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ESL-TR-82-45

ENVIRONMENTAL FATE OF HYDRAZINE FUELS IN AQUEOUS AND SOIL ENVIRONMENTS

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FEBRUARY 1983

FINAL
MAY 1979 - MAY 1981

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER
ESL-TR-82-45

2. GOVT ACCESSION NO.
AD-A125 813

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Environmental Fate of Hydrazine Fuels in Aqueous and Soil Environments

5. TYPE OF REPORT & PERIOD COVERED
Final May 79 - May 81

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
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8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
HQ AFESC/RDVC
Tyndall AFB, FL 32403

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Program Element: 62601F
JON: 19002013

11. CONTROLLING OFFICE NAME AND ADDRESS
Environics Division, Engineering and Services Laboratory, Air Force Engineering and Services Center

12. REPORT DATE
February 1983

13. NUMBER OF PAGES
23

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Availability of this report is specified on the reverse of the front cover.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrazine
Monomethylhydrazine
Unsymmetrical dimethylhydrazine
Marine water
Fresh water
Aqueous Decomposition
Soil percolation
Soil adsorption
Clay
Organic
Sand

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The fate of chemicals in aqueous environments is determined by diverse processes: chemical degradation, physical phase transfer, and dilution or dispersion. This study focused on the uncatalyzed aqueous decomposition (distilled, sea, and pond water) of hydrazine fuels. Despite their hypergolic nature, these fuels are remarkably stable in uncatalyzed aqueous solutions. Monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) were found to be extremely stable in distilled water, and had slow half-lives

(10-14 days) in ponds and seawaters. As this study minimized biological decomposition and phase transfer losses, the aqueous half-lives of 10-14 days are very conservative figures and represent "worst case" situations.

PREFACE

This report was prepared by the Air Force Engineering and Services Center, Engineering and Services Laboratory, Tyndall AFB, Florida 32403, under Program Element 62601F, Project 1900, Subtask 2013. Work documented herein was performed between May 1979 and May 1981 in response to a technical need (TN-SO-AFESC-2109-76-4501), Environmental Fate of Hydrazine Fuels issued by Space Division.

This work was performed by Captain Barbara A. Braun and Captain Joseph A. Zirrolli with support from SSgt Charles A. Mulligan. Captain Joseph A. Zirrolli was the AFESC project officer.

This report has been reviewed by Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The Air Force is the major user of the hypergolic rocket fuels, hydrazine (Hz), monomethylhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH). As such, the Air Force is responsible for health, safety, and environmental considerations associated with hydrazine fuel use. The use of these fuels poses possible adverse health hazards. During handling, fuel could inadvertently be released into the ambient air and/or surrounding aqueous environments. These fuels are highly toxic, and, as a result of recent studies (References 1 and 2), the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute of Occupational Safety and Health (NIOSH) have listed these compounds among the industrial substances suspected of being human carcinogens.

In addition to the concern for the adverse health effects of the hydrazines, there is a need to investigate their environmental decomposition products. The initial major aqueous and air products of MMH and UDMH, formaldehyde monomethylhydrazone (FMH) and formaldehyde dimethylhydrazone (FDH), respectively, have been determined by the Air Force Aerospace Medical Research Laboratory to have the same relative magnitude of toxicity as MMH and UDMH (Reference 3).

A minor decomposition product of UDMH that presents the greatest hazard is N-nitrosodimethylamine (NDMA). Nitrosoamines are considered to be among the most potent of all chemical carcinogens. There are no permissible exposure levels for NDMA (Reference 4). Dimethylamine (DMA) and trimethylamine (TMA) are also minor decomposition products or fuel contaminants of MMH and UDMH, as well as possible precursors of NDMA (Reference 5).

Most environmentally related studies conducted by the Air Force have centered on the immediate hazards of spills and protection of the worker from acute exposures to the hydrazine fuels or their vapors. Little has been done to predict the persistence of hydrazine compounds in the aqueous environment and, because of their use as propellants, chemical research has centered on high temperature decomposition and oxidation, treatments to improve fuel stability, and efforts to develop and evaluate specific catalysts for controlled decomposition (Reference 6).

In this study, the decomposition rates of MMH and UDMH in aqueous environments (distilled, seawater, and freshwater) were determined. UDMH decomposition products were identified using gas chromatography/mass spectrometry (GC/MS) techniques.

SECTION II

METHODS AND MATERIALS

A. REAGENTS

All reagents were prepared from ACS grade or better chemicals using all-glass distilled, deionized water. Trisodium pentacyanoaminoferroate (TPF) color reagent was prepared in our laboratory using the recommended method of Pinkerton, et al. (Reference 7). Hydrazine fuels were obtained from the Rocky Mountain Arsenal as the fuel grade chemical (98+ percent).

B. ANALYTICAL METHODS

The fuel concentrations were followed during the course of the experiments using colorimetric techniques. MMH was analyzed using p-dimethylaminobenzaldehyde (PDAB) (Reference 8), which reacts with MMH to form a yellow azine compound. Absorbance was measured at 460 nm with a detection limit of 0.040 mg/l MMH. UDMH was analyzed using trisodium pentacyanoaminoferroate (TPF) (Reference 7), which forms a rosy red compound. Absorbance was measured at 495 nm with a detection limit of 0.700 mg/l UDMH. Because of the time-dependence of this reaction, all readings were taken 45 to 60 minutes after addition of the samples to the reagent. Absorbance measurements were made using a 1 by 1 centimeter silica cell in a Perkin Elmer Coleman 55 single-beam digital spectrophotometer.

In addition to the colormetric analysis in the aqueous decomposition study, the concentrations of the fuels and oxidation products were followed using a Finnigan 3200 Gas Chromatograph/Mass Spectrometer (GC/MS) interfaced to a System 150 data system. The GC/MS samples were prepared by placing a 100 μl water sample in 100 μl of a solution containing 0.005 moles/liter phenol, 0.02 moles/liter sodium hydroxide, and 2.7 moles/liter acetone. Phenol was used as an internal standard. The acetone was used to transform the UDMH to its hydrazone. This solution was prepared every 3 to 4 days. Samples were chromatographed on a 1/4-inch x 4-foot glass GC column packed with Tenax® GC 60/80. The carrier gas was Helium with a flow of 30 ml/minute. Temperature was programmed at 70°-200°/10°/minute with data acquistition starting at 100°C. The MS was operated in the multiple-ion mode at 70 eV ionization voltage. The ions monitored were: 15, 42, 60, 72, 74, 94, and 100 amu.

C. AQUEOUS DECOMPOSITION

Natural waters used in these studies were obtained from a freshwater pond on Tyndall AFB, FL and from the Gulf of Mexico. New water samples were obtained and filtered through Whatman 42 ashless filter paper for each study. Two fuel concentrations were studied: 0.1 percent (2.7×10^{-2} moles MMH/liter; 1.3×10^{-2} moles UDMH/liter) and 0.05 percent (1.4×10^{-2} moles MMH/liter, 6.6×10^{-3} moles UDMH/liter) solutions.

