

AD-A082 674

BATTELLE COLUMBUS LABS ON
EVALUATION OF THE ENVIRONMENTAL FATE OF MUNITION COMPOUNDS IN S--ETC(U)
JUN 79 V O HALE, T B STANFORD, L G TAFT

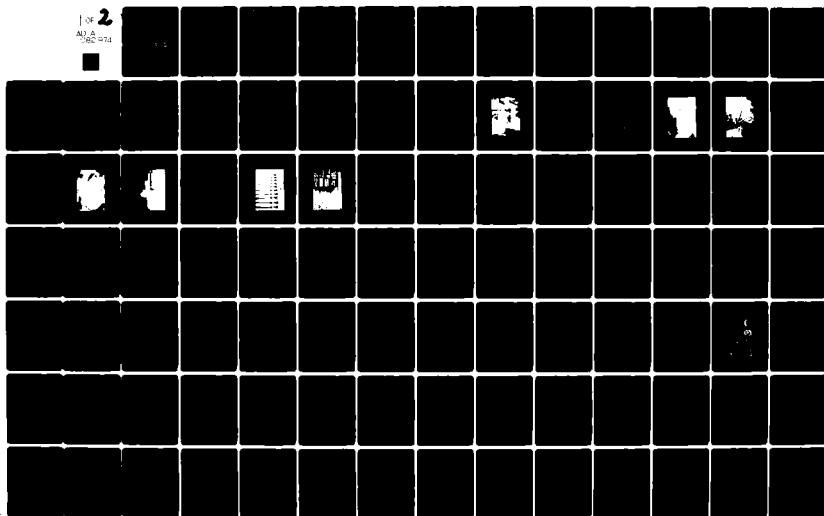
F/G 19/1

DAMD17-76-C-6065

NL

UNCLASSIFIED

1 of 2
AD-A
082 674



PHOTOGRAPH THIS SHEET

ACA082874

DTIC ACCESSION NUMBER

II

LEVEL

12

INVENTORY

Battelle Columbus Laboratories, Columbus, OH

"Evaluation of the Environmental Fate of Munition Compounds in Soil"

DOCUMENT IDENTIFICATION

Final Rpt.

Contract No. DAMD17-76-C-6065

June 1979

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

DISTRIBUTION STATEMENT

ACCESSION FOR	
NTIS	GRA&I ☒
DTIC	TAB ☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION /	
AVAILABILITY CODES	
DIST	AVAIL AND/OR SPECIAL
A	

DISTRIBUTION STAMP

DTIC
ELECTE
S APR 9 1980 D
D

DATE ACCESSIONED

DATE RECEIVED IN DTIC

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-DDA-2

ADA082874

AD _____

EVALUATION OF THE ENVIRONMENTAL
FATE OF MUNITION COMPOUNDS IN SOIL

FINAL REPORT

Verle Q. Hale, Thomas B. Stanford,
and Lee G. Taft

JUNE 1979

Supported by
U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-76-C-6065
Project Officer - Eugene P. Meier
U.S. Army Medical Bioengineering Research
and Development Laboratory

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

DOD DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited

The findings in this report are not to be construed as an
official Department of the Army position unless so designated
by other authorized documents.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Evaluation of the Environmental Fate of Munition Compounds in Soil		5. TYPE OF REPORT & PERIOD COVERED Final Report 30 June 1976 to 31 March 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Verle Q. Hale Thomas B. Stanford Lee G. Taft		8. CONTRACT OR GRANT NUMBER(s) DAMD 17-76-C-6065
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Laboratories Columbus, Ohio 43201		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62720A.3E162720A835.00.033 62720A.3E162620A835.00.033
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Medical Research & Development Command Fort Detrick, Frederick, Maryland 21701		12. REPORT DATE June 1979
		13. NUMBER OF PAGES 108
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U.S. Army Medical Bioengineering Research and Development Laboratory Fort Detrick, Frederick, Maryland 21701		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		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

EXECUTIVE SUMMARY

A study was conducted to monitor the downward movement of Tetryl (N-methyl-N,2,4,6-tetranitroaniline), RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine), and TNT (2,4,6-trinitrotoluene) and their transformation products through intact soil columns. Lysimeters were constructed by pressing steel pipes (36-inch (91.4 cm) diameter) into the ground to a depth of 5 ft (152 cm) and then withdrawing them to preserve intact soil columns. The munition compounds were mixed into the surface layer of the soils; grass was planted; and the lysimeters were irrigated on a regular schedule.

Periodic soil water samples were taken by applying vacuum to ceramic cup sampling tubes installed at depths of 6, 18, 30 and 60 inches (15, 46, 76, and 152 cm). Periodic soil samples were taken at selected intervals in the soil profiles with an Oakfield sampler. The water and soil samples were analyzed for the munition compounds and their known transformation products.

A concurrent study was made using soil columns 2 inches (5 cm) in diameter by 24 (61 cm) inches in length taken from the same soils. These columns were treated with munition compounds which were ring-labeled with ^{14}C . A primary objective of this experiment was to provide an early prediction of what should be expected in the large columns. These columns were irrigated on the same schedule as the large lysimeters. Two identical sets of columns were prepared. The leachate from the bottoms of one set was collected and analyzed for ^{14}C activity by liquid scintillation. When a significant level of activity was observed in these leachates, the soil columns were cut into 6-inch sections which were analyzed for munitions compounds and transformation products. The duplicate set of small columns was equipped with barium hydroxide traps and propylene carbonate traps to collect $^{14}\text{CO}_2$ and ^{14}C -organic compounds that might volatilize from the soil surface. Air was constantly flushed through the headspace of the columns and passed through the traps. Periodic samples from these traps were assayed for ^{14}C activity.

These studies were continued for a period of 6 months. Results showed very little detectable movement of the munition compounds or their known transformation products in this time frame. These compounds were detectable by HPLC as low as 50 ppb, but the areas under the curves of the graphs were too small to be reliably measured below 200 ppb. Separate studies indicated that this may be the combined result of soil fixation and limited water solubilities of the munition compounds. Significant amounts of the compounds were not recovered in either the water or the soil extract during partition experiments, an indication of fixation on the soil that was not reversible with the extraction solvents used.

A solubility study showed that the solubilities of munition compounds in water were not as high as reported in the literature.

Some evidence of migration and degradation was seen in the ^{14}C study. However, migration was slow and appeared late enough in the study to suggest that such an experiment should be continued for longer than 6 months. Carbon-14 activity was detected in both the column effluents and in the trapped air samples from the soil surface but the identity and concentration of these compounds or their transformation products were not determined.

High performance liquid chromatography (HPLC) analyses of the soil samples produced peaks for compounds that were neither the munition compounds nor their known transformation products. These unknowns are believed to have been derived from the munition compounds since they were not observed in analysis of untreated soils.

In the early part of this study, an attempt was made to monitor movement of the compounds in the soil profile by monitoring migration of organic carbon in the soil and organic carbon, nitrate and nitrite in the soil water. These analyses were not useful due to interference from high background levels of these parameters in the soil profiles.

The objectives of this study were only partly achieved in that, while evidence of both degradation and migration was seen in the ^{14}C study, the quantities of the munition compounds involved were too low to allow quantification. There was some evidence of chemical transformation in the basic study, but the concentrations of transformation products could not be quantified. Thus, it was not possible to maintain mass balances. Identification of unknown transformation products would have required additional methods of analysis but the quantities of unknowns which could have been recovered were insufficient for this purpose.

While the ^{14}C study results were not definitive in that they were designed to only indicate trends and not rates, these results were more meaningful than were those of the basic study.

Recommendations for similar studies are that small scale experiments utilizing radioactively labeled compounds be conducted before progressing to the more expensive and difficult studies with large lysimeters.

FOREWORD

This research was funded by the Department of the Army, U.S. Army Medical Research and Development Command.

The work was conducted during the period of August 16, 1976, to April 30, 1978, at the laboratories of Battelle's Columbus Laboratories in Columbus and West Jefferson, Ohio. The Principal Investigator was Dr. Verle Q. Hale with Dr. Thomas B. Stanford responsible for most of the analytical work and Dr. Lee G. Taft responsible for the greenhouse work and the nitrate, nitrite, and organic carbon analyses.

The study was under the general direction of Dr. Eugene P. Meier, U.S. Army Medical Bioengineering Research and Development Laboratory, to whom, as Project Officer, we express our appreciation for his understanding and patience with the many operational and analytical problems encountered.

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	2
FOREWORD	4
INTRODUCTION	13
Experimental Approach	13
Basic Study	14
¹⁴ C Study	15
METHODS	15
Lysimeters	15
Basic Study	15
Soil Selection	15
Brookston Soil	16
Bennington Soil	16
Genesee Soil	16
Princeton Soil	16
Soil Core Acquisition	17
Lysimeter Construction	17
Lysimeter Stabilization	23
Treatment of Lysimeters	23
Water Sampling	23
Soil Sampling	24
¹⁴ C Study	27
Soil Core Acquisition	27
Column Structures	27
Column Stabilization	30

TABLE OF CONTENTS
(Continued)

	<u>Page</u>
Treatment of Columns	30
Water Sampling	32
Trap Sampling	32
Soil Sampling	32
Analytical	32
Material	32
Instrumentation	34
Preparation Procedures	34
Sample Preparation	34
Water Sample Preparation (HPLC)	35
Water Sample Preparation (Scintillation Counting	35
Ba(OH) ₂ Trap Sample Preparation	35
Propylene Carbonate Trap Sample Prepara- tion	35
Sample Analyses	36
Quality Control for HPLC Analyses	36
Blank and Spiked Samples	36
Standard Curves for HPLC Analyses	36
Standard Curves for HPLC Analyses	36
HPLC Analyses	37
Liquid Scintillation Counting	38
Total Organic Carbon	38
Water	38
Soil	38

TABLE OF CONTENTS
(Continued)

	<u>Page</u>
Nitrate	38
Nitrite	38
Partition Experiment	38
Solubility Experiment	39
Solubility in Water	39
Solubility in Et ₂ O	40
Recovery Experiment	40
Results	40
Analytical	40
Quality Control for HPLC Analyses	40
Blank and Spiked Samples	40
Standard Curves for HPLC Analyses	40
Recovery Study	44
Solubility Experiment	44
Solubility in Water	44
Solubility in Diethyl Ether	50
Basic Study	51
Soil Samples	51
Water Samples	51
¹⁴ C Study	51
Water Samples	51
Ba(OH) ₂ and Propylene Carbonate Trap Samples	59
Soil Samples	59

TABLE OF CONTENTS
(Continued)

	<u>Page</u>
Water Sample (HPLC) Analysis	59
Other Analyses	59
Total Organic Carbon	59
Nitrate and Nitrite	59
Partition Experiment	59
Discussion	79
Objectives of Analysis	79
¹⁴ C Study	79
Water Samples	79
Trap Samples	82
Basic Study	83
Water Samples	83
Soil Samples	84
Solubility Study	85
Total Organic Carbon, Nitrate and Nitrite Analyses	87
Partition Experiment	87
Conclusions	88
Recommendations	90

APPENDIX A

MODEL STANDARD SOIL PROFILE DESCRIPTIONS OF THE SOIL SERIES USED IN THIS STUDY	91
---	----

LIST OF TABLES

	<u>Page</u>
Table 1. Approximate Weights Required To Press Lysimeter Pipes into the Soils and the Resulting Compaction	17
Table 2. Amount of ¹⁴ C-Labeled Munition Added to Each ¹⁴ C-Lysimeter	31
Table 3. Suspected TNT Metabolites and Source	33
Table 4. HPLC Analytical Parameters	37
Table 5. Wavelength of Maximum Absorbance and Molar Extinction Coefficients of Munition Compounds	37
Table 6. Typical Slope and Intercept Values for HPLC Standard Curves	44
Table 7. Recovery of Munition Compounds from Water and Soil Using Organic Solutions To Prepare Spiked Samples	49
Table 8. Recovery of Munition Compounds from Water Using Aqueous Solutions To Prepare Spiked Samples	49
Table 9. Water Solubility of Munition Compounds at 21°C	50
Table 10. Solubility of Munition Compounds in Diethyl Ether at Various Temperatures	51
Table 11. Tetryl Content of Soil Samples Collected from the Basic Study	52
Table 12. RDX Content of Soil Samples Collected from the Basic Study	53
Table 13. TNT Content of Soil Samples Collected from the Basic Study	54
Table 14. Tetryl Content of Water Samples Collected from the Basic Study	55
Table 15. RDX Content of Water Samples Collected from the Basic Study	56
Table 16. TNT Content of Water Samples Collected from the Basic Study	57

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 17. ^{14}C Activity of Water Samples Collected from the Tetryl Treatment of the ^{14}C Study	58
Table 18. ^{14}C Activity of Water Samples Collected from the RDX Treatment of the ^{14}C Study	58
Table 19. ^{14}C Activity of Water Samples Collected from the TNT Treatment of the ^{14}C Study	58
Table 20. ^{14}C Activity of Trap Samples Collected from the Tetryl Treatment of the ^{14}C Study	60
Table 21. ^{14}C Activity of Trap Samples Collected from the RDX Treatment of the ^{14}C Study	61
Table 22. ^{14}C Activity of Trap Samples Collected from the TNT Treatment of the ^{14}C Study	62
Table 23. Concentrations of Munition Compounds in Soils from Sacrificed ^{14}C Columns	63
Table 24. Concentrations of Munitions Compounds in Water Samples from ^{14}C Columns After 20 Weeks	65
Table 25. Total Organic Carbon in Soil Samples Collected from the Tetryl Treatment of the Basic Study	66
Table 26. Total Organic Carbon in Water Samples Collected from the Tetryl Treatment of the Basic Study	67
Table 27. Total Organic Carbon in Soil Samples Collected from the RDX Treatment of the Basic Study	68
Table 28. Total Organic Carbon in Water Samples Collected from the RDX Treatment of the Basic Study	69
Table 29. Total Organic Carbon in Soil Samples Collected from the TNT Treatment of the Basic Study	70
Table 30. Total Organic Carbon in Water Samples Collected from the TNT Treatment of the Basic Study	71
Table 31. Nitrate Content of Water Samples Collected from the Tetryl Treatment of the Basic Study	72
Table 32. Nitrite Content of Water Samples Collected from the Tetryl Treatment of the Basic Study	73

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 33. Nitrate Content of Water Samples Collected from the RDX Treatment of the Basic Study	74
Table 34. Nitrite Content of Water Samples Collected from the RDX Treatment of the Basic Study	75
Table 35. Nitrate Content of Water Samples Collected from the TNT Treatment of the Basic Study	76
Table 36. Nitrite Content of Water Samples Collected from the TNT Treatment of the Basic Study	77
Table 37. Partition Experiment Data	78
Table 38. Relationship Between Disintegration per Minute and Concentration of Pure ¹⁴ C-Labeled Compound .	80
Table 39. Radioactivity and Projected Concentrations of Intact Munitions in Princeton (TNT and RDX) and Genesee (TNT and RDX) Columns	81
Table 40. Recovery of Munition Compounds in Aqueous Samples at Concentrations Below 1 ppm	83

LIST OF FIGURES

	<u>Page</u>
Figure 1. Structures of the Munition Compounds Studied . .	14
Figure 2. Lysimeter Containing Intact Soil Core	18
Figure 3. Lysimeter Construction Details	20
Figure 4. Lysimeter Collection Tubes	21
Figure 5. Lysimeter Water Removal Vacuum System	22
Figure 6. Sampling Sleeve with Flange	25
Figure 7. Sketch of the Sampling Sleeve in Place	26
Figure 8. Open System Drainage Lysimeters for ^{14}C Study. .	28
Figure 9. Closed System Vacuum Lysimeters for ^{14}C Study. .	29
Figure 10. Percent Recovery of Spiked Water Samples	41
Figure 11. Percent Recovery of Spiked Soil Samples	42
Figure 12. Percent Deviations of Standard Solutions from Their Known Values Using HPLC Analyses	43
Figure 13. Standard Curve for Tetryl	45
Figure 14. Standard Curve for RDX	46
Figure 15. Standard Curves of TNT and Its Transformation Products	47
Figure 16. HPLC Chromatograms of Tetryl, RDX, and TNT and Suspected Transformation Products	48
Figure 17. Autoradiogram of Cross-Sections of ^{14}C Columns Showing the Distribution of ^{14}C Throughout the Soil	64
Figure 18. HPLC Chromatograms of Genesee TNT (26-Week Sample)	86

INTRODUCTION

In the manufacturing of almost any chemical, there are a number of process steps in which some of the raw materials or the finished product can escape from the process stream. This may occur as a result of equipment leaks, off-gas discharges or broken packages, equipment inadequacies or failure, carelessness, routine maintenance and housekeeping activities, or the repair, modification, or replacement of machinery. The result is that the soils within the production areas of U.S. Army ammunition plants have become contaminated with raw materials, munition compounds, and various waste materials. At low levels of soil contamination, they may be harmful to the local environment because of toxicity to vegetation and/or wildlife. Of special concern is the possibility that these materials may be transported from the immediate area of contamination to neighboring environments and thus increase the area of possible adverse effects. The most likely means of this transport is by surface or groundwater. The eroding action of surface water is an obvious way to move contaminants that are on or near the soil surface. Where such materials are buried or are incorporated in the soil, the transporting mechanism which may involve groundwater is less certain. At high levels of soil contamination, munition compounds can also constitute a potential fire and/or explosion hazard.

EXPERIMENTAL APPROACH

The objective of this research program was to determine the environmental fate of munition compounds in soils. The most important concern was to determine the persistence and potential for short-term translocation of the munition compounds and their possible transformation products downward through the soil profile to groundwater. The munition compounds studied were TNT (2,4,6-trinitrotoluene), Tetryl (N-methyl-N,2,4,6-tetranitroaniline) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). The structures of these compounds are diagramed in Figure 1.

These compounds were mixed into the surface layer of soils which were chosen to represent fine, medium, and coarse textured soils. Both an acidic and a medium texture basic soil were selected to provide a total of four soil types for this study. The soils chosen were Brookston silty clay loam (fine texture), Bennington silt loam (medium texture, acidic), Genesee silt loam (medium texture, basic), and Princeton fine sandy loam (coarse texture). See Appendix A for the soil profile descriptions. These soils represent different rates of internal drainage because of their range of textures and different abilities to fix compounds.

because of their range of organic matter and ion exchange capacities. Experts in soils and agricultural engineering were employed as consultants to help identify suitable soils, acquire the lysimeter columns, and establish the irrigation regimes.

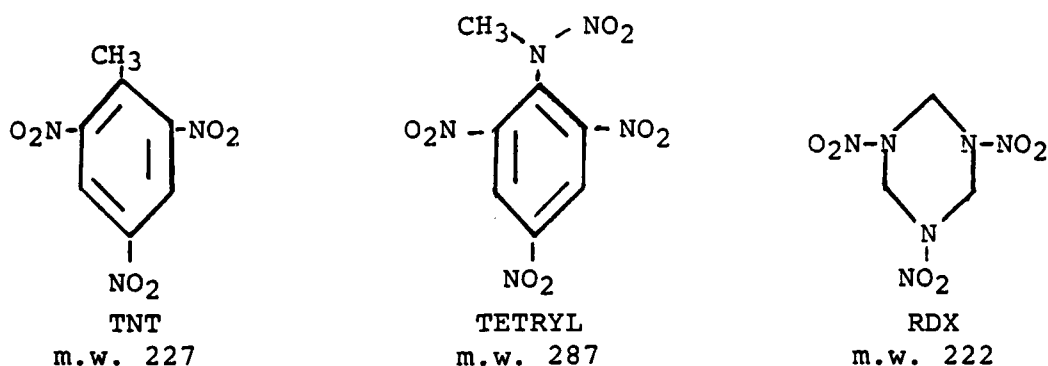


FIGURE 1. STRUCTURES OF THE MUNITION COMPOUNDS STUDIED

Basic Study

It was desired to conduct this study as much as possible on intact soil columns and, at the same time, maintain some control over weather conditions in order to assure that all treatments would be nearly identical in factors which might affect either the transformation or the translocation of the munition compounds. To accomplish both of these objectives, lysimeters were used in which intact soil columns were brought from the field into a shaded greenhouse where rainfall was excluded, temperature was controlled within optimum plant growing limits, and ambient humidity was maintained by allowing air flow from the outside.

The lysimeters were equipped with soil water samplers so that periodic water samples could be taken from various depths to follow any downward movement of the compounds. A constant vacuum was maintained on water collectors in the bottoms of the lysimeters to prevent a buildup of water with resultant anaerobic conditions. Following the additions of the munition compounds, the lysimeters were irrigated with deionized water (to simulate rain water) according to a water balance schedule worked out for each soil to assure that the lysimeters neither dried out nor became waterlogged. The movement of the compounds was monitored by periodically analyzing water and soil samples from the various depths throughout the length of the lysimeters. The samples were analyzed for the parent munition compounds and for all of the

known and suspected transformation products and impurities. The lysimeters were maintained and sampled for a period of 6 months.

¹⁴C Study

In order to predict rates of movement and to attempt to identify formation of transformation products, a concurrent pilot study was established using small columns and ¹⁴C-labeled munition compounds. Leachate from these columns was monitored for ¹⁴C activity and, in selected cases where such activity was found, the leachate was analyzed to attempt to characterize the labeled compound. The air from the tops of half of these labeled columns was also monitored for ¹⁴C activity to determine if volatile munitions compounds or degradation products were being lost from the columns. At the termination of the study, these columns were cut into sections and analyzed for munition compound distribution.

METHODS

LYSIMETERS

Basic Study

Soil Selection

The study required that four soils be chosen for use as drainage lysimeters to study the movement and transformation of three munition compounds in soil. The four soils were chosen to represent a range of pH, texture, and organic matter content that might be found in soils throughout the country. Soils were selected with the assistance of a consultant, Dr. George Hall, Agronomy Department, The Ohio State University. The general criteria for selection of soils were: (1) that they be deep enough to permit a 60-inch core to be taken, (2) that they be free of rocks and consolidated material which might inhibit subsequent soil sampling and water movement, and (3) that they be easily accessible to equipment used in the soil collection operation. After a soil and its location had been selected, an Oakfield sampler was used to ascertain profile depth and to collect soil samples for pH and textural determinations. The three soil cores were taken from within a 10 x 10 ft area. Model profile descriptions of the soils chosen are in Appendix A.

Brookston Soil. A Brookston silty clay loam (sicl) was chosen as the fine textured soil. The dominant characteristics of this soil are its high percentage of organic matter in the A and B horizons and its very poor internal drainage. The three Brookston cores were obtained from Battelle's property at West Jefferson, Madison County, Ohio. The site chosen was at the edge of a cultivated field which had been planted to soybeans the previous 2 yrs.

Bennington Soil. A Bennington silt loam (sil) was chosen as the acidic, medium textured soil. The Bennington series consists of light-colored, somewhat poorly drained soils that formed in clay loam or heavy loam glacial till of Wisconsin Age. The typical Bennington soil has a dark grayish-brown silt loam plow layer. The subsoil is more clayey than the plow layer. Internal drainage is restricted in this subsoil as indicated by the presence of mottling. The substratum consists of calcareous glacial till. The dominant character of this soil is its slow permeability in the subsoil and substratum. The three Bennington soil cores were obtained from the property of Carl E. Seliskar, Delaware County, Ohio. The site chosen was located in a pasture which had not received lime or fertilizer for at least 20 yrs.

Genesee Soil. A Genesee silt loam (sil) was chosen as being representative of an alkaline, medium textured soil. The Genesee series consists of light-colored, well-drained soils that formed in materials washed from high-lime Wisconsin till. The Genesee soils occupy flood plains throughout central Ohio. In a typical profile, the plow layer is a dark grayish-brown silt loam which is high in organic matter. It is underlain by loamy material that has little or no visible structure to indicate soil formation. The three Genesee cores were obtained from the Hartman farm in southern Franklin County, Ohio. The site chosen was an uncultivated area at the edge of a cultivated field which had a cropping history of corn.

