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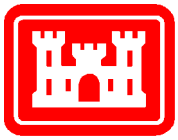

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Evaluating the Use of Snow-Covered Ranges to Estimate the Explosives Residues that Result from Detonation of Army Munitions

Thomas F. Jenkins, Thomas A. Ranney, Marianne E. Walsh,
Paul H. Miyares, Alan D. Hewitt, and Nicholas H. Collins

August 2000

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Technical Report
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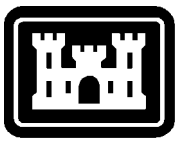

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August 2000

Prepared for
STRATEGIC ENVIRONMENTAL RESEARCH
AND DEVELOPMENT PROGRAM

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Abstract: Estimating the amounts of residues remaining after munitions detonate is complicated by the presence of residues from previous detonations and the difficulty in easily obtaining adequately sized samples to overcome spatial heterogeneity in residue deposition. This study was conducted to assess the use of snow-covered ranges to provide these types of estimates. Specifically, two snow-covered ranges were used to estimate the amount of explosives residues that result from detonation of individual mortar rounds. At Fort Drum, New York, 60-mm mortar rounds were fired, and at Camp Ethan Allen, Vermont, 81-mm mortar rounds were detonated by EOD personnel using C4 (RDX) and a blasting cap. The locations where residues were deposited were identified by the presence of soot from the detonation of TNT on the surface of the otherwise clean snow. Large surface snow samples were collected with a snow shovel and the melted snow was extracted and analyzed by gas chromatography with an electron capture detector (GC-ECD) and reversed-phase high performance liquid chromatography (RP-HPLC). For both types of rounds, the main charge was Composition B (60% RDX and 39% TNT). The major residues produced were RDX and nitroglycerine (NG), with lesser amounts of HMX and TNT. Surface concentrations ranged from as high as 4430 $\mu g/m^2$ for RDX to less than 0.05 $\mu g/m^2$ for TNT, both at Camp Ethan Allen.

The major advantages of using snow-covered ranges were: 1) the snow cover provided an uncontaminated surface, unaffected by previous detonations, 2) the black soot produced from the detonation of TNT delineated the areas where residue had deposited and 3) surface snow provides both a convenient matrix for collection of large surface area samples, essential for characterizing heterogeneously distributed residues, and a matrix free from interferences.

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Marianne E. Walsh, Chemical Engineer, and Alan D. Hewitt, Research Chemist, Geological Sciences Division; Dr. Paul H. Miyares, Research Chemist, Geochemical Sciences Division; Nicholas H. Collins, Physical Scientist, Plans and Programs Office, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL); and Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire.

The authors acknowledge Joseph Donnelly, Assistant Range Officer, SGT Daniel Stevens and SP4 Adam Grew, A. Company, 4/31 Infantry, Fort Drum, New York, and MSGT James M. Wisowaty and SSGT Andrew A. King, 158th CES Explosive Ordnance Disposal, Vermont Air National Guard, Burlington, Vermont, for assistance in conducting these tests at Fort Drum and the Ethan Allen Firing Range, Vermont.

The authors gratefully acknowledge funding for this work provided under project CP1155 by the *Strategic Environmental Research and Development Program* (SERDP), Bradley Smith, Executive Director, and Dr. Jeffrey Marquesse, Technical Director. Technical reviews were provided by Dr. C.L. Grant, Professor Emeritus, University of New Hampshire, Dr. Judith Pennington and Dr. James Brannon, Environmental Laboratory, ERDC, Vicksburg, Mississippi, and Martin H. Stutz, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland.

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ABBREVIATIONS

ACN	acetonitrile
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
1,3-DNB	1,3-dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
EOD	explosive ordnance disposal
GC-ECD	gas chromatography-electron capture detection
HE	high explosive
HMX	1,3,5,7-hexahydro-1,3,5,7-trinitro-1,3,5,7-tetrazocine
MDL	method detection limit
NG	nitroglycerine
RDX	1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine
RP-HPLC-UV	reversed-phase high performance liquid chromatography with ultraviolet detection
SARM	standard analytical reference material
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene

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INTRODUCTION

Background

Over the past several years, interest in potential environmental effects from testing and training activities at the Department of Defense's impact ranges has increased. An on-going investigation at the Massachusetts Military Reservation (MMR) has found that the underlying groundwater aquifer may be contaminated with low concentrations of RDX.* Furthermore, research conducted at CRREL has demonstrated that surface soil can be substantially contaminated with the residues of high explosives resulting from the use of LAW rockets at antitank firing ranges (Jenkins et al. 1997, Jenkins et al. 1998).

