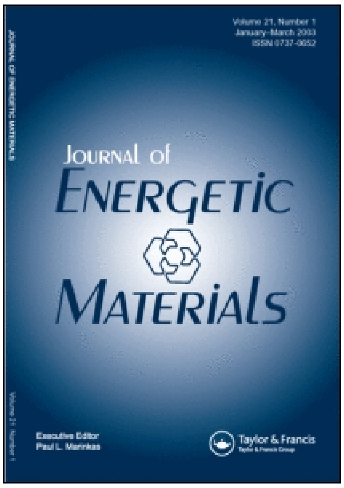

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Migration of explosives in soil: analysis of rdx, tnt, and tetryl from a 14c lysimeter study

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MIGRATION OF EXPLOSIVES IN SOIL: ANALYSIS OF RDX, TNT, AND TETRYL FROM A 14C LYSIMETER STUDY

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ABSTRACT

This report describes the chemical analysis results of 121 water and 24 soil samples from a ^{14}C lysimeter study of TNT, RDX, and tetryl performed at Battelle Columbus Laboratories. Lysimeters were constructed at Battelle by pressing steel pipes into various soils. The lysimeters were withdrawn to preserve the soil columns intact. ^{14}C ring-labeled munition compounds were than mixed into the surface layer (first 3 inches) of the soils and the lysimeters were irrigated on a regular basis over a six month period. Periodic water samples (leachate) were taken for analysis at selected intervals. The study described here was undertaken (a) to assess the environmental fate of these compounds in various soil samples - since soils within the production areas of U.S. munition plants have become contaminated with raw materials, munition compounds, as well as waste materials, and (b) to determine the persistence and

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movement of these compounds and their possible decomposition and/or biotransformation products thru the soil to groundwater. The soils (Brookston, Bennington, Genesee, and Princeton) were chosen for their range of textures (from fine to coarse) as well as their ability to fix compounds due to their various amounts of organic matter and ion exchange capacity. Of the 121 water samples (leachate) received, forty-six had ^{14}C activity greater than 100 dpm/ml and were further analyzed by GC/EC, HPLC, and TLC methods.

The data indicate that neither TNT nor any of the typical TNT biodegradation or oxidation products were observed in the "TNT water samples" either by GC/EC or HPLC. Analysis of a Princeton - "TNT water sample" with high ^{14}C activity revealed only highly polar, nonvolatile products which could neither be separated nor identified.

Analysis of the Princeton - "RDX water samples" revealed increasing amounts of RDX in the leachate (from 1.4 mg/L in the 5/2 sample to 40.0 mg/L in the 8/22 sample). HMX, the impurity in RDX synthesis, was present to the extend of 10% of the RDX amount in each water sample. The Genesee - "RDX water samples" also contained RDX but only at 1/10 the level of that of the Princeton - "RDX water samples". The Bennington and Brookston - "RDX water samples" contained virtually no RDX. TLC and ^{14}C analysis of the residue from evaporation of the Princeton - "RDX #8/22 water sample" revealed the following amounts: 40 mg/L RDX, 4 mg/L HMX, 60 mg/L ^{14}C labeled volatile decomposition products and approximately 30 mg/L of other ^{14}C labeled polar nonvolatile decomposition products.

Only three "tetryl water samples" had sufficient ^{14}C activity to warrant analysis. Tetryl could not be detected, but trace amounts of picric acid were confirmed by HPLC. TLC analysis of one of the "tetryl water samples" revealed only nonvolatile, highly polar products.

Visual observations of the various soil textures and porosities coincide with those of Battelle (e.g., Brookston - silty clay, fine texture, Benning-ton - silt loam, medium texture, Genesee - silt loam, medium texture, Princeton - fine sandy loam, coarse texture). Evidence of both degradation and migration was apparent in this ^{14}C study. The retention of the munition compounds (TNT, RDX) as well as their decomposition and/or biotransformation products on the various soils also coincide with the porosity of the soils. The theoretical material balance was also determined from the data obtained on each lysimeter segment analyzed by ^{14}C TLC, and HPLC. Two biotransformation products of TNT, the 4-amino-2,6-dinitrotoluene and the 2-amino-4,6-dinitrotoluene were found in the TNT soil extracts. The Princeton - TNT soil sample contained approximately 6% of each of the aminodinitrotoluenes (ADNT), the Genesee - TNT soil had only 0.1% of each of the ADNT's. The Bennington - TNT soil contained 0.02% of each of the ADNT's, while only 0.01% of the 4A26DNT isomer was found in the Brookston - TNT soil extract. Both the Princeton and

Genesee - RDX soil contained approximately 10% HMX, 4.5% volatile materials, and 20% polar type compounds. Known hydrolysis or alkaline degradation products, such as formic acid or formaldehyde were not found.