Princeton Soil. A Princeton sandy loam (sl) was chosen as being representative of a coarse textured soil. The Princeton series consists of dark-colored, well-drained soils formed in thick deposits of coarse silt and fine sand of Aeolian origin. The typical Princeton soil has a brown, fine sandy loam A horizon, brown and yellowish-red sandy clay loam B horizons, and brown to strong brown stratified C horizons. The three Princeton cores were obtained from the Hartman farm in southern Franklin County, Ohio. The site chosen was an uncultivated area at the edge of a cultivated field with a previous cropping history of corn.

Soil Core Acquisition

The soil cores to be used as lysimeters in this study were obtained in a manner similar to that reported by Tackett et al. (1965). The consulting assistance of Dr. Glen Schwab of the Agricultural Engineering Department, The Ohio State University, was utilized in acquiring these cores. Steel cylinders (36 inches (91.4 cm) in diameter and 66 inches (168 cm) in length) were pressed into the soil to a depth of 5 ft (152 cm). This was accomplished by sequentially placing sections of steel plate on top of the cylinders. The object was to press the pipes into the soil and avoid breaking the column which would occur if they were driven in. The steel plate and the soil cores were manipulated with a 35,000-lb capacity forklift. The soil cores were removed from the profile by excavating the soil on one side of the cylinder, rocking the cylinder toward the excavated side to fracture the bottom of the soil column and then vertically lifting the cylinder containing the intact soil core (Figure 2). A conventional backhoe was used to excavate the soil adjacent to the cylinder. A tractor-trailer rig was used to transport the steel plate from site to site and to transport the soil cores to the greenhouse. Table 1 shows the approximate weight required to press the steel cylinders into each of the four soils and the approximate compactions which occurred.

TABLE 1. APPROXIMATE WEIGHTS REQUIRED TO PRESS LYSIMETER PIPES INTO THE SOILS AND THE RESULTING COMPACTION

Soil	Weight, pounds	Compaction, inches
Brookston (sicl)	52,000	6
Bennington (sil)	82,000	0
Genesee (sil)	38,500	2
Princeton (sl)	43,000	1

Lysimeter Construction

The lysimeters were constructed of round steel pipe 36 inches in diameter. The outside bottom edge of the pipe was beveled to about 30 degrees to facilitate penetration and to displace soil to the outside of the pipe. Four equally spaced 1-inch holes



FIGURE 2. LYSIMETER CONTAINING INTACT SOIL CORE

were cut in the pipe near the bottom edge to accommodate "J" bolts as a means of attachment for the bottom plate. Three equally spaced, 2.5-inch holes were cut in the pipe 4 inches above the beveled edge to serve as ports to insert water collection tubes. The top end of the pipe was fitted with two lifting brackets spaced 180 degrees apart. The metal pipes and bottom plates were wiped down before use with acetone to remove trace organics which could confuse analysis (Figure 3).

After the soil cores were obtained, bottom plates were attached and they were transported to Battelle's greenhouse facilities at West Jefferson, Ohio. The 12 cores were placed in one room and arranged in four rows according to soil type. Once inside the greenhouse, the soil columns were sealed at the interface of the lysimeter pipe and bottom plate with silicone rubber sealant and an irrigation regime of 2 inches per week was initiated. The surface 3 inches of soil from each of the 12 columns were removed, dried, and passed through a 1/4-inch screen. Water collection tubes were installed so their depths would be 6, 18, 30, and 60 inches (15, 46, 76, and 152 cm) below the soil surface in each lysimeter. The water collection tubes for the upper three depths were installed vertically. Three water collection tubes were installed at the 60-inch (152 cm) depth by inserting them horizontally through holes in the side of the lysimeter pipes. A 2-inch diameter barrel auger was used to drill holes from the soil surface to the desired depths and a slurry made from the cuttings was used to fill the void space between the collection tube and the outside of the hole. The water collection tubes consisted of porous ceramic cups cemented to steel access tubes of required lengths and were obtained from Soilmoisture Equipment Company (Series 1900).

Two separate vacuum systems were connected to the water collection tubes. One system was connected to the three water collection tubes whenever a water sample was desired (Figure 4). The other system, connected to the three collection tubes at the bottom of the lysimeter (60-inch (152 cm) depth), was under continuous vacuum and served as a means of removing water which had percolated through the soil column. The sample collection vacuum system consisted of 1/4-inch I.D., thick wall, red rubber tubing connected with polyethylene fittings. The water removal vacuum system was equipped with a 5-gallon glass carboy which served as a water trap between the horizontal collection tubes and the vacuum pump (Figure 5). The vacuum line from the tubes to the glass carboy consisted of 5/16-inch I.D., thick-walled amber latex tubing connected with glass fittings. The portion of the line from the glass carboy to the vacuum pump was red rubber tubing with polyethylene fittings. Vacuum at 25 inches Hg was maintained by a carbon vane vacuum pump.

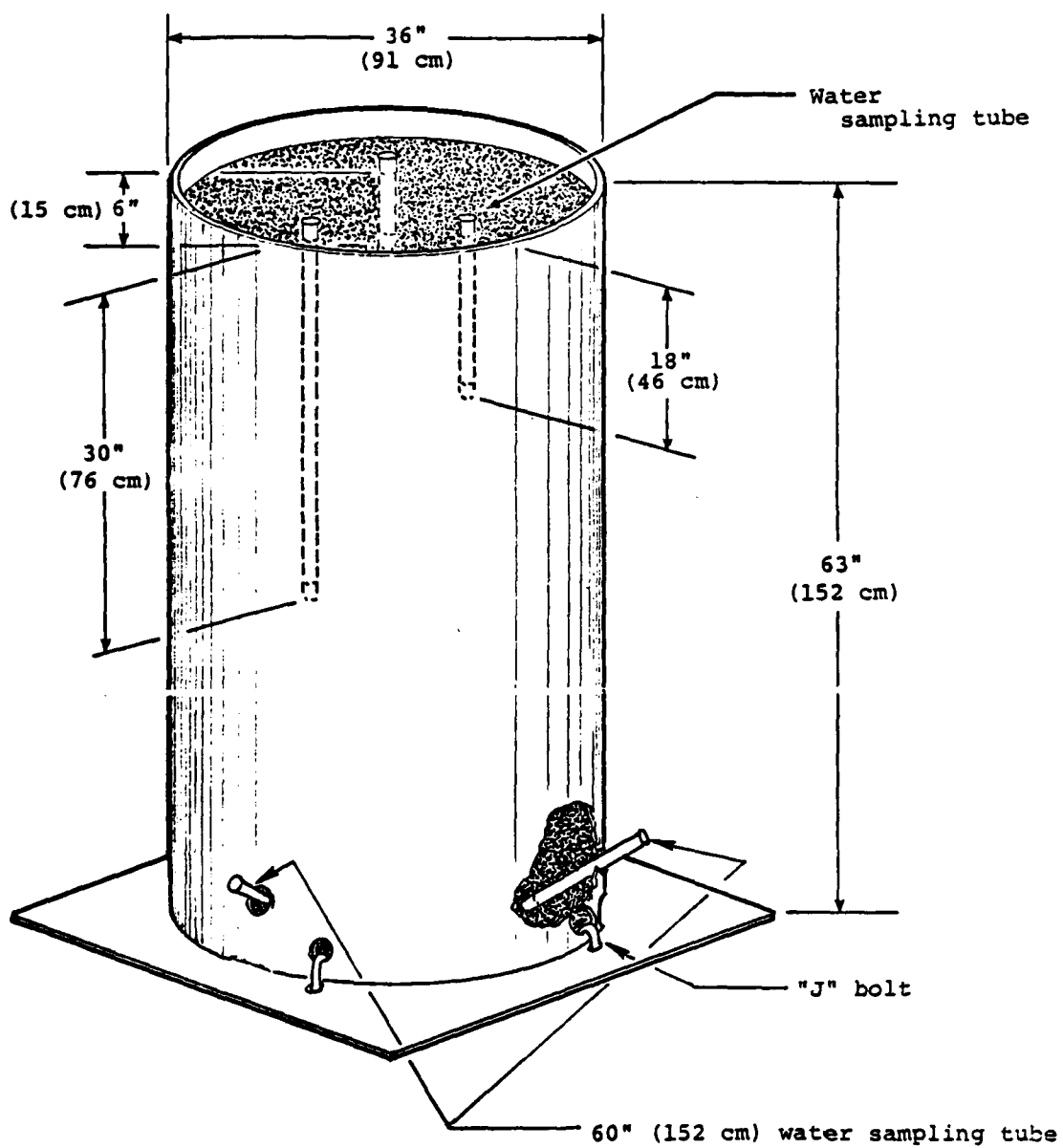


FIGURE 3. LYSIMETER CONSTRUCTION DETAILS

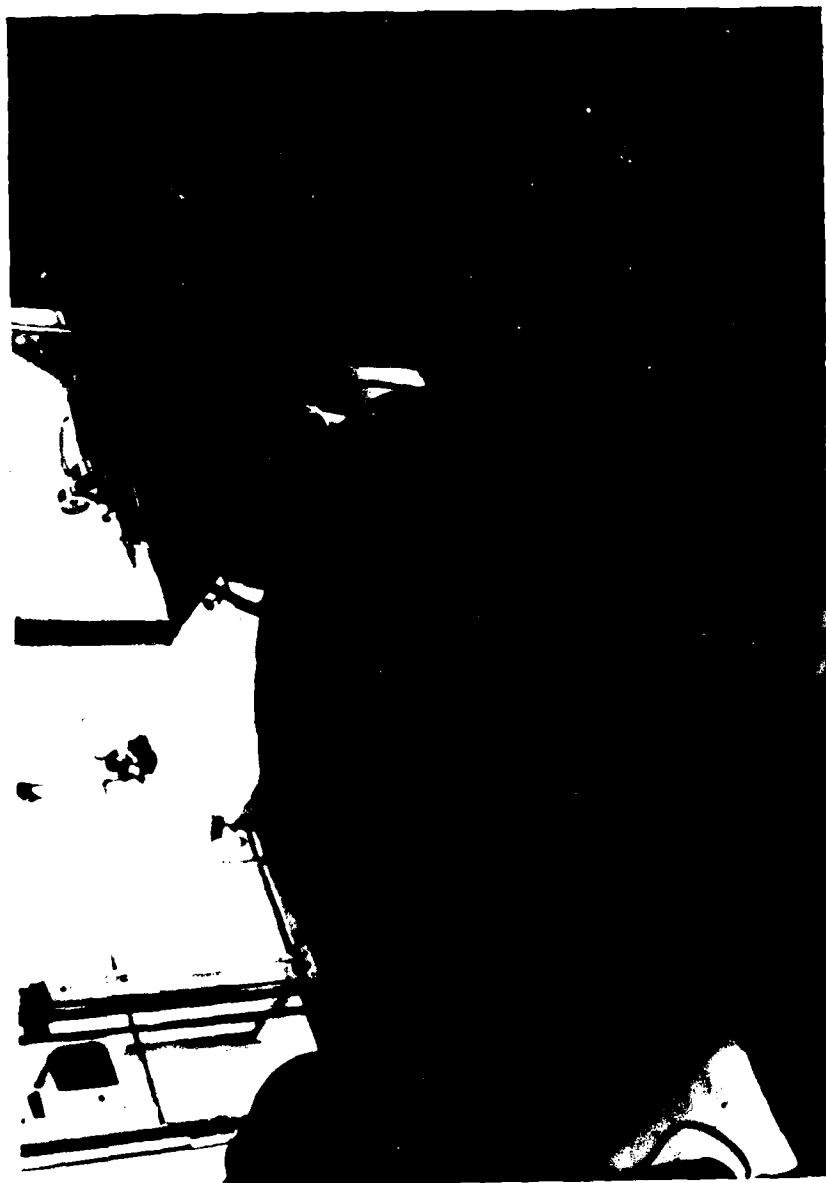


FIGURE 4. LYSIMETER COLLECTION TUBES

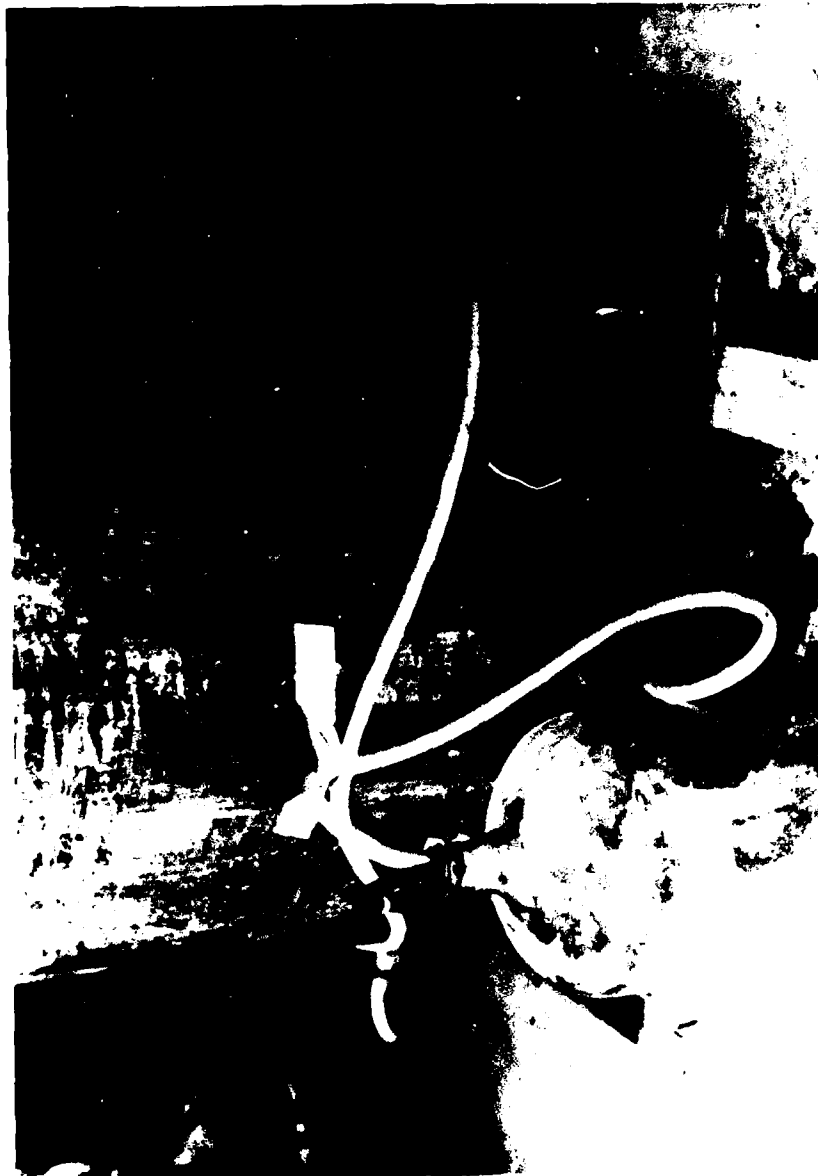


FIGURE 5. LYSIMETER WATER REMOVAL VACUUM SYSTEM

Lysimeter Stabilization

The soil cores were placed in the greenhouse the last week in December and the munition treatments were not applied until the last week in March. The intervening 3-month period was allowed for instrumentation and stabilization of the lysimeters. The initial irrigation rate of 2 inches per week was modified downward because of the limited permeability of the Bennington and Brookston soils. The final irrigation rate for each soil was determined by using various irrigation rates during the stabilization period and then empirically choosing the rate which allowed maximum water movement and a minimum of soil saturation. The final irrigation regime was chosen to be 1.0 inch per week given in three increments (Monday, Wednesday, and Friday) to the Genesee and Princeton soils and 0.5 inch per week given in three increments to the Bennington and Brookston soils. This irrigation regime was first employed on March 14, 1977, and was used throughout the course of the study. The temperature inside the greenhouse was maintained between 70 and 80°F. Relative humidity was not controlled but generally ranged from 60-80 percent. This schedule was worked out in consultation with Dr. George Taylor, Agronomy Department, The Ohio State University.

Treatment of Lysimeters

The top 3 inches of soil, which had previously been removed, dried and screened, was treated with 2 percent by weight of one of the three munition compounds: tetryl, RDX or TNT. The treated layer of soil consisted of 100 lbs of soil mixed with 2 lbs of munition compound. The treatment of the lysimeters was accomplished in the following manner: (1) the munition compound was divided into four portions weighing 0.5 lb each; (2) the soil was divided into four portions weighing 25 lbs each; (3) 1 day prior to treatment, one portion of compound and one portion of soil were transferred to a wide-mouth, 5-gal glass jar; (4) the munition-soil mixture was thoroughly mixed by placing the jar on a set of rollers inclined at about 30° and rotated for 20 min; and (5) four such jars of the munition-soil mixture were returned to the top of each lysimeter. The preceding treatments were made with tetryl on March 23, RDX on March 28, and TNT on March 30, 1977.

Water Sampling

Prior to actual treatment of the lysimeters with munition compounds, data relating to the initial nitrate and nitrite status

of the four soils were collected. This was accomplished by removing about 100 ml of water from each of the four water sampling tubes. The water samples were then refrigerated and transferred to the Battelle laboratory for analysis.

Water samples were collected the day of treatment and after each successive 2-wk interval following treatment for a period of 24 wks. The water samples were removed from the collection tubes by using a pipetting bulb attached to a length of glass tubing. On any given day, 16 samples (one compound x four soils x four depths) were collected. Each of the 16 samples was subdivided into two samples, one for organic analysis and the other for nitrate and nitrite analysis. All samples were then cooled and transported to the Battelle laboratory in an ice chest. At the laboratory, the samples were refrigerated at 4°C until analyzed.

Soil Sampling

The soil profile of each lysimeter was sampled 2 wks after treatment and at the end of every 4-wk interval thereafter through 26 wks. The 18- and 22-wk samples were not taken. The soil profile samples were a composite of three 60-inch (152 cm) deep soil cores which were separated into seven depth intervals: 0-4, 4-8, 8-12, 12-24, 24-36, 36-48, and 48-60 inches (0-10, 10-20, 20-30, 30-61, 61-91, 91-122, and 122-152 cm). Corresponding increments from the three cores were composited. These profile samples at the various depths were obtained by sequential insertion of an Oakfield sampler into the soil. Because of the high potential for contamination of the deeper soil samples from repeated insertion and withdrawal of the sampler through the highly concentrated (20,000 ppm) treated layer, an anti-sloughing device was used. This device was a sleeve with flange similar in design to the one reported by Smith et al. (1976) (Figures 6 and 7). After the soil samples were obtained, they were put in amber glass jars, transferred to BCL, and placed under refrigeration at 4°C until analyzed.

The final (26-wk) soil samples were taken in a somewhat different manner because of concern over potential contamination from the highly concentrated surface layer. Three sections of 2-inch diameter, thin-wall electrical conduit were driven into each lysimeter to a depth of 5 ft by repeated hammering with a post driver. A machined cutting tip was attached to the end of the conduit reducing the diameter of the soil core by 1/8 inch which facilitated removal of the soil core from the conduit. The conduit containing the soil core was removed from the lysimeter by the use of a 1000-lb capacity, mechanical platform jack. Once removed, the soil cores were extracted from the conduit by applying pressure to the bottom end of the soil core. Thirty-six such



FIGURE 6. SAMPLING SLEEVE WITH FLANGE



FIGURE 7. SKETCH OF THE SAMPLING SLEEVE IN PLACE

soil cores were obtained from the 12 lysimeters. The three cores from each lysimeter were separated into the seven depth intervals previously mentioned and were subsequently composited by soil depth interval.

C¹⁴ Study

This study involved the use of 24 soil cores (2-inch diameter x 24 inches long [5 x 61 cm]). Twelve of the 24 soil cores were used as an open system and the remaining 12 were used as closed system lysimeters. The open system consisted of 12 soil cores each contained in a length of 2-inch, thin-wall electrical conduit, the lower end of which was inserted in a Buchner funnel which, in turn, was inserted in a 500-ml suction flask (Figure 8). The suction flasks were wrapped in aluminum foil to exclude light which could permit photodegradation and algal growth. The closed system was constructed in the same manner except that the top of the column was sealed with a two-hole rubber stopper which was connected to a vacuum pump through a series of gas washing bottles to scrub air flushed through the head space (Figure 9).

Soil Core Acquisition

Six 2-inch diameter cores of each of the four soils used in the Basic Study were obtained by manually driving 27-inch (68 cm) sections of thin-wall electrical conduit into the soil to a depth of 2 ft (61 cm). A post driver was used to drive the conduit into the soil and it was removed by excavating the soil on one side of the conduit. The bottom end of the conduit was fitted with a beveled cutting tip which reduced the diameter of the soil core by 1/8 inch. This was necessary to reduce the friction between the soil and interior wall of the conduit in order to minimize compaction in the soil core. Once the soil cores were obtained, the ends were capped and they were transported to the greenhouse along with the large soil cores.

Column Structures

Once inside the greenhouse, the bottom inch (2.5 cm) and top 3 inches (7.6 cm) of soil were removed from each core. The top soil sample was air dried and passed through a 1/4-inch screen. The bottom cavity was filled with silica sand and a ceramic Buchner funnel containing a 1/4-inch layer of glass wool was placed over the bottom end of the soil core. Three of the six cores

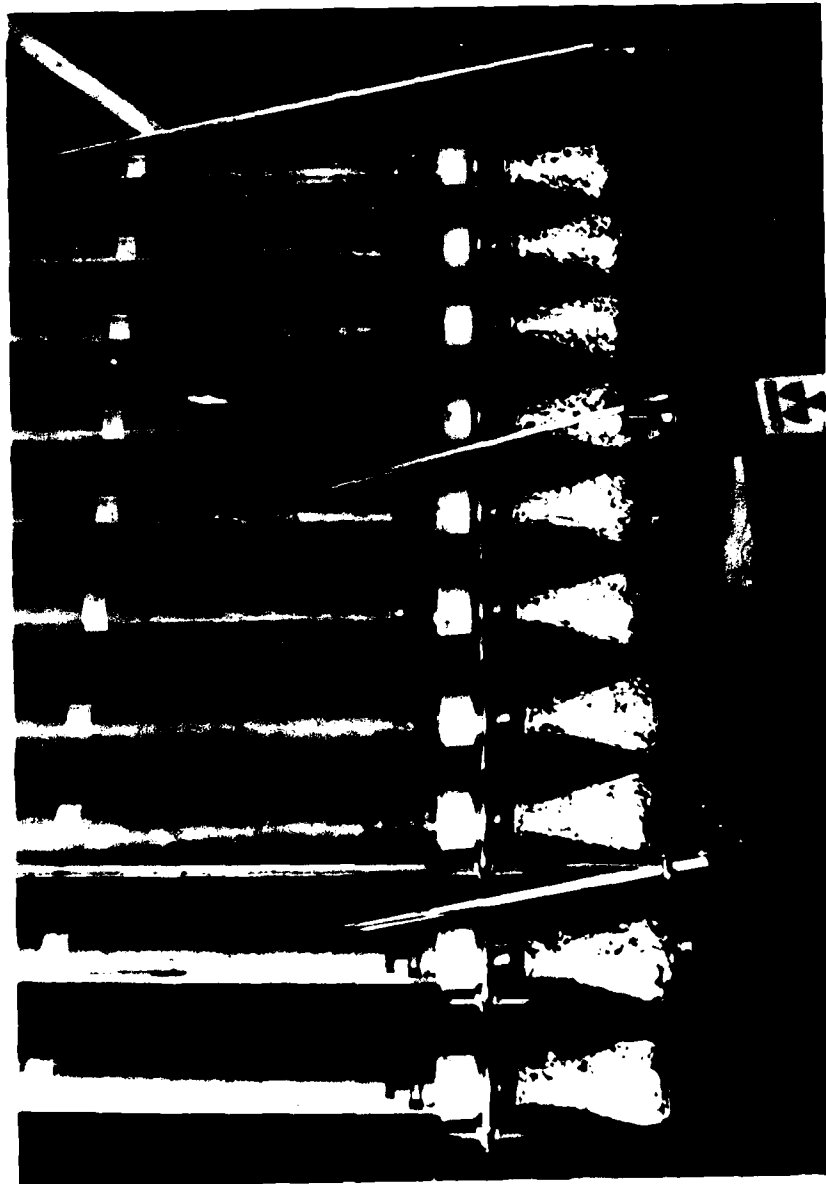


FIGURE 8. OPEN SYSTEM DRAINAGE LYSIMETERS FOR ^{14}C STUDY



FIGURE 9. CLOSED SYSTEM VACUUM LYSIMETERS FOR ^{14}C STUDY

from each soil were placed in the rack built for the closed system while the remaining three were placed in the rack built for the open system. The area between the outside of the column and the inside of the Buchner funnel was sealed with silicone sealant. A 500-ml, side-arm flask was attached to the Buchner funnel to collect the soil water effluent from each soil column.

