# Quantification and Aging of the Post-Blast Residue of TNT Landmines

ABSTRACT: Post-blast residues are potential interferents to chemical detection of landmines. To assess the potential problem related to 2,4,6trinitrotoluene (TNT), its post-blast residue was identified and quantified. In the first part of this study laboratory-scale samples of TNT (2 g) were detonated in a small-scale explosivity device (SSED) to evaluate the explosive power and collect post-blast residue for chemical analysis. Initiator size was large relative to the TNT charge; thus, issues arose regarding choice of initiator, residue from the initiator, and afterburning of TNT. The second part of this study detonated 75 to 150 g of military-grade TNT (typical of antipersonnel mines) in 55-gal barrels containing various witness materials (metal plates, sand, barrel walls, the atmosphere). The witness materials were analyzed for explosive residue. In a third set of tests, 75-g samples of TNT were detonated over soil (from Fort Leonard Wood or Sandia National Laboratory) in an indoor firing chamber (100 by 4.6 by 2.7 m high). Targeted in these studies were TNT and four explosive-related compounds (ERC): 2,4-dintrotoluene (DNT), 1,3-dinitrobenzene (DNB), 2- and 4-aminodinitrotoluene (2-ADNT and 4-ADNT). The latter two are microbial degradation products of TNT. Post-blast residue was allowed to age in the soils as a function of moisture contents (5 and 10%) in order to quantify the rate of degradation of the principal residues (TNT, DNT, and DNB) and formation of the TNT microbial degradation products (2-ADNT and 4-ADNT). The major distinction between landmine leakage and post-blast residue was not the identity of the species but relative ratios of amounts. In landmine leakage the DNT/TNT ratio was usually greater than 1. In post-blast residue it was on the order of 1 to 1/100th of a percent, and the total amount of pre-blast residue (landmine leakage) was a factor of 1/100 to 1/1000 less than post-blast. In addition, landmine leakage resulted in low DNT/ADNT ratios, usually less than 1, whereas pre-blast residues started with ratios above 20. Because with time DNT decreased and ADNT increased, over a month the ratio decreased by a factor of 2. The rate of TNT degradation in soil observed in this study was much slower than that reported when initial concentrations of TNT were lower. Degradation rates yielded half-lives of 40 and 100 days for 2,4-DNT and TNT, respectively.

KEYWORDS: forensic science, landmines, TNT, decomposition, soil, detection

Annually, landmines kill or maim more than 15,000 people; most victims are civilians (1–3). Since World War II more than 400 million landmines have been placed, at least 65 million since 1978 (1). The U.S. Department of State estimates that between 65 and 110 million uncleared landmines are currently in the soil of 62 nations; others estimate the number as high as 200 million. A 1995 report states that even with a 30-person de-mining team, only an average of 2300 m<sup>2</sup> could be cleared per day at a cost per landmine of \$200 to \$1000 (3). This figure is in sharp contrast with the average price of a mine-between \$3 and \$15. The low cost, ease of use, and effectiveness make eradication of landmines a difficult task. The explosive 2,4,6-trinitrotoluene (TNT) is the main charge in the majority of landmines, but RDX, Tetryl, and PETN are also used (4). The main charge in mines ranges in size from tiny anti-personal mines, 30 to 700 g (Fig. 1), to the anti-tank mines, 1 to 10 kg. The housing for mines varies from wooden boxes to metal or plastic shells, which provide varying degrees of leak resistance. Various options exist for triggering mines, and the presence of a booster appears to be optional. Table 1 was prepared after review of the almost 700 landmines featured in Ref 4. Only about 10% provided sufficient data for this table: explosive fill; average charge size, container; and the average charge-to-initiator ratio.

Even with myriad new technological developments, dogs remain one of the most relied-on landmine detectors worldwide. Dogs are believed to directly "smell" the explosive and, thus, avoid false positives. Several concerns arise in contemplating design of instrumentation that locates mines by chemical sensing: the amount of explosive signature available from the mine, the presence of interfering explosive-related compounds (ERC) resulting from previous military activity (i.e., post-blast residue), and the persistence of ERC (i.e., the rate of decay). This study addressed the magnitude of the initial ERC deposits and the decay rate.

The main charge in most landmines is 2,4,6-trinitrotoluene (TNT) (4). However, when "leakage" from landmines was examined at a test landmine field located at Fort Leonard Wood, MO, TNT was not the predominant signature (5,6). In many cases, explosive-related compounds (ERC) were found, instead of TNT. 2,4-Dintrotoluene (DNT) and 1,3-dinitrobenzene (DNB) are found in manufactured TNT. Both 2- and 4-aminodinitrotoluene (2-ADNT and 4-ADNT) are degradation products of TNT, formed by microbial action in the soil. 2,4-DNT and DNB also undergo degradation to form amino-nitro-toluene (ANT) and nitro-aniline, respectively, but these are difficult to detect because of the lower initial concentrations of the precursor (5,6). The results in Table 2 represent the ERC signatures for two types of landmines (designated PMA-1A and TMA-5 and described in Table 1) buried for about eight months. The depth of placement of the landmine is also indicated in Table 2.

The objective of this study was to identify and quantify postblast residue of TNT and determine the rate of degradation in two soil types. Several test setups were employed in an effort to contain and quantify residue. In a companion study, Cold Region Research

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FIG. 1—PMA-2 anti-personnel mine casing.

and Engineering Laboratory (CRREL) and Sandia National Laboratory (SNL) functioned landmines in open fields and collected what necessarily was a minute fraction of the residue (5,6). Our strategy was to attempt to quantify the residue. The first experiments were performed on 2-g samples of TNT, RDX, and Tetryl using a small-scale explosivity device (SSED) (7-10). The second collection of experiments detonated 75 or 150-g of TNT in 55 gal barrels. Various witness materials were used in the barrel teststhe barrel walls, clean sand, aluminum witness plates. Finally, 75 g of TNT was detonated in an indoor firing chamber over soil. Two soils-one loamy (Fort Leonard Wood) and one sandy (Sandia National Laboratory)-were used. After the detonation, moisture content of the soils was adjusted to 5 or 10%, and the degradation of the principal post-blast residues (TNT, 2,4-DNT, 2-ADNT, 4-ADNT, 1,3-DNB) was tracked at room temperature over several months.