INTRODUCTION

The current emphasis on environmental pollution has lead to concern about the possible contamination of soil by explosive compounds and water materials from munition and loading facilities. Soil contamination can occur as a result of equipment failure, carelessness, routine maintenance, or package breakage. Even low levels of soil contamination may prove harmful to the local environment because of toxicity to vegetation and/or wildlife. An additional concern is the possibility that these materials may be transported to neighboring environments and thus increase the area of contamination. A probable means of transfer would be through the soil to groundwater.

This study was funded to assess the environmental fate of TNT, RDX and tetryl in various soils. This report describes the chemical analysis results of 121 water and 24 soil samples from the ^{14}C lysimeter study of TNT, RDX, and tetryl performed at Battelle Columbus Laboratories.

The objectives were to (1) determine the ^{14}C activity of each water sample and compare the results with those obtained earlier by Battelle; (2) quantitatively analyze for TNT, tetryl, and RDX in the water samples where ^{14}C activity was greater than 100 dpm per mL (0.5 μg/mL); (3) analyze for transformation products in the water samples; (4) check for volatile products; (5) analyze each soil section for total ^{14}C activity and for total explosive content; and finally (6) analyze for any transformation products in the soil samples. Lysimeters were constructed at Battelle by pressing steel pipes into various soils. The soils (Brookston, Bennington, Genesee, and Princeton) were chosen for their range of textures (from fine to coarse) as well as their ability to fix compounds due to their various amounts of organic matter and ion exchange capacity.

These soils were packed into steel columns, 24 inches long and 2 inches in diameter. The top 3 inches were removed from each column, and 4 grams of one of the ^{14}C labeled explosives (TNT, RDX, tetryl) was uniformly mixed with this portion of the soil[7] and added back to the top of the steel columns (lysimeters). The ^{14}C activity of each explosive contained in the soil was such that 200 disintegrations per minute (dpm) correspond to 1 microgram of explosive. Each column contained 8.0×10^8 dpm of ^{14}C activity at the start of the lysimeter test. The lysimeters were then irrigated on a regular schedule with distilled water for 6 months at Battelle. Every 2 weeks, a water sample was taken from the bottom of each column. After 6 months, each column was cut into four 6-inch sections for analysis. A total of 121 water samples and 24 6-inch sections of soil were analyzed. The soil samples analyzed at NSWC/WO included 16 sections of TNT soil samples (Princeton, Bennington, Brookston, and Genesee), 4 Princeton RDX soil sections, and 4 Genesee RDX soil sections.

When determining the theoretical material balance (based on ^{14}C count) of the soil sections, it should be noted that Battelle had removed for its analysis 16% of each soil column (bottom 1 inch of each 6 inch section). The segments of the soil columns used for the NSWC/WO analysis include: Segment 1 (0-5 inches soil), Segment 2 (7-11 inches soil), Segment 3 (13-17 inches soil), and Segment 4 (19-23 inches soil). The analytical results are recorded by segments of each soil column and reflect ^{14}C, TLC, and HPLC analyses of the extracts of those segments. The quantities of explosive, explosive degradation products and/or biotransformation products found in each segment of soil are tabulated in Tables 9 through 14. Of the 121 water (leachate) samples received, forty-six had ^{14}C activity greater than 100 dpm/ml and were further analyzed by GC/EC, HPLC, and TLC methods. The total amount of activity found in the water samples from each column is negligible (0.1%) when compared to the original total ^{14}C activity (800,000,000 dpm) of each column.

EXPERIMENTAL

Liquid Scintillation Counting of both water and soil samples was done with a Searle Co. Scintillation Counter (model-Unilux 2-A). The sample disperser was Eastman CAB-OSIL M-5 Scintillation Grade, and the solvent was Aquasol Universal cocktail.

Gas Chromatography (GC) was utilized to assay for TNT and tetryl in the water samples. AN HP-5700 gas chromatograph with electron capture (EC) detection was used. The water samples were extracted with benzene 1:1 (2,4,6-trinitro-1,3-dimethoxybenzene was used as an internal standard). With this procedure, concentrations down to 0.3 μg/L could be observed without concentrating the extract.

High Performance Liquid Chromatography (HPLC) was used to assay both water and soil samples for TNT, tetryl, and RDX. A Waters Model ALC 202/440 isocratic HPLC with an M-6000A pump and a 254 nm detector was used. The analytical column was a reverse-phase Whatman 10 μm Partisil ODS-2 utilizing methanol/water (40/60) as the solvent at a flow rate of 2 ml/min. Using this analytical method, concentrations down to 50 μg/L could be observed with 100 μL injections at the most sensitive setting of the Waters 440 detector (0.005 AUFS). HPLC data of the explosive compounds and some of their transformation products can be found in Table 1.