In the closed system, two-hole stoppers were inserted into the tops of the columns so that air could be flushed through the head space of each of 12 columns to be monitored for carbon dioxide and volatile organics. The scrubbing system consisted of a barium hydroxide trap for carbon dioxide followed by a propylene carbonate trap for organics. The trap for carbon dioxide consisted of a Fischer Milligan gas washing bottle containing 200 ml of a 0.2 M barium hydroxide solution. The trap for organics consisted of a 250-ml, tall-form gas washing bottle containing 200 ml of propylene carbonate. A vacuum pump, operating at 25 inches Hg, was used to provide the negative pressure required to pull unfiltered, unscrubbed air through head space of the lysimeters. The flow rate through the system was controlled by a critical-flow orifice at 50 ml/min. The segment of the purge line between the head space of the columns and the critical-flow orifice, which included the traps, consisted of 1/4-inch diameter Teflon tubing. Thick-wall, 1/4-inch diameter red rubber tubing was used for the segment of the line between the critical-flow orifice and the vacuum pump.

Column Stabilization

The 2-inch soil cores were brought into the greenhouse by the last week in December and treatments were not initiated until the first week in March. The intervening 2 months were allowed for construction and stabilization of the columns. Once inside the greenhouse, the soil columns were placed under the same refrigeration regime as the larger columns of the basic study (2 inches/wk). Several of the columns passed water at high rates indicating that the water may be passing through the column at the metal-soil interface. However, with time and the addition of several milliliters of 10:1 (water to soil) slurry to the interface at the top of the columns, the rate of flow from the columns was reduced to more reasonable limits; i.e., 0.5 to 5 ml/min. All columns were brought within this range of maximum flow rate prior to treatment.

Treatment of Columns

The top 3 inches (7.6 cm) of soil of each column which had previously been removed, dried, and screened was treated with 2

percent by weight of one of the three munition compounds. The munition compound added to the soil was a combination of cold and ^{14}C -labeled material with the labeled portion comprising about 0.6 percent of the total. The total weight of the soil-munition mixture returned to each of the columns was 200 grams, containing 4 grams of compound. The soil and munition compound was mixed for 2 hrs to obtain a homogenous mixture prior to application to the column. This mixture was prepared such that the ^{14}C activity of 200 dpm would correspond to $1\text{ }\mu\text{g}$ of total (labeled and unlabeled) munition compound. In this manner, $1\text{ }\mu\text{g}$ of total munition compound would be detectable by radiocounting techniques at the 200 dpm level which was considered a lower limit of detection. Since, by definition, $1\text{ }\mu\text{Ci} = 2.22 \times 10^6\text{ dpm}$, an activity of 200 dpm corresponds to $9.01 \times 10^{-5}\text{ }\mu\text{Ci}$. Therefore, each μg of total munition compound (labeled and unlabeled) had an activity of $9.01 \times 10^{-5}\text{ }\mu\text{Ci}$; i.e., the munition compound in each treated layer had a specific activity of $9.01 \times 10^{-5}\text{ }\mu\text{Ci}/\mu\text{g}$. Therefore, the 4 g of total (labeled and unlabeled) munition applied to each column had a ^{14}C activity of $3.6 \times 10^2\text{ }\mu\text{Ci}$. Table 2 gives the amount in milligrams of each labeled compound which was added to its appropriate column.

TABLE 2. AMOUNT OF ^{14}C -LABELED MUNITION ADDED TO EACH ^{14}C -LYSIMETER

Compound	Molecular Weight	Specific Activity ($\mu\text{Ci}/\mu\text{mol}$)	mgs Added
Tetryl	287	4.56	22.9 (a)
RDX	222	3.75	21.8
TNT	227	5.57	12.7

$$\begin{aligned}
 & \text{(a) } 3.6 \times 10^2\text{ }\mu\text{Ci} \times 0.0001 \\
 & \times \frac{1\text{ }\mu\text{mole tetryl}}{4.56\text{ }\mu\text{Ci}} \times \frac{287\text{ }\mu\text{g}}{\mu\text{mole tetryl}} \\
 & = 22.9\text{ mg tetryl.}
 \end{aligned}$$

Water Sampling

Water samples were collected from the 500 ml side-arm flasks of the closed system every 2 wks after treatment. These samples were placed in amber bottles and transported to the laboratory in Columbus for analysis for ^{14}C activity via liquid scintillation techniques.

Trap Sampling

Samples were collected every 2 wks from the barium hydroxide and propylene carbonate traps. The entire contents of each trap was placed in an amber bottle and transported to Columbus for analysis via liquid scintillation techniques.

Soil Sampling

At the end of the 26-wk study period, the 12 lysimeters of the closed system were dismantled and cut up into four sections corresponding to soil depth intervals 0-6, 6-12, 12-18, and 18-24 inches (0-15, 15-30, 30-46, and 46-61 cm). Each 6-inch (15 cm) interval was analyzed for munition compound by HPLC. In addition, a 1/2-inch (1.27 cm) thick cross section was removed from the lower end of each of the 0-6-inch (0-15 cm) sections for analysis of ^{14}C distribution by autoradiography. The autoradiogram was developed after an exposure time of 14 days. These sections were not analyzed by scintillation counting.

ANALYTICAL

Material

The analytical standards used in this study were obtained from Edgewood Arsenal, Edgewood, Maryland, and were purified by recrystallization from benzene/hexane before use. Bulk quantities of production grade TNT, RDX, and tetryl were shipped from Edgewood Arsenal and were used as received for treating the lysimeters used in the Basic Study. Radiolabeled munitions were obtained from New England Nuclear, Boston, Massachusetts, with the specific activities as shown in Table 3.

All organic solvents used in the study were distilled-in-glass grade obtained from Burdick and Jackson, Muskegon, Michigan. Meta-nitrophenol (98+ percent purity) was purchased from

Eastman Organic Chemicals as was scintillation grade ethanolamine. The standards for the suspected TNT transformation products were obtained from the sources as listed in Table 3.

TABLE 3. SUSPECTED TNT METABOLITES AND SOURCE

Compound	Source
2,3-dinitrotoluene (2,3-DNT)	Aldrich Chemical Co., Milwaukee, WI
2,4-dinitrotoluene (2,4-DNT)	Edgewood Arsenal, Edgewood, MD
2,5-dinitrotoluene (2,5-DNT)	K & K Laboratories, Plainview, NY
2,6-dinitrotoluene (2,6-DNT)	Edgewood Arsenal, Edgewood, MD
3,4-dinitrotoluene (3,4-DNT)	Aldrich Chemical Co., Milwaukee, WI
3,5-dinitrotoluene (3,5-DNT)	Dr. R. J. Spanggard, Stanford Research Institute, Menlo Park, CA
2,4,6-trinitrobenzaldehyde (2,4,6-TNBA)	ICN Life Sciences Group, Cleveland, OH
1,3,5-trinitrobenzene (1,3,5-TNB)	Edgewood Arsenal, Edgewood, MD
1,3-dinitrobenzene (1,3-DNB)	Eastman Organic Chemicals, Rochester, NY
4-amino-2,6-dinitrotoluene (4-ADNT)	Mr. N. E. Burlinson, Naval Surface Weapons Center, Silver Springs, MD

The purity of each munition used in the ^{14}C and Basic studies was examined by HPLC and a comparison made of its melting point with reported values. Each unlabeled munition was recrystallized and 20 μl of its 10 ppt solution was then chromatographed by HPLC. In this fashion, a 1 percent impurity would constitute 2 μg in the chromatographed sample and, assuming similar uv extinction coefficients, this level of impurity in each munition would be easily observed as a peak in the chromatogram. The purity of the ^{14}C labeled material was similarly examined, except that fractions were also collected after every 1-min interval. Each of these

fractions was then examined by scintillation counting in order to detect the presence of any non-uv active radioactive impurity.

Instrumentation

The HPLC analyses of the water and soil samples generated in this study were accomplished using a Waters Model 6000A Solvent Delivery System equipped with a DuPont Model 834 Liquid Chromatography Automatic Sampler, an Infotronics Model CRS-204 digital integrator, and either a DuPont Model 837 Variable Multiwavelength Detector or a Perkin-Elmer Model 65T Detector/Oven.

Preparation Procedures

Both water and soil samples were analyzed in this study after prior preparation of these samples according to the procedures described below.

Sample Preparation

Soil samples were prepared for HPLC analysis as follows:

Soil (HPLC)

1. Weigh 1 g aliquot of soil and place in a tared sample vial; oven dry at 100°C for 1 hr and calculate moisture content.
2. Weigh 50 g of moist soil and place in screw cap 500 ml Erlenmeyer flask; add 50 ml of pH 7.0 phosphate buffer, 100 ml Et₂O, and spike with 50 µl of 10.0 mg/ml solution of m-nitrophenol in methanol.
3. Cap and shake for 1 hr using a wrist action mechanical shaker.
4. Pour into a 250 ml separatory funnel and let settle for 1/2 hr.
5. Separate the ether phase and reduce in volume to ~10 ml with rotary evaporator (<40°C).
6. Dry with 1 g anhydrous MgSO₄ for 1 hr, then pipet ether extract into vortex evaporator tubes.
7. Further concentrate extract to 5 ml using vortex evaporator (<40°C).
8. Filter and place filtrate in sample vial.

Water Sample Preparation (HPLC). Water samples were prepared for HPLC analysis as follows:

1. Shake water sample and withdraw a 50-ml aliquot; buffer with 5 ml pH 7.0 phosphate buffer; add 100 ml Et₂O and spike with 50 μ l of a 10.0 mg/ml solution of m-nitrophenol in methanol.
2. Cap and shake for 5 min.
3. Pour into a 250-ml separatory funnel and separate the ether phase.
4. Concentrate as described for the soil sample extracts.

Water Sample Preparation (Scintillation Counting). Water samples from the ¹⁴C lysimeters were prepared for ¹⁴C activity by scintillation counting a 5.0 ml aliquot (withdrawn from shaken sample) and added to a scintillation vial containing 15 ml of Bray's scintillation cocktail prepared as follows:

1. Dissolve 60 g naphthalene in 100 ml dioxane in graduated cylinder.
2. Add 100 ml methanol and 20 ml ethylene glycol.
3. Add 4.0 g PPO (2,5-diphenyloxazole).
4. Add 0.20 g POPOP (1,4-bis[2-(5-phenoxyoxazolyl)]-benzene).
5. Dilute to 1000 ml with dioxane after complete dissolution.

Ba(OH)₂ Trap Sample Preparation. Samples from the Ba(OH)₂ traps were prepared for scintillation counting as follows:

1. Shake the sample, withdraw a 10 ml aliquot, and place in a 50 ml three-necked flask equipped with an addition funnel and a N₂ purge line (this purge line enters below the level of liquid sample and exits into a small trap composed of a scintillation vial containing 10 ml ethanolamine).
2. Add 2 ml of 1.0 N HCl dropwise while purging with N₂.
3. Continue to purge for 5 min.
4. Add 10 ml Bray's Solution to ethanolamine trap prior to scintillation counting.

Propylene Carbonate Trap Sample Preparation. Samples from the propylene carbonate traps were prepared for scintillation

counting as follows:

1. Withdraw a 10 ml aliquot from the shaken samples.
2. Add to 10 ml Bray's Solution in a scintillation vial prior to scintillation counting.

Sample Analyses

Quality Control for HPLC Analyses

Blank and spiked water and soil samples and standard solutions of each munition compound were processed as a part of normal sample preparation and analysis schedule during the latter phases of this study. The initial planning for this program did not consider nor include these quality assurance procedures. However, such procedures were requested and made a part of the extension to the Basic Study, beginning in September 1977.

Blank and Spiked Samples. Blank samples consisted of distilled water and untreated (dried) soil of each of the four soil types. At the request of the U.S. Army, no blank soil lysimeter was included in this study; and it was, therefore, not possible to obtain true "blank" soil samples. However, additional soil which had been collected from each site during the acquisition of the lysimeters was used to prepare blanks for the HPLC analyses. Spiked samples were prepared at the 1 and 10 ppm levels by injecting blank soil and water samples with measured volumes of standard solutions for each munition compound. These control samples as well as a randomly chosen standard solution of each munition compound were prepared and/or analyzed with every group of 20 soil or water samples examined during the extension phase of this study. Either 1 or 10 ppm spiked samples were analyzed with each sample group and the blank soil was selected arbitrarily from one of the four soil types.

Standard Curves for HPLC Analyses

Standard Curves for HPLC Analysis. The UV response factors for each munition and suspected transformation product were measured by preparing and analyzing standard solutions with concentrations from 1-100 ppm. A regression analysis was made for the ratio of peak area of munition to that of added internal standard over this concentration range and the resulting best fitted line was used in quantitating unknown samples. This curve was monitored as described above and redetermined whenever calculated values for standard solutions deviated more than 10 percent of their known values.

HPLC Analysis

Table 4 lists the parameters which were used in the HPLC analysis of the water and soil samples in this study.

TABLE 4. HPLC ANALYTICAL PARAMETERS

Analyte	RDX	Tetryl and TNT
Column	(25 μ m x 4 mm Zorbax-ODS DuPont Instruments) (a)	
Mobile Phase	30% CH ₃ OH/70% H ₂ O	40% CH ₃ CN/60% H ₂ O
Flow Rate	1.2 ml/min	1.6 ml/min
Column Temperature	Ambient	Ambient
Column Pressure	3000 psig	2500 psig
Neff	5000-7000 plates	5000-8000 plates
Detection Wavelength(b)	230 nm	230 nm

(a) This column was used for both analytical procedures.

(b) A detection wavelength of 230 nm was selected because the average uv response of these materials maximized in this region as shown by the data in Table 5.

TABLE 5. WAVELENGTH OF MAXIMUM ABSORBANCE AND MOLAR EXTINCTION COEFFICIENTS OF MUNITION COMPOUNDS (a)

Munition	Log ϵ	λ max(nm)
Tetryl	4.40	225 (in ethanol)
RDX	4.00	236 (in methanol)
TNT	4.29	227 (in ethanol)

(a) Values cited in Organic Electronic Spectral Data, Vol 1, Interscience Publishers, Inc., New York (1960).

Liquid Scintillation Counting

The ^{14}C activity of the water samples examined in this study were determined using a SEARLE Mark III Liquid Scintillation System, Model 6880. These analyses employed a single counting channel present for ^{14}C with automatic correction for quenching. Spiked samples and blanks were processed with each sample set and all sample sets were counted for 0.1 min.

Total Organic Carbon

Water. Water samples were analyzed for total organic carbon (TOC) by methods outlined in Methods for Chemical Analysis of Water and Wastes (1971). Basically, this method involved acidification of the sample and analysis via a Beckman Model IR 315 infrared analyzer.

Soil. Soil samples were analyzed for total organic carbon by methods for dry combustion of solids outlined in Methods of Soil Analyses (1965). This method involved acidification with HCl to remove carbonate-carbon and analysis using a LECO Model WR-12 carbon determinator equipped with a high temperature induction furnace.

Nitrate

Water samples were analyzed for nitrate (NO_3^-) by a Dion-X System Ten ion chromatograph.

Nitrite

Water samples were analyzed for nitrite (NO_2^-) by methods outlined in Methods for Chemical Analysis of Water and Wastes (1971). Basically, this method involved the diazotization of sulfanilamide by nitrite and subsequent coupling with N-(1-naphthylethylenediamine). This generated a red color whose absorbance was measured in a spectrophotometer at 450 nm.

Partition Experiment

The partitioning of each munition between soil and water is measured by the ratio of the concentration of the compound in the

soil phase vs that in the water phase at equilibrium

$$P = \frac{C_s}{C_w}$$

where

C_s = concentration of solute in soil phase (ppm)
 C_w = concentration of solute in water phase (ppm).

An understanding of the chemical and physical properties of munition compounds would logically begin with a study of their partitioning behavior, especially as it relates to the mechanism of transport. This data would then aid in designing and interpreting a more comprehensive study.

C_s and C_w were determined after shaking 10.0 g of each soil with 1000 ml distilled water which had been spiked with known amounts of munition compound. The aqueous concentrations used were 21.4 $\mu\text{g/ml}$ for tetryl, 23.5 $\mu\text{g/ml}$ for RDX, and 28.6 $\mu\text{g/ml}$ for TNT. Each soil-water mixture was shaken for 1 hr after which the two phases were separated and the water phase filtered. The filter paper and residue were combined with the soil and both the water and soil phases were prepared and analyzed as described previously.

Solubility Experiment

Solubility in Water. Initial attempts to generate water solutions of 100 ppm of these compounds for use in the partition experiment were unsuccessful. These solutions were prepared by spiking measured volumes of water with known amounts of each munition in methanol or acetone solution. However, upon standing, each of these mixtures soon became saturated with and contained undissolved compounds.

In order to generate true aqueous solutions of each compound, 0.1 to 0.5 g of each compound was precisely weighed and added to 2100 milliliters distilled water and shaken for 3 days at 21°C in the dark. Two such solutions were prepared for each compound and a blank water sample was also processed using these same procedures. These solutions were carefully filtered through 0.22 μm filter paper and the residue air-dried and weighed. Each solution was then examined by UV spectroscopy and aliquots withdrawn, extracted, and analyzed by HPLC as described above for water samples. In this manner, true aqueous solutions were generated for each compound and their concentrations accurately determined.

Solubility in Et₂O. The solubility of RDX, tetryl, and TNT in diethyl ether was determined using a thermostated water bath. Measured amounts of munitions (0.1 to 0.5 g) were added to 140 ml (100 g) of diethyl ether in a 500-ml round bottom flask immersed in the water bath. The mixture was swirled frequently as it was allowed to equilibrate for 1 hr. The mixture was removed and quickly filtered through a tared glass filter frit. This filter was air-dried and the amount of dissolved compound determined by the weight difference between compound added and recovered.

Recovery Experiment

The efficiency of the extraction procedure used for water and soil samples was examined by preparing and analyzing samples of known concentration. Initially, these spiked samples were generated by injecting known amounts of each compound in organic solution into blank water and soil samples and allowing the organic solvent to evaporate. However, these techniques may not generate samples representative of actual samples in which the compound exists in a highly dispersed solution (water samples) or adsorbed to soil particles (soil samples). Therefore, to verify the efficiency of recovery from authentic water solutions of each munition, the recovery study was repeated using spiked water samples which were generated without the use of organic solvents. Spiked water samples generated in the Solubility Experiment described above were also extracted and analyzed and the recoveries determined for each compound in these samples. Two 50-ml aliquots of each of these solutions were extracted using the normal procedures while a third 50-ml aliquot was extracted three times in sequence and each of these extracts analyzed individually.

RESULTS

Analytical

Quality Control for HPLC Analyses

Blank and Spiked Samples. The data in Figure 10 were obtained from the analyses of spiked water samples while Figure 11 represents the analyses of spiked soil samples.

Standard Curves for HPLC Analyses. Figure 12 displays the results of the analyses of standard solutions conducted during the analysis of water and soil samples.

