and 15 days, except for the solution in the modified beaker which was sampled only on Day 0 and Day 10. The NaOH trap contents were removed and replaced with fresh 1N NaOH after 2, 4, 7, and 10 days.

Sample aliquots were subjected to liquid scintillation counting (LSC) in Formula 947™ or in Atomlight™ scintillation cocktail (New England Nuclear). The percent of the radioactivity attributable to $^{14}\text{CO}_2$ was determined by first, precipitating of the carbonate with barium chloride solution, and then counting of the clear, supernatant liquid in Atomlight™.

After adjustment of the pH to 3-4 with dilute formic acid the samples were analyzed by high performance liquid chromatography (HPLC) using a Varian® Model 5000 liquid chromatograph and a 25 cm x 4.6 mm Zorbax® (du Pont) column

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at 30°C. The mobile phase was acetonitrile/water (20/80/vv) adjusted to pH 3 with formic acid, and the flow rate was 1 ml/min. Typical retention times were 6.6 min for methomyl and 4.4 min. for the oximino compound. Sample eluent collected at 1 min. intervals and correlated with the chromatogram was quantitated by LSC.

Aliquots of the 15-day exposure, 100 ppm solution (original level) showed a single peak for the photoproduct with a retention time of 5-6 minutes. Samples (1 ml) of the 5-6 min. fractions were individually equilibrated with 1 ml fractions of ethyl acetate, ethyl ether, and benzene. Identification of compounds was made by use of a Finnigan 4500 gas chromatograph/mass spectrometer. The GC column was 3' x 0.25 in. OD packed with Porapak® Q (200/235 mesh) and injection port and column temperatures were maintained at 225° and 180°C respectively. The mass spectrometer was operated in the selected ion monitoring mode at m/e 41, the molecular ion of acetonitrile. A 25 ug/ml acetonitrile sample was the standard against which the 15-day, 100 ppm solution was compared. Both the standard and the sample were analyzed by GC/MS with the spectrometer in the scanning mode.

RESULTS

Reference to Table II will show that methomyl proved to be stable to hydrolysis at pH 4, the pH chosen for this study. From Table I it is seen that methomyl photolyzed rapidly at

both 100 ppm and 10 ppm levels with the half life being on the order of 2-3 days with the 100 ppm solution. Oximino did not appear to be a photolysis product. Instead, the principal photoproduct, a volatile material, was shown by GC/MS to be acetonitrile. The retention time of the photoproduct, characterized as a single peak in the fractions on the Zorbax® column was 5-6 minutes.

Figures 1 and 2 depict the photolysis of methomyl in pH 5 buffer.

TABLE I

Hydrolysis of [¹⁴C]Methomyl at pH 5

(Dark Control)

% of Original Radioactivity As:

<u>Initial Methomyl Concentration</u>	<u>Days Exposure</u>	<u>Methomyl</u>	<u>Oximino Compound</u>
<u>100 ppm</u>	0	94	2
	1	94	1
	3	98	1
	6	93	1
	9	92	2
	14	91	2
<u>10 ppm</u>	0	93	2
	1	94	2
	3	93	1
	6	90	2
	9	94	2
	14	92	2

TABLE II

Photolysis of [¹⁴C]Methomyl at pH 5

% of Original Radioactivity As:

<u>Initial Methomyl Concentration</u>	<u>Days Exposure</u>	<u>Total ¹⁴C</u>	<u>Methomyl</u>	<u>Oximino Compound</u>	<u>Unknown Products*</u>
<u>100 ppm</u>					
	0	100	90	3	5
	1	93	50	1	39
	2	100	42	1	55
	3	106	35	1	68
	7	67	9	<1	56
	15	74	3	<1	66
<u>10 ppm</u>					
	0	100	89	3	6
	1	108	83	2	22
	2	138	105	1	30
	3	112	67	1	41
	7	64	31	1	29
	15	55	13	1	39

* The unknown photoproduct was subsequently identified as acetonitrile.