Thin Layer Chromatography (TLC) was utilized to separate and quantitate the explosives and their transformation products in both water and soil samples. Merck Silica Gel HF-254, coated on glass plates, was used as the absorbent. Benzene, methanol, and a mixture of benzene/ether/ethanol (50:30:20) were the three solvent systems used. UV-visible spots on the TLC plate were scraped off and their ^{14}C activities determined directly by scintillation counting. TLC data of the explosive compounds and some of their transformation products can be found in Table 1.

TABLE 1. HPLC and TLC Data of Explosive Compounds

Compound	HPLC Retention Times (min.)	HPLC Relative Response Factor (254 nm)	TLC R_F (benzene)
TNT	13.3	0.84	0.83
PiH	6.8	1.00	0.80
4A26DNT	16.8	0.43	0.28
2A46DNT	18.7	0.80	0.28
2,6DA4NT	3.0	0.97	0.03
2,4DA6NT	3.4	0.48	0.03
RDX	5.4	0.33	0.32
HMX	2.8	0.32	0.17
Cyclohexanone	5.2	15.80	----
Tetryl	13.0	0.65	0.70
Picric Acid	1.0	1.40	0.00

The soil extraction procedure consisted of scraping each soil segment from the metal casing. Ten to twenty grams of the soil were dried overnight at 70°C, then reweighed to determine the water content in each segment. Each ^{14}C-"TNT soil segment" was extracted with 800 mL benzene. The soil was stirred in the extracting solvent for 20 minutes, filtered and extracted a second time with 800 mL of fresh benzene and the extracts combined. The above soil was re-extracted a third and fourth time with acetone (500 mL each) and filtered. The acetone extracts were combined. The benzene and acetone extracts were then reduced in volume at room temperature to the point where all extracted products remained in solution. These solutions or dilutions thereof were used in the liquid scintillation counter, HPLC, or TLC to identify and quantitate the ^{14}C-TNT and other transformation products. The residual ^{14}C activity left on the extracted soil was determined by liquid scintillation counting techniques after drying the soils at 50°C overnight. The same procedures were used for the ^{14}C RDX soil samples, however, due to the relative insolubility of RDX in benzene, only acetone was used as the extraction solvent (total acetone - 800 mL).

RESULTS AND DISCUSSION

All 121 water samples received from Battelle were analyzed for ^{14}C activity (Tables 2, 3, and 4). The counts obtained at NSWC indicate a close correlation with those reported by Battelle. The "TNT-water samples" with ^{14}C activities greater than 100 dpm/mL, were analyzed directly (i.e., no extraction or filtering) by reverse-phase liquid chromatography. TNT was not found by this method where concentrations down to 50 μg/mL are observable using 100 μL injections. None of the known TNT biotransformation products[1] (e.g., 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene or the diamino derivatives of TNT) were observed by this method. Nor were other commonly known TNT degradation products[2,3] found (i.e., trinitrobenzene, trinitrobenzyl alcohol, trinitrobenzaldehyde, or trinitrobenzoic acid).

TABLE 2. ^{14}C Activity of TNT Water Samples[(a)]

Samples	Battelle Data (dpm)	NSWC Data (dpm)[(b)]
Bennington-TNT	all < 500	all < 500
Brookston-TNT	all < 500	all < 500
Genesee-TNT		
4/20/77[(c)]	684	(d)
6/15	597	(d)
6/29	610	(d)
7/13	1,358	(d)
7/27	1,097	699
8/10	1,944	1,367
8/24	2,220	849
Princeton-TNT		
4/20/77	825	(d)
5/4	5,130	5,250
5/18	16,753	17,174
6/1	18,651	18,543
6/15	15,662	15,076
7/13	13,451	13,261
7/27	16,734	14,072
8/10	11,676	11,340
8/24	10,627	10,660

(a) Sample size = 5 mL
(b) Error of NSWC ^{14}C measurement = ± 200 dpm
(c) Sample number = date when sample was taken by Battelle
(d) Samples filtered and solid material checked for ^{14}C activity-neither filtrate or solids showed activity above 500 dpm.