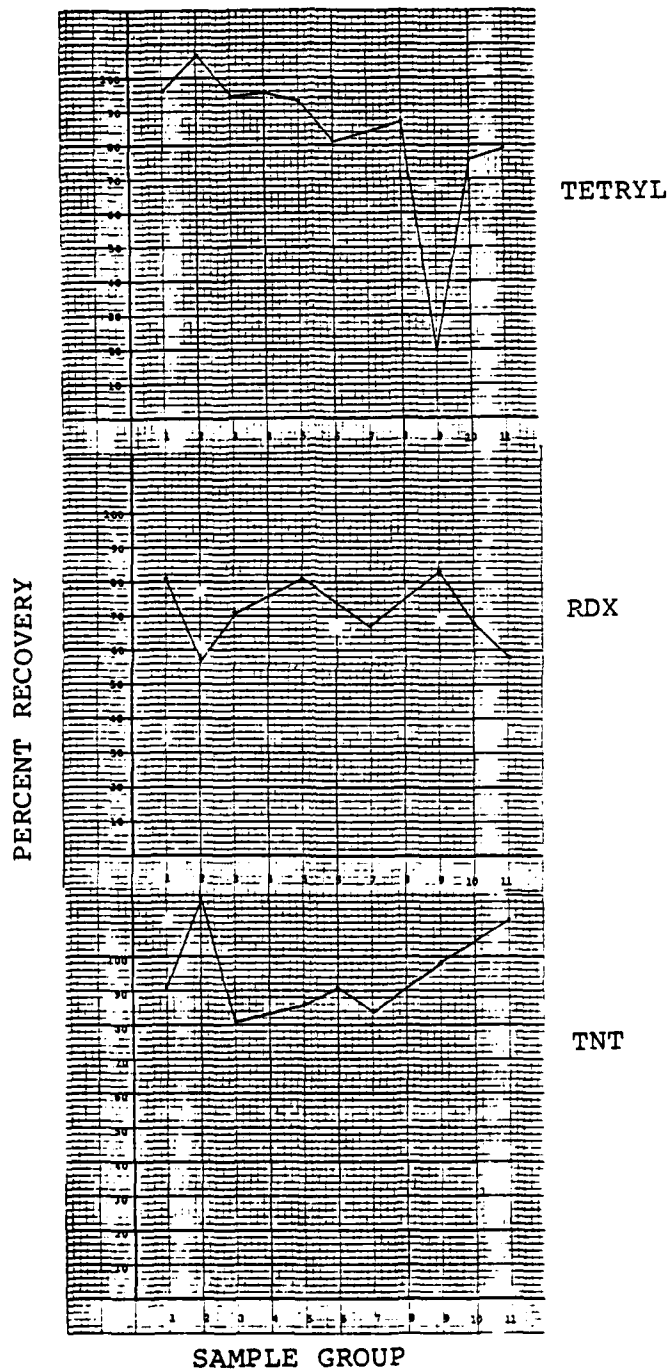


FIGURE 10. PERCENT RECOVERY OF SPIKED WATER SAMPLES

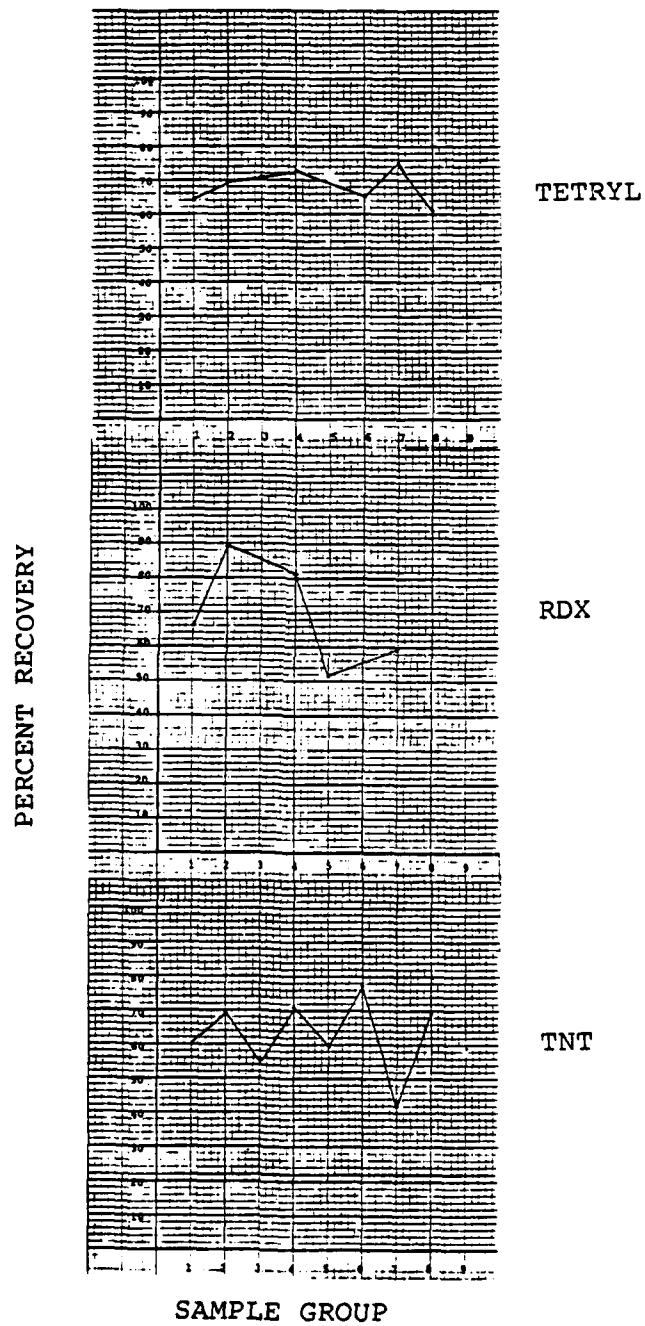


FIGURE 11. PERCENT RECOVERY OF SPIKED SOIL SAMPLES

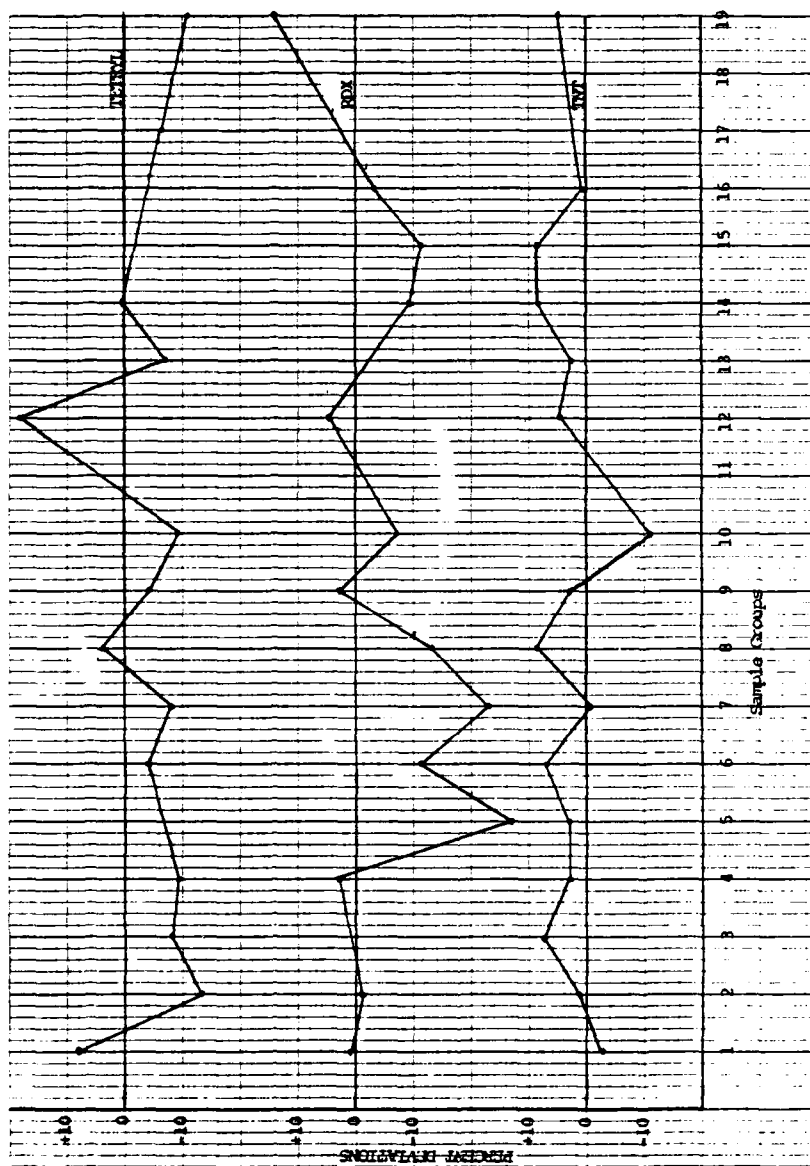


FIGURE 12. PERCENT DEVIATIONS OF STANDARD SOLUTIONS FROM THEIR KNOWN VALUES USING HPLC ANALYSES

The standard curves (HPLC) generated for each munition compound and suspected transformation product were linear for solutions corresponding to sample concentrations in the range of 1-100 ppm. Examples of these curves are shown in Figures 13-15 and their slopes and intercepts are given in Table 6.

TABLE 6. TYPICAL SLOPE AND INTERCEPT VALUES FOR HPLC STANDARD CURVES

Compound	Units		Correlation Coefficient
	Slope	Intercept	
Tetryl	1.313	-0.202	0.995
RDX	2.733	0.199	0.996
TNT	1.627	0.067	0.999
DNB	0.852	0.015	0.999
TNB	1.312	0.015	0.999
DNT ₁ (2,4- and 2,6-DNT) ^(a)	1.062	-0.006	0.999
DNT ₂ (2,3-2, 5-3,4- and 3,5-DNT)	1.078	-0.010	0.999
4-ADNT	1.039	-0.013	0.999

(a) See Table 3.

The DNT's were not individually resolved under the chromatographic conditions employed, but they were eluted in two groups (Figure 16). These two peaks (DNT₁ and DNT₂) were quantitated based on the total weight of all DNT isomers in each peak.

Recovery Study

Initial recovery data collected from water and soil injected with organic solutions of each compound are reported in Table 7. Recovery data obtained from aqueous solutions of each compound (generated as described in the Methods section of this report) are tabulated in Table 8.

Solubility Experiment

Solubility in Water. Table 9 lists the data obtained in measuring the water solubility of each compound using the techniques described in the Methods section of this report.

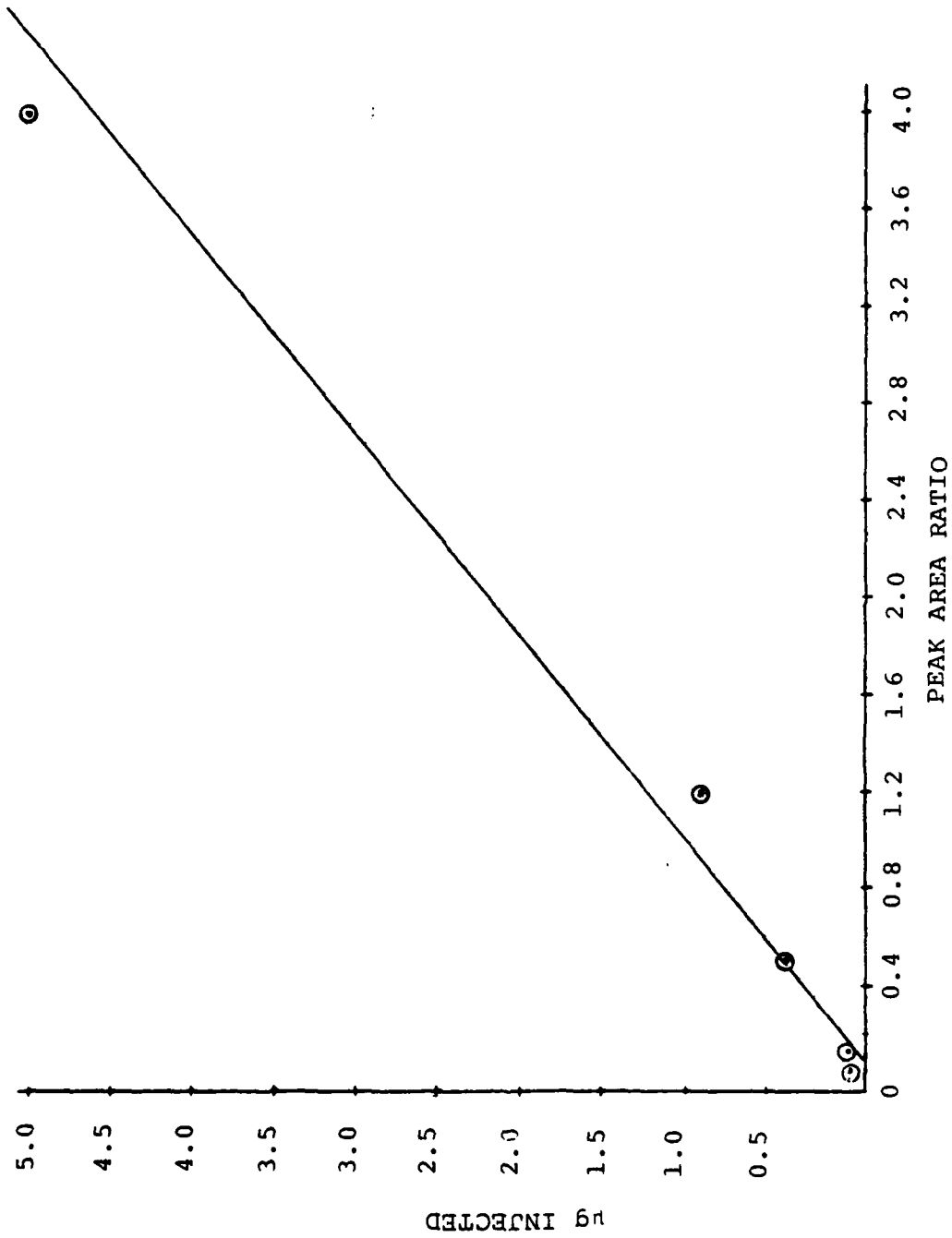


FIGURE 13. STANDARD CURVE FOR TETRYL

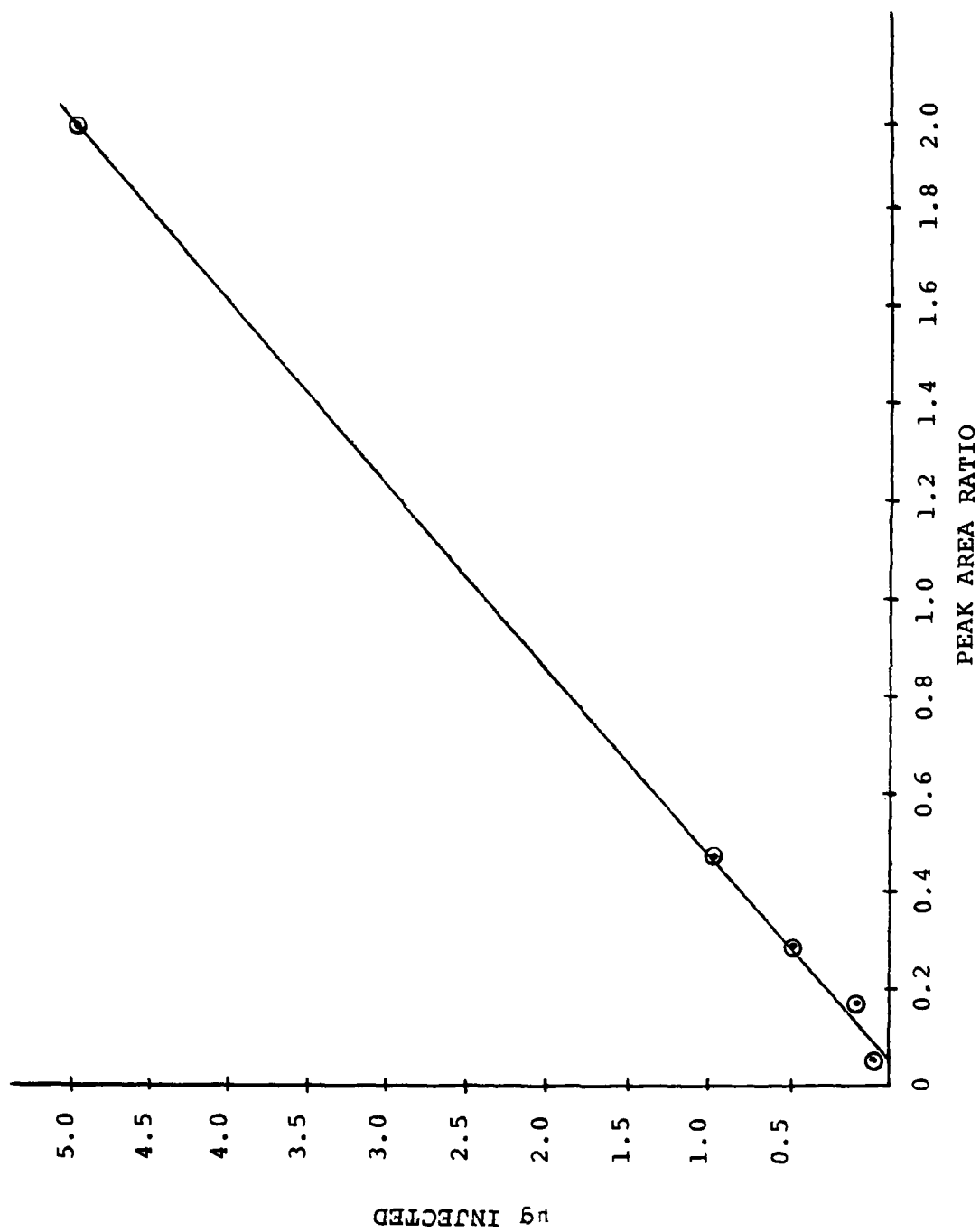


FIGURE 14. STANDARD CURVE FOR RDX

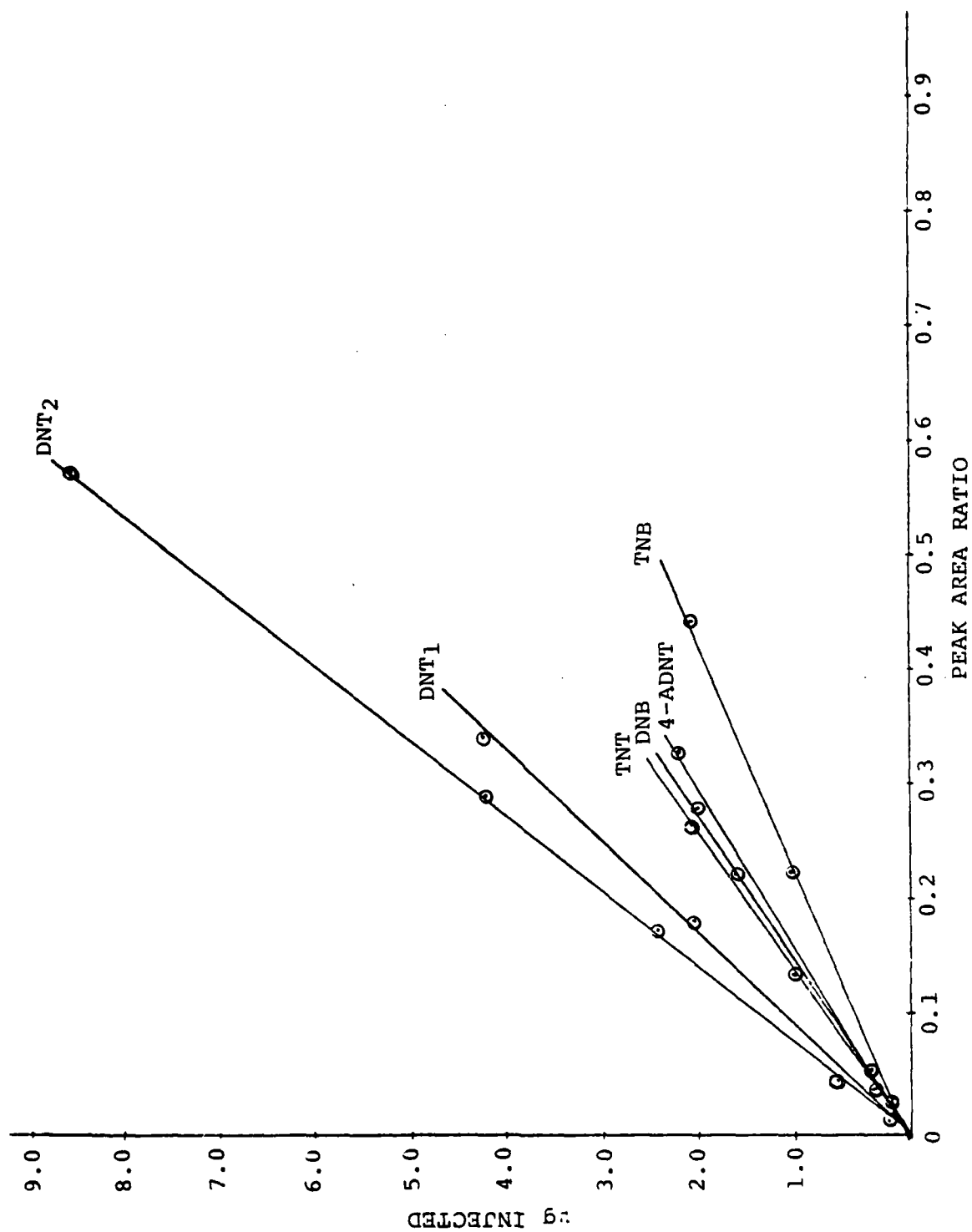


FIGURE 15. STANDARD CURVES OF TNT AND ITS TRANSFORMATION PRODUCTS

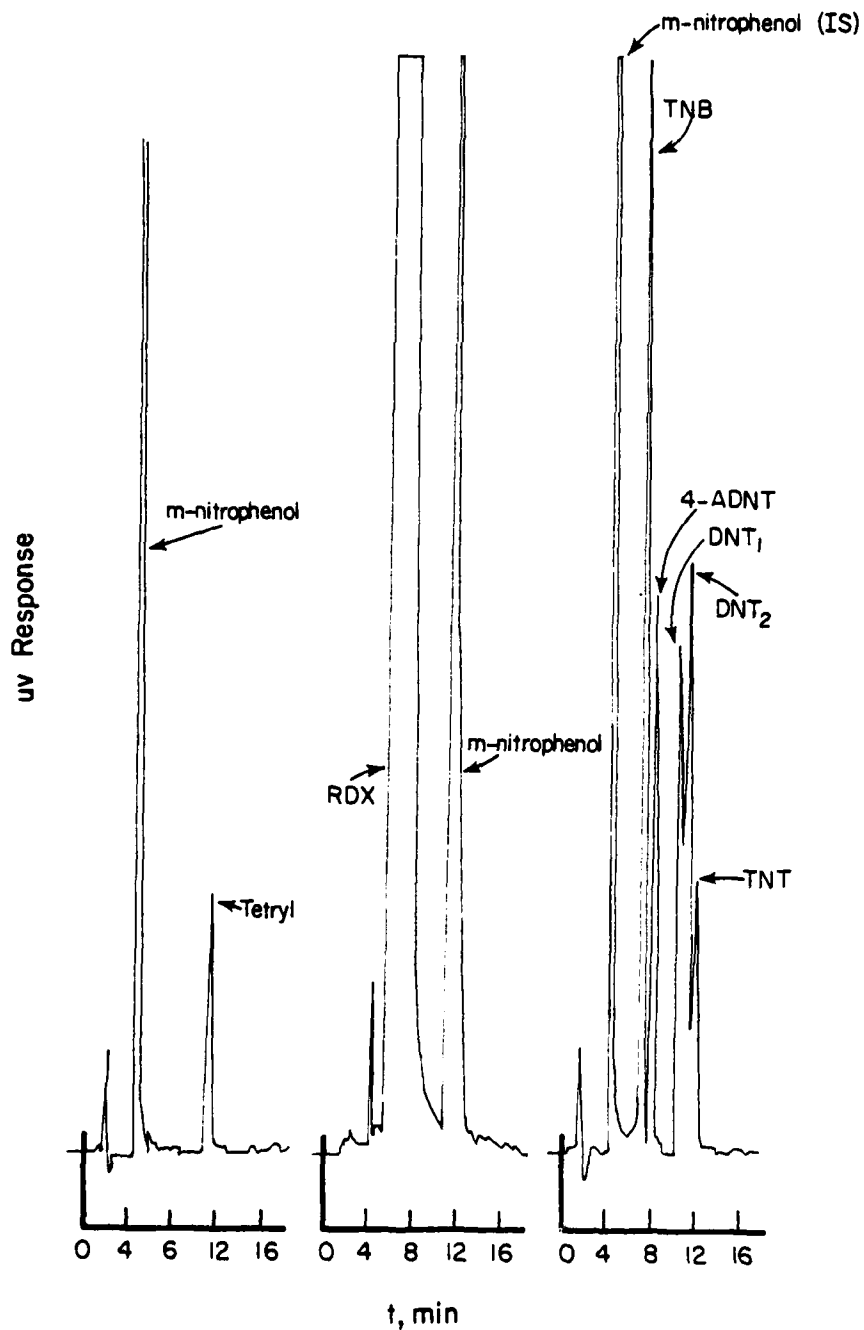


FIGURE 16. HPLC CHROMATOGRAMS OF TETRYL, RDX, AND TNT AND SUSPECTED TRANSFORMATION PRODUCTS

(See Table 4 for chromatographic conditions;
IS = internal standard.)

TABLE 7. RECOVERY OF MUNITION COMPOUNDS FROM WATER AND SOIL (a)
USING ORGANIC SOLUTIONS TO PREPARE SPIKED SAMPLES

Compound	Spiked (b) (ppm)		Found (b) (ppm)		Percent Recovered (b)	
	Soil	Water	Soil	Water	Soil	Water
Tetryl	10	10	8.3	9.7	83	97
RDX	10	10	7.7	8.1	77	81
TNT	10	10	9.0	9.8	90	98
1,3-DNB	10	10	8.9	9.8	89	98
1,3,5-TNB	10	10	9.8	9.6	98	96
4-ADNT	10	10	9.0	9.2	90	92
DNT ₁ (2,4- and 2,6- DNT)	20	20	19.4	19.6	97	98
DNT ₂ (2,3-, 2,5-, 3,4-, and 3,5-DNT)	40	40	39.2	38.8	98	97

(a) Brookston soil.

(b) Average of three determinations.

TABLE 8. RECOVERY OF MUNITION COMPOUNDS FROM
WATER USING AQUEOUS SOLUTIONS TO
PREPARE SPIKED SAMPLES

Compound	Spiked (ppm)	Found (ppm)	Percent Recovered
<u>TETRYL</u>			
Single Extraction	21.4	18.4	86.0
Multiple Extraction	21.4	19.1	89.3
1st Extraction		19.0	88.5
2nd Extraction		0.1	0.5
3rd Extraction		0.0	
<u>RDX</u>			
Single Extraction	23.5	18.5	78.7
Multiple Extraction	23.5	17.2	73.2
1st Extraction		15.7	66.8
2nd Extraction		1.5	6.4
3rd Extraction		0.0	

TABLE 8. (Continued)

Compound	Spiked (ppm)	Found (ppm)	Percent Recovered
<u>TNT</u>			
Single Extraction	28.6	27.8	97.2
Multiple Extraction	28.6	26.7	93.4
1st Extraction		26.3	92.0
2nd Extraction		0.4	1.4
3rd Extraction		0.0	

TABLE 9. WATER SOLUBILITY OF MUNITION
COMPOUNDS AT 21°C

Compound (saturated)	Found (ppm)		HPLC (ppm)	Reported (b) (ppm)
	Gravimetric (a)	UV		
TNT	85.8 ± 0.9	86.7	83.4	130
RDX	23.6 ± 2.0	23.5	18.5	NA (c)
Tetryl	21.4 ± 1.4	21.4	18.4	75

(a) Average of two samples ± 2X (standard deviation).

