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Thomas F. Jenkins

US Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH

Alan D. Hewitt

US Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH

Clarence L. Grant

University of New Hampshire, Durham, NH

Sonia Thiboutot

Defence R&D Canada—Valcartier, Val-Belair, Que., Canada

Guy Ampleman

Defence R&D Canada—Valcartier, Val-Belair, Que., Canada

See next page for additional authors

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Authors

Thomas F. Jenkins, Alan D. Hewitt, Clarence L. Grant, Sonia Thiboutot, Guy Ampleman, Marianne E. Walsh, Thomas A. Ranney, Charles A. Ramsey, Antonio J. Palazzo, and Judith C. Pennington

Identity and distribution of residues of energetic compounds at army live-fire training ranges

Thomas F. Jenkins^{a,*}, Alan D. Hewitt^a, Clarence L. Grant^c,
Sonia Thiboutot^b, Guy Ampleman^b, Marianne E. Walsh^a,
Thomas A. Ranney^d, Charles A. Ramsey^e, Antonio J. Palazzo^a,
Judith C. Pennington^f

^a *US Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH 03755, USA*

^b *Defence R&D Canada—Valcartier, Val-Belair, Que., Canada G3J 1X5*

^c *University of New Hampshire, Durham, NH 03824, USA*

^d *Science and Technology Corporation, Hanover, NH 03755, USA*

^e *EnviroStat, Inc., P.O. Box 636, Fort Collins, CO 80522, USA*

^f *US Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS 39180, USA*

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Abstract

Environmental investigations have been conducted at 23 military firing ranges in the United States and Canada. The specific training facilities most frequently evaluated were hand grenade, antitank rocket, and artillery ranges. Energetic compounds (explosives and propellants) were determined and linked to the type of munition used and the major mechanisms of deposition.

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1. Introduction

Over the past few years environmental investigations have been conducted at 23 military installations in the United States and Canada (Fig. 1). The objectives of these studies were to identify the types and distribution

of energetic residues (ERs) present in the surface soils at various types of army, live-fire training ranges. The concern is that these ERs could serve as sources for off-site migration of various compounds in ground water or surface water. The intent of this paper is to summarize the knowledge that has been gained from these studies.

The energetic compounds used in military high explosives include 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine (HMX). Those used

* Corresponding author. Tel.: +1 603 6464385.

E-mail address: Thomas.F.Jenkins@erdc.usace.army.mil (T.F. Jenkins).

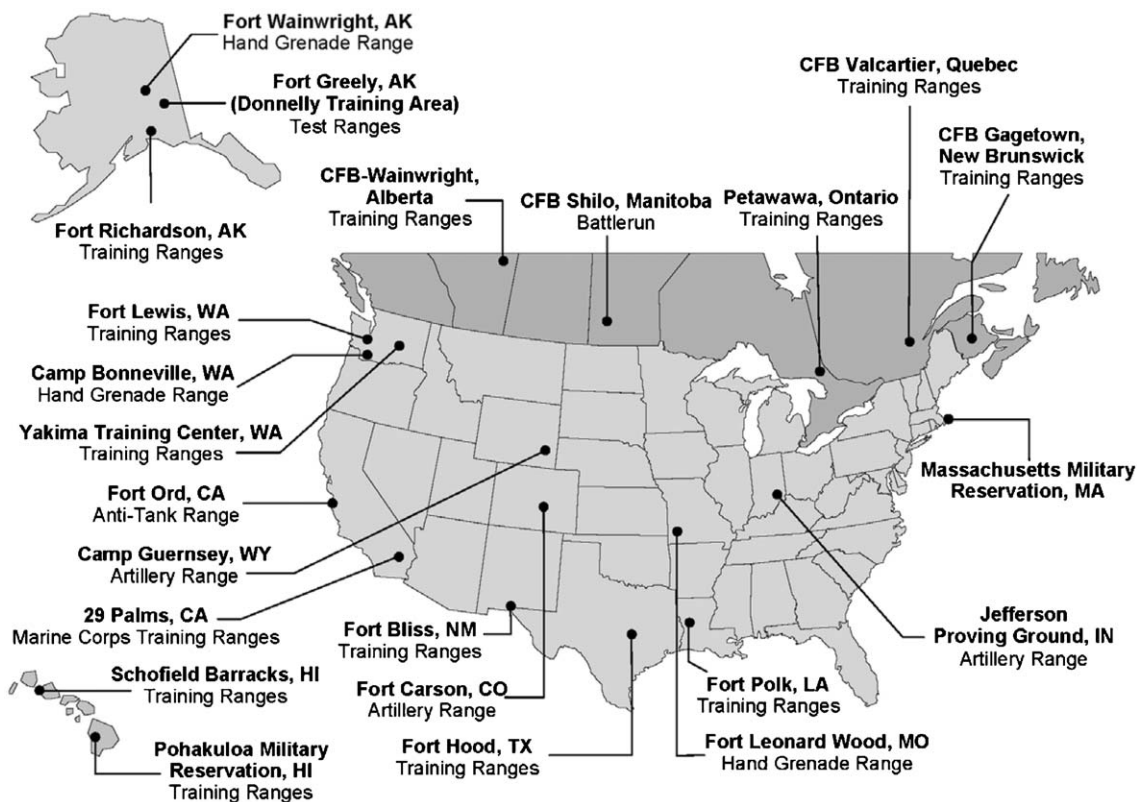


Fig. 1. US and Canadian Army installations where field-sampling experiments were conducted.

in propellants include nitrocellulose (NC), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), and nitroguanidine (NQ). Residues of these compounds are deposited onto the surface during live-fire training, generally as particles, fibers and slivers (Radtke et al., 2002; Walsh et al., 2002; Taylor et al., 2004; Walsh et al., 2004).