## **Experimental Section**

## Two-Gram Tests

The detonation chamber was a heavy-walled, bolted-closure, stainless-steel vessel with interior dimensions (3 by 9 in.), giving about 1-L volume; its lid was held on with eight bolts. The energetic material (2 g) was packed in a tapered 0.303-in. brass cartridge with the base thicker than the open end (7-10). Since the object of these tests was to examine residue from the detonation, it was necessary to first examine the residue produced by the initiating device. Three different initiators were examined: Star 8 detonators and exploding bridge wire detonators RP-3 and RP-2 from Reynolds Initiation Systems, Inc. After reviewing the results, the smallest detonator (RP3) was used in the residue analysis tests. Table 3 shows the composition of the detonators and their observed post-blast residue. Although the detonation chamber was vented, sufficient post-blast vapor remained to allow sampling with a Solid Phase Micro-Extraction Fiber (SPME) within a minute after the detonation. A polydimethyl-siloxane (PDMS) SPME was exposed to the chamber atmosphere for 1 min and then desorbed onto a Hewlett Packard (HP) Model 5890 Gas Chromatograph/HP model 5971 with mass selective detector (GC/MS). A GC Chrompack PoraPLOT Q capillary column (25 by 0.25 mm) was used for separations (11). The condensed blast residue was extracted from the cylinder walls with acetonitrile (50 mL). The solvent was filtered through a Gelman 0.2  $\mu$ m nylon Acrodisc 13 syringe filter and concentrated to 1 to 2 mL with a stream of nitrogen gas. Three instruments were used for chemical analysis of condensed blast residue: a HP Model 5890 gas chromatograph (GC) equipped with a J&W DB-5 capillary column (30 by 0.32 mm) and electron capture detector (ECD); a HP Model 1100 high-pressure liquid chromatograph (HPLC) with diode array detector; and a HP Model 5890 GC with HP Model 5971 mass selective detector (GC/MS). Chromatograph conditions are given in Table 4.

#### Barrel Tests with Aluminum Witness Plates

The 55-gal barrel tests used amounts of explosive comparable to that found in anti-personnel landmines. A preliminary test using a 150-g charge of TNT dramatically split the barrel. Furthermore, extensive efforts to clean the barrel walls prior to blast failed to remove contaminants that significantly interferred with residue analysis. These difficulties were overcome by reducing the TNT charge to 75 g and lining the barrel with a double layer of aluminum foil on top of which 32, flame-cleaned aluminum witness plates (10.2 by 10.2 cm) were affixed. The plates were evenly distributed in three rows of eight (17, 42, and 70 cm from the top of the 86-cm-high barrel); four witness plates were attached to the bottom and the lid of the barrel. The witness plates covered about 16% of the barrel walls. In most cases, SPME fibers were held over the open barrel (lids were blown off) for 2 min immediately (within 5 min) after the blast. Then each witness plate was wrapped in aluminum foil and heat-sealed in polyethylene bags for transport to the lab. The retrieved witness plates were individually soaked in acetonitrile (100 mL) for 48 h; soot was manually scraped from each plate. The acetonitrile was concentrated to 2 mL under a stream of nitrogen gas. The concentrated solution was filtered (0.2 µm PTFE Acrodisc syringe filters) into Agilent amber, widemouth, crimp-top 2-mL vials and stored at  $-20^{\circ}$ C awaiting GC/ECD analysis. The ERCs (TNT, 1,3-DNB; 2,6-DNT; 2,4-DNT; 2-ADNT; and 4-ADNT) were identified by retention time and quantified using two different chromatographic columns (Restec RTx-225 and J&W DB-5MS) for confirmation.

#### Firing Chamber Tests

This test was devised to purposely contaminate soil with residue from TNT detonations. Soil from Ft. Leonard Wood (FLW) and Sandia National Laboratory (SNL) was sieved (No. 2 sieve) and dried on a glass plate in an oven at 60°C for 1 h. After drying, the soil was stored in a 1-gal paint can that had been cleaned with methanol, acetonitrile, and acetone. Two indoor detonations of 75 g of TNT were performed in a well-ventilated room approximately 100 m long, 4.6 m wide, and 2.7 m high (328 ft by 180 in.  $\times$  96 in.). About 3 lb of the witness soil was sprinkled over two (63.5 by 119 cm) aluminum trays double-wrapped with aluminum foil and placed side by side to give a total surface of 127 by 119 cm. For each detonation a different soil was used (FLW or SNL). No attempt was made to completely cover the trays with soil. Around the trays, the floor was covered with a double layer of aluminum foil, out to about 2.54 m. The military-grade TNT (~75 g), suspended  $\sim 60$  cm above the center of the trays, was detonated using a Number 12 detonator. Following the detonation, the soil was poured into a stainless steel bowl that had been previously rinsed with tap water, distilled water, acetone, and acetonitrile. The soil was mixed for 20 min using an aluminum-wrapped wooden spoon.