TABLE 3. ^{14}C Activity of Tetryl Water Samples$^{(a)}$

Samples	Battelle Date (dpm)	NSWC Data (dpm)$^{(b)}$
Bennington-tetryl		
6/22/77$^{(c)}$	1,809	1,448
Brookston-tetryl		
6/2277	3,752	3,065
Genesee-tetryl		
4/27/77	1,382	(d)
5/25	1,215	529
6/22	1,472	(d)
7/6	1,392	(d)
7/20	1,160	(d)
8/3	2,190	(d)
8/17	1,335	(d)
Princeton-tetryl	all < 500	all < 500

(a) Sample size = 5 mL
(b) Error of NSWC ^{14}C measurement = ± 200 dpm
(c) Sample number = date when sample was taken by Battelle
(d) Samples filtered and solid material checked for ^{14}C activity-neither filtrate nor solids showed activity above 500 dpm

TABLE 4. ^{14}C Activity of RDX Water Samples[(a)]

Samples	Battelle Data (dpm)	NSWC Data (dpm)[(b)]
Bennington-RDX		
6/27/77[(c)]	5,220	3,898
6/11/77	543	< 500
Brookston-RDX	all < 500	all < 500
Genesee-RDX		
4/4/77	885	742
4/18	1,815	2,700
5/2	2,504	2,243
5/16	9,125	10,549
5/30	5,279	4,744
6/13	36,056	34,262
6/27	34,180	42,252
7/11	6,994	6,975
8/8	17,030	16,057
8/22	24,566	22,121
Princeton-RDX		
4/18/77	676	794
5/2	4,490	4,317
5/16	11,317	12,807
5/30	22,783	23,202
6/27	65,557	68,795
7/11	94,382	102,609
7/25	104,465	121,019
8/8	124,913	129,294
8/22	134,999	138,281

(a) Sample size = 5 mL

(b) Error of NSWC ^{14}C measurement = ± 200 dpm

(c) Sample number = date when sample was taken by Battelle

The azoxytoluenes, also identified by NSWC[4] during earlier TNT biodegradation investigations were not found in these water samples.

TNT was not found by the GC/EC method in any of the "TNT-water samples". Concentrations down to 0.3 $\mu g/L$ could typically be detected by this method without concentrating the 1:1 benzene extract.

A small quantity of the Princeton "TNT water sample #5/18", with 17,174 counts (which showed no TNT present by GC or HPLC), was evaporated to dryness at room temperature, then recounted. The counts remained constant, indicating an absence of volatile decomposition products. This sample was also extracted with benzene (1:1) and the benzene layer counted for ^{14}C activity. A level of 100 dpm/5 mL was observed indicating that the TNT decomposition products were quite polar and water soluble.

Using the same three most active water samples (Princeton-"TNT 5/18", Princeton-"RDX 8/22", and Bennington-"tetryl 6/22"), thin layer chromatographic analyses were obtained on the solid residues from each of these water samples. It was hoped that this method would isolate some decomposition products. A 5.0 mL aliquot of the water sample was taken to dryness at room temperature, redissolved in 0.5 mL of water and the entire amount spotted on a TLC plate. Standards of the known biotransformation and hydrolysis products for each explosive were run on the same plate as the unknown residues. Areas of the plate were removed directly into the scintillation vial for ^{14}C counting.

Table 5 contains the TLC analysis data of the Princeton-"TNT 5/18 sample" which showed no evidence of TNT or its known biotransformation products. No evidence of any other benzene chromatographable polynitroaromatic compounds associated with the photochemical, thermal, or alkaline decomposition of TNT (i.e., PiCHO, $PiCH_2OH$, $PiCH_2CH_2Pi$, PiH, etc.) was found.

TABLE 5. Analysis of TNT, TNT-Biotransformation Standards and Princeton-"TNT 5/18" by TLC

TNT and TNT Biotransformation Standards

	R_F(benzene)	R_F(Magic)	R_F(MeOH)
TNT	0.78	1.00	1.0
$2NH_2$-4,6-DNT	0.20	1.00	1.0
$4NH_2$-2,6-DNT	0.23	1.00	1.0
$2,4NH_2$-6-NT	0.03	0.94	1.0
$2,6NH_2$-4-NT	0.03	0.96	1.0

Princeton-TNT 5/18

R_F(benzene)	$\%^{14}C$	R_F(Magic)$^{(a)}$	$\%^{14}C$	R_F(MeOH)	$\%^{14}C$
0.61-0.79	0	0.58-0.91	3	0.83-0.95$^{(b)}$	59
0.44-0.61	0	0.07-0.58$^{(b)}$	65	0.07-0.83$^{(b)}$	13
0.26-0.44	0	0.0-0.07$^{(b)}$	30	0.00-0.07$^{(b)}$	11
0.0-0.07	98				

(a) Magic Solvent = benzene/ether/ethanol, 50:30:20
(b) No distinct spots-tailing occurring

The "RDX water samples" with sufficient ^{14}C activity (Table 4) were also analyzed by HPLC. HPLC analysis results of RDX and HMX can be found in Table 6 as well as quantitative TLC analysis data for RDX. HMX is the expected impurity in production grade RDX and is usually present at a concentration of 8-13%. The final column in Table 6 represents the total ^{14}C activity in each water sample converted to RDX in μg/mL. The data show that the actual concentration of RDX in the Princeton and Genesee water samples is ~28% and ~8% respectively of the ^{14}C activity. Note that the ^{14}C activity of the Princeton RDX samples dated 6/27 to 8/22 is higher than the solubility of RDX in water (45 μg/mL at 25°C), indicating that RDX decomposed in the soil and the products were flushed out in the leachate.