At US and Canadian Army bases, we have studied hand grenade, antitank rocket, and mortar and artillery ranges. Different types of munitions containing a variety of energetic formulations are used during training. Generally, ERs at firing points are compounds used in propellant formulations, whereas ERs at the impact areas are compounds used as high explosives in munition warheads.

2. Methods

2.1. Soil sampling

Soil sampling methods for the various types of ranges have evolved to address the nature of the deposition and distribution of ERs. Stainless steel scoops were used to sample non-cohesive soils such as sands and gravels,

and specially designed corers were used in more cohesive soils such as silts and clays (Walsh, 2004). Because of the presence of subsurface unexploded ordnance (UXO), soil sampling was often limited to surface and near-surface depths. When allowed, soil profiling has shown that major residue concentrations are in the top several centimeters (Jenkins et al., 2001; Pennington et al., 2003; Hewitt et al., 2005a).

When soil sampling was conducted to estimate mean concentrations for a given area, multi-increment composite sampling was used to address the high degree of spatial heterogeneity (Walsh et al., 1997, 2005; Jenkins et al., 1999, 2004a,b, 2005; Hewitt et al., 2005a). The number of increments and mass needed per composite to provide a reliable estimate of the mean concentration depends on residue deposition and the size of the area being investigated (Jenkins et al., 2005). Generally 30 to 50 increments were adequate for 10-m × 10-m (100 m²) areas, and 50–100 increments were often adequate for larger areas, i.e., 100-m × 100-m (10000 m²). Discrete samples were used to characterize residues in areas where solid explosives were observed on the soil surface, or for depth profiling near these high-concentration sources.

2.2. Sample processing and subsampling

Sample processing and subsampling have also evolved to address heterogeneity, size distribution, and the composition of explosives and propellant particles (Walsh et al., 2002, 2005). Currently, air-dried soils are sieved (#10, <2 mm) to remove oversized material, then the <2-mm fraction is mechanically ground on a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) ring mill. Soils from impact ranges are ground for 90 s. From firing points, where ERs can be present as fibers, they are ground for five 60-s intervals with a short cooling period between grinds. Ground samples are mixed thoroughly, spread to form a 1-cm-thick layer, and 10-g subsamples are formed by combining ≥ 30 random increments.

2.3. Sample analysis

The 10-g portions of soil are extracted with 20 ml of acetonitrile using either an ultrasonic bath or shaker table for 18 h. Extracts are analyzed using either RP-HPLC Method 8330 (EPA, 1994) or GC-ECD Method 8095 (EPA, 1999). Many samples were analyzed by both methods to increase confidence in the identity of detected analytes and to obtain results for various ERs that can differ in concentration by several orders of magnitude. Besides the major nitroaromatic and nitramine high explosives and propellants used by the Army, the major environmental transformation products known to form in aerobic surface and near-surface soils (1,3,5-trinitrobenzene (TNB), 2-amino-4,6-dinitrotoluene [2ADNT], and 4-amino-2,6-dinitrotoluene [4ADNT]) were also quantified.

3. Results and discussion

3.1. Hand grenade ranges

Hand grenade ranges are generally only a few hectares in size and poorly vegetated because of the large number of individual detonations. The greatest density of craters lie at distances between 15 and 35 m from the throwing pits, and depending on the range design, were in an area 20–60 m wide. At some ranges craters are filled in and the surface is leveled frequently; at others, they are left intact. The multitude of detonations within the confined area tends to mix the top 10–15 cm of soil (Jenkins et al., 2001).

Most training at hand grenade ranges in the United States and Canada is with M67 and C-13 fragmentation grenades, both of which contain an explosive charge of 185 g of Composition B that is 60% military grade RDX, 39% military grade TNT, and 1% wax. Military-grade RDX contains about 90% RDX and 10% HMX.

Eleven active and two closed hand grenade ranges were sampled (Table 1). The analytes detected include RDX, TNT, HMX, TNB, 2ADNT, and 4ADNT. RDX was generally present at the highest concentration with mean surface concentrations from <0.01 to 51 mg/kg. These ranges fall into two groups: one group of six ranges had mean RDX concentrations less than 0.12 mg/kg and the other group of seven ranges had concentrations between 0.45 and 51 mg/kg (Table 1). Standard deviations are not included in this and other summary tables because the distributions were generally non-Gaussian and the sampling strategies varied as we gained more knowledge about these sites (Jenkins et al., 2005). Remnants of partially detonated grenades and some chunks of the high-explosive fill were observed at many of the seven ranges with higher RDX concentrations. It is unclear whether these partial detonations occurred when the rounds were thrown or when duds were blown-in-place using C4 explosive (91% RDX). In either case, high-concentrations of residues were attributed to these partial detonation events.

The relatively high-concentrations of RDX, HMX, and TNT in the surface soils cannot be explained by hand grenades that detonated as designed (high-order detonations). Hewitt et al. (2005a) estimated that about 0.025 mg of RDX and less than 0.001 mg of TNT are deposited on the soil surface when a hand grenade detonates as designed. To attain a 0.5-mg/kg RDX concentration in the top 10 cm of a 20-m \times 20-m area with a soil density of 2.0 g/cc would require more than one million detonations. Thus it is the low-order detonations that occasionally occur on these ranges that are responsible for the largest part of the energetic residues present at hand grenade ranges.