Degradation studies were performed in 150 ml stoppered Pyrex® reagent bottles which were soaked in Chem-Solv® glassware cleaner to remove organic material, rinsed with deionized, distilled water, soaked in a 50-percent solution of nitric acid, and again rinsed with deionized, distilled water. This rigorous cleaning was necessary to achieve reproducible results. Without cleaning, randomly accelerated degradation rates were observed, possibly the result of trace metals which catalyze the breakdown of hydrazines.

The fuel solutions were first prepared in volumetric flasks and mixed thoroughly using Teflon®-coated magnetic stir bars. One hundred ml aliquots were then transferred, in triplicate, to the cleaned 150 ml stoppered Pyrex® reagent bottles. All experiments were conducted at room temperatures. Samples were taken periodically, with sampling becoming less frequent as the study progressed and the degradation rate decreased. Each colorimetric analysis was done in triplicate. The GC/MS samples were taken in duplicate, at the same time samples were withdrawn for colorimetric analysis, and were analyzed after 5 hours.

D. SOIL PERCOLATION/ADSORPTION

Four soil types varying in sand, clay, and organic content were used in these studies. The soils were characterized by Dr. M. Hayes, University of Birmingham, England, and their properties are listed in Table 1.

TABLE 1. SOIL PROPERTIES

NAME	MOISTURE content (%)	SAND (%)	CLAY (%)	ORGANIC (% carbon)	pH	CEC[a] (meq/100g)
Sand	-	100.0	-	-	-	-
Clay	1.5	69.3	27.9	Tr[b]	3.7	18.8
Organic	0.2	96.1	1.0	1.0	6.4	20.4
VAFB[c]	0.4	99.1	0.4	Tr[b]	6.1	7.3

[a] Cation exchange capacity.
[b] Trace.
[c] Vandenberg Air Force Base soil.

As shown, all soils were mostly sand with low cation exchange capacities. The sand used was cleaned Ottawa sand while the other samples were natural soils. The clay and organic soils were obtained on Tyndall AFB. All soils were sieved (500 micrometers) and dried at 80°C for 24 hours before use.

1. Soil Percolation

Glass columns (60 cm X 10 cm i.d.) were dry packed with 200 grams of soil, forming a soil column 20 cm in height. After washing with 1 liter of deionized, distilled water, the columns were drained and excess free water removed with gentle air pressure. Fuel solutions (10 ml, 0.1 percent v/v) were applied to the column head and, after 15 minutes of equilibration, the columns were leached with 2 liters of deionized, distilled water at 5 ml/minute. Leachate fractions were collected every 6 minutes (30 ml volume), centrifuged for 20 minutes at 35,000 RCF to remove suspended particles, and then analyzed by colorimetry.

Duplicate columns were run with each fuel and soil mixture. Additionally, a blank soil column (no fuel added) was leached in the same manner to insure that each soil leachate itself did not interfere in fuel colorimetric assays.

2. Soil Adsorption

Adsorption studies were performed in capped, polycarbonate centrifugation tubes using 3 grams of each soil type mixed for 20 minutes in 30 milliliters of 0.002 percent v/v aqueous fuel solution. Tubes were then centrifuged at 35,000 RCF, the fuel solution decanted, and the soil pellet extracted with 30 milliliters of 0.1 N HCl in the same manner. Each fuel solution and acid extraction was performed in triplicate and assayed by colorimetry. The amount of "fuel adsorbed" was calculated as the difference between the initial fuel solution concentration and the fuel solution concentration after soil mixing.

SECTION III

RESULTS

A. AQUEOUS DECOMPOSITION.

1. Stability of Aqueous Hydrazine Fuel Solutions.

The aqueous chemistry of hydrazine fuels in both laboratory deionized, distilled water and natural waters is remarkably stable. However, our initial studies were marked by assay fluctuations which were greater than the normal variance of the colorimetric methods. Typically, during an aqueous study, the PDAB assay for MMH and the TPF procedure for UDMH yield coefficients of variation (standard deviation of the mean divided by the mean value) for each time point of 2 percent and 3 percent, respectively. This contrasts with an 8-percent variation per time point among the triplicate reaction vessels in the study (each time point is the mean of three colorimetric assays per reaction vessel). Often this increased variation was due to an abnormally increased rate of fuel degradation in one of the three runs (Figure 1).

Since hydrazine oxidation can be catalyzed by metal ions, the glass reaction vessels were subsequently stringently acid-cleaned (see Section II) before each study. Variation among triplicate reaction vessels which had been acid-cleaned then dropped to 3 percent for both MMH and UDMH studies--representative of the normal assay variablity. The effect of this acid cleaning on the calculated first-order decomposition rate is shown in Table 2. For MMH, the average half-life, as measured in marine water (13 days), did not change although the method of cleaning did increase the precision by 50 percent. The reverse is true for UDMH in marine water. While the relative variation remained constant, the half-life doubled to approximately 12 days. This faster decay rate in detergent- cleaned beakers may also reflect volatilization losses as UDMH is 10 times more volatile than MMH and the latter studies were performed in stoppered vessels (Method 2).