At MMR, there is a source of RDX contamination within the impact area, but it has not been conclusively identified. Candidates include leakage of explosives from the large amount of unexploded ordnance in the subsoil from over a half century of training, buried ordnance, residues from past disposal practices, or the accumulated residues from the very large number of detonations of high explosive munitions over the half century of use. Definitive resolution of these candidate sources is highly complex.

The major products of detonation of high explosives are typically CO_2, CO, H_2O, N_2, and solid carbon or soot (USAMC 1972). However, forensic examination of post-blast residues reveals trace quantities of intact explosives following a detonation (Yinon and Zitrin 1993). Of particular interest is the prevalence of RDX and NG in these residues. No systematic study has identified the extent of contamination with residues of explosives at DoD testing and training ranges resulting from these activities. A major reason for the lack of this information is the difficulty in obtaining reliable data to make these assessments. Experiments conducted at existing impact areas must cope with contamination from previous use of the ranges. In addition, the residues produced will be spatially heterogeneous because of the particulate nature of deposition. Very large surface areas would have to be sampled to overcome this difficulty. Extensive soil sampling and analysis is operationally difficult and often prohibitively expensive.

A previous experiment conducted with 60- and 81-mm mortars and a 105-mm howitzer on ice-covered terrain revealed the presence of darkened ash (soot) around detonation craters (Collins and Calkins 1995). While sampling for residues was not a major objective of this work, snow around 81- and 105-mm detonation craters was sampled and analyzed for explosives residues. No explosives were detected above the method detection limit of the RP-HPLC method; however, visual inspection of the chromatograms did reveal small peaks corresponding to RDX.* These observations suggested to us using a snow cover to isolate post-blast residues.

Objective

This study evaluates the use of snow-covered ranges for determining the explosives residues produced by detonations of HE-containing mortar rounds. Two scenarios were tested. In the first, a snow cover was used to estimate the amount of residues that are deposited on a range when an army munition is fired and detonates on

* Personal communication with J. Clausen, Ogden Environmental, Westford, Massachusetts, 1999.

* Personal communication with M.E. Walsh, CRREL, 1999.

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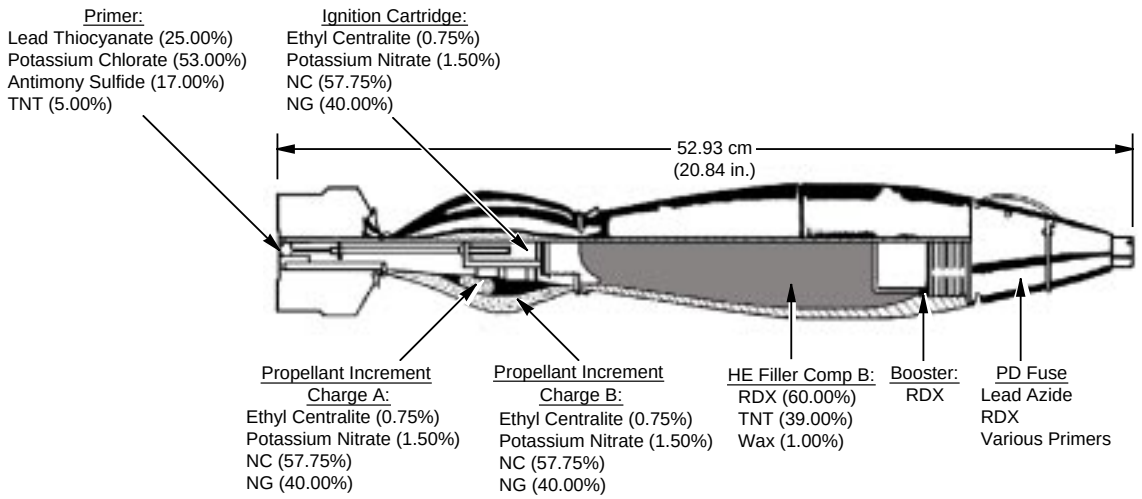


Figure 1. Diagram of 81-mm mortar rounds detonated with C4 at Camp Ethan Allen Firing Range.

impact. In the second, the residues that result from the practice of attaching C4 to an item of unexploded ordnance and detonating it in place were examined. Because concentrations would likely be low, we used much larger samples than did Collins and Calkins (1995), and a new gas chromatographic electron capture (GC-ECD) method developed recently by Walsh and Ranney (1998, USEPA 1999), which provides much lower MDLs than the earlier RP-HPLC method.