3.2. Antitank rocket range impact areas

Antitank rocket ranges are several hundred hectares in size and there is a direct line of sight to the targets, i.e., derelict armored vehicles placed about 100 m down-range. The weapon most often fired at the ranges sampled is the 66-mm M72 light anti-armor weapon (LAW). This item contains M7 double-base propellant that is 54.6% NC, 35.5% NG, 7.8% potassium perchlorate, 0.9% ethyl centralite, and 1.2% carbon black. The warhead contains 0.3 kg of the melt-cast explosive octol (70% HMX and 30% TNT) with either a tetryl or RDX booster.

Field experiments were conducted at six active and one closed antitank rocket range(s). The primary residue detected at impact areas was HMX with concentrations in surface soils adjacent to targets generally in the hundreds of mg/kg (Table 2). HMX concentrations decline with distance from the target (Jenkins et al., 1997, 1998). TNT, RDX, 4ADNT, and 2ADNT are often detectable as well, but concentrations are several orders

Table 1
Summary of results for energetic compounds detected in surface soils at hand grenade ranges

Installation	Samples analyzed	Mean concentration (mg/kg)					
		HMX	RDX	TNT	TNB	4ADNT	2ADNT
Range A ^{a,c}	23 [*]	1.8	7.5	9.3	0.05	0.15	0.13
	5 ^{**} (50)	1.0	4.4	1.5	ND ^{***}	ND	ND
Range B ^{a,c}	27 [*]	0.02	0.08	0.03	ND	0.01	ND
Range C ^{b,d}	48 [*]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Range D ^{a,d}	18 ^{**} (30)	0.19	0.45	<0.01	<0.01	<0.01	<0.01
Range E ^{a,e}	15 ^{**} (20)	0.05	0.71	0.06	<0.01	0.02	0.02
Range F ^{a,d}	25 ^{**} (1, 5, 10, 20, 40)	2	11	1.2	0.15	ND	ND
Range G ^{a,f}	3 ^{**} (30)	9.1	51	36	0.28	0.40	0.03
Range H ^{a,f}	7 ^{**} (30)	0.53	5.6	0.78	<0.01	<0.01	<0.01
Range I							
Old range ^{b,d}	11 [*]	ND	5.1	0.4	ND	ND	ND
Old range ^{b,g}	5 ^{**} (30)	0.02	0.12	0.12	<0.01	<0.01	<0.01
New range ^{a,h}	5 ^{**} (30)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
New range ^{a,i}	15 ^{**} (25)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Range J ^{a,d}	2 ^{**} (30)	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
Range K ^{a,d}	9 ^{**} (25, 100)	0.18	0.65	0.16	<0.01	<0.01	<0.01

* Discrete samples.

** Multi-increment samples with (*n*) increments per sample.

*** Not determined.

^a Active ranges.

^b Closed ranges.

^c Jenkins et al. (2001).

^d Unpublished data.

^e Ampleman et al. (2003).

^f Pennington et al. (2004).

^g Dube et al. (1999).

^h Thiboutot et al. (2003).

ⁱ Thiboutot et al. (2004).

of magnitude lower. The low solubility of HMX allows it to accumulate on the surface while the more soluble TNT dissolves and undergoes environmental transformations to ADNTs (McCormick et al., 1976). The ADNTs can covalently bind to soil organic matter, thereby becoming immobilized (Thorn et al., 2002), but the fraction that does not covalently bind appears to be more mobile than TNT in the soil profile.

Ruptured LAW rockets were observed on the surface of many of these ranges. It has been observed that when this weapon fails to hit a target, the side wall of the warhead frequently ruptures upon surface impact, thereby depositing crystalline explosive. This mode of deposition is thought to be the major source of ERs.

Because antitank rockets are propelled all the way to the target, propellants can still be present when these rockets detonate or rupture upon impact. For these reasons pieces of propellant are also often visible on the soil surface in the area around the targets, and NG is often present in impact area soil samples (Table 2). Although potassium perchlorate is also present in this propellant, it was not detected in soils from several antitank ranges.

3.3. Antitank rocket range firing points

Sampling was conducted at six antitank rocket range firing points. In all cases NG was the primary ER detected (Table 3). Surface soil concentrations from 0 to 25 m behind the firing line were generally in the hundreds of mg/kg, whereas concentrations between the firing line and the target were generally several orders of magnitude lower.

3.4. Artillery ranges

Artillery ranges are the largest training ranges in the army inventory, typically covering hundreds of square kilometers. Firing positions are often arranged around the circumference of the range with firing fans overlapping in a central impact area. Artillery and mortar rounds travel several kilometers before impacting near the targets. Only a few errant rounds impact outside of the central impact zone, an area that typically covers several square kilometers. Most rounds that arrive near targets are set to detonate upon impact, forming a crater, the size depending on the type of round and the

Table 2
Summary of results for energetic compounds detected in surface soils adjacent to targets at antitank rocket ranges

Installation	Samples analyzed	Mean concentration (mg/kg)					
		HMX	RDX	TNT	4ADNT	2ADNT	NG
Range L ^{a,c,d}	16*	803	4.6	24			NA [†]
	5*	399	0.76	3			NA
	20*	662	<0.1	4			NA
	4** (30)	898	2.8	7			7.8
Range M ^{a,c}	11*	987	5.3	126			NA
Range N ^{b,e}	8***	307	0.25	0.2	0.69	0.55	NA
Range O ^{a,d}	10	680	<1	4			NA
	5**	874	0.5	6	0.8	0.7	25
	8**	489	0.5	2	0.4	0.5	34
Range P ^{a,f}	6** (30)	23	0.8	0.04	0.05	0.12	NA
Range K ^{a,g}	3** (50)	745	0.32	73			2.5

* Composite samples.