(b) Values cited in T. Urbanskii, The Chemistry and Technology of Explosives, Vol. 1, Pergamon Press, London (1964).

(c) NA - Not available.

Concentrations were determined for each munition compound using gravimetric, UV, and HPLC techniques. The gravimetric results were corrected for contributions observed in the blank sample and the UV and HPLC data were obtained after combining the two duplicate solutions generated for each compound.

Solubility in Diethyl Ether. Table 10 lists the data obtained from determination of the solubility of tetryl, RDX, and TNT in diethyl ether at 20, 25, and 30°C.

TABLE 10. SOLUBILITY OF MUNITION COMPOUNDS
IN DIETHYL ETHER AT VARIOUS
TEMPERATURES

Compound	Temperature (g/100 g ether)		
	20°C	25°C	30°C
<u>TETRYL</u>			
Observed	0.249	0.339	0.365
Reported (a)	0.418	0.457	0.493
<u>RDX</u>			
Observed	0.016	0.018	0.047
Reported (a)	0.055	NA (b)	0.075
<u>TNT</u>			
Observed	2.011	2.227	2.497
Reported (a)	3.290	3.800	4.560

(a) Values cited in T. Urbanskii, The Chemistry and Technology of Explosives, Vol. 1, Pergamon Press, London (1964).

(b) NA = Not available.

Basic Study

Soil Samples. Tables 11-13 list the data collected in analyzing the soil samples generated during the Basic Study. These samples were prepared and quantitated using methods described earlier.

Water Samples. Tables 14-16 list the data collected from the analysis of water samples generated during the Basic Study. These samples were prepared and quantitated using methods described earlier.

¹⁴C Study

Water Samples. Tables 17-19 list the data collected from the radioassay of water samples generated during the ¹⁴C Study. The method of sample preparation and analysis is as described earlier.

TABLE 11. TETRYL CONTENT OF SOIL SAMPLES
COLLECTED FROM THE BASIC STUDY

(Data reported in ppm tetryl.)

Soil	Depth (cm)	Weeks After Treatment				
		2	6	10	18	26
Brookston (sicl)	0-10	-- (a)	--	--	Not	10,200
	10-20	--	613.5	123.2	sampled	191.3
	20-30	--	540.0	14.5		38.3
	30-61	<0.5	13.0	24.6		30.1
	61-91	<0.5	1.3	2.5		20.8
	91-122	<0.5	1.8	0.6		<0.5
	122-152	<0.5	6.8	5.7		3.7
Bennington (sicl- acid)	0-10	--	--	--	Not	32,900
	10-20	3.2	583.3	476.2	sampled	435.7
	20-30	1.9	11.8	35.3		19.9
	30-61	43.0	58.1	36.4		94.5
	61-91	4.8	32.2	29.2		493.0
	91-122	51.1	6.8	151.5		974.6
	122-152	18.3	19.9	21.3		5.8
Princeton (sl)	0-10	--	--	--	Not	27,400
	10-20	94.2	532.4	138.0	sampled	270.2
	20-30	43.7	3.0	110.8		1,737.0
	30-61	15.0	43.3	20.6		471.9
	61-91	55.9	12.2	14.7		638.3
	91-122	<0.5	15.7	33.0		664.2
	122-152	1.80	29.8	46.6		2,425.0
Genesee (sil)	0-10	14,075	--	--	12,900	21,000
	10-20	103.9	835.0	243.2	12,018.3	2,330.0
	20-30	267.9	208.2	599.1	2.1	<0.5
	30-61	201.2	25.5	61.6	0.2	<0.5
	61-91	79.0	38.8	32.4	0.0	<0.5
	91-122	10.6	299.2	152.1	2.1	274.3
	122-152	9.0	68.7	14.4	0.1	999.1

(a) Sample not analyzed.

TABLE 12. RDX CONTENT OF SOIL SAMPLES
COLLECTED FROM THE BASIC
STUDY

(Data reported in ppm RDX.)

Soil	Depth (cm)	Weeks After Treatment				
		2	6	10	18	26
Brookston (sicl)	0-10	—	—	—	Not sampled	13,600
	10-20	43.3	7.7	42.1		330.5
	20-30	29.8	37.7	—		83.9
	30-61	11.5	7.5	<0.5		14.1
	61-91	3.5	5.7	<0.5		31.8
	91-122	6.5	<0.5	<0.5		43.9
	122-152	2.5	1.0	2.7		112.3
Bennington (sicl- acid)	0-10	—	—	—	Not sampled	29,000
	10-20	39.2	4.9	100.50		—
	20-30	36.1	41.5	90.3		245.5
	30-61	5.8	13.6	18.2		—
	61-91	7.4	1.2	<0.5		120.1
	91-122	<0.5	2.0	67.3		16.1
	122-152	—	1.5	<0.5		225.4
Princeton (sl)	0-10	—	—	—	Not sampled	23,000
	10-20	32.4	33.4	99.9		73.0
	20-30	77.0	25.0	36.7		113.1
	30-61	23.7	46.5	43.9		68.3
	61-91	1.6	9.4	10.7		75.6
	91-122	<0.5	9.8	<0.5		223.8
	122-152	<0.5	30.7	<0.5		270.4
Genesee (sil)	0-10	—	—	—	7,700	47,000
	10-20	20.8	88.8	146.7	2.7	250.9
	20-30	19.6	37.9	33.2	0.1	157.3
	30-61	4.0	11.8	23.6	0.2	158.4
	61-91	3.6	7.0	32.0	<0.5	375.8
	91-122	3.9	1.5	25.1	0.2	81.6
	122-152	2.0	21.0	69.3	0.4	95.3

TABLE 13. TNT CONTENT OF SOIL SAMPLES COLLECTED FROM THE BASIC STUDY

(Data reported as ppm TNT.)

Soil	Depth (cm)	Weeks after Treatment				
		2	6	10	18	26
Brookston (sicl)	0-10	--	--	--	--	20,100
	10-20	23.9	9.7	76.5	8.1	1,237.0
	20-30	27.2	19.2	3.9	<0.5	146.8
	30-61	11.3	10.5	1.3	<0.5	0.8
	61-91	1.4	10.4	0.1	<0.5	0.4
	91-122	18.6	<0.5	0.2	<0.5	6.0
	122-152	5.8	<0.5	0.2	<0.5	14.9
Bennington (sil, acid)	0-10	--	--	--	Not sampled	17,400
	10-20	477.7	23.2	1.1		1,039.0
	20-30	201.5	9.9	0.1		123.6
	30-61	40.8	1.4	0.2		4.5
	61-91	17.0	5.0	<0.1		15.3
	91-122	16.6	3.0	14.7		--
	122-152	40.4		0.2		544.6
Princeton (sl)	0-10	--	--	--	Not sampled	6,010
	10-20	1,291.8	49.3	58.2		238.6
	20-30	356.7	86.7	0.6		238.6
	30-61	144.0	15.8	0.4		131.3
	61-91	69.3	5.8	0.1		396.6
	91-122	16.4	8.3	<0.1		284.5
	122-152	18.5	2.7	0.8		261.1
Genesee (sil)	0-10	--	--	--	21,000	21,500
	10-20	132.1	--	80.8	13.37	25.0
	20-30	61.4	10.4	5.4	6.14	80.2
	30-61	4.7	2.5	<0.5	<0.5	151.0
	61-91	3.2	47.5	<0.5	<0.5	--
	91-122	2.5	20.0	<0.5	<0.5	--
	122-152	8.2	116.7	<0.5	<0.5	--

TABLE 14. TETRYL CONTENT OF WATER
SAMPLES COLLECTED FROM
THE BASIC STUDY

(Data reported in ppm tetryl.)

Soil	Depth (cm)	Weeks After Treatment (a)		
		2	4	6
Brookston (sicl)	15	<0.5	<0.5	1.5
	46	2.5	--	<0.5
	76	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5
Bennington (sil)	15	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5
	152	1.3	<0.5	<0.5
Princeton (sl)	15	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5
	76	2.2	<0.5	<0.5
	152	--	<0.5	<0.5
Genesee (sil)	15	<0.5	<0.5	<0.5
	46	0.9	<0.5	0.6
	76	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5

(a) All samples were <0.5 for 8-, 10-, 12-, 14-, 16-, 18-, 20-, 22-, and 24-week collections.

TABLE 15. RDX CONTENT OF WATER SAMPLES COLLECTED FROM THE BASIC STUDY

(Data reported in ppm RDX.)

Soil	Depth (cm)	Weeks After Treatment (a,b)						
		2	4	6	8	10	12	14
Brookston (sicl)	15	<0.5	<0.5	<0.5	4.0	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Bennington (sil, acid)	15	<0.5	<0.5	38.68	<0.5	<0.5	<0.5	<0.5
	46	<0.5	<0.5	1.89	<0.5	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Princeton (sl)	15	2.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Genesee (sil)	15	<0.5	1.5	<0.5	<0.5	<0.5	<0.5	<0.5
	46	<0.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	76	1.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	152	<0.5	5.3	<0.5	<0.5	<0.5	<0.5	<0.5

(a) All samples were <0.5 for 16-, 18-, 20-, 22-, and 24-week collections.

(b) A major component was observed in each of the 22- and 24-week collections which eluted just prior to RDX.

TABLE 16. TNT CONTENT OF WATER SAMPLES COLLECTED FROM THE BASIC STUDY

(Data reported in ppm TNT.)

Soil	Depth (cm)	Weeks After Treatment (a,b,c)			
		2	4	6	8
Brookston (sicl)	15	<0.5	<0.5	<0.5	0.7
	46	<0.5	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5	0.3
	152	<0.5	<0.5	<0.5	<0.5
Bennington (sil, acid)	15	<0.5	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5	0.3
	76	<0.5	<0.5	<0.5	1.8
	152	<0.5	<0.5	<0.5	<0.5
Princeton (sl)	15	<0.5	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5	1.8
	76	<0.5	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5	1.12
Genesee (sil)	15	<0.5	<0.5	<0.5	<0.5
	46	<0.5	<0.5	<0.5	<0.5
	76	<0.5	<0.5	<0.5	<0.5
	152	<0.5	<0.5	<0.5	<0.5

- (a) All samples were <0.5 for 10-, 12-, 14-, 16-, 18-, 20-, 22-, and 24-week collections.
- (b) Possible traces (<0.5 ppm) of the DNT isomer(s) were observed in the 15 cm sample from Brookston soil (24-week).
- (c) These samples (Bennington, 15 cm, 22-week; Princeton, 15 and 46 cm, 22-week; and Genesee, 152 cm, 22-week) had two large peaks near the retention times of the DNT's, but these were shown not to be one of the DNT isomers by spiking the samples with authentic standards.

TABLE 17. ^{14}C ACTIVITY OF WATER SAMPLES COLLECTED FROM THE TETRYL TREATMENT OF THE ^{14}C STUDY

(Data reported in dpm; background activity of about 100 dpm has not been subtracted.)

Soil	Weeks After Treatment											
	2	4	6	8	10	12	14	16	18	20	22	24
Brookston (sicl)	12	74	48	199	140	70	71	3,752	224	152	95	58
Bennington (sil, acid)	165	177	83	82	35	128	59	1,809	247	164	23	130
Princeton (sl)	24	167	97	284	117	36	5,736	83	237	95	73	60
Genesee (sil)	72	96	121	1,382	326	1,215	36	1,472	1,392	1,160	2,190	1,335

TABLE 18. ^{14}C ACTIVITY OF WATER SAMPLES COLLECTED FROM THE RDX TREATMENT OF THE ^{14}C STUDY

(Data reported in dpm; background activity of about 100 dpm has not been subtracted.)

Soil	Weeks After Treatment											
	2	4	6	8	10	12	14	16	18	20	22	24
Brookston (sicl)	36	60	12	42	102	71	76	83	73	179	186	328
Bennington (sil, acid)	24	36	50	47	94	12	108	5,220	543	176	157	35
Princeton (sl)	52	88	676	4,490	11,317	22,783	28,879	65,557	94,382	104,465	124,913	134,999
Genesee (sil)	404	885	1,815	2,504	9,125	5,279	36,056	34,180	6,994	20,105	17,030	24,566

TABLE 19. ^{14}C ACTIVITY OF WATER SAMPLES COLLECTED FROM THE TNT TREATMENT OF THE ^{14}C STUDY

(Data reported in dpm; background activity of about 100 dpm has not been subtracted.)

Soil	Weeks After Treatment											
	2	4	6	8	10	12	14	16	18	20	22	24
Brookston (sicl)	60	107	330	35	47	225	48	83	85	82	71	82
Bennington (sil, acid)	77	116	440	71	70	348	261	178	59	35	94	47
Princeton (sl)	96	83	825	5,130	16,753	18,651	15,662	11,913	13,451	16,734	11,676	10,627
Genesee (sil)	23	60	684	222	667	453	597	610	1,358	1,097	1,944	2,220

Ba(OH)₂ and Propylene Carbonate Trap Samples. Tables 20-22 list the data collected in the analysis of the trap samples generated during the ¹⁴C Study. The method of sample preparation and analysis is as described earlier.

Soil Samples. At the end of the ¹⁴C Study, one set of these columns was sacrificed. These columns were segmented into 6-inch increments and the bottom inch of each segment analyzed for munition compound via HPLC. Table 23 lists the data collected in analyzing these soil samples. The method of sample preparation and analysis is described under the Methods section of this report.

Figure 17 shows the cross-sectional distribution of ¹⁴C as determined by autoradiograms of a soil slice taken at the 6-inch depth for each soil and munition compound combination. The purpose of these autoradiograms was to determine how evenly the ¹⁴C moved through soil and whether channeling occurred. The only significant evidence of channeling is with TNT in the Bennington soil. This, however, is an artifact resulting from the fact that the soil slice was not coherent enough to allow its removal from the pipe section which was left in place as a retainer.

Water Samples (HPLC) Analysis. Selected effluent samples from the ¹⁴C lysimeters were extracted and analyzed by HPLC. These samples consisted of the 24-wk effluent samples withdrawn from each of these columns. The results of these analyses are given in Table 24.

Other Analyses

Total Organic Carbon. Tables 25-30 show the results of the TOC analyses on soil and water samples from the Basic Study. These analyses were conducted in the early part of the study using the methods described in the Methods section of this report.

Nitrate and Nitrite. Tables 31-36 present data from nitrate and nitrite analyses which were performed on water samples from the Basic Study using the procedures described in the Methods section of this report.

Partition Experiment

Table 37 lists the water and soil concentrations obtained in the partition experiment for each compound examined. The values

TABLE 20. ¹⁴C ACTIVITY OF TRAP SAMPLES COLLECTED FROM THE TETRYL TREATMENT
OF THE ¹⁴C STUDY

(Data reported in dpm; background activity of about 100 dpm has not been subtracted.)

Soil	Weeks After Treatment										
	1	2	4	6	8	10	12	14	16	18	20
	BARIUM HYDROXIDE TRAPS										
Brookston (sicl)	38	111	91	122	953	195	135	652	1,336	3,280	2,110
Bennington (sil, acid)	56	185	490	875	523	2,458	226	302	2,868	4,276	1,415
Princeton (sl)	209	847	109	750	122	124	293	157	1,131	2,234	4,907
Genesee (sil)	70	651	948	562	7,342	933	4,157	1,378	194	6,261	7,468
	PROPYLENE CARBONATE TRAPS										
Brookston (sicl)	54	57	83	109	41	67	66	27	41	41	81
Bennington (sil, acid)	68	55	82	643	55	55	27	55	41	41	27
Princeton (sl)	70	68	27	82	40	109	54	82	27	81	41
Genesee (sil)	95	109	83	353	95	189	67	67	55	54	52

TABLE 21. ¹⁴C ACTIVITY OF TRAP SAMPLES COLLECTED FROM THE
RDX TREATMENT OF THE ¹⁴C STUDY

(Data reported in dpm; background of about
100 dpm has not been subtracted.)

Soils	Weeks After Treatment									
	1	2	4	6	8	10	12	14	16	20
<u>BARIUM HYDROXIDE TRAPS</u>										
Brookston (sil)	241	131	364	5,102	126	416	187	138	31,279	17,018
Bennington (sil, acid)	314	2,010	4,638	11,302	37,899	9,804	2,640	526	76,879	48,122
Princeton (sil)	10,835	6,439	20,158	27,137	27,053	15,261	13,943	8,330	188,565	107,534
Genesee (sil)	3,954	7,502	195	439	--(a)	10,204	2,335	2,685	27,144	12,207
<u>PROPYLENE CARBONATE TRAPS</u>										
Brookston (sil)	179	0	42	110	0	287	67	55	81	28
Bennington (sil, acid)	134	55	55	695	511	41	14	95	41	41
Princeton (sil)	138	41	125	97	965	616	463	14	68	27
Genesee (sil)	--	45	69	425	328	68	363	109	256	41

(a) Insufficient sample for analysis.

TABLE 22. ¹⁴C ACTIVITY OF TRAP SAMPLES COLLECTED FROM THE TNT TREATMENT OF THE ¹⁴C STUDY

(Data reported in dpm; background of about 100 dpm has not been subtracted.)

Soil	Weeks After Treatment									
	1	2	4	6	8	10	12	14	16	18
<u>BARIUM HYDROXIDE TRAPS</u>										
Brookston (sicl)	0	160	134	556	123	--(a)	52	482	161	3,055
Bennington (sil, acid)	474	89	86	249	1,251	72	785	1,419	929	2,934
Princeton (sl)	408	131	72	706	143	--	2,902	439	2,249	10,294
Genesee (sil)	107	89	2,293	188	104	--	4,061	1,505	56	1,763
<u>PROPYLENE CARBONATE TRAPS</u>										
Brookston (sicl)	124	69	69	55	55	123	41	82	95	108
Bennington (sil, acid)	55	110	123	68	180	151	82	14	82	55
Princeton (sl)	82	137	191	82	289	138	136	96	68	27
Genesee (sil)	68	41	55		179	441	365	81	41	54

(a) Insufficient sample for analysis.

TABLE 23. CONCENTRATIONS OF MUNITION COMPOUNDS IN SOILS FROM SACRIFICED 14C COLUMNS

Soil	Depth (cm)	Compound (ppm except where otherwise indicated)						
		Tetryl	RDX	TNT	DNT ₁	DNT ₂	DNB	4-ADNT
Brookston (sicl)	12.5-15	trace	4.4	trace	20.9	<0.5	trace	<0.5
	28-30.5	trace	27.1	trace	<0.5	<0.5	trace	<0.5
	43.2-45.7	<0.5	17.9	trace	<0.5	<0.5	<0.5	<0.5
	58.5-61	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Bennington (sil, acid)	12.5-15	14.7	9.4	trace	trace	trace	<0.5	6.9
	28-30.5	3.9	<0.5	<0.5	<0.5	<0.5	<0.5	1.8
	43.2-45.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	58.5-61	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Princeton (sl)	12.5-15	103.3	34.2	16.5	<0.5	56.5	0.5	15.2
	28-30.5	49.1	10.3	0.5	<0.5	trace	<0.5	2.9
	43.2-45.7	15.4	4.8	trace	<0.5	<0.5	<0.5	trace
	58.5-61	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Genesee (sil)	12.5-15	trace	142.8	2.4	<0.5	1.5	<0.5	41.5
	28-30.5	<0.5	59.4	trace	<0.5	<0.5	<0.5	trace
	43.2-45.7	<0.5	15.3	<0.5	<0.5	<0.5	<0.5	<0.5
	58.5-61	<0.5	13.1	<0.5	<0.5	<0.5	<0.5	<0.5

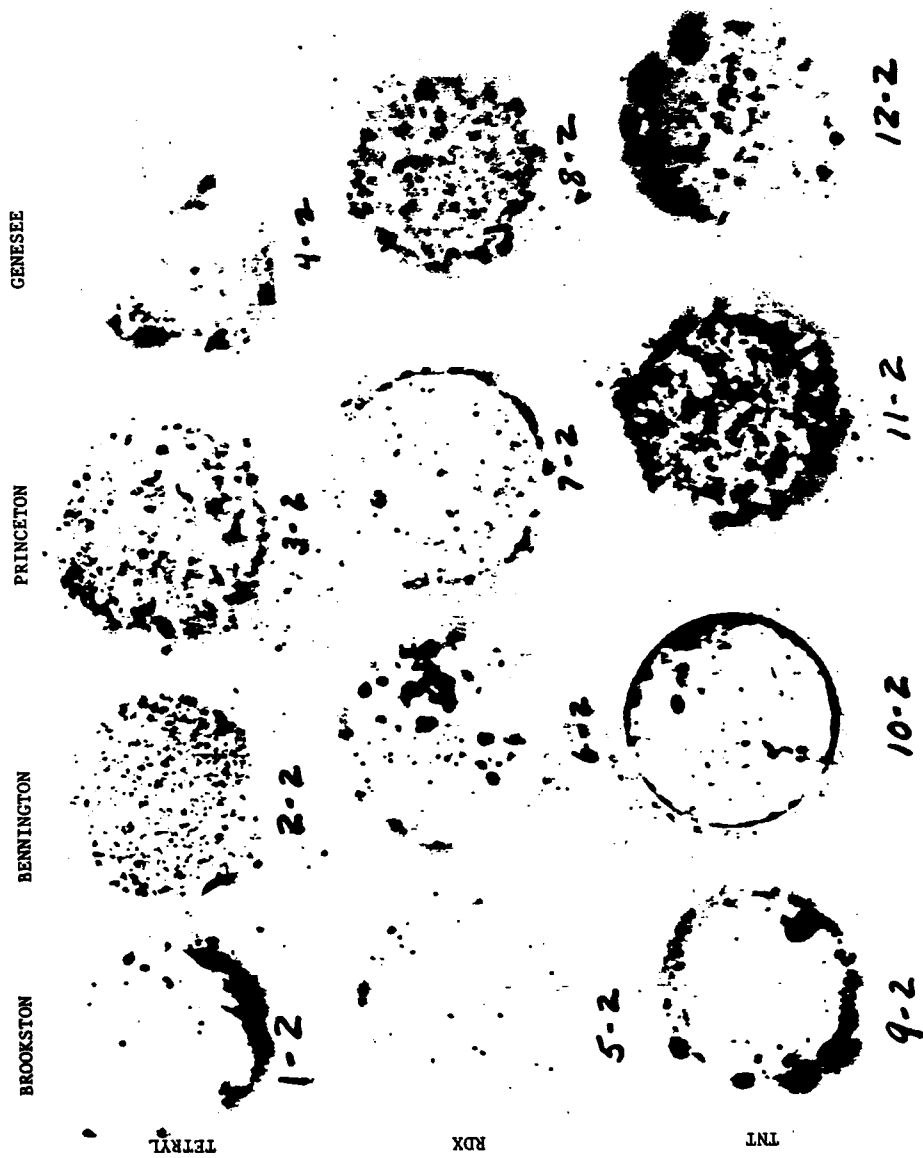


FIGURE 17. AUTORADIOGRAM OF CROSS-SECTIONS OF ^{14}C COLUMNS SHOWING THE DISTRIBUTION OF ^{14}C THROUGHOUT THE SOIL

TABLE 24. CONCENTRATIONS OF MUNITIONS COM-
POUNDS IN WATER SAMPLES FROM
14C COLUMNS AFTER 20 WEEKS

Soil	Tetryl	TNT (a) (ppm)	RDX
Brookston (sicl)	<0.5	<0.5	<0.5
Bennington (sil, acid)	<0.5	<0.5	<0.5
Princeton (sl)	-- (b)	<0.5	<0.5
Genesee (sil)	<0.5	< 0.5	<0.5

(a) None of the TNT degradation products were observed above the detection limit.