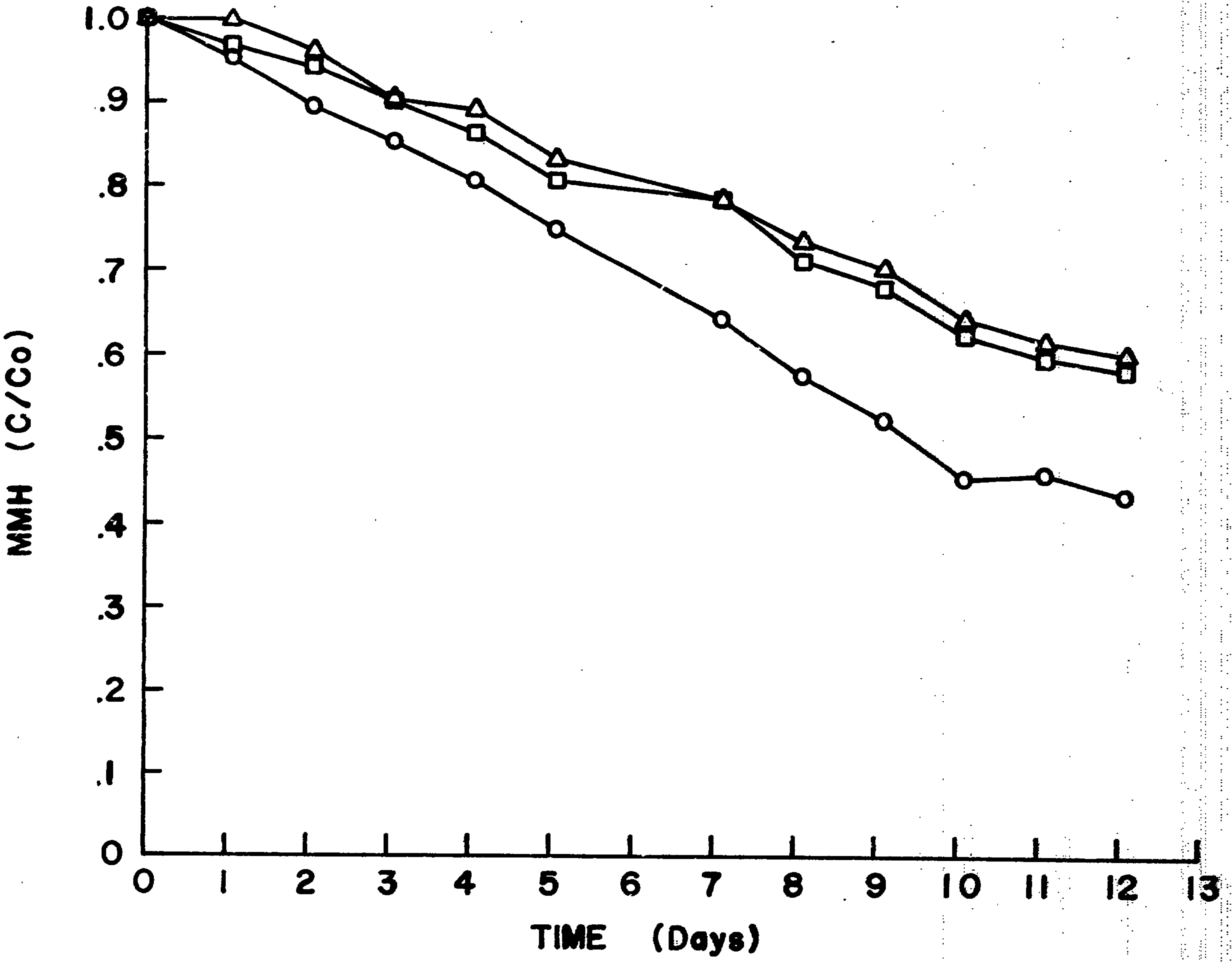


Figure 1. Aqueous Decomposition of 0.1 Percent MMH in Seawater.

TABLE 2. ESTIMATION OF AQUEOUS HALF-LIVES[a] OF HYDRAZINE FUELS: FACTORS AFFECTING ACCURACY AND PRECISION

Fuel	Method 1[b] (Days)	Method 2[c] (Days)
	mean std dev	mean std dev
MMH	12.6 ± 4.5, n=9	13.1 ± 2.2, n=6
UDMH	5.8 ± 1.2, n=3	12.6 ± 2.8, n=4

[a] Results are expressed as pseudo-first-order rate half-lives determined by linear regression of natural logarithm (Fuel) versus time.

[b] Performed in open 250 ml beakers, cleaned with laboratory detergent followed by distilled, deionized water rinses.

[c] Performed in stoppered 100 ml glass reagent bottles, acid-cleaned as described in Methods.

2. Monomethylhydrazine Decomposition

The aqueous decomposition of MMH in either distilled or natural waters is quite slow in the absence of catalytic metal ions or active aeration (Figure 2). In deionized, distilled water, less than 20 percent of the initial MMH had decomposed after 300 hours. Although in freshwaters and seawaters the degradation rates are statistically faster, they are still surprisingly slow, considering the hypergolic nature of this rocket fuel. With such slow reaction rates it is difficult to extrapolate accurate half-lives. Thus, the results listed in Table 3 are conservative estimates. These half-lives (approximately 2 weeks) do not change significantly in different natural waters, nor are they dependent upon the initial MMH concentration.

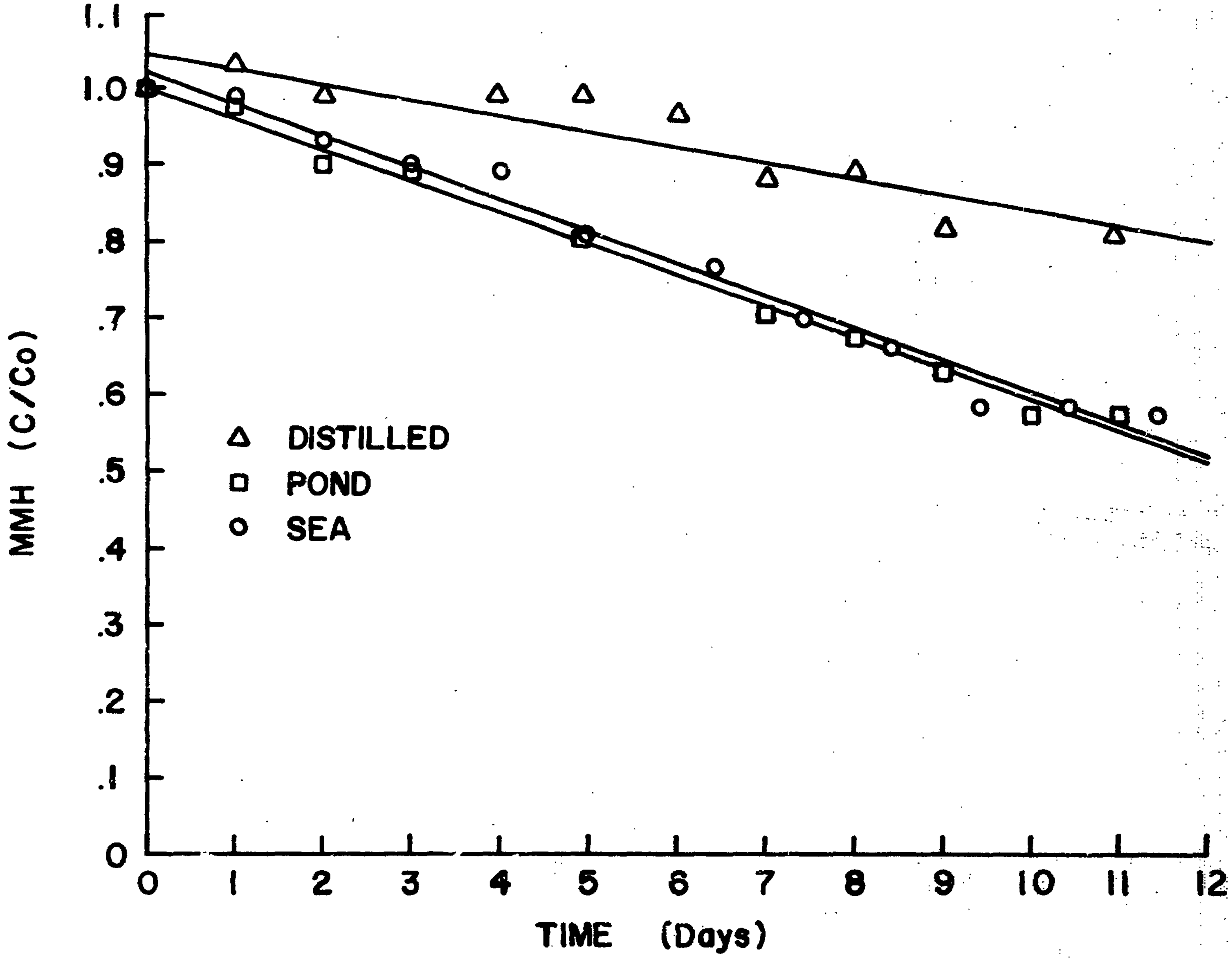


Figure 2. Aqueous Decomposition of 0.1 Percent MMH.