** Multi-increment samples with (*n*) increments per sample.

*** Discrete samples.

[†] NA—not analyzed for NG.

^a Active ranges.

^b Closed range.

^c Thiboutot et al. (1998).

^d Jenkins et al. (2004a).

^e Jenkins et al. (1998).

^f Pennington et al. (2002).

^g Unpublished data.

Table 3
Summary of results for nitroglycerin (NG) near firing points at active anti-tank rocket ranges

Installation	Samples analyzed	Mean NG concentration (mg/kg)								
		In front					Behind			
		0–10 m	10–20 m	20–30 m	30–40 m	40–50 m	0–10 m	10–20 m	20–30 m	30–40 m
Range P ^a	2 (30)*	3								
Range G ^b	4 (30)*						1200	9.4		
Range I ^{c,d}	4 (30)*	176	65			14	1130			
	15 (30)*	160	160	87	55	12	4700	2320	380	84
Range Q ^c	10 (30)*	1	0.5	<0.1			1			
Range L ^f	13 (30)*		4.2	0.8	0.1	0.4	910	490	104	
Range K ^g	8 (40)*						2240	380		

* Multi-increment samples with (*n*) increments.

^a Pennington et al. (2002).

^b Pennington et al. (2004).

^c Thiboutot et al. (2003).

^d Thiboutot et al. (2004).

^e Pennington et al. (2003).

^f Jenkins et al. (2004a).

^g Unpublished data.

physical properties of the soil. Occasionally a round impacts without detonating, resulting in either a surface or subsurface UXO. In a very few cases a round partially detonates upon impact, or perhaps a UXO is sympathetically breached by shrapnel from another detonation.

Both events result in what is called a low-order detonation.

The major munition systems currently being fired into the ranges studied include 155-mm howitzers, 105-mm howitzers, 120-mm main tank guns, 81-mm mor-

tars, 60-mm mortars, and 120-mm mortars. Others include 90-mm recoilless rifle rounds, 4.2-in. mortar rounds, 8-in. artillery rounds, bombs, 40-mm grenades, 106-mm high-explosive plastic (HEP) rounds, 2.75-in. rockets, and wire-guided missiles. Munitions are delivered using single-, double-, and triple-base gun propellants, and composite rocket and missile propellants. Single-base propellant is composed of NC and 2,4-DNT, double-base propellant is composed of NC and NG, and triple-base propellant is composed of NC,

NG, and nitroguanidine. Composite rocket and missile propellants typically contain ammonium perchlorate as a crystalline oxidizer, and may contain additional energetic compounds such as HMX and NG (Akhavan, 1998). The high explosives used in artillery and mortar warheads are generally either TNT or Composition B.

The areas sampled include firing points, targets, detonation craters, and areas where a round had undergone a low-order detonation.

Table 4
Summary of sampling results for surface soils at artillery firing points

Installation	Type of weapon fired	Type of propellant	Mean surface soil concentration (mg/kg)		
			2,4-DNT	2,6-DNT	NG
Range A ^a	105-mm howitzer	Single base			
FP 1			4.3	NA	<0.01
FP 2			9.1	0.35	<0.01
FP 3			1.1	NA	NA
FP 4			0.66	NA	NA
Range P ^b	120-mm tank gun	Single, triple base			
MPRC: 10 m from fixed firing point		24	0.40	4.6	
MPRC: 20 m from fixed firing point		8.2	0.13	1.3	
MPRC: 30 m from fixed firing point		2.2	<0.01	0.64	
MPRC: 50 m from fixed firing point		0.68	<0.01	0.33	
MPRC: 75 m from fixed firing point		0.19	<0.01	0.50	
Range P ^b	155-mm howitzer	Single, triple base			
7 m from firing point			<0.03	<0.02	26
12 m from firing point			<0.03	<0.02	3.0
22 m from firing point			3.2	0.05	6
32 m from firing point			0.27	<0.02	1.85
Range Q ^c	155-mm howitzer	Single, triple base			
Non-detects: 12 samples			<0.002	<0.001	<0.001
Maximum value found			0.97	<0.001	<0.001
Range R ^d	(600 rounds fired) [*]	105-mm howitzer	Single base		
At muzzle of 105-mm howitzer			63	<0.01	<0.01
5-m from muzzle			84	<0.01	<0.01
10-m from muzzle			57	<0.01	<0.01
15-m from muzzle			15	<0.01	<0.01
20-m from muzzle			4.0	<0.01	<0.01
Range K ^e	Various mortars	Single, double base	0.91	<0.01	3.58
Range G ^f					
Max in seven composite samples	105-mm and 155-mm	Single, triple base	0.04	<0.01	0.35
Range S ^g	Mostly mortars	Mostly double base	0.11	<0.01	12

^{*} Surface samples collected from top 0.5 cm of surface soil.

^a Walsh et al. (2005).