(b) Insufficient sample.

TABLE 25. TOTAL ORGANIC CARBON IN SOIL SAMPLES
COLLECTED FROM THE TETRYL TREATMENT
OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (a) (percent)	
		2	6
Brookston (sicl)	0-10		
	10-20	4.3	3.8
	20-30	2.3	3.0
	30-61	1.9	1.5
	61-91	1.2	-- (b)
	91-122	0.58	--
	122-152	0.44	--
Bennington (sil, acid)	0-10		
	10-20	0.46	0.88
	20-30	0.26	0.30
	30-61	0.40	0.43
	61-91	0.78	--
	91-122	0.81	--
	122-152	0.66	--
Princeton (sl)	0-10		
	10-20	0.98	0.83
	20-30	0.74	0.44
	30-61	0.21	0.23
	61-91	0.19	--
	91-122	0.11	--
	122-152	0.13	--
Genesee (sil)	0-10		
	10-20	3.4	3.4
	20-30	2.9	3.2
	30-61	2.2	2.2
	61-91	1.8	--
	91-122	1.2	--
	122-152	1.6	--

(a) Analyses were discontinued after 6 weeks because data were not helpful.

(b) Dash indicates samples not analyzed.

TABLE 26. TOTAL ORGANIC CARBON IN WATER SAMPLES
COLLECTED FROM THE TETRYL TREATMENT
OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)							
		0	2	4	6	8	10	12	14
Brookston (sicl)	15	15	15	14	17	17	NA	19	16
	46	12	14	13	11	12	11	16	14
	76	9	NA	NA	NA	NA	NA	NA	NA
	152	7	NA	NA	NA	NA	NA	NA	NA
Bennington (sil, acid)	15	10	8	8	7	7	6	6	7
	46	7	9	14	6	12	3	10	7
	76	12	NA	NA	NA	NA	NA	NA	NA
	152	10	NA	NA	NA	NA	NA	NA	NA
Princeton (sl)	15	17	21	11	13	12	13	14	14
	46	14	17	13	12	8	7	11	9
	76	16	NA	NA	NA	NA	NA	NA	NA
	152	8	NA	NA	NA	NA	NA	NA	NA
Genesee (sil)	15	20	16	16	16	14	19	16	18
	46	19	14	16	14	12	13	12	16
	76	12	NA	NA	NA	NA	NA	NA	NA
	152	13	NA	NA	NA	NA	NA	NA	NA

TABLE 27. TOTAL ORGANIC CARBON IN SOIL
SAMPLES COLLECTED FROM THE
RDX TREATMENT OF THE BASIC
STUDY

Soil	Depth (cm)	Weeks After Treatment ^(a) (percent)	
		2	6
Brookston (sicl)	0-10		
	10-20	3.2	4.5
	20-30	2.6	3.4
	30-61	2.2	1.7
	61-91	0.62	-- ^(b)
	91-122	0.48	--
	122-152	0.60	--
Bennington (sil, acid)	0-10		
	10-20	0.41	0.82
	20-30	0.33	0.37
	30-61	0.46	0.35
	61-91	0.66	--
	91-122	0.65	--
	122-152	0.67	--
Princeton (sl)	0-10		
	10-20	0.86	1.3
	20-30	0.30	0.40
	30-61	0.17	0.11
	61-91	0.11	--
	91-122	0.12	--
	122-152	0.15	--
Genesee (sil)	0-10		
	10-20	3.3	3.2
	20-30	3.2	3.1
	30-61	2.4	2.4
	61-91	2.0	--
	91-122	1.5	--
	122-152	1.4	--

(a) Analyses were discontinued after 6 weeks because data were not helpful.

(b) Dash indicates samples not analyzed.

TABLE 28. TOTAL ORGANIC CARBON IN WATER SAMPLES
COLLECTED FROM THE RDX TREATMENT OF
THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)							
		0	2	4	6	8	10	12	14
Brookston (sicl)	15	11	11	6	8	8	8	9	16
	46	6	12	6	12	6	10	9	17
	76	24	NA	NA	NA	NA	NA	NA	NA
	152	9	NA	NA	NA	NA	NA	NA	NA
Bennington (sil, acid)	15	6	10	4	4	4	9	5	6
	46	8	14	7	10	5	10	5	10
	76	9	NA	NA	NA	NA	NA	NA	NA
	152	5	NA	NA	NA	NA	NA	NA	NA
Princeton (sl)	15	9	16	6	9	10	10	12	14
	46	14	17	6	7	8	6	7	8
	76	14	NA	NA	NA	NA	NA	NA	NA
	152	6	NA	NA	NA	NA	NA	NA	NA
Genesee (sil)	15	18	14	14	13	15	9	12	18
	46	19	19	10	12	15	13	11	14
	76	17	NA	NA	NA	NA	NA	NA	NA
	152	11	NA	NA	NA	NA	NA	NA	NA

TABLE 29. TOTAL ORGANIC CARBON IN SOIL
SAMPLES COLLECTED FROM THE
TNT TREATMENT OF THE BASIC
STUDY

Soil	Depth (cm)	Weeks After Treatment ^(a) (percent)	
		2	6
Brookston (sicl)	0-10		
	10-20	4.0	3.8
	20-30	2.4	2.8
	30-61	1.4	1.6 ^(b)
	61-91	0.71	--
	91-122	0.49	--
	122-152	0.96	--
Bennington (sil, acid)	0-10		
	10-20	0.80	0.50
	20-30	0.37	0.24
	30-61	0.48	0.29
	61-91	0.57	--
	91-122	0.73	--
	122-152	0.58	--
Princeton (sl)	0-10		
	10-20	0.76	--
	20-30	0.52	--
	30-61	0.40	--
	61-91	0.20	--
	91-122	0.16	--
	122-152	0.15	--
Genesee (sil)	0-10		
	10-20	3.4	--
	20-30	2.8	--
	30-61	2.2	--
	61-91	1.5	--
	91-122	1.9	--
	122-152	1.4	--

TABLE 30. TOTAL ORGANIC CARBON IN WATER SAMPLES
COLLECTED FROM TNT TREATMENT OF THE
BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)							
		0	2	4	6	8	10	12	14
Brookston (sicl)	15	13	14	8	8	11	20	14	14
	46	15	10	5	9	6	10	7	NA
	76	13	NA	NA	NA	NA	NA	NA	NA
	152	8	NA	NA	NA	NA	NA	NA	NA
Bennington (sil, acid)	15	4	8	5	6	4	6	6	14
	46	5	12	5	8	6	14	10	11
	76	15	NA	NA	NA	NA	NA	NA	NA
	152	8	NA	NA	NA	NA	NA	NA	NA
Princeton (sl)	15	15	23	12	15	18	14	21	18
	46	12	16	9	6	8	7	8	9
	76	10	NA	NA	NA	NA	NA	NA	NA
	152	9	NA	NA	NA	NA	NA	NA	NA
Genesee (sil)	15	16	20	14	17	13	13	23	15
	46	12	18	10	12	12	12	16	15
	76	16	NA	NA	NA	NA	NA	NA	NA
	152	9	NA	NA	NA	NA	NA	NA	NA

TABLE 31. NITRATE CONTENT OF WATER SAMPLES COLLECTED FROM
THE TETRYL TREATMENT OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)						
		0	2	4	6	8	10	12
Brookston (sicl)	15	135	188	153	169	358	NA	373
	46	18.4	28	74	63	166	111	265
	76	4.9	20	96	111	169	NA	NA
	152	0.44	0.12	0.68	0.8	NA	NA	NA
Bennington (sil, acid)	15	40	64	118	159	210	250	262
	46	2.35	18	112	38	NA	13	116
	76	1.44	6.2	32	12	NA	NA	NA
	152	2.12	0.5	1.1	1	NA	NA	NA
Princeton (sl)	15	154	325	394	205	473	692	743
	46	108	154	118	178	297	512	450
	76	43.3	50	74	81	132	NA	NA
	152	13.7	7.2	18	6.4	NA	NA	NA
Genesee (sil)	15	220	361	243	321	267	310	360
	46	136	161	190	233	328	380	512
	76	107	127	132	282	179	NA	NA
	152	9.7	48	47	52	24	NA	NA

TABLE 32. NITRITE CONTENT OF WATER SAMPLES COLLECTED
FROM THE TETRYL TREATMENT OF THE BASIC
STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)						
		0	2	4	6	8	10	12
Brookston (sicl)	15	0.33	0.39	0.60	0.31	0.78	NA	0.70
	46	0.11	0.19	0.11	0.29	1.5	0.66	0.86
	76	0.25	0.61	0.60	0.43	0.67	NA	NA
	152	0.03	0.06	0.05	0.17	0.11	NA	NA
Bennington (sil, acid)	15	0.05	0.24	0.28	0.35	0.48	1.46	0.28
	46	0.03	0.38	0.53	0.34	0.37	0.23	0.67
	76	0.05	0.18	0.82	0.19	0.49	NA	NA
	152	0.40	1.0	0.34	1.38	1.2	NA	NA
Princeton (sl)	15	0.04	3.6	1.48	1.79	0.49	1.44	0.39
	46	0.15	0.57	0.31	0.58	0.51	0.13	0.30
	76	0.03	0.06	0.32	0.37	0.41	NA	NA
	152	0.40	1.0	0.82	1.36	1.2	NA	NA
Genesee (sil)	15	0.06	1.4	0.44	0.45	0.92	1.24	0.71
	46	0.08	0.46	0.14	0.17	0.07	0.10	0.12
	76	0.03	0.20	0.26	0.40	0.16	NA	NA
	152		2.5	0.95	1.30	2.7	NA	NA

TABLE 33. NITRATE CONTENT OF WATER SAMPLES COLLECTED
FROM THE RDX TREATMENT OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)					
		0	2	4	6	8	10
Brookston (sicl)	15	115	206	203	223	286	315
	46	8.4	31	21	57	49	120
	76	15	25	15	60	35	NA
	152	0.63	0.04	0.15	4.3	NA	NA
Bennington (sil, acid)	15	23	35	57	74	105	138
	46	5.7	118	68	63	40	128
	76	0.66	2.1	34	43	15	NA
	152	0.04	0.08	0.68	4.1	NA	NA
Princeton (sl)	15	121	370	300	221	308	278
	46	63	92	118	200	400	1000
	76	51	57	53	59	72	NA
	152	11	3.6	1.6	2.8	NA	NA
Genesee (sil)	15	256	214	523	420	613	420
	46	170	458	252	168	328	350
	76	107	177	160	98	NA	NA
	152	12	3.1	14	3.7	NA	NA

TABLE 34. NITRITE CONTENT OF WATER SAMPLES COLLECTED
FROM THE RDX TREATMENT OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)					
		0	2	4	6	8	10
Brookston (sicl)	15	0.14	0.13	0.43	0.49	0.12	0.73
	46	0.16	0.15	0.46	1.17	0.72	0.82
	76	0.17	0.41	0.49	0.91	0.15	NA
	152	0.15	0.05	0.03	0.21	0.04	NA
Bennington (sil, acid)	15	0.08	0.25	0.13	0.27	0.20	0.37
	46	0.03	0.61	0.89	0.74	4.7	2.47
	76	0.26	0.82	0.39	0.91	2.9	NA
	152	0.15	0.17	0.16	0.64	0.06	NA
Princeton (sl)	15	0.06	2.3	1.5	1.0	0.47	1.44
	46	0.15	1.9	0.36	0.56	0.41	0.51
	76	0.25	0.14	0.66	0.95	0.59	NA
	152	0.04	0.46	0.36	0.35	0.62	NA
Genesee (sil)	15	0.05	0.41	0.33	0.27	0.21	0.84
	46	<0.01	0.38	0.30	0.53	0.39	0.80
	76	0.07	0.09	0.66	0.51	0.25	NA
	152	1.2	1.0	2.6	0.44	2.6	NA

TABLE 35. NITRATE CONTENT OF WATER SAMPLES COLLECTED
FROM THE TNT TREATMENT OF THE BASIC STUDY

Soil	Depth (cm)	Weeks After Treatment (ppm)					
		0	2	4	6	8	10
Brookston (sicl)	15	120	142	184	215	216	238
	46	82	37	26	32	39	61
	76	212	87	9.5	5.2	NA	NA
	152	0.12	0.37	<0.1	1	NA	NA
Bennington (sil, acid)	15	24	54	64	100	218	153
	46	5.1	21	5.6	280	7	62
	76	2.9	5.7	5.2	16	7	NA
	152	2.7	5.4	1.8	2.4	87	NA
Princeton (sl)	15	198	365	326	290	570	345
	46	63	172	176	258	311	307
	76	29	31	36	46	NA	NA
	152	1.6	0.17	0.34	1.7	NA	NA
Genesee (sil)	15	213	350	444	441	588	590
	46	175	205	243	308	398	450
	76	132	153	178	218	212	NA
	152	48	41	76	66	NA	NA

TABLE 36. NITRILE CONTENT OF WATER SAMPLES COLLECTED
FROM THE TNT TREATMENT OF THE BASIC STUDY

(Data reported as ppm-NO₂.)

Soil	Depth (cm)	Weeks After Treatment (ppm)					
		0	2	4	6	8	10
Brookston (sicl)	15	0.21	0.30	0.16	0.21	0.16	1.89
	46	0.24	<0.01	0.26	0.18	0.09	0.75
	76	0.95	0.33	0.26	0.32	0.05	NA
	152	0.07	<0.01	0.08	0.08	0.02	NA
Bennington (sil, acid)	15	0.32	11.11	0.13	0.25	0.12	0.41
	46	0.12	0.25	0.13	0.84	0.56	1.44
	76	0.07	0.25	0.99	0.48	0.80	NA
	152	1.1	0.24	0.53	0.56	0.22	NA
Princeton (sl)	15	0.12	2.04	0.89	0.58	0.37	0.60
	46	0.17	0.53	0.20	0.30	0.19	2.55
	76	0.13	0.95	1.7	1.2	0.31	NA
	152	0.58	0.01	0.03	0.08	0.03	NA
Genesee (sil)	15	0.02	0.74	1.4	0.80	0.92	1.09
	46	1.1	0.07	0.13	0.23	0.36	0.52
	76	0.18	0.21	0.30	0.32	0.23	NA
	152	2.8	0.36	0.30	0.06	0.01	NA

TABLE 37. PARTITION EXPERIMENT DATA

Soil	Initial Aqueous Concentration (ppm)	C_w (a)	C_s (b)	P (c)
<u>TNT</u>				
Brookston (sicl)	28.6	24.3	122.6	5.0 (14.4)
Genesee (sil)	28.6	23.6	117.6	4.9 (17.8)
Princeton (sl)	28.6	25.7	64.6	2.5 (8.2)
Bennington (sil, acid)	28.6	24.5	81.0	3.3 (13.5)
<u>TETRYL</u>				
Brookston (sicl)	21.4	13.7	36.5	2.7 (34.3)
Genesee (sil)	21.4	13.6	37.1	2.7 (35.3)
Princeton (sl)	21.4	16.5	31.9	1.9 (11.5)
Bennington (sil, acid)	21.4	17.1	51.7	3.0 (7.6)
<u>RDX</u>				
Brookston (sicl)	23.5	28.0	219.3	7.8
Genesee (sil)	23.5	31.6	200.8	6.4
Princeton (sl)	23.5	22.6	4.8	0.2
Bennington (sil, acid)	23.5	29.1	52.8	1.8

(a) C_w = concentration in the aqueous phase.

(b) C_s = concentration in the soil phase.

(c) Values in parentheses are calculated using the concentration difference in the water phase to determine C_s .

of P are also given and are calculated as the ratio of Cs to Cw using both the measured value for Cs and the extrapolated value for Cs based on the measured loss of compound from the water phase. This latter value for Cs is determined by dividing the loss of munition (μg) in the water phase by the weight (g) of soil.

DISCUSSION

Objectives of Analysis

With the assumption that the migration of munition compounds through soil proceeds by water transport, it was anticipated that this migration would be manifested by concentration gradients in both the water and soil samples withdrawn from various depths in the soil profile. The appearance and migration of any transformation products should produce a similar gradient which would also be reflected by similarly varying patterns in the ^{14}C activity of the column effluents obtained in the ^{14}C Study. Consequently, the objective of the analysis of these samples was to monitor for anticipated changes in the concentration gradient for each selected munition compound and the presence and movement of any transformation products which may be found. To this end, soil and water samples were systematically withdrawn and analyzed for specific compounds with attention to the appearance of any "new components" during the course of this study.

^{14}C Study

Water Samples. Tables 17-19 present the levels of radioactivity found in the effluent samples from the ^{14}C lysimeters. Blank and spiked samples were not processed during the analysis of these samples, although an examination of single samples of untreated soils of each of the four soil types used in this study revealed ^{14}C levels at or below the instrumental background (100 dpm).

Several of these samples displayed relatively high dpm values and were presumed to contain correspondingly high levels of munition or munition-related material.

The ^{14}C -labeled compounds were examined by HPLC to determine their purities. Methanol solutions containing 1-2 μg of each ^{14}C -labeled compound were chromatographed and fractions collected and analyzed by radioassay. These compounds were all shown to be free of any radioactive impurities above the 1 percent level.

Using the specific activities for each compound given in Table 3, the calculations in Table 38 indicate the levels of pure compound these values may represent.

TABLE 38. RELATIONSHIP BETWEEN DISINTEGRATION PER MINUTE AND CONCENTRATION OF PURE ^{14}C -LABELED COMPOUND

Compound	100 dpm		100,000 dpm	
	Total (μg)	Concentration (ppb)	Total (μg)	Concentration (ppb)
TNT	1.6×10^{-3} (a)	0.3 (b)	1.6	300
RDX	2.7×10^{-3}	0.5	2.7	500
Tetryl	2.8×10^{-3}	0.5	2.8	500

(a) $0.152 \mu\text{mol}/\mu\text{Ci} \times 227.1 \mu\text{g}/\mu\text{mol} \times 1 \mu\text{Ci}/2.22 \times 10^6 \text{ dpm } \mu\text{Ci} \times 100 \text{ dpm} = 1.6 \text{ ng}$.

(b) $1.6 \text{ ng}/5 \text{ ml} = 0.3 \text{ ppb}$.

Several of the samples analyzed for ^{14}C had activities in excess of 100,000 dpm and these samples were extracted and analyzed by HPLC according to the procedures described in the Analytical Procedures section of this report. However, the concentrations of any TNT, RDX, and tetryl in these samples were too low to be detected by HPLC.

It is important to remember that since the ^{14}C columns were treated with 1:150 mixture of labeled to non-labeled munition, 0.5 ppm concentrations of ^{14}C -labeled material might represent as much as 75 ppm of total intact munition, assuming the labeled and non-labeled materials behave identically in the soil column. Table 39 illustrates the correspondence between some of the ^{14}C activities observed for Princeton-PDX column effluent (see Table 19) and concentrations of intact ^{14}C -labeled and non-labeled munition.

HPLC analyses of the 24-wk ^{14}C water samples (see Table 19) and of the sacrificed ^{14}C columns indicate that no parent munition is migrating through these columns in concentrations above 0.5 ppm. Consequently, the high levels of radioactivity observed in samples 13-20 must be due to materials generated from the intact munition. Such transformation products may have been generated from the thermal, biological, photolytic, or chemical degradation of the parent compound accompanied by possible

TABLE 39. RADIOACTIVITY AND PROJECTED CONCENTRATIONS OF INTACT MUNITIONS IN PRINCETON (TNT AND RDX) AND GENESEE (TNT AND RDX) COLUMNS

Soil	Munition	Parameter	Weeks After Treatment									
			8	10	12	14	16	18	20	22	24	
Princeton	TNT	¹⁴ C activity (dpm)	5,130	16,753	18,651	15,462	11,913	13,451	16,734	11,676	10,627	
		¹⁴ C munition (ppm) (a)	0.02	0.05	0.06	0.05	0.04	0.04	0.05	0.04	0.03	
	RDX	Total munition (ppm) (a)	2.3	7.4	8.4	7.0	5.4	6.1	7.5	5.3	4.8	
		¹⁴ C activity (dpm)	4,490	11,117	22,783	28,879	65,557	94,382	104,465	124,913	134,999	
	Total munition (ppm) (a)	¹⁴ C munition (ppm) (a)	0.02	0.06	0.11	0.14	0.33	0.47	0.52	0.62	0.68	
Total munition (ppm) (a)		3.4	8.5	17.1	21.7	49.2	70.8	78.3	93.7	101.3		
Geneese	TNT	¹⁴ C activity (dpm)	222	667	453	597	610	1,358	1,097	1,944	2,220	
		¹⁴ C munition (ppm) (a)	0.0007	0.002	0.001	0.002	0.002	0.003	0.003	0.006	0.007	
	RDX	Total munition (ppm) (a)	0.10	0.3	0.2	0.3	0.3	0.6	0.5	0.9	1.0	
		¹⁴ C activity (dpm)	2,504	9,125	5,279	36,056	34,180	6,994	20,105	17,030	24,566	
	Total munition (ppm) (a)	¹⁴ C munition (ppm) (a)	0.01	0.05	0.03	0.18	0.17	0.03	0.10	0.09	0.12	
Total munition (ppm) (a)		1.9	6.8	4.0	27.0	25.6	5.2	15.1	12.8	18.4		

(a) Values calculated using the following relationships: 100,000 dpm $\pm$ 0.3 ppm ¹⁴C-TNT (where 100,000 dpm $\times$ 1 μ Cl/2.22 $\times$ 10⁶ dpm $\times$ 227.1 μ g/ μ mol TNT $\times$ 1/657 μ Cl/ μ mol)/5 ml volume of sample = 0.3 μ g/ml; similarly, 100,000 dpm $\pm$ 0.5 ppm ¹⁴C-RDX, 100,000 dpm $\pm$ 0.5 ppm ¹⁴C-Tetryl.

exchange reactions in which ^{14}C carbons are transferred to non-munition-related compounds in the soil columns. However, the absence of any large unidentified components in the chromatograms of the sacrificed ^{14}C soil samples or the selected water samples indicates that such transformation products are apparently not highly uv active. Such compounds as aliphatic amines and nitro compounds, as well as formaldehyde, etc., might be anticipated in the case of RDX as tetryl decomposition processes but because of high polarity (water solubilities) as low uv extinction may not appear in the chromatograms of these samples.

The monitoring and identification of these ^{14}C -labeled materials eluting from these columns are very important in describing the "breakthrough" which seems to have occurred in some of the ^{14}C columns. The high sensitivity to detection afforded by radiocounting techniques combined with the separation and isolation of components by HPLC may be used to identify and monitor these specific compounds. Each highly active sample should be fractionated first by direct injection HPLC and each fraction examined for radioactivity. Active fractions could then be submitted for structural characterization by mass spectrometry, nuclear magnetic reassurance, and infrared spectroscopy, as applicable. Once identified, continued radiomonitoring would provide a sensitive means of detection for the migration rates of these materials through these columns. Such a preliminary study would perhaps be most valuable in predicting such behavior in the larger lysimeter study and serve as a sensitive prediction for breakthrough of specific compounds in the larger study. It appears from the data collected thus far that migration of parent compounds is very limited. However, there does appear to be a gradual increase in production/migration of some munition-related material whose identity is as yet undefined.

Therefore, it would seem feasible to extend the ^{14}C study until actual breakthrough of intact munition is observed. These data coupled with identification and monitoring of the ^{14}C -labeled materials would provide a good approximation to the behavior of these munitions in real world conditions.