Table 7 contains the analysis data of the Princeton-"RDX

8/22 sample" which indicated the presence of HMX, RDX, and 50% ^{14}C volatile material. Other known hydrolysis or alkaline degradation products, such as formic acid or formaldehyde, could not be determined by TLC. However, in separate experiments on the Princeton-"RDX 8/22 water sample", tests for formaldehyde and formic acid were carried out. The chromatropic acid test for formaldehyde was negative, but this test is misleading if NO_2^- and NO_3^- are present. Therefore, the "nitrobenzene method" of Hoffsommer and Glover[5] was used to determine NO_2^- and NO_3^- concentrations. Results of this test showed a nitrate concentration of $2.31 \times 10^{-3}M$ and a nitrite concentration of $5.8 \times 10^{-4}M$. The combined $NO_2^- + NO_3^-$ concentration found is approximately 50% more than the value expected from the decomposition of the theoretical RDX value of 138 $\mu g/mL$ (Table 6) less the actual 36 $\mu g/mL$ RDX. This result suggests several possibilities: (1) RDX could be decomposing on the soil, releasing NO_2^- and/or NO_3^- which is flushed out of the lysimeter with water but leaving the ^{14}C tagged species absorbed on the soil; (2) a background concentration of NO_2^-/NO_3^- in the soil would give high readings; or (3) more than three of the six RDX nitrogen atoms are ending up as NO_2^- and/or NO_3^-.

TABLE 6. Analysis of RDX and HMX in Water Samples

Sample Number (date)	RDX by TLC ($\mu g/mL$)	RDX by HPLC ($\mu g/mL$)	HMX by HPLC ($\mu g/mL$)	RDX by ^{14}C Activity ($\mu g/mL$)$^{(a)}$
Princeton-RDX				
5/22/77	1.2	1.4		4.3
5/16	3.4	4.0	0.36	12.8
5/30	6.0	6.0	0.60	23.2
6/27	17.8	18.0	1.80	68.8
7/11	26.6	27.0	2.70	102.6
7/25	31.4	34.0	3.40	121.0
8/22	36.0	40.0	3.60	138.0
Genesee-RDX				
4/18/77	0.28	0.14		2.7
5/2	0.22	0.14		2.2
5/16	1.06	0.52	0.04	10.5
5/30	0.48	0.40	0.04	4.7
6/13	3.40	4.00	0.36	34.3
6/27	4.20	4.20	0.46	42.2
7/11	0.70	0.58	0.06	7.0
8/8	0.16	1.62	0.14	16..*****22 2.20
2.54	0.24	22.1		
Bennington-RDX				
6/27/77	0.78	0.68	0.06	3.9

(a) Theoretical RDX based on ^{14}C activity in water sample, assuming no decomposition.

TABLE 7. Analysis of RDX/HMS, RDX Degradation Products and Princeton-"RDX 8/22" by TLC

RDX/HMX Standards

	Rf(benzene)	Rf(Magic)
RDX	0.11	1.00
HMX	0.03	0.94
Formic Acid	0.00	0.00
Formamide	0.00	0.47

Princeton-RDX 8/22(a)

Rf(benzene)	%^{14}C	Rf(Magic)(b)	%^{14}C	Rf(MeOH)	%^{14}C
0.68-1.0	0	0.77-1.0	33	0.77-1.0	31
0.30-0.68	0	0.07-0.77	12	0.07-0.77	13
0.08-0.30	26	0.0-0.07	7	0.0-0.07	5.3
0.0-0.08	23				

(a) 50% of ^{14}C activity due to volatile material
(b) Magic Solvent = benzene/ether/ethanol, 50:30:20

TLC analysis was also obtained on the solid residue from the Princeton-"RDX water sample #8/22" with 138, 281 counts. The data indicate 40% volatile decomposition products with 25% of the activity due to benzene-soluble material (mostly RDX).