^b Pennington et al. (2002).

^c Pennington et al. (2003).

^d Jenkins et al. (2001).

^e In preparation.

^f Pennington et al. (2004).

^g Hewitt et al. (2005a).

3.5. Artillery range firing points

Firing points for 105-mm and 155-mm howitzers, various mortars, and 120-mm tank guns have been sampled (Table 4). Most sampling occurred where 105-mm howitzers were fired with a single-base propellant, and 2,4-DNT was present at low mg/kg concentration. For samples with 2,4-DNT concentrations above 3 mg/kg, the impurity 2,6-DNT was often detected. NC was not determined but would be expected to be present at higher concentrations than 2,4-DNT.

For soil samples collected at a multi-purpose range complex in front of a fixed firing point for 120-mm tank guns, both 2,4-DNT and NG were detected at 75 m, the farthest distance from the firing point sampled (Table 4) (Pennington et al., 2002). The propellants used with 155-mm howitzers can be either single base for short-range targets or a combination of single base and triple base for longer ranges. The major ER for 155-mm howitzer training was NG, although some 2,4-DNT was also detected.

Concentrations of NG and 2,4-DNT at 155-mm howitzer firing points were generally two-orders of magnitude lower than 2,4-DNT at 105-mm howitzer firing positions. NG was the largest concentration ER at mortar firing points.

3.6. Artillery impact ranges

The US Army Environmental Center (AEC) and the US Army Center for Health Promotion and Preventive Medicine (CHPPM) conducted Regional Range Studies to assess the overall environmental impacts of residues from firing activities on several artillery ranges. The AEC/CHPPM group used a random sampling strategy to collect soil samples from across the entire impact range. Most of these samples did not contain detectable ERs (USACHPPM, 2001, 2002, 2004).

At several Canadian ranges samples have been collected at various distances between firing points and targets. Concentrations of ERs were generally near or below analytical detection limits (Ampleman et al., 2003; Thiboutot et al., 2003). Samples were also collected using a grid node ($\approx 100 \text{ m}^2$) sampling design on two impact ranges. Only three of the 145 samples had detectable ERs and when detected, concentrations were below 1 mg/kg (Walsh et al., 2004). Using a non-judgmental sampling design for an entire impact range has consistently shown that most of the range has undetectable levels of ERs.

Based on crater density most of the detonations occur around targets. Samples were collected at five different artillery ranges around nine separate targets.

Table 5
Analytical results for soil samples collected near artillery targets

Installation	# of increments per sample	Distance from target (m)	Mean concentration (mg/kg)						
			HMX	RDX	TNT	4ADNT	2ADNT	TNB	
Range T ^a	30	1	0.14	<0.03	<0.02	<0.03	<0.04	<0.02	
	30	5	<0.03	0.003	0.003	0.02	0.01	<0.003	
	30	10	<0.03	<0.003	0.013	0.04	0.03	<0.003	
	30	15	<0.03	<0.003	<0.001	0.01	0.007	<0.003	
Range Q ^b	Target 1	30	2	3.1	2.1	0.69	0.1	<0.01	<0.01
	Target 1	30	5	0.03	0.01	0.57	0.08	<0.01	<0.01
	Target 2	30	2	<0.03	<0.003	<0.001	<0.002	<0.01	<0.01
	Target 3	30	2	<0.03	<0.003	<0.001	0.04	<0.01	<0.01
	Target 4	30	2	0.02	0.01	0.02	0.02	<0.01	<0.01
	Target 5	30	2	0.08	0.37	<0.01	0.002	<0.01	<0.01
	Target 5	30	5	0.04	0.03	<0.001	<0.01	<0.01	<0.01
Range U ^c	10	0–2	<0.01	0.011	0.005	<0.01	<0.01	<0.01	
	10	2–5	<0.01	0.006	0.02	0.012	0.013	<0.01	
	10	5–10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
	10	10–20	0.003	0.045	<0.01	<0.01	<0.01	<0.01	
Range V ^d	10	0–2	5.6	6.5	0.62	0.23	0.31	<0.01	
	10	2–5	0.46	2.1	5.6	0.51	0.61	0.01	
Range W ^c	100	*	<0.01	<0.001	0.004	0.010	0.015	0.001	

* 100-m \times 100-m area centered among four targets.

^a Pennington et al. (2002).

^b Pennington et al. (2003).

^c Hewitt et al. (2005a).

^d Jenkins et al. (2004b).

Two of the targets had ERs present in the surface soil above 1 mg/kg, whereas the concentrations around most of the other targets samples were below 0.1 mg/kg (Table 5). At the targets with 1 mg/kg or higher levels of ERs, rounds that had low-ordered were observed within the same impact range. Overall, the concentrations of ERs near artillery targets are moderate to low, and spatially there is no defined concentration gradient.