314 MT-4         P         Yugoslav         Cylinder         TNT         3.8         none         0.00           549 TM-500         P         Yugoslav         Brick         TNT         0.5         det only         0.64         781           429 PMR-3         P         Yugoslav         Stake         TNT         0.4         det only         0.64         641           564 TMA-4         T         Yugoslav         Disk         TNT         5.5         Tetryl         10.60         519           25 AT 11         T         W German         Cylinder         RDX/TNT         0.9         Tetryl         0.00         472           169 M21         T         U.S.         Disk         Comp B         4.9         RDX/PbN <sub>6</sub> 11.20         438           494 SACIMAC-10         T         Italy         TNT         10.0          0.03         333           399 PMA-1         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313	11
549 TM-500       P       Yugoslav       Brick       TNT       0.5       det only       0.64       781         429 PMR-3       P       Yugoslav       Stake       TNT       0.4       det only       0.64       641         564 TMA-4       T       Yugoslav       Disk       TNT       5.5       Tetryl       10.60       519         25 AT 11       T       W German       Cylinder       RDX/TNT       0.9       Tetryl       0.00       472         169 M21       T       U.S.       Disk       Comp B       4.9       RDX/PbN <sub>6</sub> 11.20       438         494 SACIMAC-10       T       Italy       TNT       10.0        0.03       333         399 PMA-1       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313         401 PMA-1A       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313	
429 PMR-3       P       Yugoslav       Stake       TNT       0.4       det only       0.64       641         564 TMA-4       T       Yugoslav       Disk       TNT       5.5       Tetryl       10.60       519         25 AT 11       T       W German       Cylinder       RDX/TNT       0.9       Tetryl       0.00       472         169 M21       T       U.S.       Disk       Comp B       4.9       RDX/PbN <sub>6</sub> 11.20       438         494 SACIMAC-10       T       Italy       TNT       10.0        0.03       333         399 PMA-1       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313         401 PMA-1A       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313	40
564 TMA-4         T         Yugoslav         Disk         TNT         5.5         Tetryl         10.60         519           25 AT 11         T         W German         Cylinder         RDX/TNT         0.9         Tetryl         0.00         472           169 M21         T         U.S.         Disk         Comp B         4.9         RDX/PbN <sub>6</sub> 11.20         438           494 SACIMAC-10         T         Italy         TNT         10.0          0.03         333           399 PMA-1         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313           401 PMA-1A         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313	40
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169 M21         T         U.S.         Disk         Comp B         4.9         RDX/PbN <sub>6</sub> 11.20         438           494 SACIMAC-10         T         Italy         TNT         10.0          0.03         333           399 PMA-1         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313           401 PMA-1A         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313	
494 SACIMAC-10       T       Italy       TNT       10.0        0.03       333         399 PMA-1       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313         401 PMA-1A       P       Yugoslav       box       TNT       0.2       No 8 det       0.64       313	
399 PMA-1         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313           401 PMA-1A         P         Yugoslav         box         TNT         0.2         No 8 det         0.64         313	40
401 PMA-1A P Yugoslav box TNT 0.2 No 8 det 0.64 313	10
	6
540 TM-200 P Yugoslav brick TNT 0.2 det only 0.64 313	
42 B MK 1 T Egypt disk TNT 7.0 0.03 233	
492 SACI 54/7 T Italy disk TNT 7.0 0.03 233	
496 SACIMAC-7 T Italy TNT 7.0 30.00 233	
309 MP-APVL F4 T Chile cylinder TNT 2.0 Pentolite 10.20 196	
495 SACIMAC-5 T Italy TNT 5.5 0.03 183	
170 M24 T U.S. rocket Comp B 0.9 Tetral 4.86 176	
491 SACI 54/5 T Italy disk TNT 5.0 0.03 167	
539 TM 100 D Yugoslav cylinder TNT 0.1 dot oply 0.64 156	
298 MODEL 52 T. Swiss cylinder TNT 12.2 TNT 0.00 152	
548 TM 46 T Soviet TNT emotel 5.7 Total 27.90 151	
464 DTM DALL T Creek box TNT C 4 DETN 50.00 101	
$\begin{array}{cccccccc} 404 \text{ PIMI-BAII} & \text{Czecri } & \text{Dox} & \text{INI} & \text{6.4 PEIN} & \text{50.00} & \text{129} \\ 613 \text{ True } & \text{64} & \text{True } & \text{64} & \text{True } & \text{64} & \text{700} \\ \end{array}$	
613 Type 84 T China disk TNT/RDX(50/50) 5.0 TNT 0.04 125	40
Soviet disk INI, amatol 5.9 INI 50.00 118	12
1/2 M26 P U.S. cylinder Comp B 0.2 Tetryl 1.50 113	
243 MI AC ID 47 T French disk TNT 5.4 PbN6 0.05 108	
645 VALMARA 59 P Italy cylinder Comp B 0.5 TNT 0.01 104	
566 TMB-1 T Soviet disk TNT, amatol 5.0 TNT 50.00 100	12
293 MODEL 37 T Swiss disk TNT 3.0 TNT 30.00 99	
168 M2 P U.S. cylinder TNT 0.2 Tetryl 1.61 96	
<sup>173</sup> M34 T U.S. <sup>scatterable</sup> Comp H6 1.4 RDX 17.40 78	4
<sup>306</sup> MON-200 P Soviet disk TNT 12.0 TNT 163.00 74	
547 TM-44 T Soviet TNT, amatol 5.4 picric acid 75.00 72	
239 MI AC CP 48/55 T French disk Hexolite 6.7 Pentolite 0.10 67	5
383 PDM-1 W Soviet box TNT 10.0 TNT 150.00 67	
567 TMB-2 T Soviet disk TNT, amatol 5.0 TNT 75.00 67	
466 PTMI-BAIII T Czech disk TNT 7.2 TNT 115 63	
200 MAT-76 T Romania disk TNT 9.4 TNT 0.16 58	
583 TRUPPMINA 10 P Sweden disk TNT 0.1 Tetryl 2.00 56	
403 PMA-3 P Yugoslav disk TNT 0.0 det only 0.64 54	
545 TM-41 T Soviet cylinder TNT or amatol 4.0 picric acid 75 53	
470 PTMI-K T Czech disk TNT 4.9 99 49	
573 TMD-B T Soviet box Amatol, TNT 9.0,9.7 TNT 0.20 49	
646 VALMARA 69 P Italy cylinder TNT 0.6 RDX 12.20 47	
398 PM-60 T E. German disk TNT 10.0 TNT,PETN 218 46	
554 TM-62M T Soviet disk TNT or TNT/RDX or 7.0 Pentryt 175 40 TNT/RDX/AI	8
555 TM-62P T Soviet disk TNT 5.7-8.3 Pentrvt 175 40	
556 TM-62P3 T Soviet disk TNT or TNT/RDX 6.5-7.5 Pentrvt 175 40	
561 TMA-1 T Yugoslav disk TNT 5.6 TNT/Tetryl 0.15 37	

TABLE 1—Summary of available landmines (from Ref 4).

(continues)

# of 700	Name	Туре	Country	Shape	Explosive	Charge Kg	Booster	Booster g	Charge/ Booster	note
594	Туре 59	Т	China	disk	TNT or TGA 60/24/16	6.2	TNT	174	36	
551	TM-57	Т	Soviet	disk	TNT or TGA 60/24/16	6.0	TNT	174	35	
589	Type 51 (wood)	)	China	box	TNT	6.8	TNT	0.20	34	
240	MI AC CP 48T	Т	French	cylinder	TNT	7.3	Pentolite	0.23	32	ļ
359	OZM-72	Ρ	Soviet	cylinder	TNT	0.7	Tetryl	23	30	
238	MI AC CP 48	Т	French	disk	TNT or picric acid	6.9	Pentolite	0.23	30	
354	NV-41	Т	Soviet	box	TNT	5.9	TNT	200	30	
463	PTMI-BA	Т	Czech	disk	TNT	5.9	TNT	200	30	
572	TMD-44	Т	Soviet	box	TNT,ammonite 80	4.8-6.7	TNT	200	29	9
419	PMN	Ρ	Soviet	disk	TNT	0.2	Tetryl	7	29	
565	TMA-5	Т	Yugoslav	box	TNT	5.5	RDX	200	28	
215	MC-71	Т	Romania	2 cones	TNT	5.1	TNT	225	23	
526	T.MI.35(S)	Т	old German	disk	TNT	5.3	Penthrite	250	21	
37	AUPS	Ρ	Italy	disk	Comp B	0.1	PETN. TNT, or Tetryl	6	18	2
420	PMN-2	Р	Soviet	disk	TG-40(TNT/RDX)	0.1		6	18	
467	PTMI-D	Т	Czech	box	TNT	6.2	TNT	400	16	
529	T/78	Ρ	Egypt	brick	TNT	0.2	RDX	13	15	
527	T.MI.42	Т	old German	disk	TNT	4.7	PETN	350	13	
244	MI AC ID 51	Т	French	disk	TNT	6.5	RDX	0.50	13	
246	MI AC ID 52	Т	French	disk	TNT	6.5	RDX	0.50	13	
693	YAM-5K	Т	Soviet	box	TNT, amatol	5.0	TNT	400	13	
694	YAM-5M	Т	Soviet	box	TNT, amatol	5.0	TNT	400	13	
695	YAM-5U	Т	Soviet	box	TNT, amatol	5.0	TNT	400	13	
299	MODEL 64	Р	Swiss	cylinder	TNT	0.4	PETN	41	10	
294	MODEL 42	Т	Swiss	box	TNT	4.5	Tetryl	0.50	9	
163	M16A2	Ρ	U.S.	cylinder	TNT	0.5	Comp A5	70	7	3
402	PMA-2	Ρ	Yugoslav	disk	TNT	0.1	Hexagen	15	7	7
9	Aluminum	Т	old German	disk	Cheddite	4.1	TNT	600	7	1
255	MI AP DV 56	Ρ	French	cylinder	TNT	0.1	Tetryl	0.02	5	
256	MI AP DV 59	Ρ	French	cylinder	TNT	0.1		0.01	5	
153	LMG	Т	Soviet	rocket	TNT	3.2	TNT	780	4	
603	Type 72	Ρ	China	disk	TNT or TNT/RDX 1/1	0.1	RDX/wax	0.02	2	
608	Type 72C	Ρ	China	disk	TNT or TNT/RDX 1/1	0.0	RDX/wax	0.02	2	
528	T.MI.43(P)	Т	old German	disk	TNT	5.5	PETN	3400	2	
607	Type 72B	Ρ	China	disk	TNT or TNT/RDX 1/1	0.0	RDX/wax	24	1	
575	TMM1	Т	Yugoslav	disk	TNT	5.6				
576	TMM1	Т	Cuba	box wood	TNT				Charge	-
587	TS-50	Р	Italy,Egypt	disk	T4 (like CompB)				Booster	
662	VS 2.2	Т	Italy	cylinder	TNT/RDX	1.9				stde
664	VS-50	Р	Italy,Egypt	disk	RDX	0.0		avera	ge =	147