Of the three "tetryl water samples" which had sufficient ^{14}C activity to warrant analysis (Table 3), none showed any LC absorption corresponding to tetryl. However, a peak coresponding to picric acid,[6] a known hydrolysis product of tetryl, was observed by LC in each of these samples. Picric acid comprised 14% of the total ^{14}C activity in the Bennington "6/22 tetryl sample", 5% in the Brookston "6/22 tetryl sample", and 10% in the Genesee "5/11 tetryl sample". The concentration of picric acid in these samples was determined by measurement of ^{14}C activity in isolated TLC spots and by peak area in

HPLC. Quantitation of picric acid was verified using TLC by removing the spot corresponding to picric acid and counting its ^{14}C content.

Tetryl was not found in any of the "tetryl-water samples" by the GC/EC method. The limit of detection of tetryl is less than 0.3 μg/L in the samples extracted with benzene (1:1).

TLC analysis (Table 8) were obtained on the solid residue of the Bennington "tetryl-water sample" #6/22, containing 1,448 counts. Identical volatility and extraction data were observed as with the TNT water sample, indicating polar/water-soluble decomposition products.

TABLE 8. Analysis of Tetryl, Picric Acid, and the Bennington-Tetryl 6/22 Sample by TLC

Tetryl/Picric Acid Standards

	Rf(benzene)	Rf(Magic)
Tetryl	0.7	1.0
Picric Acid	0.0-0.17	0.45

Bennington-Tetryl 6/22

Rf(benzene)	%^{14}C	Rf(Magic)	%^{14}C
0.79-1.0	0	0.92-1.0	80
0.62-0.79 (picric)	0	0.07-0.92	14
0.44-0.62	0	0.0-0.07	6
0.26-0.44	0		
0.07-0.26	52		
0.0-0.07	48 (picric)		

The results of this study indicate that all objectives were met. Evidence of both degradation and migration was seen in the ^{14}C study. Several of the decomposition and/or biotransformation products found in the soil and water samples were identified and quantified. Theoretical material balance was determined on each soil column segment analyzed by HPLC and ^{14}C TLC (see Tables 9 and 10).

All 121 water samples received from Battelle were analyzed for ^{14}C activity. The counts obtained at NSWC indicate a close correlation with those reported by Battelle. Based on Battelle's activity figures, a ^{14}C activity of 100 dpm/mL corresponds to a concentration of 0.5 mg/L of the explosive and/or its transformation products in the water samples. Forty-six water samples had ^{14}C activity greater than 100

TABLE 9. TNT Soil Sample Summary

	COLUMN SEGMENTS	MATERIALS	TLC DATA (GRAMS)	HPLC DATA (GRAMS)	TOTAL TL DATA (GRAMS
BENNINGTON TNT SOIL SAMPLE SUMMARY TOTAL WEIGHT IN SEGMENTS 1, 2, AND 3 = 3.731g = 93% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	TNT	2.82		
		2A + 4A	0.168		
		TLC ORIGIN	0.232		
		UNEXTRACTABLE	0.548		
	SEGMENT 2 7-11"	TNT	0.0001	0.0009	
		2A + 4A	0.001	0.0006	
		TLC ORIGIN	0.0004		
		UNEXTRACTABLE	0.008		
	SEGMENT 3 13-17"	TNT	3 μg		
		2A + 4A	14 μg		
		TLC ORIGIN	11 μg		
		UNEXTRACTABLE	283 μg		
	SEGMENT 4 19-23"	NOT ANALYZED			
	SEGMENTS 1+2+3	TNT			2.774
		2A + 4A			0.169
		TLC ORIGIN			0.232
		UNEXTRACTABLE			0.556
BROOKSTON TNT SOIL SAMPLE SUMMARY TOTAL WEIGHT IN SEGMENTS 1 AND 2 = 3.88g = 97% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	TNT	2.94	2.93	
		2A + 4A	0.070		
		TLC ORIGIN	0.077		
		UNEXTRACTABLE	0.756		
	SEGMENT 2 7-11"	TNT	0.0001	0.00013	
		2A + 4A	0.0006		
		TLC ORIGIN	0.0004		
		UNEXTRACTABLE	0.030		
	SEGMENT 3 13-17"	NOT ANALYZED			
	SEGMENT 4 19-23"	NOT ANALYZED			
	SEGMENTS 1+2	TNT			2.94
		2A + 4A			0.07
		TLC ORIGIN			0.08
		UNEXTRACTABLE			0.79
GENESEE TNT SOIL SAMPLE SUMMARY TOTAL WEIGHT = 3.93g = 98% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	TNT	2.122	2.20	
		2A + 4A	0.269		
		TLC ORIGIN	0.043		
		UNEXTRACTABLE	1.300		
	SEGMENT 2 7-11"	TNT	0.018	0.015	
		2A + 4A	0.008	0.009	
		TLC ORIGIN	0.009		
		UNEXTRACTABLE	0.137		
	SEGMENT 3 13-17"	TNT	0.0001	0.0001	
		2A + 4A	0.0002	0.00014	
		TLC ORIGIN	0.0002		
		UNEXTRACTABLE	0.018		
	SEGMENT 4 19-23"	TNT	<1.0 μg	0.04 μg	
		2A + 4A	2.4 μg	4.0 μg	
		TLC ORIGIN	20.0 μg		
		UNEXTRACTABLE	0.0027		
	SEGMENTS 1+2+3+4	TNT			2.14
		2A + 4A			0.277
		TLC ORIGIN			0.052
		UNEXTRACTABLE			1.46
PRINCETON TNT SOIL SAMPLE SUMMARY TOTAL WEIGHT = 3.47g = 87% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	TNT	1.550	1.78	
		2A + 4A	0.057		
		TLC ORIGIN	0.106		
		UNEXTRACTABLE	0.329		
	SEGMENT 2 7-11"	TNT	0.140	0.107	
		2A + 4A	0.412	0.45	
		TLC ORIGIN	0.604		
		UNEXTRACTABLE	0.229		
	SEGMENT 3 12-17"	TNT	0.0007		
		2A + 4A	0.003		
		TLC ORIGIN	0.011		
		UNEXTRACTABLE	0.056		
	SEGMENT 4 19-23"	TNT	6.0×10^{-6}		
		2A + 4A	6.2×10^{-5}		
		TLC ORIGIN	3.1×10^{-4}		
		UNEXTRACTABLE	0.004		
	SEGMENTS 1+2+3+4	TNT			1.69
		2A + 4A			0.47
		TLC ORIGIN			0.72
		UNEXTRACTABLE			0.59