TABLE 3. ESTIMATED HALF-LIVES[a] OF HYDRAZINE FUELS IN NATURAL WATERS

Fuel	Initial Concentration (millimolar)	Assay	Pond Water (Days)	Seawater (Days)
			mean ± std dev	mean ± std dev
MMH[e]	19.0	color[b]	13.1 ± 1.1, n=6	13.1 ± 2.2, n=6
	9.5	color[b]	18.0 ± 2.3, n=6	24.1 ± 8.8, n=6
UDMH[e]	13.1	color[c]	22.2 ± 6.9, n=4	12.6 ± 2.8, n=4
	6.5	color[c]	16.3 ± 6.9, n=4	12.6 ± 1.1, n=3
	6.5	MS[d]	8.8 n=1	4.7 n=1
A-50[f]				
Hz[g]	1.8	color[b]	8.3 ± 0.6, n=5	
UDMH[g]	0.9	color[c]	7.3 ± 1.0, n=5	

[a] Results are expressed as pseudo-first-order rate half-lives determined by linear regression of natural logarithm (Fuel) versus time.

[b] Fuel assayed by PDAB colorimetry.

[c] Fuel assayed by TPF colorimetry.

[d] Fuel assayed by GC/MS.

[e] Studies performed in stoppered glass reagent bottles, acid-washed.

[f] Studies performed in open glass reagent bottles, acid-washed.

[g] Component of A_{50}. Single sample.

3. Unsymmetrical Dimethylhydrazine Decomposition.

When studied in stringently cleaned and stoppered vessels, the aqueous decompostion rates observed for UDMH in natural waters are comparable to MMH's rate (Table 3, Figure 3). One study performed with Aerozine 50 (50 percent hydrazine, 50 percent UDMH by weight) suggests a slightly faster rate, but this may reflect volatilization losses from unstoppered vessels.

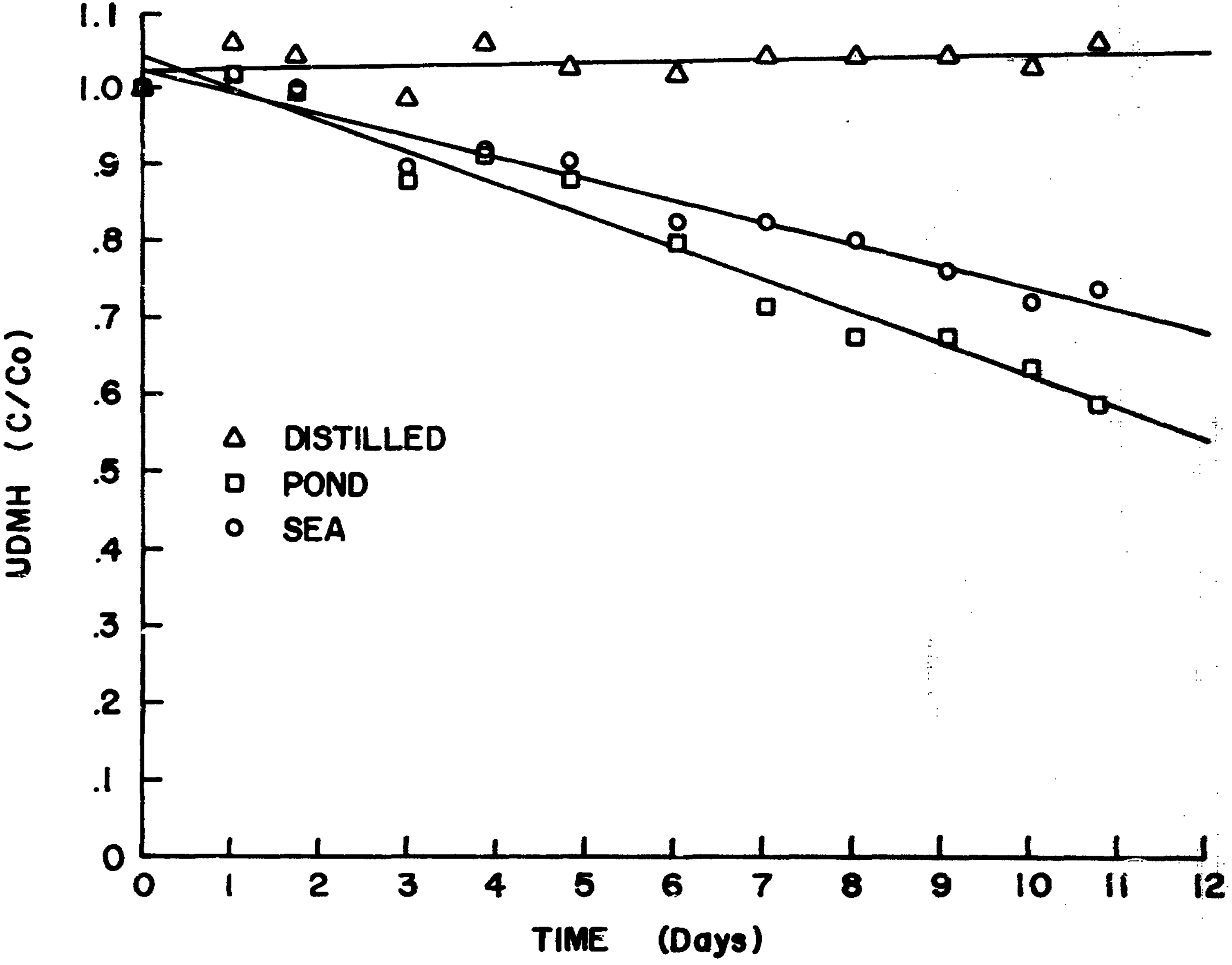


Figure 3. Aqueous Decomposition of 0.1 Percent UDMH.

To more accurately extrapolate the aqueous half-lives of UDMH and to characterize the decomposition products, the low concentration studies (6.5 millimolar UDMH) were extended to over 30 days (about 2 half-lives or 70-80 percent decomposition). In these runs, the fuel degradation time course appeared logarithmic (Figure 4) and a good statistical regression of the logarithmic time course was obtained (Figure 5). These half-lives of about 2 weeks did not differ in either ponds or seawaters. However, GC/MS courses showed the actual degradation rate of UDMH to be twice as fast, or on the order of 5-9 days (Table 3). This discrepancy is caused by a lack of specificity with the colorimetric assays. It has been shown that a major decomposition product of the hydrazine fuels, the hydrazine hydrazone, positively interferes in each respective colorimetric assay. For MMH this interferent in the PDAB assay is formaldehyde monomethylhydrazone (FMH, II). For UDMH in the TPF procedure, formaldehyde dimethylhydrazone (FDH, IV) is the positive interferent (Figure 6).