TABLE 1—Continued

Cheddite = chlorate or perchlorate explosives usually coated with plastic to keep out water.
 Comp B = TNT/RDX 50/50.
 Comp A5 = RDX with stearic acid (1 to 1.5% or 1.6% and 0.4% graphite).
 Comp H6 = RDX 45%, TNT 30%, Al 20%, D-2 comp 5, CaCl2 0.5%.

- 5. Hexolite = mixtures of RDX & TNT.
- 6. Entry 400 PMA-1A is corrupt.

- b. Entry 400 PMA-1A is corrupt.
  7. Hexagen = 90% RDX, 8% wax & graphite (in database, but usually just RDX).
  8. Pentryt (Pentrit is PETN, possibly the same).
  9. 200 g. With Trotyl (TNT) main charge, 160 g.
  10. No 8 = 11 mg PbN6, 190 mg Pb cresol, 450 mg PETN.
  11. Cylindrical block of TNT with two holes drilled to allow detonating cord for initiation; there is also a fuze well.

12. Picture cutout to see inside.

	Micrograms of ERC from Mine										
Depth, cm	1,3-DNB	2,4-DNT	TNT	4-ADNT	2-ADNT	2,6-DNT					
		PMA	A-1A, 200g TNT in t	DOX							
0-2.5 2.5-5 2.5-5 surface under 0-2.5 surface 0-2.5 2.5-5	34 188 20.9 20.6	115 87 6 9 39 16 58 93 8	32 19 3 23 2 129 17	566 413 17 38 81 27 357 246 16	469 431 18 44 77 8 357 209 11						
		TMA-5, 5.5	kg TNT + 200 g RI	DX booster							
0-5 5-10 10-15 surface 0-5 5-10 10-15	17.7 79 2.1 10.4 146	6 266 566 6 96 383 1123	4 27 49 3 28 155 1533	2 149 316 17 95 300 790	8 222 369 17 146 452 806	3.1 7 3 11.7					

TABLE 2—CRREL findings of ERCs at Fort Leonard wood (5,6).

CRREL = Cold-region research & engineering laboratory. ERCs = Explosive related compounds.

TABLE 3—Initiators for SSED.

	star #8	RP-2	RP-3									
Spe	cifications											
Dimensions	Dimensions (2" x 0.25") ((											
PETN (mg)	450	32	29									
Other energetics (mg)	Pb azide (11)	RDX (18)	none									
	Pb cresol (190)	binder										
Detonation Products with E	xplosive Charge	using #8, RP2 8	RP3 detonators									
Explosive Charge TNT Tetryl RDX												
Explosive Charge	?,?,L	,L,L	S,M,M									
Benzonitrile	_,S,S	_,S,_										
Benzoic acid	_,S,_	_,S,_	_,S,_									
Naphthalene	S,M,M	S,S,S	S,S,									
Acenaphthylene	S,M,M	S,S,S	S,S,S									
Naphthlenecarbonitrile	_,S,S	, ,S	_,S,_									
Phenanthrene/anthracene	_,S,_	S,S,S	S,S,_									
Fluoranthene	S,S,S	S, ,	S,S,S									
Pyrene	_ ,S,S	S, ,	S,S,S									
Hexanedioic acid esters	L,_,_	L,_,_	M,_,_									
Phthalates	M,,_	S,S,S	S,_,_									
* Products assigned by match > 90% to GC/MS library. Small (S), medium (M) and large (L)												
refer to the relative size of mass spectrometry total ion chromatography peaks. Ordering is #8,												
	1 D	8-10										

 $SSED = Small-Scale Explosivity Device^{-10}$ 

		MF f	iber	Plates	s & Soil	S	SED	Plate(TNT & ERC) & Soil(ERC		
Instrument:	(	GC/M	S	GC	/MS	G	C/ECD	GC	/ECD	
	HP5	5890/	5971	HP589	90/5971	HF	P 5890	HP	5890	
Column:	Por	aPLO	DTQ	J&W [	DB-5MS	J&W DB-5MS		J&W DB-5M	S RTx-225	
	25 x	0.25	5 mm	30 m x	30 m x 0.22mm 30 m		x 0.22mm	6m x 0.53 mr	n 6m x 0.53 mm	
Sample in:	SPME fib	er		CH₃CN o	r acetone	ac	etone	CH₃CN		
Injector °C	100			100		200		2	50	
Detector °C	C				300	20 mir	3	00		
Transfer line °C	180			310						
GC oven	-805	5 min	15°C/min	75	20°C/min	75	20°C/mir	1	0030 s, 2C/min	
	180				20 min	300	20 mir	1	203C/min	
								13520C/min		
								2	803.5 min	
	DB-5MS			Restec		ana na	Analysis	TNT		
	RT(min.)	RRT	MDL	RT(min.)	RRT	MDL				
			ng/mL			ng/mL	Instrument:	HPLC		
2,6 DNT	6.5	1	20	6.92	1	20		HP1100		
1,3 DNB	7.87	1.04	20	7.21	1.04	20	Column:	Hypersil BDS-C	18	
2,4 DNT	10.45	1.41	30	7.68	1.11	35		10 cm x 4 mr	n	
TNT	10.9	2.94	10	9.8	1.42	10		Photodiode arr	ay	
4-A-DNT	19.16	3.75	15	18.8	2.72	20	Solvent:	CH₃CN		
2-A-DNT	19.48	3.86	15	22.04	3.18	20	Detector:	214, 235, 254	nm	
							Solvents:	H2O/methanol		
RT=retention time	RT=retention time; RRT=relative retent			MDL=minin	num detectio	<sup>n limit</sup> Flow rate:		0.72 mL/min		
							Methanol	20	6%	
							Gradient:	40%, 55%, 70%	%	

TABLE 4—Experimental methods, detection limits, GC retention times.