TABLE 10. RDX Soil Sample Summary

	COLUMN SEGMENTS	MATERIALS	TLC DATA (GRAMS)	HPLC DATA (GRAMS)	TOTAL TLC DATA (GRAMS)
GENESEE RDX SOIL SAMPLE SUMMARY TOTAL WEIGHT = 3.290g = 82% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	RDX	1.904	2.129	
		HMX	0.386	0.252	
		TLC ORIGIN	0.342		
		UNEXTRACTABLE	0.571		
		VOLATILE	—		
	SEGMENT 2 7-11"	RDX	0.036	0.034	
		HMX	0.006	0.006	
		TLC ORIGIN	0.013		
		UNEXTRACTABLE	0.010		
		VOLATILE	0.003		
	SEGMENT 3 13-17"	RDX	0.003	0.0024	
		HMX	0.0004	0.0004	
		TLC ORIGIN	0.001		
		UNEXTRACTABLE	0.005		
		VOLATILE	0.0008		
	SEGMENT 4 19-23"	RDX	0.003		
		HMX	0.0003		
		TLC ORIGIN	0.001		
		UNEXTRACTABLE	0.004		
		VOLATILE	0.0007		
	SEGMENTS 1+2+3+4	RDX			1.946
		HXM			0.393
		TLC ORIGIN			0.3576
		UNEXTRACTABLE			0.590
		VOLATILE			0.004
PRINCETON RDX SOIL SAMPLE SUMMARY TOTAL WEIGHT = 3.398g = 85% THEORETICAL MATERIAL BALANCE	SEGMENT 1 0-5"	RDX	1.513	1.560	
		HMX	0.210	0.185	
		TLC ORIGIN	0.162		
		UNEXTRACTABLE	0.409		
		VOLATILE	0.101		
	SEGMENT 2 7-11"	RDX	0.638	0.699	
		HMX	0.113	0.063	
		TLC ORIGIN	0.094		
		UNEXTRACTABLE	0.059		
		VOLATILE	0.040		
	SEGMENT 8 13-17"	RDX	0.014		
		HMX	0.012		
		TLC ORIGIN	0.006		
		UNEXTRACTABLE	0.004		
		VOLATILE	0.001		
	SEGMENT 4 19-23"	RDX	0.014		
		HMX	0.0024		
		TLC ORIGIN	0.0016		
		UNEXTRACTABLE	0.003		
		VOLATILE	0.011		
	SEGMENTS 1+2+3+4	RDX			2.169
		HMX			0.337
		TLC ORIGIN			0.264
		UNEXTRACTABLE			0.475
		VOLATILE			0.153

dpm/mL and were further analyzed by GC, HPLC, and TLC.

Neither TNT nor any of the typical TNT biodegradation or oxidation products were observed in the "TNT water samples" either by GC/EC or HPLC. Analysis of a Princeton - "TNT water sample" with high ^{14}C activity revealed only highly polar, nonvolatile decomposition products which could neither be separated nor identified.