Trap Samples. The radioassay of the propylene carbonate trap samples (see Tables 21-23) indicates that no volatile ^{14}C -labeled organics were collected in these traps. The $\text{Ba}(\text{OH})_2$ traps showed significant activities in some cases, indicating the formation of $^{14}\text{CO}_2$ in these cores. The RDX and TNT columns were most notable in this regard, especially in the cases of the Princeton and Genesee soils.

The barium hydroxide traps, however, showed significantly higher activities, indicating that $^{14}\text{CO}_2$ was released in some cases. Most notably with RDX, increasingly higher activities in

the $\text{Ba}(\text{OH})_2$ traps associated with each soil column were observed with time. It is evident that chemical or biological activity resulted in ring cleavage of the munition compound to produce $^{14}\text{CO}_2$.

Basic Study

Water Samples. The water samples analyzed in this study were devoid of munition compounds at concentrations sufficient for quantitation using the HPLC procedures employed in this study. Experiments were conducted to determine the recovery of very low levels of these compounds in aqueous samples. Spiked aqueous samples were prepared in duplicate as described in the Solubility Experiment and these samples were prepared and analyzed using the normal procedures. These data are presented in Table 40 and indicate that recovery decreases significantly below 1 ppm using the sample preparation procedures employed in this study. Based on this recovery study, a detection limit of 500 ppb is given for each of the compounds examined for water samples. As will be discussed later, the water solubilities of these compounds were significantly lower than their reported values and much slower than anticipated (see discussion on Solubility Study in Discussion and Analytical Results sections of this report).

TABLE 40. RECOVERY OF MUNITION COMPOUNDS
IN AQUEOUS SAMPLES AT CONCENTRATIONS BELOW 1 PPM

Compound	Spiked (ppb)	Found (a) (ppb)	Percent Recovery
Tetryl	1000	560	56
	500	200	40
	100	<50(b)	0
	50	<50(b)	0
RDX	1000	410	41
	500	195	39
	100	<50(b)	0
	50	<50(b)	0
TNT	1000	680	68
	500	210	42
	100	<50(b)	0
	50	<50(b)	0

(a) Average of two determinations.

(b) Munition compounds were detected in these samples, however, the scales were too small to be readably quantitated.

Blank and spiked water samples were prepared and analyzed during the latter phases of this study with every set of 40 water samples generated from the Basic Study. The spiked samples prepared by spiking distilled water with organic solutions of each munition compound and these recoveries were between 70 and 90 percent in most cases. Blank samples contained only small amounts of impurities in all cases and were devoid of any components which may have interfered significantly with the analytical method.

During the course of analyzing these water samples, few instances were observed in which possible transformation products may have occurred in the water samples analyzed. The 22- and 24-wk RDX water samples generated from the Basic Study all displayed a major peak which eluted just prior to RDX. The amounts of this material appeared to vary randomly in these samples and close inspection of earlier samples from these lysimeters revealed that a few of these contained a similar component in trace amounts. Several of the 22-wk TNT water samples generated from the Basic Study also contained major unidentified materials. These materials had retention times similar to those of the DNT isomers. These samples were spiked with authentic standards of these isomers and it appears that these unidentified materials were not dinitrotoluenes.

Soil Samples. Soil samples generated from the Basic Study displayed concentrations of munition compounds at varying levels throughout the study. The 0-4-inch depth on each soil column included the treated layer and was highly concentrated. These samples were prepared as discussed in the Methods section of this report but were not analyzed with the other samples. The extracts of these highly concentrated samples were diluted 1000-fold and analyzed separately to prevent cross contamination of the much less concentrated samples withdrawn from the lower depths. These samples were analyzed only for the 18-wk and 26-wk soil samples and in most cases varied significantly from the treatment concentration of 20,000 ppm. This may be the result of inhomogeneity of the treated soil layer because the crystalline compound was merely mixed into the soil.

The recovery of compounds from each soil was examined in order to establish the efficiency of the extraction-concentration procedures used in sample preparation and also to verify the detection limits for the quantitation of these compounds. These studies were conducted using Brookston soil which has a relatively high sorption capacity compared to the other soils used in this study. (See clay and organic matter contents of the soils in Appendix A.) These recoveries proved to be essentially quantitative; however, it is not clear whether or not the procedure used to generate the spiked soil samples actually resulted in

sorption of the compounds on the soil. Consequently, these recoveries may be somewhat higher than would be obtained for truly sorbed compounds and may not reflect the extent of any irreversible sorption which may be expected to occur.

Blank and spiked soils were processed as a part of the quality control procedures used in the latter phase of this study. Spiked samples were prepared as described in the recovery studies discussed above and recoveries ranged between 55 and 80 percent. The blank samples contained several organic components; however, none of the components eluted with the same retention time as RDX, tetryl or TNT and its suspected transformation products. A minor component was observed near the internal standard using HPLC conditions for the determination of RDX. Under these conditions, this component eluted just after the internal standard and resulted in approximately a 10 percent error in the area measurement of the internal standard.

Other components appeared consistently in the chromatograms obtained from the analyses of the soil samples withdrawn from the TNT and tetryl lysimeters. These components were not found at comparable concentrations in the blank soils. Such components were observed primarily in the Genesee and Princeton soils throughout the study and are believed to have derived from the munition compounds (Figure 18). Their concentrations seem to be depth dependent and were consistent in successive samples withdrawn from particular depths. Specifically, the shallow depth samples from the Genesee soils consistently displayed large quantities of the unidentified components when examined under conditions suitable for the separation of TNT and its transformation products. The concentrations of these materials appear to rapidly decrease with depth in the samples obtained during a given sampling period. The Princeton soil samples withdrawn from the tetryl and TNT lysimeters displayed a large number of major unidentified components which were not found in comparable concentrations in the blank samples. These materials also appear to decrease in concentration with depth; however, there was a dramatic increase in their concentration at the 48-60-inch depth. This pattern was observed in Princeton soil samples prepared and analyzed throughout the study.

Solubility Study

The solubilities of each munition compound were verified at several temperatures in both water and diethyl ether. In both solvents, the measured values differed significantly from those reported in the literature. The water solubilities were the most surprising in that the generation of saturated solutions apparently requires many hours of vigorously shaking the compounds in

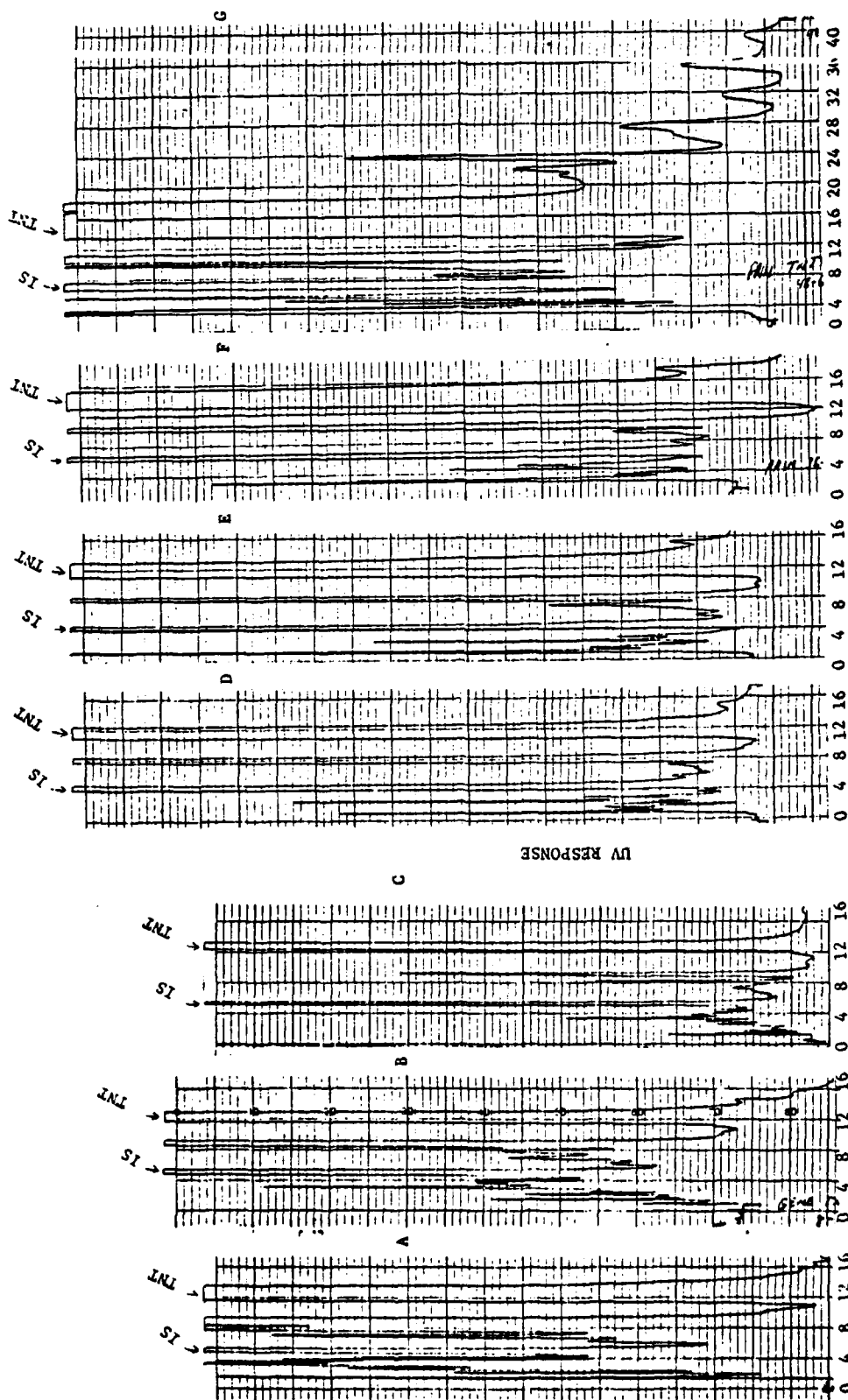


FIGURE 18. HPLC CHROMATOGRAMS OF GENESEE SOIL-TNT (26-WEEK SAMPLE)

(A = 30-61 cm, B = 61-91 cm, C = 91-122 cm and Princeton TNT—26-week samples,
D = 20-30 cm, E = 30-61 cm, F = 61-91 cm, and G = 91-122 cm.)

water. The compounds used in this study were purified by recrystallization before use and their melting points confirmed, although no information is available concerning the purity of the material used to determine the values reported in the literature. The HPLC chromatograms of the assay solutions were devoid of materials other than the compound and the internal standard. If water transport is the method of migration of these materials in soil, then their water solubilities are important data which may confirm or deny this postulated method of migration. If these materials are only slightly and very slowly soluble, then their migration rates by this postulated mechanism would be expected to be determined for each compound. From the slopes of these curves (mole fraction of compound vs temperature), the heats of solution may be determined and the solubility of each material calculated for any temperature (within the specified range). An accurate prediction of migration of these compounds through different soils will also require a knowledge of their partitioning between each soil and water, as discussed below.

Total Organic Carbon, Nitrate and Nitrite Analyses

The objective of these analyses was to provide an additional means of monitoring movement of munition compounds through the lysimeters. It was hypothesized that movement of either intact compounds or their transformation products would be detected by increased levels of TOC, NO_3 , and/or NO_2 at the lower sampling depths. In order for these results to be meaningful, the increase with time and depth would have to be rather large, at least several orders of magnitude at the concentrations with which we were dealing.

These kinds of increases were not consistently seen in the analyses which were conducted on the samples taken early in the study. The low solubilities of the munition compounds apparently resulted in slow enough movement that any increased concentration throughout the profile was masked by the background levels in the soil. Consequently, these analyses were discontinued.

Partition Experiment

The sorption of organics on soils is a well-known phenomenon and is especially pronounced for highly polar compounds such as those examined in this study (see Bailey, G. W., and J. W. White, "Factors Influencing the Adsorption, Desorption, and Movement of Pesticides in Soil", Residue Rev. 32:29-92 [1970]). Consequently, any movement of these materials through a soil phase would be

expected to depend upon the extent and rate of the sorption-desorption processes. The equilibrium between a sorbed and non-sorbed compound in a water-soil system is defined by the partition coefficient, P , and was measured for each soil-munition compound combination used in this study. These values were determined by measuring the ratio of concentrations of each compound in the separated water and soil phases. However, mass balance calculations made using these measured concentrations indicate that some of these materials are irreversibly sorbed to a large extent on each soil studied. Because of the difficulties in preparing spiked soil samples containing known amounts of sorbed munition compound, the extent of this irreversible sorption is not known. The irreversible sorption of these materials becomes especially important at their low soil concentrations which were observed in this study (see Table 38). At the 200 ppm level, the irreversible sorption of 1 mg of munition compound on 10 g of soil will result in only a 50 percent recovery and the calculation of the partition coefficient based on this material, assuming total recovery, will be in error by 100 percent. By calculating P based on the difference in concentration of the compound in the water phase before and after sorption onto the soils, more reliable partition coefficients are obtained. The "before" concentrations were obtained from the Solubility in Water Experiment from which the water solutions of known concentrations were prepared for use in the partition experiment. The "after" values were measured in the water phase after exposure to the soil. An unexplained anomaly occurred in the case of RDX in that the "after" concentration was greater than the "before" concentration. The blank water samples did not contain any materials which may have interfered with the RDX or internal standard and thereby possibly caused these anomalous results. This anomaly may be due to errors in determining the "before" concentration as only a single such determination was made. Because of the inherent inhomogeneity of soil as well as the apparently high time-dependency of the water solubility process, these partition experiments should be replicated at a series of different concentrations and exposure times.

CONCLUSIONS

1. Results of the Basic Study indicate that, over the 6-month period, parent munition compounds in the water remained at too low a concentration to be quantifiable by the analytical methods used. This appears to be the result of both soil fixation as shown by the partitioning experiment and very slow water solubilities of the compounds. There are no drinking water criteria or standards for these compounds.

2. While the results were not consistent, analyses of soil samples gave more indication of movement of munition compounds than did water samples.
3. There was a significant evolution of $^{14}\text{CO}_2$, especially from the Genesee and Princeton soils, indicating chemical or biological degradation of munition compounds at or near the surface of the soil. There was also some movement of ^{14}C -labeled compounds downward through the soil columns which may have been increasing toward the end of the experiment. These actions were detectable because of the high specific activities of the ^{14}C -tagged parent compounds, however; and the actual quantities of the compounds and/or their transformation products were too low to be quantified by the HPLC analyses. Since the ^{14}C levels increased with time in both the leachates and the trap samples, we believe that such an experiment should be continued for a longer period of time than 6 months.
4. Solubilities of the munition compounds in both water and diethyl ether were found to be much lower than have been reported in the literature. If it is to be assumed that the primary mechanism for transport of these materials in the soil is dependent upon solubility and precipitation phenomena, then these properties need to be examined more thoroughly.
5. Analyses for total organic carbons in the soil and water and for nitrate and nitrite in the water throughout the soil profile were not useful in monitoring munition compound movement. The relatively low levels of TOC, NO_3 , and NO_2 originating from the compounds were masked by indigenous soil materials.
6. Several unidentified peaks appeared in the HPLC chromatograms of many of the samples analyzed in this study. The retention times of these materials did not correspond to those of munition compounds or suspected transformation products. However, because of their irregularity of appearance and concentrations, it was not possible to determine if these materials were munition or soil related. Such uncertainties point out the need for having included blank lysimeters in this study.
7. Because leachable levels of the munition compounds could not be quantified, it was not possible to maintain mass balances either during or at the end of the experiment.

RECOMMENDATIONS

Based on the experiences gained from this program, several recommendations can be made to enhance the efficiency, i.e., results obtained for effort applied. These recommendations are:

1. Studies using radioactively-labeled compounds should be conducted before going to the large lysimeters. These studies might include:
 - leaching through small columns
 - soil thin-layer chromatography to learn something of migration rates
 - determination of sorption coefficients
 - biological degradation rates.
2. If a small column experiment were planned as an independent study instead of a pilot study for large lysimeters, it could be designed to give some definitive data by enlarging it to include the effects of such things as temperature and soilborne solutes.
3. The study should be allowed to continue until the quantities of leached compounds are large enough to be measured. Perhaps some alternative methods for chemical analysis need to be explored.
4. The method used in this program to obtain the large lysimeters was very satisfactory.
5. One of the problems encountered in taking soil samples in the lysimeters was the likelihood of cross contamination of samples. A different sampling system needs to be developed.
6. Because of the complexity of the soil and water matrix in terms of possible uv active organic constituents, the use of blank lysimeters is extremely important. Only by comparing samples obtained from such blanks with those from treated lysimeters can new or unsuspected transformation products be discerned.

APPENDIX A

MODEL STANDARD SOIL PROFILE DESCRIPTIONS OF
THE SOIL SERIES USED IN THIS STUDY

APPENDIX A

MODEL STANDARD SOIL PROFILE DESCRIPTIONS OF
THE SOIL SERIES USED IN THIS STUDY

APPROVED BY PRINCIPAL SOIL CORRELATOR
 MIDWEST REGIONAL TSC

Established Series
 Rev. JD-FWS
 5/17/67

Andy J. Standish
 8/29/67

BROOKSTON SERIES

The Brookston series is a member of a fine-loamy, mixed, noncalcareous, mesic family of Typic Argiaquolls. The Brookston soils typically have silty clay loam or clay loam dark colored A horizons 11 to 18 inches thick that grade into gray mottled clay loam B horizons with moderate development. Solums are normally 3 to 4 feet thick and slightly acid to neutral in reaction.

Typifying Pedon: Brookston silty clay loam - cultivated field.
 (Colors for moist soil)

- Ap 0-8" Very dark gray (10 yr 3/1) light silty clay loam: weak coarse granular structure; firm; cloddy when dry; abundant fine roots; neutral; abrupt smooth boundary (7 to 10 inches thick).
- Al2 8-14" Very dark gray (10 yr 3/1) silty clay loam with common fine faint dark yellowish-brown (10 yr 4/4) and dark gray (10 yr 4/1) mottles: weak coarse subangular blocky structure breaking to moderate medium granular structure; friable; abundant roots; neutral; clear wavy boundary (4 to 11 inches thick).
- Blgt 14-20" Dark gray (10 yr 4/1) silty clay loam with common fine faint dark yellowish-brown (10 yr 4/4) and yellowish-brown (10 yr 5/6) mottles; moderate medium and coarse subangular blocky structure; firm; very dark gray (10 yr 3/1) and gray (10 yr 5/1) thin discontinuous clay films on ped faces and as lining in voids; few fine roots; neutral; clear wavy boundary 4 to 10 inches thick).
- IIB2lgt 21-31" Gray (N 5/) clay loam with common fine distinct dark brown (10 yr 4/3) and yellowish-brown (10 yr 5/4) mottles; moderate medium subangular blocky structure; firm; few 2-5 mm glacial pebbles; very dark grayish-brown (10 yr 3/2) filled root channels; very dark brown (10 yr 2/2) silty clay loam material in old crayfish channels; dark gray (10 yr 4/1) clay films on most peds and as lining in few voids; neutral; gradual wavy boundary (1 to 14 inches thick).

- IIB22gt 31-40" Gray (10 yr 5/1) clay loam with many medium distinct yellowish-brown (10 yr 5/4 and 5/8) and dark yellowish-brown (10 yr 4/4) mottles; moderate coarse subangular blocky structure; firm; very dark gray (10 yr 3/1) thin discontinuous clay films on ped surfaces; few fibrous roots in upper horizon; numerous glacial pebbles; neutral; clear irregular boundary (7 to 15 inches thick).
- IIB3 40-46" Yellowish-brown (10 yr 5/6) and dark yellowish-brown (10 yr 4/4) clay loam with common medium distinct gray (10 yr 5/1) mottles; weak coarse subangular blocky structure; firm; small irregular pockets of loamy material; numerous glacial pebbles; neutral; clear irregular boundary (4 to 12 inches thick).
- IIC 46-66" Brown (10 yr 5/3) loam; massive; friable; with dark yellowish-brown (10 yr 4/4) and brown (7.5 yr 5/4) thin clay films along old root and worm hole voids; fingers of gray (10 yr 5/1) and very dark gray (10 yr 3/1) silty clay loam as fillings and linings of old krotovinas; moderately alkaline (calcareous).

Type Location: Howard County, Indiana; SW1/4 of NE1/4, Sec. 5, T23N, R4E, 516 feet east of center line gravel road, and 345 feet south of ditch; 1/2 mile east of U.S. Hwy. 31, 1/3 mile south of U.S. Hwy. 35.

Range in Characteristics: The solum thickness generally ranges from about 30 to 50 inches but in some areas it is as shallow as 24 inches. Mean annual soil temperature ranges between 49 and 57 F. The reaction of the solum is slightly acid to neutral and in some areas it ranges to mildly alkaline. Loess cap is 0 to 20 inches thick. The A horizons range in color from black (10 yr 2/1) to very dark grayish-brown (10 yr 3/2); in texture from loam to silty clay loam; in structure from weak to moderate, medium to coarse granular, or weak to moderate, fine to medium subangular blocky; in consistency from friable to firm; in thickness from 11 to 18 inches but typically is 12 to 16 inches. The B2 horizons range in color of neutral (N) to 10 yr, 2.5Y and 5Y hues, in value of 4 to 6 and chromas of 1 to 2 with few to common, faint to distinct mottles of 10 yr to 2.5Y or 7.5Y hues in values of 4 to 6 and chromas of 1 to 8; clay and organic films have colors of very dark gray (10 yr 3/1) to gray (10 yr 5/1); in texture from silty clay loam to clay loam with some horizons ranging to loam (the weighted average clay content of the top 20 inches of the argillic is between 27 and 35 percent and the weighted average sand content is >15 percent fine sand or coarser); in structure from moderate, medium to coarse subangular blocky to moderate, medium to coarse angular blocky structure (structure may also be weak to moderate, medium to coarse prismatic); in consistency from

AD-A082 874

BATTELLE COLUMBUS LABS OH
EVALUATION OF THE ENVIRONMENTAL FATE OF MUNITION COMPOUNDS IN S--ETC(U)
JUN 79 V O HALE, T B STANFORD, L G TAFT DAMD17-76-C-6065
ML

UNCLASSIFIED

2 of 2
AD-A082 874



END
DATE
FILMED
5-80
DTIC

friable to firm. The upper B2 horizon is often lower in sand than the lower horizons. Clay films in the Bt horizons range from easily seen on all peds and linings in voids to difficult to observe and only on some peds and linings in some voids. The C horizon includes hues of 10 yr and 2.5Y, values of 5, 6, or 7, and chromas of 1, 2, or 3; texture is usually a loam but may be a light clay loam or silt loam; reaction is mildly to moderately alkaline (and is usually calcareous).

Competing Series and Their Differentiae: Similar or related soils are in the Mermill, Rensselaer, Westland, Mahalasville, Patton, Ragsdale, Drummer, Virden, Sable, Kokomo, Colwood, Lenawee, Barry, Pewamo, Abington, *Naven, Marengo, and Millgrove series. The Mermill soils have a coarser textured solum and contain a higher content of gravel in the lower part. The Rensselaer soils are formed in stratified sandy and silty materials and the lower solum has a higher sand content. The Westland soils have more gravel in the lower solum and overlie calcareous gravel and sand. Mahalasville soils have an upper solum low in sand content and a lower solum which is loamy (it is in a fine-silty family). The Patton soils do not have an argillic horizon and have a low sand content in the solum (Haplaquoll, fine-silty). The Ragsdale soils have a lower sand content in the solum (Argiaquoll, fine-silty). The Drummer soils have a cambic rather than argillic horizon and less sand in the upper solum (Typic Haplaquoll, fine-silty). The Virden soils have higher chromas in the B horizon and leached of carbonates in the C. Sable soils lack an argillic horizon and the solum contains less sand (Typic Haplaquoll, fine-silty). The Kokomo soils have a thicker A1 horizon and a finer textured B. The Colwood and Lenawee soils are developed in stratified materials, have more variable textured sola and lack argillic horizons. The Barry soils have coarser textured B and C horizons. The Pewamo soils have finer textured B and C horizons. The Abington soils have thicker A horizons and a lower solum with a higher gravel content. The *Naven soils have developed in two-story parent material consisting of loamy outwash over clayey slack-water deposits. They have coarser textured upper sola with a higher sand content and finer textured lower sola, with a lower sand content. The Marengo soils are more acid. The Millgrove soils are derived from gravelly beach ridges and outwash material and have gravelly sandy loam and gravelly sand substratum. Ber-ville soils have more gravel throughout the solum.