The soil was then weighed and sealed in doubled plastic bags. The bagged samples were transported in an insulated chest containing dry ice to the laboratory, where they were stored in the laboratory freezer ( $-20^{\circ}$ C). Time from detonation to packing in dry ice was approximately 1 h. In the laboratory the soils (FLW and SNL) were removed from the freezer and tumbled for 8 h at  $-5^{\circ}$ C to assure homogeneous distribution of explosive residue. After the mixing, five samples (5 g each) were extracted with acetonitrile and analyzed for homogeneity of the ERCs. The results showed satisfactory homogeneity with about 80 mg of TNT in each soil type with standard deviation less than 1%. Ninty-six samples (5 g each) of each soil were weighed into snap-top plastic vials. To half of them 0.25 mL of water containing 60 mg of RDX/L (0.015 mg RDX/5 g soil) were added; to the other samples 0.25 mL of water and 0.25 mL of the RDX spiked water were added. The RDX was used as an internal standard for the chromatographic analyses. Samples were allowed to equilibrate at room temperature in a covered, insulated box. The sampling schedule was more frequent early in the aging cycle. At recorded time intervals, 5-g soil samples were extracted with 5 mL of acetonitrile, followed by sonication (12 h) at 10°C (12,13). The acetonitrile extract was filtered twice using syringe filters (1.0 µm then 0.20 µm Acrodisc PTFE filters); the extract was stored in Agilent amber, wide-mouth, crimp-top 2-mL vials in a freezer (-20°C) until analysis. Quantification of most ERCs was accomplished using a HP5890 GC/ECD. The acetonitrile extracts (1 µL) were directly injected (250°C) into a split/splitless port equipped with a deactivated Supelco glass inlet liner and a DB-5MS fused-silica column (6-m by 0.53-mm ID) with 1.5- $\mu$ m film thickness of 5%-(phenyl)-95%-dimethyl polysiloxane (J&W Scientific). Since the concentrations of TNT were above the linear range (~200  $\mu$ g/L) of the ECD detector, the acetonitrile extracts were re-analyzed using a reverse-phase high-performance liquid chromatography using a HP Model 1100 system with photodiode array detector (12,13). Samples (1  $\mu$ L) were introduced via autosampler. Conditions, retention times, and detection limits are shown in Table 4.

## **Results and Discussion**

## Two-Gram Detonation Tests

Three initiators (Star 8, RP-3 EBW, and RP-2-EBW) were used for 2-g charges of explosive in the SSED. When the detonators were functioned without an explosive charge, PETN (and RDX in the case of RP-2) was observed remaining from the detonator. When the detonators functioned against a charge, it was notable that the charge was not generally observed when the large detonator (Star 8) was employed. The presence of TNT and Tetryl residue was confirmed when the EBW initiators were used, but RDX was only tentatively, not conclusively, identified. Other species were observed; Table 3 reports those species identified by GC/MS using a spectral library of reliability 90% or better. Most of these products were attributed to the initiator. Various phthalates probably were produced by the wire insulation of the detonator, while the condensed-ring products could also come from the insulation or from soot of the explosives. As a result of this preliminary investigation, the smallest initiators (RP-3 EBW) were used for the majority of chemical analysis tests. In each of these tests unconsumed explosive (TNT, RDX, or Tetryl) was extracted from the cylinder walls. However, neither SPME fibers nor acetonitrile extracts of the cylinder walls showed the targeted ERCs. Only in the TNT blast was benzonitrile observed among both the condensed-phase and the SPME products. The 2-g detonation could be conveniently conducted in our laboratory; however, there was concern that postblast residue from a confined 2-g blast might not be representative of larger detonations. TNT is an oxygen-deficient explosive and a small container could restrict after-burning of the TNT that would occur in free-field detonation. To determine whether after-burn was significant in the SSED, the 2-g tests, normally performed under air, were performed under oxygen and under nitrogen (Table 5). In both cases, the flaked TNT performed poorly in the explosivity test. About 89% of the 0.303 brass cartridge remained attached to the base after detonation of the flaked TNT as compared to 30% using powdered military grade TNT (Table 5). However, the purpose of these tests was to analyze for the amount of TNT remaining under nitrogen versus under oxygen. There was a factor of 10 less TNT remaining when the TNT was initiated under oxygen instead of nitrogen (Table 5). This suggested that after-burning was an important consideration at the 2-g scale, at least with an oxygen-deficient explosive like TNT. It was concluded that the restricted volume of the SSED affected the amount of explosive residue remaining but not the performance of the explosive.

#### Barrel Tests with Witness Plates

88 TNT in air

89 TNT in air

98 TNT in air

The 32 witness plates from each 55-gal barrel test were analyzed individually using GC/ECD. TNT, 1,3-DNB, 2,6-DNT, 2,4-DNT, 2-ADNT, and 4-ADNT were identified and quantified using two different chromatographic columns (RTx-225 and DB-5MS). Not surprisingly, the witness plate results show that TNT and the ERCs were distributed symmetrically in a pattern such that they were most concentrated lateral to the location of the suspended TNT charge (Table 6). Results were relatively reproducible. On average, 16-mg TNT was recovered from each plate. Extrapolating to the 32 plates covering 15.6% of the barrel suggested that approximately 4.5% of the TNT survived the detonation. The amounts of ERCs observed were significantly less than the TNT (Table 7). In each

RP-2

RP-3

RP-3

2.0000

2.0002

2.0002

test 2,4-DNT was the most prominent ERC. Preliminary studies showed that our GC/MS analysis of SPME fibers did not have sufficient sensitivity to detect TNT nor the ERCs; thus, GC/ECD (DB-5MS column) was used. The disadvantage of this method, of course, was that only targeted compounds could be conclusively identified. However, with this increased sensitivity, TNT, DNB, and DNT were observed on the SPME fibers. For five experiments, air samples were taken using three different SPME fibers-PDMS/divinylbenzene, polyacrylate, and carboxen/PDMS-the latter giving slightly lower readings, but no conclusion should be drawn from that one result. Table 8 reports the average found in the five trials, reported in terms of micrograms (µg) of ERCs thermolyzed from the fibers. Regardless of the witness material-plate or air (sampling vapor)-the amounts of ERCs observed were significantly less than the TNT, and their amounts relative to TNT were approximately the same. In each test, 2,4-DNT was the most prominent (Table 8).