CH_3HNH_2 (I) MMH	$CH_3NHN{=}CH_2$ (II) FMH
$(CH_3)_2NNH_2$ (III) UDMH	$(CH_3)_2NN{=}CH_2$ (IV) FDH

This laboratory has determined that these hydrazones have an absorptivity equal to that of the parent hydrazine in each respective assay. Therefore, the conversion of UDMH to FDH is not detected by the TPF colorimetric procedures.

B. SOIL PERCOLATION AND ADSORPTION

1. Soil Percolation

Soil leaching results shown in Table 4 indicate that the hydrazine family of fuels interacts strongly with all natural soils. It is surprising to note the recovery differences between cleaned sand and VAFB soil, which itself is greater than 99 percent sand.

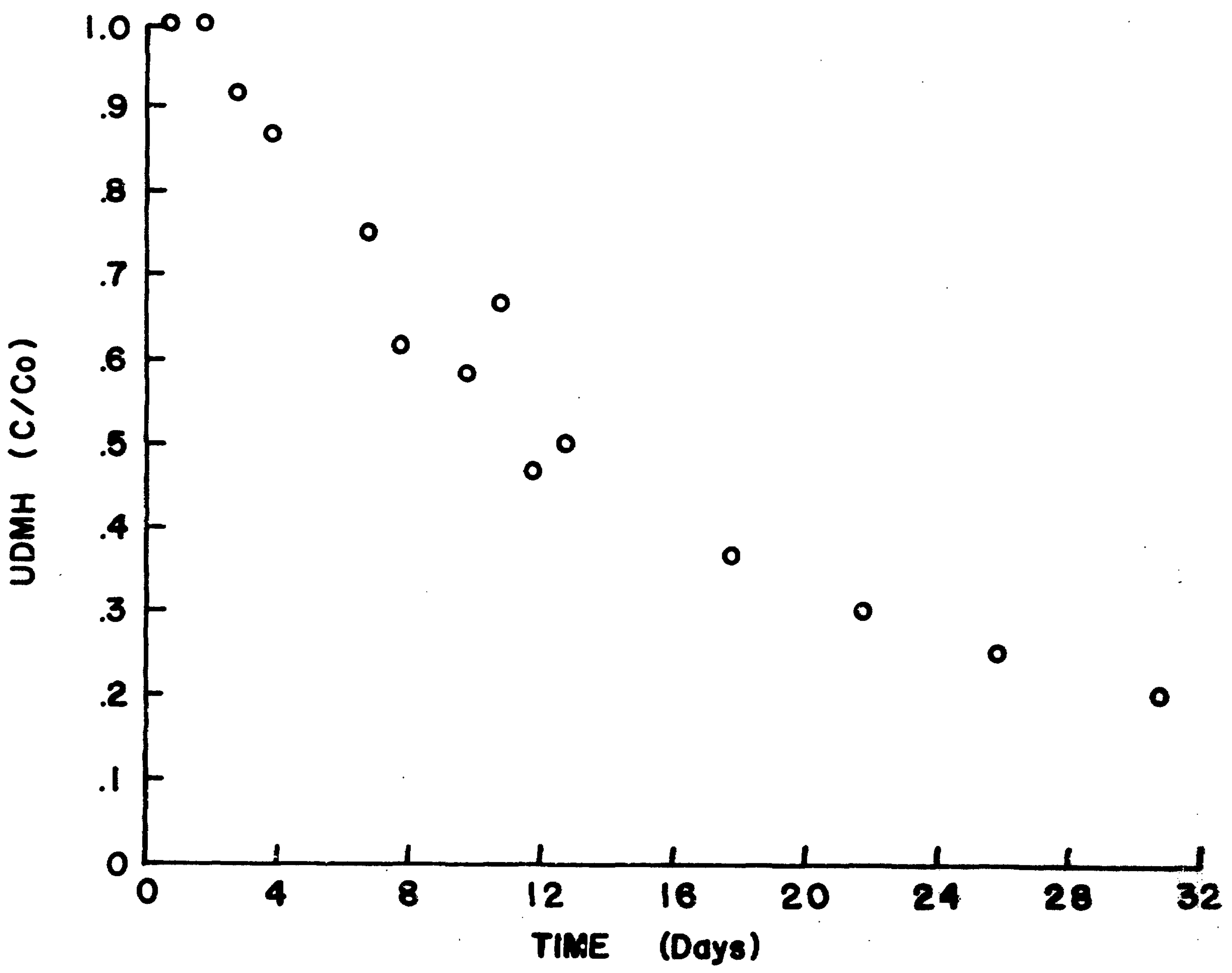


Figure 4. Aqueous Decomposition of 0.05 Percent UDMH in Seawater.