3.7. Artillery ranges near low-order (partial) detonations

Discrete locations and areas where residues (particles) of high explosives were visible on the surface have been sampled on several ranges (Table 6). For example, at one site a grid was positioned around an 81-mm mortar round that had low-ordered. The 10-m × 10-m grid was subdivided into 100 1-m × 1-m cells and a discrete sample

Table 6 Analytical results for some surface soil samples collected near low-order (partial) detonations at artillery ranges

Installation	Description of surface soil samples	Mean concentration (mg/kg)						
		HMX	RDX	TNT	4ADNT	2ADNT	TNB	2,4-DNT
Range R ^a	Beneath a low-order 2.75-in rocket warhead	40	340	130	1	0.8	0.2	0.04
Range A ^b	Beneath a low-order 155-mm round			15100	110	102	15	40
Range T ^c	Beneath a ruptured 500-lb bomb			9440			50	
Range P ^c	Near a low-order 155 mm	5.2	54					
Range Q ^d	Beneath a low-order 2.75-inch rocket warhead	302	1130	14	3.3	2.8		
Range Q ^d	Beneath a low-order 155-mm round			2520			148	
Range Q ^d	Beneath a 90-mm round	149	678	1110	12	18	9	1.3
Range X ^c	Beneath a chunk of Composition B from low-order 155 mm	94	825	537	0.05	0.11	4	
Range I ^f	Within a crater from a low-order 500-lb bomb			42200				

^a Walsh et al. (2001).
^b Jenkins et al. (2001).
^c Pennington et al. (2002).
^d Pennington et al. (2003).
^e Hewitt et al. (2005a).
^f Thiboutot et al. (2003).

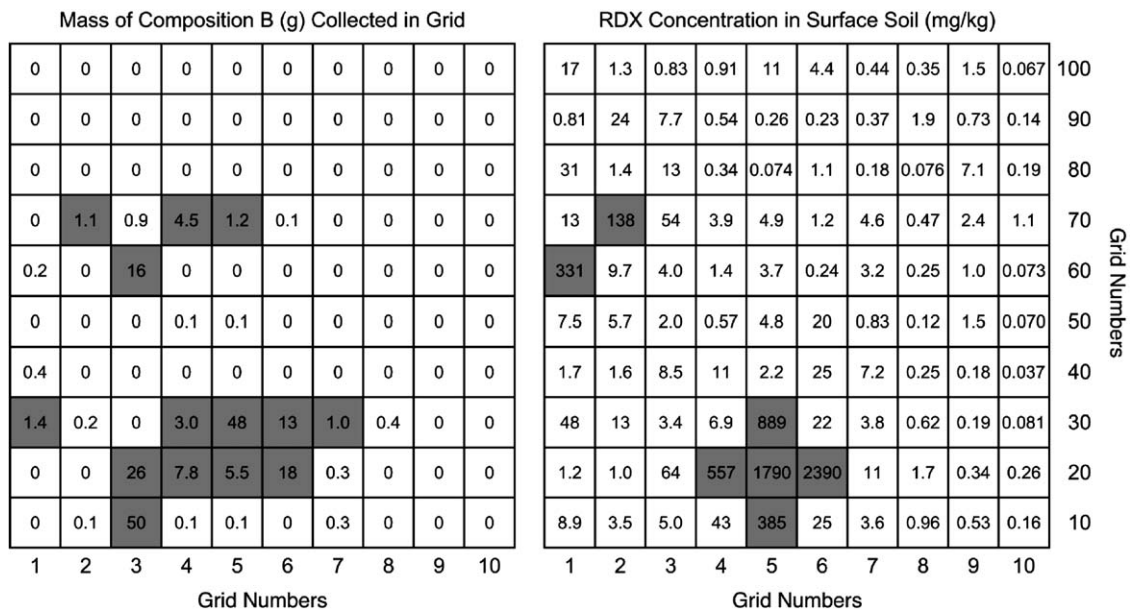


Fig. 2. Mass of Composition B and soil RDX concentrations and their relative position in the sampling grid near a low-order 81-mm mortar round at an artillery range impact area.

was collected from each cell (Jenkins et al., 2004b). In addition, the mass of the pieces of Composition B present on the surface of each cell was weighed. The RDX soil concentrations among the 100 discrete samples varied from 0.037 to 2390 mg/kg (Fig. 2). The highest concentrations, i.e., those >100 mg/kg, were isolated in two small areas near where the greatest mass of chunks of pure explosive were found on the surface.

Most of these low-ordered rounds have been found in areas well away from recognizable targets. One possible explanation is that rounds that have low-ordered near targets are much more likely to be blow-in-place or removed by UXO technicians when targets are serviced during range management operations. Based on these findings (Fig. 2 and Table 6), low-order detonations and UXO items that have been ruptured by other detonations represent the main source of explosives residues on artillery ranges.

4. Summary and conclusions

The types of residues, their concentrations, and distributions differ depending on the type of range and munition used. For hand grenade ranges, the major residue deposition occurs when grenades undergo a low-order detonation, either when thrown or when duds are blown-in-place using C4 explosive. The major ERs on these ranges are RDX and TNT from Composition B, the explosive charge in M67 and C13 fragmentation grenades. For ranges where a recent partial detonation has occurred, concentrations are generally in the low mg/kg range and the distributions are more evenly dispersed than at other types of ranges due to the hundreds of individual detonations that continuously redistribute the near-surface materials.

At antitank rocket ranges the major residue in surface soils in the target area is HMX from the octol in the warhead of 66-mm M72 LAW rockets. A concentration gradient is present in surface soils relative to the distance from targets. HMX concentrations near targets are generally in the hundreds to low thousands of mg/kg with TNT concentrations about one one-hundredth that of HMX. The high levels of HMX can be attributed to the high dud and rupture rate of the M72 rockets.

At antitank rocket range firing points, NG is present from the double-base propellant used in the 66-mm M72 rockets. Concentrations as high as the low percent level are sometimes found in soil up to 25 m behind the firing line due to the back blast from this weapon. NG is also found between the firing line and the target, but concentrations are generally several orders of magnitude lower than behind the firing line.