#### Firing Chamber Tests

The soil containing the post-blast residue [TNT and the ERC's (2,4-DNT, 1,3-DNB, 2-ADNT, and 4-ADNT)] was shipped to the laboratory where it was moistened and allowed to equilibrate in the dark at room temperature. For each soil, five "day zero" samples were analyzed to assess homogeneity; it appeared to be satisfactory (Table 9). Analysis of the soil at time zero indicated about 80 mg of TNT in 5 g of the witness soil (77 mg/5 g FLW and 84mg/5-g SNL) immediately following detonation. This value was higher than expected; therefore, the test was rerun in our laboratory with the same result and in the CRREL laboratory where they confirmed our high estimates of TNT [87.5 mg/5 g soil (SNL) and 105 mg/5 g soil (FLW)]. If the soil were thoroughly homogenized, this quantity represented  $\sim$ 22 g of TNT spread over the 3 lb of soil used as witness material.

#### $0.080 \text{ g TNT/5 g soil} \cdot [3 \text{ lb soil} \cdot 454 \text{ g/lb}] = 22 \text{ g TNT}$

Since only 75 g of TNT was initiated, 22 g indicated the detonation was significantly incomplete ( $\sim$ 30% remaining in the soil). This amount of undetonated TNT is extremely high and would represent a poorly functioning device. The TNT blocks used in the firing chamber tests and in the witness-plate-in-barrel tests were from a lot of military-grade TNT provided by Sandia National Laboratory; they were quite brittle. One block was analyzed for ERCs. The results are shown in Table 10 along with the relative ratios of the

0.697

0.638

0.622

0.303

0.362

0.378

% TNT

25%

48%

2%

2%

				-			
					Fraction C	Cartridge	
Sample	TNT (g)	Initiator	Cartridge Start	Weight (g) End	Remaining	Shattered	TNT
			2	g TNT flake			
122 Sample 1 N <sub>2</sub>	2.0011	RP-3	10.944	9.708	0.887	0.113	0.503
123 Sample 2 $N_2$	2.0002	RP-3	11.051	9.854	0.892	0.108	0.954
124 Sample 3 $O_2$	2.0044	RP-3	10.993	10.874	0.989	0.011	0.034
125 Sample 4 $O_2^2$	2.0066	RP-3	10.922	9.703	0.888	0.112	0.046
			2 g	TNT powder			
87 TNT in air	2.0001	#8	11.030	3.305	0.300	0.700	

3.334

3.976

4.154

10.997

10.996

10.980

TABLE 5—Detonation of TNT in nitrogen versus oxygen in SSED.

Micrograms (ug) sample on each plate as analyzed on RTX-225 GC column														
Barrel #	Row	Plate	TNT	st dev	1,3 DNB	st dev	2,6 DNT	st dev	2,4 DNT	st dev	2-ADNT	st dev	4-ADNT	st dev
Barrel 1	R1	1	28947		4.24		3.02		22.53		NA		NA	
		2	25359		1.82		1.66		13.94		NA		NA	
		3	16121		3.68		6.18		23.43		NA		NA	
		4	9350		0.96		1.03		5.66		1.13		1.83	
		194	10613		0.92		1.36		6.94		1.15	`	1.76	
		6	14596		3.39		4.42		18.38		2.44		4.31	
		7	12611		1.96		2.22		13.92		1.51		2.35	
		8	10677		1.11		1.46		7.95		1.63		2.55	
		Average	16034	7273	2.26	1.32	2.67	1.80	14.09	6.94	1.57	0.53	2.56	1.03
	R2	9	3785		3.48		3.54		23.46	1	NA		NA	
		10	33144		3.28		3.19		18.62		NA		NA	
		11	41614		9.89		6.90		28.08		NA		NA	
		12	16630		4.76		4.73		18.74		2.01		2.65	
		13	18744		14.94		13.34		24.35		3.17		4.19	
		14	18610		7.32		7.34		26.28		3.88		5.02	
		15	17659		5.56		7.26		24.83		2.93		3.97	
		16	18661		5.52		6.73		24.97		3.69		5.04	
		Average	21106	11434	6.84	3.91	6.63	3.18	23.66	3.37	3.14	0.74	4.17	0.98
	R3	17	12230		0.74		2.10		6.19		NA		NA	
		18	11256		1.00		0.85		4.82		NA		NA	
		19	27904		1.76		2.12		16.78		NA		NA	
		20	18074		5.21		9.30		26.23		3.90		2.85	
		21	15148		1.76		3.66		21.40		4.89		7.63	
		22	10616		0.45		1.14		5.67		1.79		3.34	
		23	13079		0.85		1.18		6.86		2.02		4.33	
		24	10807		0.38		0.69		3.15		0.90		1.81	
		Average	14889	5832	1.52	1.58	2.63	2.86	11.39	8.79	2.70	1.64	3.99	2.23
	Тор	29	29295		5.13		1.85		13.82		NA		NA	
		30	-	Т	his plate	was	not reco	vered	after the	e deto	onation			
		31	10437		10.19		0.80		6.71		NA		NA	
		32	64186		0.47		0.44		1.77		NA		NA	
		Average	34639	27270	5.26	4.86	1.03	0.73	7.44	6.06			3.37	0.97
	Bot	25	23257		0.94		1.24		8.47		NA		NA	
	tom	00	40004		4.40		0.40		45.40		0.40		0.00	
		26	13694		1.19		2.18		15.49		2.42		2.92	
		27	33543		6.46		5.13		25.98		NA		NA	
		28	36290	10325	10.97	4 79	5.33	2.07	25.37	8 42	NA		NA	0.22
KIA-225		Average	26696	10020	4.89	4.70	3.4/	2.07	18.83	0.42	20		3.14	0.22
SumE	RL		626937		120		112		491		39		57	

TABLE 6—Witness plate ERCs from 75 g TNT in 55 gal barrel.

	Detonat	ted		·	Total Micr	ograms of	EPC four	ad on Dia	tos in or	ch Barr		
Derest	50101101					ograms or	ERC IOUI					
Barrel	gram TI	NT	# Plates	% Barrel(1)	TNT (ug)	% TNT (2)	ug/ plate	1,3 DNB	2,6 DNT	2,4DNT	2-ADNT	4-ADNT
1	7	6.9	31	15.1%	626937	5.40%	20224	120	112	491	59	109
2	7	75.6	31	15.1%	487730	4.28%	15733	104	75	395	70	124
3	7	6.2	32	15.6%	451625	3.80%	14113	157	113	544	41	49
4	7	4.3	13	6.3%	207686	4.42%	15976	52	46	191	20	27
			Average	RTx-225	522097	4.48%	16512					
				total TNT (g)	3.35	4.46%	% out of	75 g TN	F			
1	7	6.9	31	15.1%	481955	4.15%	15547	159	94	580	82	76
2	7	5.6	31	15.1%	464829	4.08%	14994	143	66	395	93	76
3	7	6.2	32	15.6%	493825	4.16%	15432	133	8	525	97	74
4	7	4.3	13	6.3%	158771	3.38%	12213	55	9	162	23	31
			Average	DB-5MS	480203	3.94%	14547					
			(3)	total TNT (g)	3.08	4.10%	% out of	75 g TN <sup>-</sup>	Γ -			
(1)	[(4"*4"	')*#	plates}/	3288 in <sup>2</sup>		(3)	Average	ug TNT/	(0.156*e	6)		

TABLE 7—Summary TNT and ERCs on plates in barrels.