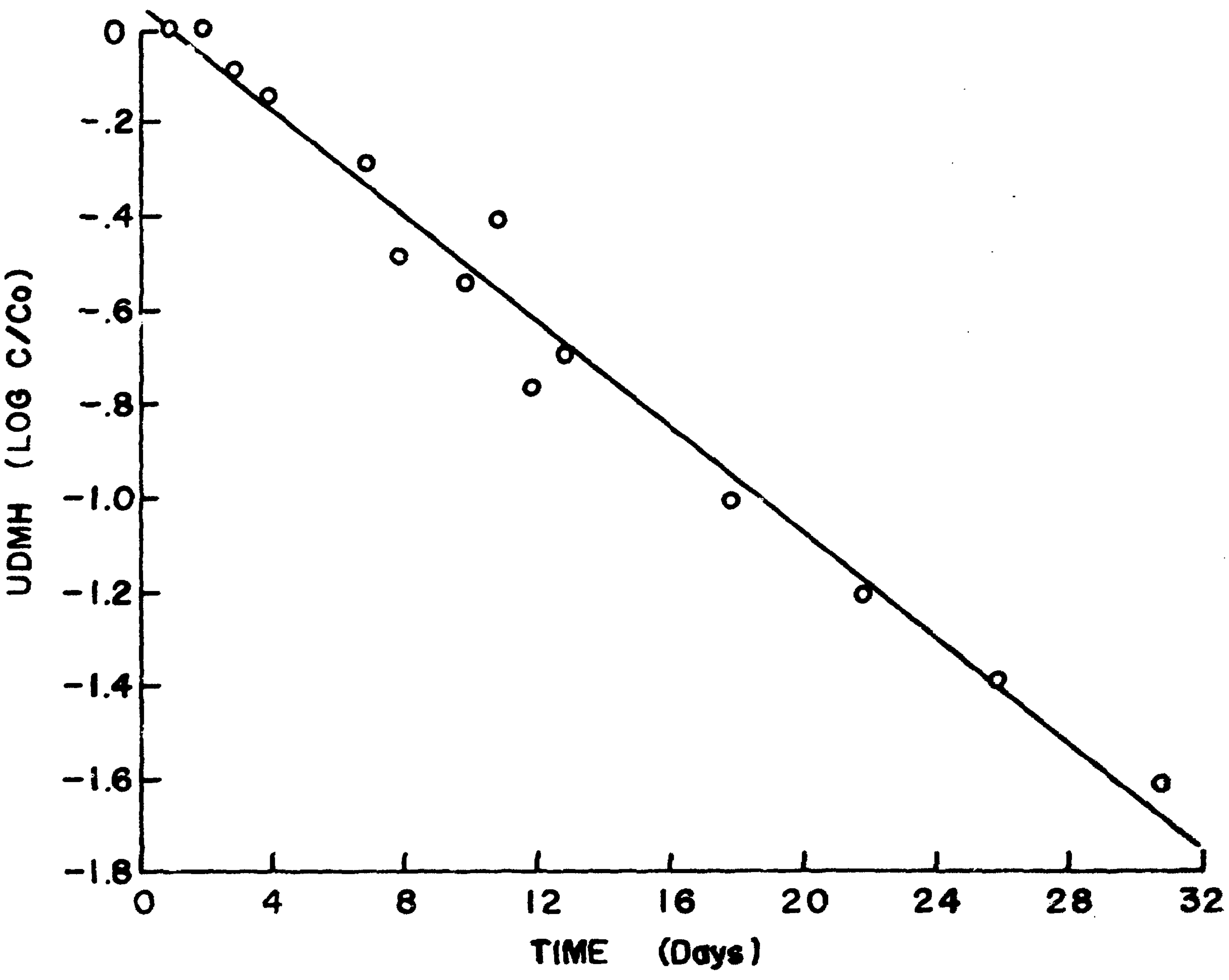


Figure 5. Logarithmic Regression of 0.05 Percent UDMH in Seawater.

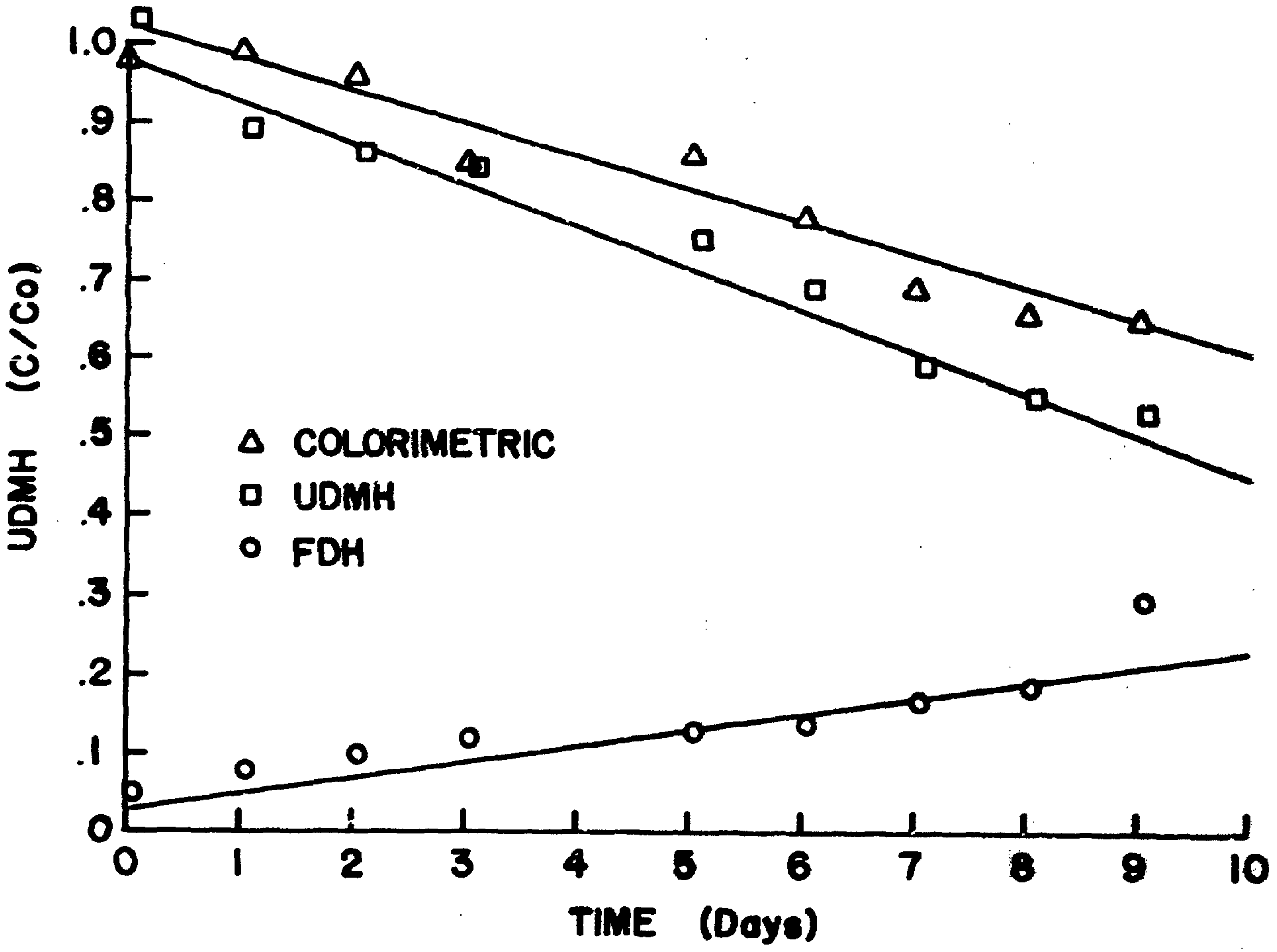


Figure 6. Comparison of the Colorimetric and GC/MS Analyses of UDMH in Pond Water.

TABLE 4. PERCENTAGE[a] OF FUEL RECOVERED FROM SOIL COLUMNS

Soil	Fuel Hz	 MMH	 UDMH
Sand	89.1 ± 0.4	86.9 ± 0.7	99.9 ± 0.1
VAFB	1.6 ± 0.1	5.5 ± 1.7	42.5 ± 1.5
Organic	1.3 ± 0.6	6.5 ± 0.3	21.9 ± 1.8
Clay (10%)[b]	7.6 ± 2.0	6.3 ± 1.6	7.2 ± 0.8

[a] Values are expressed as the average result of two soil columns plus/minus one-half the range of values.

[b] One part clay soil was mixed with nine parts pure sand to form a column which had good water percolation properties.

The difference between cleaned sand and a natural sandy soil is demonstrated graphically with UDMH in Figures 7 and 8. These composite graphs display both the cumulative total recovery of UDMH from each column (line graph) as well as the amount of fuel recovered in each successive 30-milliliter sample collection (bar graph). As shown in Figure 7, UDMH does not interact with cleaned sand; over 90 percent of the fuel is recovered in the first sample, with the remainder collected in the second. However, in the natural sandy soil, UDMH is adsorbed and then leaches through the column (Figure 8). No fuel is recovered in the first fraction and a broad band of UDMH slowly elutes. After 600 milliliters of water leaching (18 sample collections), less than 50 percent of the UDMH is recovered. These results highlight the great impact that trace soil components have on the environmental behavior of hydrazines.