Setting: These soils occur on nearly level to slightly depressed topography; slope gradients are less than 2 percent. The regolith is Wisconsin age loamy till. The climate is midcontinental type with hot summers and cold winters. The average daily maximum air temperature in July is as high as 88 F and the average daily minimum temperature drops to about 22 F in January. The mean annual soil temperature is between 47 and 59 degrees; mean annual precipitation is approximately 30 to 44 inches.

Principal Associated Soils: The well drained Miami, moderately well drained Celins, somewhat poorly drained Crosby and Conover, and very poorly drained Kokomo form a drainage sequence with the Brookston soils and are the most closely associated series.

Drainage and Permeability: Brookston soils are naturally very poorly drained; surface runoff is very slow to ponded; permeability is slow. Most areas are artificially drained with tile and open ditches.

Use and Vegetation: Mostly cultivated crops: crops include corn, soybeans, oats, wheat, and legume grass. Tomatoes, sugar beets, and field beans are important crops in some areas. A small proportion is in permanent pasture or woodlots. Native vegetation was deciduous forest, mixed with swamp grasses and sedges.

Distribution and Extent: Indiana, southern Michigan, and western Ohio and eastern Wisconsin. The series is extensive - more than 100,000 acres.

Series Established: White County, Indiana, 1915.

Remarks: The series was formerly classified as a Humic Gley. A considerable proportion of the soils now classified and mapped as the Pewamo, Hoytville and Barry series were formerly mapped as Brookston. Some areas still recognized as Brookston but falling within the fine family may be within the range in characteristics for Pewamo. They may be recognized as Pewamo soils but phased because of underlying loam till rather than silty clay loam till. Areas mapped as Brookston in the past which are associated with the Russell soils are dominantly in loess material and will be within the Ragsdale series or other series. The Chalmers series as mapped is a very close competitor to Brookston; a part of it will probably be within the Brookston series and the remainder in other series. Chalmers need to be adequately differentiated or else made inactive. Relationship of Della, Lear, *Runnymede, *Kouts to the Brookston series is not clear at the present time but they are not believed to seriously conflict.

APPROVED BY PRINCIPAL SOIL CORRELATOR
MIDWEST REGIONAL TSC: 7/7/71

Established Series
Rev. HPU-FWS
7/7/71

John E. McAllister
Rit

GENESEE SERIES

The Genesee series is a member of the fine-loamy, mixed, mesic family of Fluventic Eutrochrepts. Genesee soils typically have brown silt loam A horizons, dark, yellowish-brown and yellowish-brown loam and silt loam B horizons, and brown loamy C horizons.

Typifying Pedon: Genesee silt loam - cultivated field
(Colors are for moist soil.)

- | | | |
|-----|--------|---|
| Ap | 0-8" | Brown (10 yr 5/3) silt loam; moderate fine and medium granular structure; friable; neutral; abrupt smooth boundary (7-10 inches thick). |
| B21 | 8-14" | Dark yellowish-brown (10 yr 3/4) silt loam; weak medium subangular blocky structure parting into moderate medium granular structure; friable; mildly alkaline; clear smooth boundary (4-9 inches thick). |
| B22 | 14-24" | Dark yellowish-brown (10 yr 4/4) loam; weak medium subangular blocky structure parting into moderate and weak medium granular structure; friable; moderately alkaline; gradual smooth boundary (6-14 inches thick). |
| B23 | 24-32" | Yellowish-brown (10 yr 5/4) loam; weak medium subangular blocky structure parting to weak fine granular structure; friable; slight effervescence; gradual wavy boundary (6-10 inches thick). |
| C | 32-44" | Brown (10 yr 5/3) stratified loam, sandy loam, and silt loam; massive friable; slight effervescence; moderately alkaline. |

Type Location: Fayette County, Indiana; 490' S and 325' E of the NW corner of the SW1/4 of Sec. 32, T. 15 N., R. 13 E.

Range of Characteristics: The column ranges from 24-60 in. in thickness. The profile ranges from slightly acid to mildly alkaline in the upper part and is calcareous within the B or within depths of 40 in. It is loam or silt loam but in some pedons ranges to a light silty clay loam, clay loam or sandy loam. The Ap horizon is brown (10 yr 3/3), dark grayish-brown (10 yr 4/2), brown (10 yr 5/3), or dark yellowish-brown (10 yr 3/4). It ranges from slightly to mildly alkaline. In undisturbed

areas, the A₁ is 1-2 in thick and is very dark brown (10 yr 2/2) to very dark gray (10 yr 3/1). The B horizon typically is yellowish-brown (10 yr 5/4) or dark yellowish-brown (10 yr 4/4) but ranges to brown (10 yr 4/2). It is commonly silt loam to loam but in some pedons ranges to light silty clay loam, clay loam, or sandy loam. The average of the 10-40 in control section commonly is 18-24 percent clay but ranges up to 27 percent clay. The average content of fine sand and coarser in the 10-40 in control section is greater than 15 percent. It has weak or moderate, medium or fine subangular blocky or granular structure. It ranges from neutral to moderately alkaline. The C horizon consists of strata of brown or yellowish-brown loam, silt loam, sandy loam, and fine sand, usually becoming coarser with depth. It is mildly to moderately alkaline and contains free carbonates and has slight or moderate effervescence.

Competing Series and Their Differentiae: These are the Armiesburg, Chagrin, Cuba, Dorchester, Drury, Eel, Haymond, Huntsville, Jules, Landes, Moshannon, Ross and Sharon series. Armiesburg, Huntsville, Landes and Ross soils have mollic epipedons. Cuba and Sharon soils are more acid and have fine-silty and coarse-silty textures, respectively. Chagrin and Moshannon soils lack free carbonates within depths of 40 in and, in addition, the Moshannon soils have hues of 5 yr or redder. Dorchester and Jules have free carbonates throughout their control sections and have fine-silty textures, respectively. Drury soils lack free carbonates within depths of 40 in and have fine-silty textures. Eel soils have mottles with chroma of 2 or less within depths of 24 inches. Haymond soils lack free carbonates within depths of 40 inches and have coarse-silty textures.

Setting: The Genesee soils are chiefly on the flood plains along the streams in areas of Wisconsin glaciation and are subject to periodic flooding. Slope gradients range from 0 to 2 percent. They formed in alluvium washed mainly from areas of calcareous loamy neutral to moderately alkaline glacial drift.

Principal Associated Soils: Moderately well drained Eel soils, somewhat poorly drained Shoals soils and very poorly drained Sloam soils form a drainage sequence with the Genesee soils and are the most common associates. In some areas the somewhat poorly drained Wayland soil is an associate.

Drainage and Permeability: Well drained; permeability is moderate; surface runoff is slow.

Use and Vegetation: Commonly cleared and cropped to corn and soybeans. The native vegetation consisted of forest, chiefly of beech, elm, hickory, hackberry, buckeye, sugar maple and ash.

Distribution and Extent: Indiana, southern Michigan, western Ohio and western New York. The series is of large extent.

Series Established: Livingston County, New York, 1908.

Remarks: The Genesee series was formerly classified as an Alluvial
Soils.

National Cooperative Soil Survey

U. S. A.

Halowayhub

Established Series
Rev. FWS
5/29/74

PRINCETON SERIES

The Princeton series is a member of the fine-loamy, mixed, mesic family of Typic Hapludalfs. Princeton soils typically have brown fine sandy loam A horizons, brown and yellowish-red sandy clay loam B2 horizons, and brown and strong brown stratified C horizons.

Typifying Pedon: Princeton fine sandy loam - on a gentle slope of 4 percent in an alfalfa field at 540' elevation. (Colors are for moist soil unless otherwise stated.)

- | | | |
|------------------|--------|--|
| Ap | 0-8" | Brown (10 yr 4/3) fine sandy loam; weak fine granular structure; very friable; many medium roots; neutral; abrupt smooth boundary (6-10 in. thick). |
| Bl _t | 8-11" | Strong brown (7.5 yr 5/6) loam; weak thick platy structure parting to weak fine and very fine subangular blocky; friable; common medium roots; thin very pale brown (10 yr 7/3) silt coatings on faces of peds; thin discontinuous dark yellowish-brown (10 yr 4/4) clay films on faces of peds; neutral; clear wavy boundary (0-8 in. thick). |
| B2 _{1t} | 11-26" | Brown (7.5 yr 4/4) sandy clay loam; moderate medium subangular blocky structure; firm; common medium and fine roots; thin continuous reddish-brown (5 yr 4/4) clay films on faces of peds; medium acid; gradual wavy boundary (10-20 in. thick). |
| B2 _{2t} | 26-41" | Yellowish-red (5 yr 5/6) sandy loam; weak coarse subangular blocky structure; friable; thin discontinuous reddish-brown (5 yr 4/4) clay films on faces of peds; few fine roots; medium acid; gradual wavy boundary (4-16 in. thick). |
| C&B _t | 41-60" | Brown (7.5 yr 4/4) loamy fine sand and fine sandy loam banded; weak coarse subangular blocky structure; very friable; few fine roots; thin discontinuous brown (7.5 yr 4/4) clay films on faces of some peds; medium acid; gradual wavy boundary (10-24 in. thick). |
| C | 60-80" | Strong brown (7.5 yr 5/6) and brown (7.5 yr 4/4) stratified loamy fine sand and fine sand; single grained; loose; slightly acid. |

Type Location: Vigo County, Indiana; 260' E and 360' S from NW corner of NE1/4 Section 5, T. 10 N., R. 9 W.

Range in Characterisitics: Solum thickness is 40-60 in. The Ap horizon is dark grayish-brown (10 yr 4/2), brown (10 yr 4/3 or 5/3), or dark yellowish-brown (10 yr 4/4). A2 or B1 horizons or both are present in some pedons. The B2t horizon has 10 yr, 7.5 yr or 5 yr hue, value of 4-6, and chroma of 4-6. It typically is sandy clay loam but subhorizons in some pedons are fine sandy loam, loam, or clay loam (the 20-in. control section averages between 18 and 25 percent clay). The B2t horizon has moderate to weak medium to coarse subangular blocky structure and firm to friable consistency. It is commonly medium to strongly acid, but thin horizons in some pedons are slightly acid or very strongly acid. Between 40 and 60 in. and B and C horizons are commonly banded loamy fine sand and fine sandy loam. The C horizon commonly is stratified with loamy sand, fine sand, fine sandy loam, and coarse silt. It is slightly acid to moderately alkaline.

Competing Series and Their Differentiae: These are the Belmore, Chili, Coggon, Conestoga, Douds, El Dara, Grellton, Hayden, Hebron, Hickory, High Gap, Hollinger, Kendallville, Kennan, Kidder, Leroy, Letort, Lindley, Mandeville, Martinsville, McHenry, Miami, Mifflin, Military, Norden, Ockley, Owosso, Pecatonica, Rawson, Renova, Riddles, Rockbridge, Roseville, Sisson, Strawn, Summitville, Teanaway, Theresa, Waymor, Westville, Whalan, Woodbine, and Wynn. Belmore, Chili, Hayden, Hickory, Kendallville, Kennan, Kidder, Leroy, Lindley, Mandeville, Ockley, Owosso, Riddles, Rockbridge, and Summitville soils contain coarse fragments in some part of the B horizon. In addition, Belmore, Kendallville, and Ockley soils formed in stratified materials; Hayden, Hickory, Lindley, and Riddles soils formed in glacial till; and Owosso soils have more sand in the upper part of the solum. Coggon and Douds soils are mottled in the lower part of the solum. Conestoga soils contain less sand in the solum and have a high mica content. El Dara soils are more acid. Grellton soils contain less sand in the lower part of the solum. Hebron soils have more clay in the lower part of the solum and in the C horizon. High Gap, Mifflin, Military, Norden, and Whalan soils have bedrock at depths of less than 40 in. Hollinger soils have a high percentage of mica in the Bt horizon and have micaceous saprolite in the C horizon. Letort soils have more silt in the solum. Martinsville and Sisson soils formed in stratified waterlaid materials. McHenry, Miami, Strawn and Theresa soils have sola less than 40 in. thick. Pecatonica and Westville soils have redder hue. Rawson, Roseville, Waymor, Woodbine, and Wynn soils contain more clay in the solum. Relay soils have hues yellower than 10 yr. Renova soils have silt loam and silty clay loam in the upper

part of the solum. Teanaway soils have firm reddish-brown sandy clay in the lower part of the B horizon and in the C horizon.

Setting: Princeton soils are on nearly level to rolling hummocky topography where slopes are usually short and broken. Princeton soils formed in thick deposits of coarse silt and fine sand of Aeolian origin. The climate is humid. Mean annual temperature is about 56°F and mean annual precipitation is about 42 in. near the type location.

Principal Associated Soils: Princeton soils are in a drainage sequence with the somewhat poorly drained Ayrshire soils on nearly level topography and the very poorly drained Lyles soils in depressions.

Drainage and Permeability: Well drained; medium to rapid runoff; moderate permeability in the solum and moderately rapid in the C horizon.

Use and Vegetation: Soils are mostly cultivated. Corn, soybeans, wheat, and alfalfa are major crops; vegetables, melons, apples, and peaches are grown to some extent.

Distribution and Extent: Southern Indiana and southeastern Illinois. The series is of moderate extent.

Series Established: Gibson County, Indiana, 1922.

Remarks: The Princeton series was formerly classified as Gray Brown Podzolic.

National Cooperative Soil Survey
U.S.A.

Established Series
Rev. DMc-GMS-JEW
5/13/76

BENNINGTON SERIES

The Bennington series is a fine, illitic, mesic Aeric Ochraqualfs. Bennington soils have dark grayish-brown silt loam Ap horizons and brown mottled strongly acid light silty clay or silty clay loam Bt horizons overlying compact clay loam or loam C horizons.

Typical Pedon: Bennington silt loam - cultivated. (Colors are for moist soil.)

- | | | |
|-------|--------|--|
| Ap | 0-7" | Dark grayish brown (2.5 y 4/2) silt loam; weak fine granular structure; friable; strongly acid; abrupt smooth boundary (5-10 in. thick). |
| A2 | 7-8" | Grayish-brown (2.5 y 5/2) and light olive brown (2.5 y 5/4) silt loam; common medium distinct dark grayish-brown (10 yr 4/2) and yellowish-brown (10 yr 5/4) mottles; weak fine subangular blocky and weak platy structure; friable; very strongly acid; abrupt smooth boundary (0-5 in. thick). |
| B&A | 8-11" | Light olive brown (2.5 y 5/4) silty clay loam; many medium distinct brown (7.5 yr 5/4) mottles; strong medium subangular and angular blocky structure; firm; grayish-brown (2.5 y 5/2) silt coatings on surfaces of peds; thin discontinuous clay films on surfaces of peds; very strongly acid; clear smooth boundary (2-6 in.). |
| B2ltg | 11-16" | Olive brown (2.5 y 4/4) light silty clay; common medium distinct strong brown (7.5 yr 5/6) mottles; fine distinct dark yellowish-brown (10 yr 4/4) mottles on surfaces of peds; strong medium subangular blocky structure; firm; medium continuous gray (5 y 5/1) clay films on surface of peds; very strongly acid; gradual smooth boundary (3-10 in. thick). |
| B22tg | 16-25" | Dark yellowish-brown (10 yr 4/4) heavy silty clay loam; many fine and medium distinct brown and strong brown (7.5 yr 5/4) mottles; moderate medium angular blocky structure; firm; thin continuous dark gray (5 y 4/1) clay films on surface of peds; 2 percent coarse fragments; very strongly acid in upper part, medium acid in lower part; gradual smooth boundary (4-10 in. thick). |

- B23tg 25-29" Dark brown (10 yr 4/3) silty clay loam; many fine and medium distinct yellowish-brown (10 yr 5/4) mottles; weak medium subangular blocky structure; firm; thin discontinuous dark gray (5 6 4/1) clay films on surface of peds; 2 percent coarse fragments; neutral; gradual wavy boundary (0-10 in. thick).
- B3g 29-37" Brown (10 yr 4/3) silty clay loam; many fine and medium distinct light yellowish-brown (10 yr 6/4) mottles; weak medium subangular blocky structure; firm; few thin gray (5 y 5/1) clay coatings; mildly alkaline; 5 percent coarse fragments; occasional small limestone fragments; abrupt wavy boundary (0-15 in. thick).
- C1 37-42" Dark gray (10 yr 4/1) and brown (10 yr 4/3) light clay loam; common light brownish-gray (10 yr 6/2) lime seams; massive; firm; 5 percent coarse fragments; moderately alkaline (2-10 in. thick).
- C2 42-60" Brown (10 yr 4/3), yellowish-brown (10 yr 5/4), and dark yellowish-brown (10 yr 4/4) heavy loam; few light brownish-gray (10 yr 6/2) lime seams; massive; firm; 5 percent coarse fragments; moderately alkaline.

Type Location: Delaware County, Ohio; Berkshire Twp.; SE1/4 sec. 5, T. 4 N., R. 17 W; 150' S of SR 37, 70' W of farm lane; 0.75 mi W of Berkshire.

Range of Characteristics: Solum thickness ranges from 28-50 in. Depth to carbonates ranges from 26-46 in. Reaction is from medium to strongly acid in surface horizons unless limed, from medium to very strongly acid in the upper and middle B horizon, from medium acid to mildly alkaline in the lower B, and mildly to moderately alkaline in the C. Calcium carbonate equivalent of the C horizon ranges from 8-22 percent. Coarse fragments, dominantly partially weathered sandstone and shale, comprise 0-5 percent to a depth of 20 in., 2-15 percent in the solum below 20 in., and 2-20 percent in the C. The Ap horizons range from dark gray (10 yr 4/1) to grayish-brown (2.5 y 5/2). In uncultivated areas, A1 horizons, 1-5 in. thick, are black (10 yr 2/1) to dark grayish-brown (10 yr 4/2). The A2 horizons (if present in uncultivated areas) are below an Ap, are 10 yr or 2.5 y hues, and have values of 5 or 6 and chromas of 2-4. They are commonly mottled either with colors of higher chroma or of lower chroma. Textures of A horizons are loam or silt loam. The B1 or B&A horizons are 10 yr or 2.5 y hues, values of 3-5, and chromas of 3-6 and are mottled. Texture is silt loam, silty clay loam, or clay loam. Structure is weak or moderate fine or medium subangular blocky or weak platy. In

many pedons, there is a coating of A2 material less than 2 mm thick on surfaces of peds. The B2 horizons are 10 yr or 2.5 y hues, values of 4 or 5, and chromas of 3-6 with subhorizons with chroma of 2 allowed. Mottles are distinct or prominent and of both high and low chroma. Coatings of peds are dominantly of low chroma with hues of 10 yr, 2.5 y, or N, values of 4 or 5, and chromas of 0-2. Texture is clay loam, silty clay loam, clay, or silty clay. The texture control section averages between 35-42 percent clay. Individual subhorizons range from 27-44 percent clay. Structure ranges from moderate to strong blocky; some pedons have weak or moderate prismatic which parts to blocky. Many pedons have B3 horizons similar to B2 horizons but which contain less clay. The B3 is noncalcareous or partially leached of calcium carbonate. The C horizons range from dark gray (10 yr 4/1) and dark grayish-brown (2.5 y 4/2) to brown (7.5 yr 5/4) with light gray to grayish-brown lime streaks. Texture range includes clay loam, loam, silty clay loam, and silt loam with clay contents of 24-33 percent. The C is massive or platy and is calcareous. Coarse fragments are principally sandstone and shale with some limestone cobbles.

Competing Series and Their Differentiae: These are the Blount, Brockport, Caneadea, Churchville, Del Rey, Fulton, Lockport, Mahoning, Nappanee, Odessa, Pyrmont, Remsen, and Rhinebeck series in the same family and the Cardington, Condit, and Crosby series in related families. Blount soils have more than 40 percent clay in the texture control section and more than 22 percent calcium carbonate equivalent in the C horizon. Brockport and Lockport soils have bedrock within a depth of 40 in. Caneadea, Del Rey, Fulton, Odessa, and Rhinebeck soils have formed in uniform textured lacustrine deposits. Churchville soils have a lithologic discontinuity between depths of 20-36 in. and have more than 10 percent coarse fragments in the lower materials. Mahoning soils have moderate to strong prismatic structure in the B2 horizon and have a more abrupt boundary from A to B horizons and a lower ratio of clay control from B to C horizons. Nappanee soils have less acid solum and weakly expressed argillic horizons. Pyrmont soils have sola less than 20 in. thick and depth to carbonates is less than 18 in. Remsen soils have a weighted clay content of more than 45 percent in the argillic horizon. Cardington soils lack evidence of wetness immediately below the surface horizon. Condit soils have low chromas in more than 60 percent of the matrix in all parts between the Ap horizon and a depth of 30 in. Crosby soils have mixed mineralogy.

Setting: The Bennington soils are on nearly level to gently sloping areas of Wisconsin age till plains and moraines. The slope range is from 0-6 percent. The soils developed in calcareous till of moderate lime content which contains significant amounts

of sandstone and shale fragments. The climate is humid continental. Mean annual precipitation is 35-40 inches and mean annual temperature is about 51°C. Mean summer temperature is about 71°F.

Principal Associated Soils: Bennington soils are in a drainage sequence with the well-drained Alexandria soils, the moderately-drained Cardington soils, the poorly-drained, light-colored Condit soils, and the very poorly-drained, dark-colored Pewamo and Marengo soils. In nearby lacustrine deposits are Fitchville and Luray soils. Chili, Jimtown, and Bogart soils are on nearby terraces. Chagrin, Lobdell, Orrville, and Holly soils are on nearby flood plains.

Drainage and Permeability: Somewhat poorly drained. Runoff is medium on the gently sloping areas, slow in the nearly level areas. Permeability is moderately slow and slow.

Use and Vegetation: A large proportion is cultivated. General farming is practiced, including the raising of livestock. Commonly grown crops are corn, soybeans, small grains, and hay or forage crops. Some areas are in pasture or woodland. The original vegetation was deciduous forest with maple, beech, elm, ash, sycamore, black walnut, and oak as prominent species.

Distribution and Extent: Central and north central Ohio. The Bennington soils are of large extent.

Series Established: Licking County, Ohio, 1930.

Remarks: The Bennington soils were classified as Gray Brown Podzolic soils in the 1938 classification system. Existing data on clay mineralogy are not conclusive.

Additional Data: Laboratory data are available for the following profiles in Ohio: AS-12, CR-21, DL-2, DL-11, DL-16 (the typical pedon), DL-17, DL-21, DL-23, DL-32, ER-31, FA-S7, FA-S10, Fr-4, LC-E1, MD-20, MH-45, PY-18, RC-23, SA-14.

National Cooperative Soil Survey
U.S.A.

25 copies

Commander
US Army Medical Bioengineering
Research and Development Laboratory
ATTN: SGRD-UBG
Fort Detrick, Frederick, MD 21701

4 copies

HQDA (SGRD-SI)
Fort Detrick
Frederick, MD 21701

12 copies

Defense Technical Information Center (DTIC)
ATTN: DTIC-DDA
Cameron Station
Alexandria, Virginia 22314

1 copy

Dean
School of Medicine
Uniformed Services University of the
Health Sciences
4301 Jones Bridge Road
Bethesda, Maryland 20014

1 copy

Superintendent
Academy of Health Sciences, US Army
ATTN: AHS-COM
Fort Sam Houston, Texas 78234