(2) ugTNT\*(75000000\*% of 3288sq.in. barrel) where detonation was with 75 g TNT

TABLE 8—Micrograms	of TNT detected after	· blast and percentage	of ERC based on TNT.
IIIDDD 0 IIICIOSIUIIIS	of Int acteered after	brast and percentage	of Life bused on 1111.

colur	nn ERC/TNT	mg TNT	ug	1,3 DNB	ug	2,6 DNT	ug	2,4 DNT	ug	2-ADNT	ug	4-ADNT
RTX-2	25 plate*	16.5	4.0	0.024%	3.2	0.020%	15.2	0.092%	1.5	0.009%	2.2	0.014%
DB-5N	1S plate*	14.6	4.6	0.031%	1.7	0.011%	15.5	0.106%	2.8	0.019%	2.4	0.017%
DB-5N	IS SPME	0.02	4.6E-04	0.002%	2.6E-04	0.001%	1.0E-03	0.005%		not det	ermi	ned
	ppm SPME**	90500		2.0		1.1		4.4				

\* Values from average residue in each row and multiplying by the number of plates in row and summing over the barrel.

\*\* Ave. ERC's (ug)--5 SPME fibers was divided by barrel volume (231L) to estimate mg ERC/cm3 of air ~ ppm.

The meaning of this number is open to question because the lid of each barrel flew off upon blast.

			s	tart	31	days	Fraction	rate constant	half-life	SNL 69d/F	LW 63d	Fraction	rate constant	half-life
ERC	Soil	water	mg	std dev	mg	std dev	Lost	1/sec	days	mg	std dev	Lost	1/sec	days
TNT	Ft L.W.	10%	77	4	64	24	0.17	6.8E-08	118	37	13	0.52	1.3E-07	60
		5%	77	4	55	9	0.29	1.3E-07	63	41	4	0.47	1.2E-07	69
	Sandia NL	10%	84	7	69	1	0.18	7.4E-08	109	57	3	0.32	6.4E-08	126
		5%	84	7	73	2	0.13	5.1E-08	157	61	6	0.27	5.4E-08	149
			ug		ug		avg.	8.0E-08		ug		avg.	9.2E-08	
2,4-DNT	Ft L.W.	10%	43	3	22	1	0.50	2.6E-07	31	18	4	0.58	1.6E-07	50
		5%	43	3	28	4	0.36	1.6E-07	49	19	2	0.56	1.5E-07	53
	Sandia N L	10%	52	4	25	0.1	0.52	2.7E-07	30	21	1	0.60	1.5E-07	53
		5%	52	4	27	0.9	0.48	2.4E-07	33	20	1	0.61	1.6E-07	51
1						1	avg.	2.3E-07				avg.	1.6E-07	
1,3-DNB	Ft L.W.	10%	4.6	0.3	4.1	1	0.11	4.5E-08	178	3.8	1	0.18	3.7E-08	
		5%	4.6	0.3	3.7	0.3	0.20	8.2E-08	98	4.8	0.0			
	Sandia N L	10%	6.2	0.4	4.5	0.1	0.28	1.2E-07	66	5.8	0.4	0.06	1.0E-08	
		5%	6.2	0.4	5.0	0.2	0.20	8.1E-08	99	5.6	0.3	0.10	1.7E-08	
							Gained					Gained		
2-ADNT	Ft L.W.	10%	1.4	0.1	3.0	0.3	1.17	2.9E-07	28	2.2	0.0	0.54	-8.0E-08	
		5%	.1.4	0.1	2.5	0.4	0.76 ·	2.1E-07	38	1.8	0.3	0.26	-4.3E-08	
	Sandia N L	10%	1.4	0.2	3.0	0.06	1.16	2.9E-07	28	2.5	0.2	0.77	-9.6E-08	
		5%	1.4	0.2	2.7	0.1	0.91	2.4E-07	33	1.6	0.2	0.17	-2.7E-08	
							1							
4-ADNT	Ft L.W.	10%	0.7	0.07	1.6	0.05	1.30	3.1E-07	26	1.5	0.1	1.16	-1.4E-07	
		5%	0.7	0.07	1.2	0.1	0.75	2.1E-07	39	0.9	0.1	0.29	-4.6E-08	
	Sandia N L	10%	0.8	0.17	1.3	0.1	0.67	1.9E-07	42	0.9	0.1	0.15	-2.3E-08	
		5%	0.8	0.17	1.1	0.09	0.44	1.4E-07	58	0.7	0.1			

TABLE 9—Post-blast (75 g) TNT and ERCs in soil (5 g).

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ERCs to the TNT. The amounts and ratios are almost identical to those found after detonation over soil in the firing chamber tests, but about an order of magnitude lower from those found on the witness plate tests and much lower than those Jenkins found when a PMA2 was detonated over snow (15). We believe the increase in TNT/ERC ratios in the latter two tests is related to the decrease in undetonated TNT—30% in the soil in the firing chamber versus 2 to 4% on the plate in the barrel versus ~0.008% from the PMA2 (100 g TNT with 13 g RDX booster) in snow. If TNT detonates while the ERCs do not, the ratio ERC/TNT will be larger, the more complete the TNT detonation.

While the poor detonation of TNT was unexpected, the resultant contaminated soil is representative of that exposed to a variety of functioning and incompletely functioning devices. Therefore, this soil was used to study environmental degradation of TNT and ERCs as might be found at firing ranges and in areas of military activity. Over a period of two months, 5-g samples were removed from the insulated box and analyzed for TNT and other ERCs. The results are illustrated graphically in Figs. 2 and 3. The 0, 31, and 69-day data are tabulated in Table 9 using an average of three samplings. The degree of variability is represented by the standard deviation. While the TNT content on the Fort Leonard Wood soil appeared homogeneous on day "0," subsequent samples exhibited higher TNT variability. With this exception, the data trend was reasonably consistent. Over the period monitored, we observed a 50% drop in TNT and 2,4-DNT and an increase of up to 100% in the TNT microbial breakdown products 4-ADNT and 2-ADNT (Table 9). With two exceptions, the loss or gain was faster in soils with 10% moisture content than in those with 5%. There was no clear trend regarding the change of concentrations depending on soil type (FLW or SNL). For TNT, 2,4-DNT, and 1,3-DNB, rate constants (k) were estimated using the average fraction remaining on the 31<sup>st</sup> day. Assuming these were first-order rate constants, half-lives  $(t_{1/2})$  were