FIGURE 1

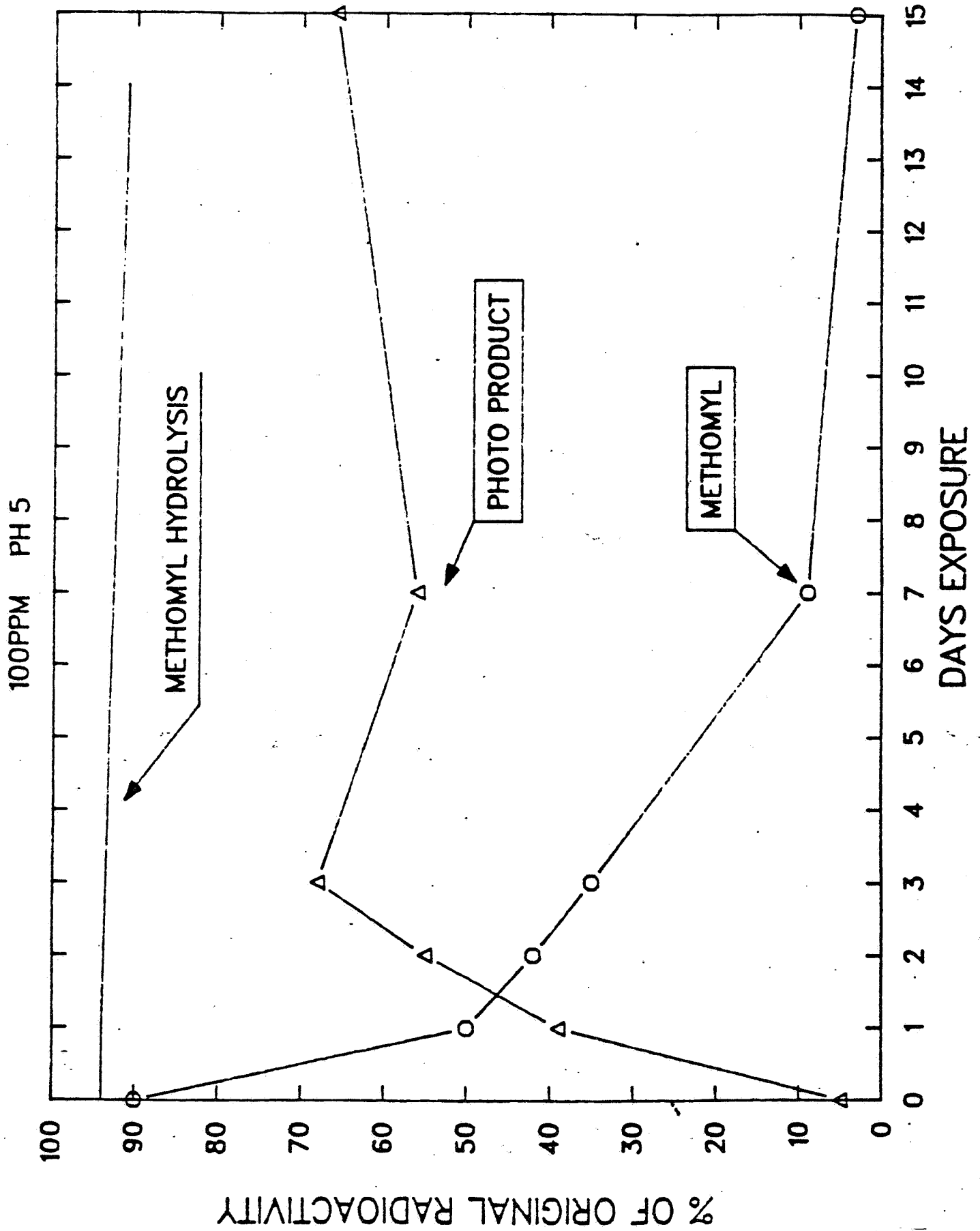


FIGURE 2