Analysis of the Princeton - "RDX water samples" revealed increasing amounts of RDX in the leachate (from 1.4 mg/L in the 5/2 sample to 40.0 mg/L in the 8/22 sample). HMX, the impurity in RDX was present to the extent of 10% of the RDX amount in each water sample. The Genesee - "RDX water samples" also contained RDX but only at 1/10 the level of that of the Princeton - "RDX water samples". The Bennington and Brookston - "RDX water samples" contained virtually no RDX. TLC and ^{14}C analysis of the residue from evaporation of the Princeton - "RDX #8/22 water sample" revealed the following amounts: 40 mg/L RDX, 4 mg/L HMX, 60 mg/L ^{14}C labeled volatile decomposition products and approximately 30 mg/L of other ^{14}C labeled polar nonvolatile decomposition products. The combined NO_2^- + NO_3^- concentration found in the Princeton - "RDX 8/22 water sample" is approximately 50% more than the value expected from the decomposition of the theoretical RDX value. This suggests several possibilities: (1) RDX could be decomposing on the soil, releasing NO_2^- and/or NO_3^- which is flushed out of the lysimeter with water but leaving the ^{14}C tagged species absorbed on the soil; (2) a background concentration of NO_2^- /NO_3^- in the soil would given high readings; or (3) more than three of the six RDX nitrogen atoms are ending up as NO_2^- and/or NO_3^-.

Only three "tetryl water samples" had sufficient ^{14}C activity to warrant analysis. Tetryl could not be detected, but trace amounts of picric acid were confirmed by HPLC. TLC analysis of one of the "tetryl water samples" revealed only nonvolatile, highly polar products.

The soils (Brookston, Bennington, Genesee, and Princeton) were chosen for their range of textures (from fine to coarse) as well as their ability to fix compounds due to their various amounts of organic matter and ion exchange capacity.

Visual observations of the various soil textures and porosities coincide with those of Battelle (e.g., Brookston - silty clay, fine texture, Bennington - silt loam, medium texture, Genesee - silt loam, medium texture, Princeton - fine sandy loam, coarse texture). Evidence of both degradation and migration of the munition compounds was apparent in this ^{14}C study. The retention of the munition compounds (TNT, RDX) as well as their decomposition and/or biotransformation products on the various soils also coincide with the porosity of the soils. The theoretical material balance (Tables 9 and 10) was also determined from the data obtained on each lysimeter segment analyzed by ^{14}C TLC and HPLC. Two biotransformation products of TNT, the 4-amino-2,6-dinitrotoluene and the 2-

amino-4,6-dinitrotoluene were found in the TNT soil extracts. The Princeton - TNT soil sample contained approximately 6% of each of the aminodinitrotoluenes (ADNT), the Geneseee - TNT soil had only 0.1% of each of the ADNT's. The Bennington - TNT soil contained 0.02% of each of the ADNT's, while only 0.01% of the 4A26DNT isomer was found in the Brookston - TNT soil extract. Both the Princeton and Genesee - RDX soil contained approximately 10% HMX, 4.5% volatile materials, and 20% polar type compounds. Known hydrolysis or alkaline degradation products, such as formic acid or formaldehyde were not found.

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NOMENCLATURE

Lysimeter Study = study conducted to monitor the downward motion of material through intact soil columns.

dpm = disintegrations per minute

GC/EC = Gas Chromatography/Electron Capture

HMX = 1,3,5,7-tetranitro - 1,3,5,7-tetraazacyclooctane

HPLC = High Performance Liquid Chromatography

$\mathrm{NO_2^-}$ = Nitrite

$\mathrm{NO_3^-}$ = Nitrate

PiCHO = 2,4,6-trinitrobenzaldehyde

$\mathrm{PiCH_2CH_2Pi}$ = hexanitrobibenzyl

$\mathrm{PiCH_2OH}$ = 2,4,6-trinitrobenzyl alcohol

RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane, cyclo-1,3,5-trimethylene-2,4,6-trinitramine, cyclonite

tetryl = N,2,4,6-tetranitro-N-methylaniline

TLC = Thin Layer Chromatography

TNT = 2,4,6-trinitrotoluene

2A = 2A46DNT = 2$\mathrm{NH_2}$46DNT = 2-amino-4,6-dinitrotoluene

2,4$\mathrm{NH_2}$-6-NT = 24DA6NT = 2,4-diamino-6-nitrotoluene

2,6$\mathrm{NH_2}$-4NT = 26DA4NT = 2,6-diamino-4-nitrotoluene

4A = 4A26DNT = 4$\mathrm{NH_2}$-2,6-DNT = 4-amino-2,6-dinitrotoluene

PiH = 1,3,5 trinitrobenzene