Fuel interaction in natural soils reflects two general processes: (1) chemical decomposition of the fuel and (2) fuel adsorption to soil components. In VAFB and organic soil types, the fuel-soil interaction (Table 4) reflected the chemical reactivities of the respective fuels: Hz greater than MMH which is greater than UDMH. This may indicate that fuel decomposition is the major process in these soils. Supporting this trend are the significantly larger recoveries of UDMH as compared with Hz or MMH. Both Hz and MMH, having hydrogen bonded to each nitrogen atom, can decompose to form reactive diimide intermediates.

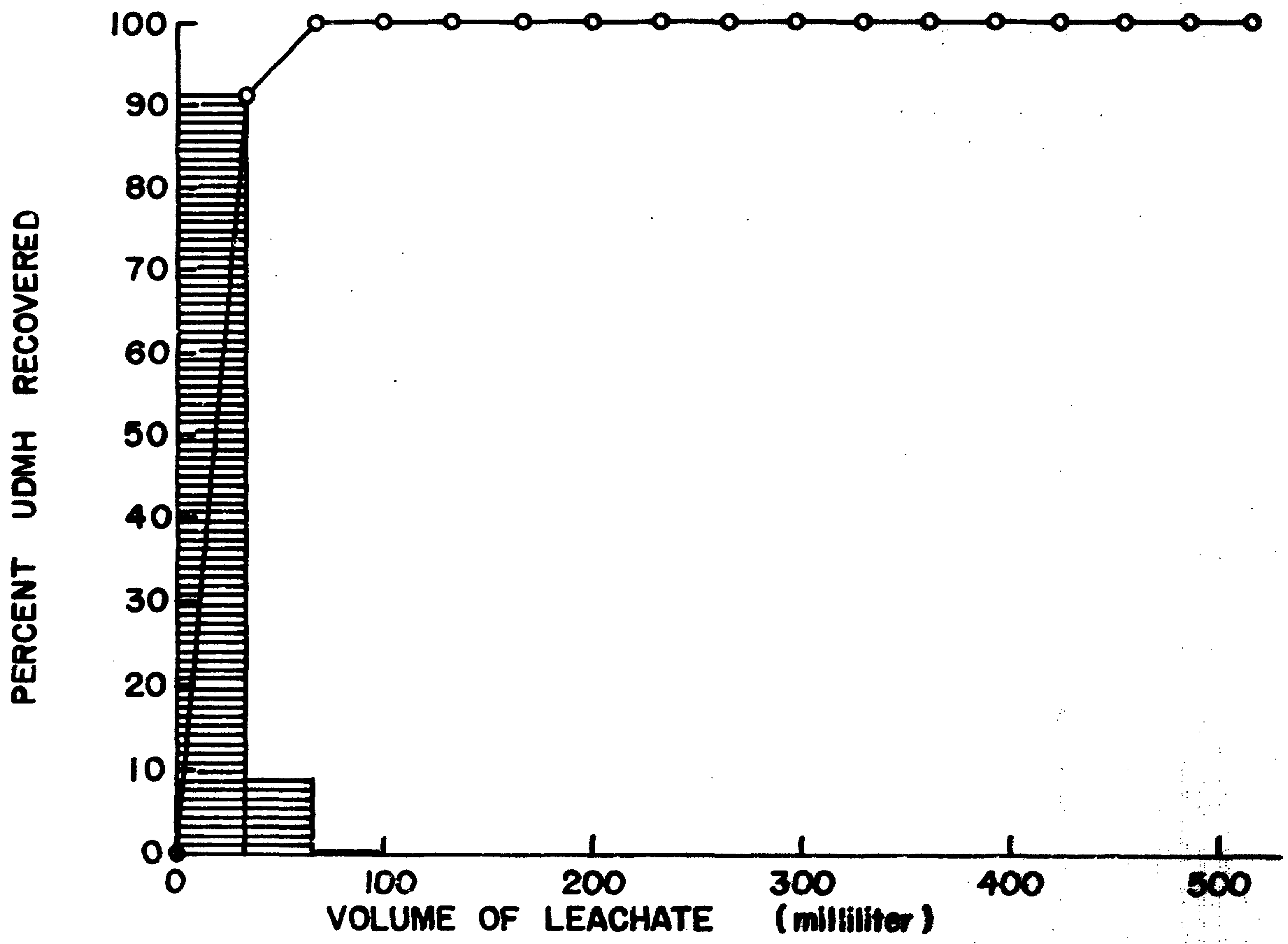


Figure 7. UDMH Percolation Through Cleaned Sand.

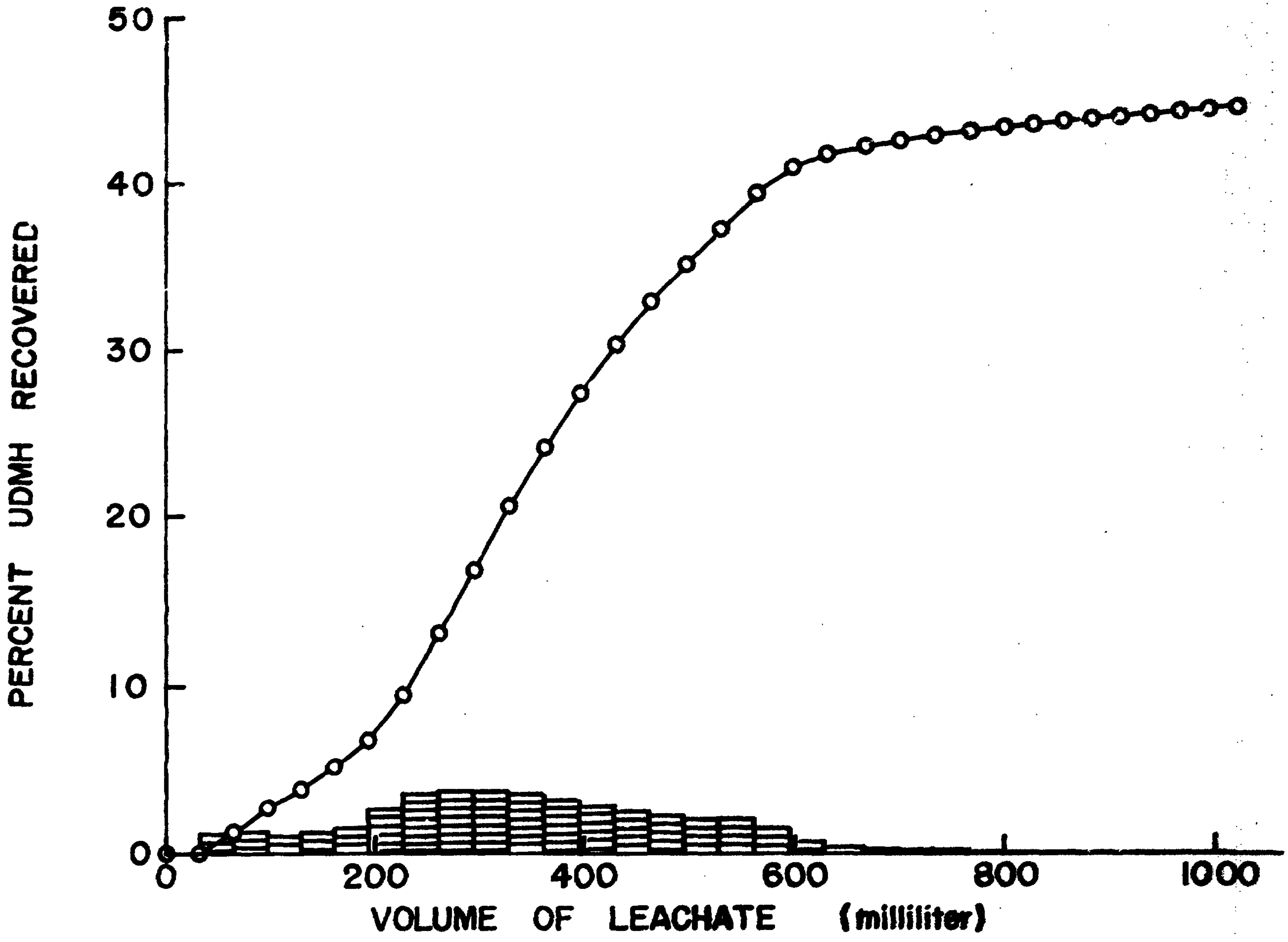
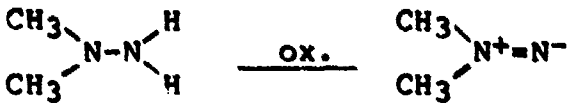