Source of Species	ug/g soil	E	RC's Detecte	ed as % of TN	IT		#	2,4DN	T/ADNT
	TNT	1,3 DNB	2,6 DNT	2,4 DNT	2ADNT	4ADNT	runs	2ADNT	4ADNT
TNT as received %	0	0.004%		0.017%	0.001%	0.000%	2	17	44
Post-Blast	~30%								
Soil, Chamber, 0 day	16187	0.007%		0.059%	0.002%	0.001%	10	37	73
Soil, Chamber, 31 days	13337	0.007%		0.039%	0.004%	0.002%	6	9	20
Soil, Chamber, 63-69 d	9836	0.011%		0.041%	0.004%	0.002%		10	22
Witness plates, Barrel	4%	0.028%	0.015%	0.100%	0.014%	0.015%	107	8	7
PMA2 (100g TNT), snow <sup>15</sup>	0.008	ND	ND	3.3%	1.2%	1.7%	14		
Landmina Laakaga							1		
	0.057	220/	20/	000/	770/	719/	1 44	1 0 02	0.88
average above TIVIA5	0.257	JZ 70	270	00%	11/0	7 1 70	44	0.03	0.00
I MA5-mean surface	0.0042			309%	405%	398%		0.91	0.93
PMA1A-mean surface	0.0038			832%	1147%	1166%		0.72	0.71
ug/g soil max.	0.023								

TABLE 10—TNT and ERCs available: a comparison of post-blast and mine leakage.

\* Jenkins TF, George V. Personal communication.



FIG. 2—Changes in TNT and ERCs concentrations in Sandia soil moistened with 10% water.



FIG. 3—Changes in TNT and ERCs concentrations in Fort Leonard wood soil moistened with 5% water.

TABLE 11—Half-li	fe estimates measi	ired at CRREL (15	5, 16).
Soil	2,4-DNT	1,3-DNB	TNT
Half Life	e in Days Determi	ned at 22°C	
Fort Leonard Wood Windsor Sandy Loam Charlton Silty Loam Fort Edwards Clay	25.7 49.5 53.3 1.5	9.9	1.3 1.9 3.5,2.4 <1
Half Life	e in Days Determin	ned at -4°C	
Fort Leonard Wood Windsor Sandy Loam Charlton Silty Loam Fort Edwards Clay	86 178 233 13.3	84	80 16.5 19.8 1.4

calculated using the equation:

## $t_{1/2} = 0.693/k$

Table 9 lists these values: 2,4-DNT decomposed faster than TNT (2  $\times 10^{-7}$  s<sup>-1</sup> compared to 6  $\times 10^{-8}$  s<sup>-1</sup>). The TNT rate constant is in reasonable agreement with estimates made from preliminary detonations in barrels over sand, where TNT post-blast residue on the sand was quantified at 12 and 18 months intervals; a rate constant of about 10-8 s-1 was found. CRREL estimated half-lives of 2,4-DNT, TNT, and 1,3-DNB in Fort Leonard Wood soil at ambient temperature (Table 11). For 2,4-DNT they obtained a half-life of 26 days, while in this study we determined it to be 31 to 49 days (10%, 5% moisture). This is in reasonable agreement. However, we differ greatly in our estimates of the half-lives of TNT and 1,3-DNB (Table 11). A significant difference between these studies is that the target compounds were deposited by detonation in our study instead of as aqueous solutions. Deposition by detonation gave no control of the initial concentrations. We believe the initial high concentrations of TNT in this study probably inhibited microbial degradation of TNT. Thus, rather than a half-life on the order of one day as observed by CRREL, we see a TNT half-life nearer 100 days (Table 11). This is a matter of great concern when considering the detection of landmines in areas that have already seen military activity.

It was observed that TNT post-blast residue differed from landmine leakage. During the 2.5-year study at a test minefield in Fort Leonard Wood, MO, Jenkins et al. (CRREL) found mine leakage produced surface concentrations of TNT in the 1-ppb range in some samples, while others showed no detectable TNT. However, 2,4-DNT and ADNT concentrations were as great or greater than TNT (16). It was recommended that detection schemes target, 2,4-DNT. In post-blast residue, the amount of TNT can greatly exceed the ERCs (Table 10). Therefore, relatively high 2,4-DNT concentrations accompanied by relatively low TNT concentrations (i.e., a high 2,4-DNT/TNT ratio) would be an indication of landmine leakage as opposed to post-blast residue. Data in Table 10 suggest the ERC/TNT ratio may be useful in differentiating the source of residue:

	DNT/TNT	ADNT/TNT	DNT/ADNT
Blast (30% TNT left)	$\sim 10^{-4}$	$\sim 10^{-5}$	~20-60
Blast (0.008% TNT left) <sup>15</sup>	$\sim 10^{-2}$	$\sim 10^{-2}$	~7-11
Surface mine leakage <sup>16</sup>	1-10's	1-10's	< 1

Low concentrations of TNT associated with landmines tend to more rapidly disappear due to bacterial action than the greater concentrations associated with post-blast. Therefore, high DNT/TNT ratios should be a conclusive identifier of landmine leakage. A further indicator that nitroarenes are from landmines is the ratio 2,4-DNT/ADNT. Generally, post-blast residue yields DNT/ADNT ratios above 10, while the ratio of these species from landmine leakage is generally below 1 (Tables 2 and 10). However, since ADNTs are more difficult to detect than TNT, this observation may not be as useful with the current generation of mine detectors.

## Conclusions

TNT detonation products, other than the target ERCs, were not detected or identified. The GC/ECD system used in this study had high sensitivity, but identification is based solely on retention times. The two GC/MS systems in our laboratory had significantly less sensitivity for the targeted ERCs. This restricted our study only to the targeted ERCs, which were observed in both post-blast samples and pre-blast TNT. Numerous other peaks in the GC/ECD chromatograms could not be identified unless their concentrations were sufficiently high to be detected by GC/MS. In the firing chamber

tests, it appeared that the dinitro species (2,4-DNT, 1,3-DNB, 2-ADNT, and 4-ADNT) survived detonation. Their amount and ratio to TNT were relatively unchanged from pre-blast to post-blast: DNT/TNT =  $\sim 10^{-4}$  and ADNT/TNT =  $\sim 10^{-5}$ . We attributed this to a poor detonation that left about 30% of the TNT unreacted. In an earlier study where only  $\sim 4\%$  of the TNT survived, we found the ERC/TNT ratio an order of magnitude higher. Jenkins also observed large ERC/TNT ratios in the explosion of a PMA2, which left only 0.008% TNT: DNT/TNT= $\sim 10^{-2}$  and ADNT/TNT= $\sim 10^{-2}$ . These ratios allow clear differentiation of post-blast residue from landmine leakage where the ERC/TNT ratios are greater than 1. When the post-blast residue was allowed to equilibrate with moistened soil, the amino-dinitrotoluenes increased, while 2,4-dinitrotoluene, 1,3-dinitrobenzene, and TNT decreased. The rate of TNT or 2,4-DNT loss was higher on the soils containing 10% rather than 5% moisture, but no clear dependence on soil type was observed. Halflives for the disappearance of 2,4-DNT and TNT were calculated; they were around 40 and 100 days, respectively.

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