Most of the total acreage at artillery ranges has undetectable levels of ERs. At artillery and mortar firing

points, detectable ERs are usually either 2,4-DNT or NG, depending on the type of propellant used for the specific firing platform, and residues can be deposited at distances up to 100 meters in front of the muzzle.

Near targets on artillery ranges, most detonations are high-order and deposit very little residue (Hewitt et al., 2005b). The major deposition is due to low-order detonations, which can deposit chunks and soil-size particles (<2 mm) of pure explosive. Concentrations of TNT and RDX from Composition B are often hundreds or thousands of mg/kg in surface soils next to these detonations. The distribution of energetic residues on an artillery impact range is best described as randomly distributed point sources. Some of these point sources may be due to low-order detonations that are from blowing-in-place of surface UXO. At present the detection of these point source areas has been visual, but research is underway to try to develop a near-real-time detection capability.

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References

- Akhavan, J., 1998. *The Chemistry of Explosives*. Royal Society of Chemistry, Cambridge, UK.
- Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Gagnon, A., Bouchard, M., Martel, R., Lefebvre, R., Ranney, T.A., Jenkins, T.F., Pennington, J.C., 2003. Evaluation of the impacts of live-fire training at CFB Shilo (final report). Defence Research Development Canada—Valcartier, Technical Report TR 2003-066, Val-Belair, Quebec.
- Dube, R., Ampleman, G., Thiboutot, S., Gagnon, A., Marois, A., 1999. Characterization of potentially explosives-contaminated sites at CFB-Gagetown, 14 Wing Greenwood and CFAD Bedford. Defence Research Establishment Valcartier, Quebec Report # DREV-TR-1999-137.
- Environmental Protection Agency, 1994. Nitroaromatics and Nitramines by HPLC, Second Update SW846 Method 8330.
- Environmental Protection Agency, 1999. Nitroaromatics and Nitramines by GC-ECD, Fourth Update SW846 Method 8095.
- Hewitt, A.D., Jenkins, T.F., Ramsey, C.A., Bjella, K.L., Ranney, T.A., Perron, N.M., 2005a. Estimating energetic residue loading on military artillery ranges: large decision units. Technical Report, ERDC/CRREL TR-05-7, US Army Engineer Research and Development Center, Hanover, New Hampshire.
- Hewitt, A.D., Jenkins, T.F., Walsh, M.E., Walsh, M.R., Taylor, S., 2005b. RDX and TNT residues from live-fire and blow-in-place detonations. *Chemosphere* 61, 888–894.
- Jenkins, T.F., Walsh, M.E., Thorne, P.G., Thiboutot, S., Ampleman, G., Ranney, T.A., Grant, C.L., 1997. Assessment of sampling error associated with the collection and analysis of soil samples at a firing range contaminated with HMX. US Army CRREL Special Report 97-22, Hanover, New Hampshire.
- Jenkins, T.F., Walsh, M.E., Thorne, P.G., Miyares, P.H., Ranney, T.A., Grant, C.L., Esparza, J., 1998. Site characterization for explosives at a military firing range impact area. US Army CRREL Special Report 98-9, Hanover, New Hampshire.
- Jenkins, T.F., Grant, C.L., Walsh, M.E., Thorne, P.G., Thiboutot, S., Ampleman, G., Ranney, T.A., 1999. Coping with spatial heterogeneity effects on sampling and analysis at an HMX-contaminated antitank firing range. *Field Anal. Chem. Technol.* 3, 19–28.
- Jenkins, T.F., Pennington, J.C., Ranney, T.A., Berry Jr., T.E., Miyares, P.H., Walsh, M.E., Hewitt, A.D., Perron, N.M., Parker, L.V., Hayes, C.A., Wahlgren, E., 2001. Characterization of eExplosives contamination at military firing ranges. ERDC TR-01-05, US Army Engineer Research and Development Center, Hanover, New Hampshire.
- Jenkins, T.F., Ranney, T.A., Hewitt, A.D., Walsh, M.E., Bjella, K.L., 2004a. Representative sampling for energetic compounds at an antitank firing range. ERDC/CRREL TR-04-7, US Army Engineer Research and Development Center, Hanover, New Hampshire.
- Jenkins, T.F., Hewitt, A.D., Ranney, T.A., Ramsey, C.A., Lambert, D., Bjella, K.L., Perron, N., 2004b. Sampling strategies near a low-order detonation and a target at an artillery impact area. ERDC/CRREL TR-04-14, US Army Engineer Research and Development Center, Hanover, New Hampshire.
- Jenkins, T.F., Hewitt, A.D., Walsh, M.E., Ranney, T.A., Ramsey, C.A., Grant, C.L., Bjella, K.L., 2005. Representative sampling for energetic compounds at military training ranges. *Environ. Forensics* 6, 45–55.
- McCormick, N.G., Feeherry, F.E., Levinson, H.S., 1976. Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds. *Appl. Environ. Microbiol.* 31, 949–958.
- Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J.M., Lynch, J., Ranney, T.A., Stark, J.A., Walsh, M.E., Lewis, J., Hayes, C.A., Mirecki, J.E., Hewitt, A.D., Perron, N., Lambert, D., Clausen, J., Delfino, J.J., 2002. Distribution and fate of energetics on DoD test and training ranges: interim report 2. ERDC TR 02-8, US Army Engineer Research and Development Center, Vicksburg, Mississippi.
- Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J.M., Lewis, J., Delaney, J.E., Clausen, J., Hewitt, A.D., Hollander, M.A., Hayes, C.A., Stark, J.A., Marois, A., Brochu, S., Dinh, H.Q., Lambert, D., Gagnon, A., Bouchard, M., Martel, R., Brousseau, P., Ranney, T.A., Gauthier, C., Taylor, Ballard, J.M., 2003. Distribution and fate of energetics on DoD Test and training ranges: interim report 3. Technical Report, ERDC TR-03-2, US Army Engineer Research and Development Center, Vicksburg, Mississippi.
- Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J., Clausen, J., Hewitt, A.D., Brochu, S., Dube, P., Lewis, J., Ranney, T., Faucher, D., Gagnon, A., Stark, J., Brousseau, P., Price, C., Lambert, D., Marois, A., Bouchard, M., Walsh M., Yost, S., Perron, M., Martel, R., Jean, S., Taylor, S., Hayes, C., Ballard, J., Walsh, M., Mirecki, J., Downe, S., Collins, N., Porter, B., Richard, K., 2004. Distribution and fate of energetics on DoD test and training ranges: interim report 4. Technical Report, ERDC TR-04-4, US Army Engineer Research and Development Center, Vicksburg, Mississippi.
- Radtke, C.W., Gianotto, D., Robeto, F.F., 2002. Effects of particulate explosives on estimating contamination at a historical explosives testing area. *Chemosphere* 46, 3–9.
- Taylor, S., Hewitt, A., Lever, J., Hayes, C., Perovich, L., Thorne, P., Daghlian, C., 2004. TNT particle size distributions from detonated 155-mm howitzer rounds. *Chemosphere* 55, 357–367.
- Thiboutot, S., Ampleman, G., Gagnon, A., Marois, A., Jenkins, T.F., Walsh, M.E., Thorne, P.G., Ranney, T.A., 1998. Characterization of antitank firing ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn. Defence Research Establishment Valcartier, Quebec Report # DREV-R-9809, Val-Belair, Quebec.

- Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Bouchard, M., Hewitt, A., Jenkins, T., Walsh, M., Bjella, K., 2003. Environmental condition of surface soils, and biomass prevailing in the training area at CFB Gagetown, New Brunswick. Defence Research and Development Canada Valcartier. DRDC Valcartier TR 2003-152, Val-Belair, Quebec.
- Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Bouchard, M., Hewitt, A., Jenkins, T., Walsh, M., Bjella, K., 2004. Environmental condition of surface soils, CFB Gagetown training area: delineation of the presence of munitions-related residues (Phase III, final report). Defence Research and Development Canada Valcartier. DRDC Valcartier TR 2004-205, Val-Belair, Quebec.
- Thorn, K.A., Pennington, J.C., Hayes, C.A., 2002. 15 N NMR investigations of the reduction and binding of TNT in an aerobic bench scale reactor simulating windrow composting. *Environ. Sci. Technol.* 36, 3739–3805.
- USACHPPM, 2001. Final Geohydrologic Study No. 38-EH-8879-99, Training range site characterization and risk screening, Camp Shelby, Mississippi, 7–23 September 1999. US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, Maryland.
- USACHPPM, 2002. Site characterization and risk screening, regional range study, Jefferson Proving Ground, Madison, Indiana, September 2002. US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, Maryland.
- USACHPPM, 2004. Geohydrologic Study No. 38-EH-6807-02, Training range site characterization and risk screening, regional range study, Dona Ana Range, Fort Bliss, Texas, May 2002. US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, Maryland.
- Walsh, M.R., 2004. Field sampling tools for explosives residues developed at CRREL. ERDC/CRREL TN 04-1, US Army Engineer Research and Development Center, Hanover, New Hampshire.
- Walsh, M.E., Collins, C.M., Bailey, R.N., Grant, C.L., 1997. Composite sampling of sediments contaminated with white phosphorus. US Army Cold Regions Research and Engineering Laboratory Special Report 97-30, Hanover, New Hampshire.
- Walsh, M.E., Collins, C.M., Racine, C.H., Jenkins, T.F., Gelvin, A.B., Ranney, T.A., 2001. Sampling for explosives residues at Fort Greely, Alaska: Reconnaissance visit July 2000. Technical Report TR-01-05. US Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire. Available from: <<http://www.crrel.usace.army.mil/techpub/>>.
- Walsh, M.E., Collins, C.M., Hewitt, A.D., Walsh, M.R., Jenkins, T.F., Stark, J., Gelvin, A., Douglas, T., Perron, N.M., Lambert, D., Bailey, R., Myers, K., 2004. Range characterization studies at Donnelly Training Area, Alaska 2001 and 2002. US Army Engineer Research and Development Center ERDC/CRREL TR-04-3, Hanover, New Hampshire.
- Walsh, M.E., Ramsey, C.A., Jenkins, T.F., 2002. The effects of particle size reduction by grinding on subsampling variance for explosives residues in soil. *Chemosphere* 55, 1267–1273.
- Walsh, M.E., Ramsey, C.A., Collins, C.M., Hewitt, A.D., Walsh, M.R., Bjella, K.L., Lambert, D.J., Perron, N.M., 2005. Collection methods and laboratory processing of samples from Donnelly Training Area Firing Points, Alaska, 2003. US Army Engineer Research and Development Center ERDC/CRREL TR-05-6, Hanover, New Hampshire.