Figure 8. UDMH Percolation Through VAFB Soil.

R=H, Hz R=H, Diimide
R=CH3, MMH R=CH3, Methyldiimide

These unstable diimide products then rapidly decompose. Unsymmetrical dimethyl hydrazine (UDMH), with both methyl groups on one nitrogen, cannot readily form a diimide intermediate. Instead, the slower oxidative loss of two hydrogens occurs and produces a more stable diazene (Reference 22) product.



UDMH Diazene

In contrast, fuel interaction with clay soil did not show any specific trends - all fuel recoveries were of the same low magnitude (Table 4). The clay soil was the only acidic soil studied (Table 1) and the hydrazines are all very basic chemicals (Table 5).

TABLE 5. HYDRAZINE BASICITY

Fuel	pKa[a]	pKa[b]
Hz	8.00	7.95
MMH	7.91	7.87
UDMH	7.13	7.21

[a] pKa's determined in the Engineering and Services Laboratory by B. A. Braun.

[b] Reference 21.

These results indicate physical adsorption as the major process occuring between fuel and clay soil. Additionally, fuel decomposition would be minimized in an acidic medium (Reference 13).

The soil percolation tests are not designed to differentiate between decomposition and adsorption processes. Certainly both processes occur in all soils and each will be greatly influenced by specific soil components. However, these percolation studies do show that regardless of the hydrazine type, fuel migration through all natural soils is slow and limited.

2. Soil Adsorption

These studies attempted to determine what roles chemical degradation and physical adsorption played in fuel-soil interaction. As described in Section II, "adsorbed fuel" was calculated as the difference between fuel solution concentrations before and after soil mixing. This calculated value actually represents both physical adsorption and chemical degradation of the fuel during soil mixing. The amount of fuel physically adsorbed to the soil is more accurately measured as that fuel which is acid extractable from the soil after fuel-soil mixing. The extent of fuel degradation occurring during the fuel-soil mixing phase can then be estimated as the difference between the "adsorbed" and "extracted" fuels. When soils are mixed with fuel solutions made up in 0.1 N HCl, there were no fuel-soil interactions; i.e., no fuel was adsorbed or degraded during the soil mixing.

The results of these adsorption studies are listed in Table 6. The data again show no fuel interaction with clean sand (as in the percolation studies) but strong effects in all natural soils. While the results are variable, several trends are noticeable in fuel-natural soil interactions. First, all fuels interact the strongest with clay type soils. This interaction appears to be mainly physical adsorption for Hz and MMH, while UDMH is both adsorbed and chemically transformed. Thus, large percentages of the initially adsorbed Hz and MMH fuels can be recovered by acid extraction. Second, Hz and MMH tend to interact more strongly in all soil types than UDMH - again reflective of their greater reactivities.

Overall, these studies demonstrate the complexity of the fuel-soil interaction. There is no single dominating process; both chemical decomposition and physical adsorption are important in all fuel-soil interactions.

TABLE 6. FUEL (v/v) BEHAVIOR IN SOIL ADSORPTION STUDIES

SOIL	FUEL[a]	ADSORBED[b]	EXTRACTED[c]	NONRECOVERED[d]
Sand	Hz	1	2	-
VAFB	Hz	58	44	14
Organic	Hz	53	25	28
Clay[e]	Hz	77	59	18
Sand	MMH	0	3	-
VAFB	MMH	51	46	5
Organic	MMH	46	26	20
Clay[e]	MMH	73	64	8
Sand	UDMH	0	5	-
VAFB	UDMH	31	20	11
Organic	UDMH	26	15	11
Clay[e]	UDMH	80	30	50

[a] Initial fuel solution was 0.002 percent (v/v).

[b] Percentage of fuel either decomposed or adsorbed during soil-fuel mixing.

[c] Percentage of fuel extractable from soil with 0.1N HCL.

[d] Fuel percent difference between adsorbed/decomposed and that extracted - may indicate amount of fuel decomposed.

[e] Clay soil was not diluted with pure sand in these studies.

SECTION IV

CONCLUSION

Hydrazines are effective rocket fuels with a long and successful history. As a major user of such energetic and toxic fuels, the Air Force has a concerned interest in both personnel safety and environmental protection. However, accidental spills may release hydrazines into air, water, and soil phases. As part of a larger Air Force effort to assess the environmental effect of such events, the aqueous half-lives of monomethylhydrazine and unsymmetrical dimethylhydrazine were determined.

The fate of a chemical in an aqueous environment is determined by diverse processes: degradation (chemical and biological), phase transfer (volatilization and sedimentation), and dilution or dispersion. This project focused on the uncatalyzed aqueous decomposition rates; biological and phase transfer losses were minimized through water sample filtration and closed experimental vessels. Thus, the aqueous half-lives of 10-14 days are very conservative and represent "worst case" situations. Despite their energetic properties, hydrazines are remarkably stable in uncatalyzed aqueous solutions.

The "real world" situation, however, is not as simple or stable. Volatilization losses from solution can be significant (Reference 17) and atmospheric oxidation rates are much faster, on the order of hours (References 9, 10, 11, and 12). Also, aerobic biodegradation proceeds in waters having hydrazine fuel concentrations less than 2 mg/l (Reference 20) and this is a significant removal process after sufficient fuel dilution occurs. Other investigators have reported enhanced aqueous oxidation rates due to trace metal ion catalysis (References 13, 15, 16, and 17), aeration (Reference 19), organic matter content (Reference 14), temperature (References 13 and 14), and pH (References 13 and 16). While all these factors combine to form the complexity of the "real world" situation, the results of this study and others indicate that aeration and dispersion processes will determine the aqueous persistence of hydrazine fuels.

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