METHODS

Overview of mortar round detonations, Camp Ethan Allen and Fort Drum

Two mortar detonation experiments were completed. The first was conducted at Camp Ethan Allen Firing Range, Vermont, on 6 March 2000. Three 81-mm mortar rounds were placed on a pristine snow surface and individually detonated by EOD personnel from the Vermont Air National Guard using a C4 charge (1.25 lb [0.57 kg]) and an M7 blasting cap that was attached to the outside of the casing. The second experiment was conducted at Fort Drum, New York, on 13 March 2000. Three 60-mm mortar rounds were fired by U.S. Army personnel and the rounds were allowed to detonate on impact in a snow-covered range.

The main charge in a 81-mm mortar round is 2.1 lb (0.95 kg) of Composition B, which is 60% RDX and 39% TNT (Fig. 1). The propellant increment charges A and B were removed from the round before detonation. The propellant is composed of 40% nitroglycerine, 57.8% nitrocellulose, 1.5% potassium nitrate, and 0.7% ethyl centralite. A smaller portion of these propellant chemicals was present in the ignition cartridge, however, and that was not removed before detonation (Fig. 1). The C4 used to detonate the 81-mm mortar rounds is composed of 91% RDX and 9% plasticizers (polyisobutylene, motor oil, di(2-ethylhexyl)-sebacate). The rounds used for these tests were loaded in 1975.

The main charge in the 60-mm mortar rounds used at Fort Drum is 0.79 lb (0.43 kg) of Composition B (Fig. 2). The propellant used with this munition is M204,

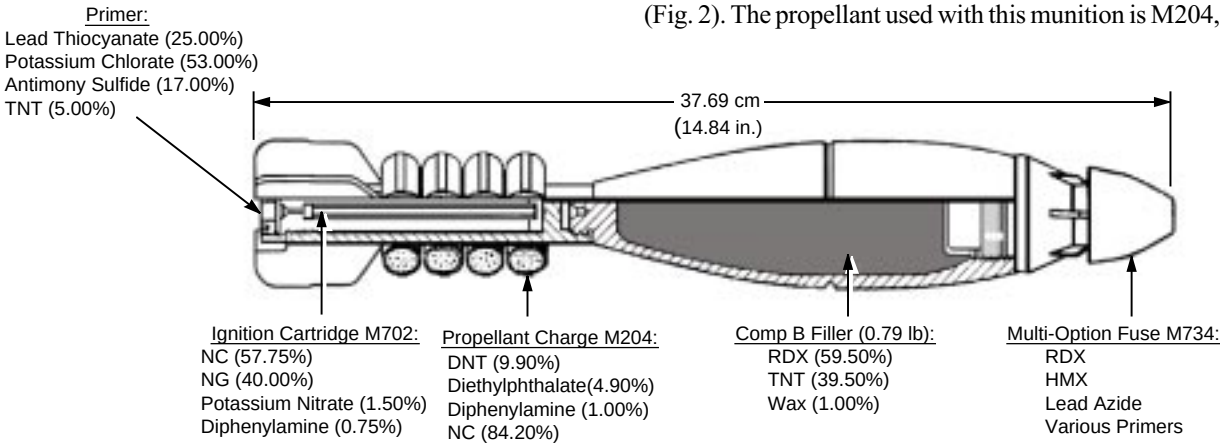


Figure 2. Diagram of 60-mm mortar rounds that were fired at Fort Drum, New York.

Figure 3. An 81-mm mortar round placed on its side on the surface of the snow.

which is composed of 84.2% nitrocellulose, 1.0% diphenylamine, 4.9% diethylphthalate, and 9.9% dinitrotoluene. An ignition cartridge composed of 57.75% nitrocellulose, 40.0% NG, 1.5% potassium nitrate, and 0.75% diphenylamine is also present in this round.

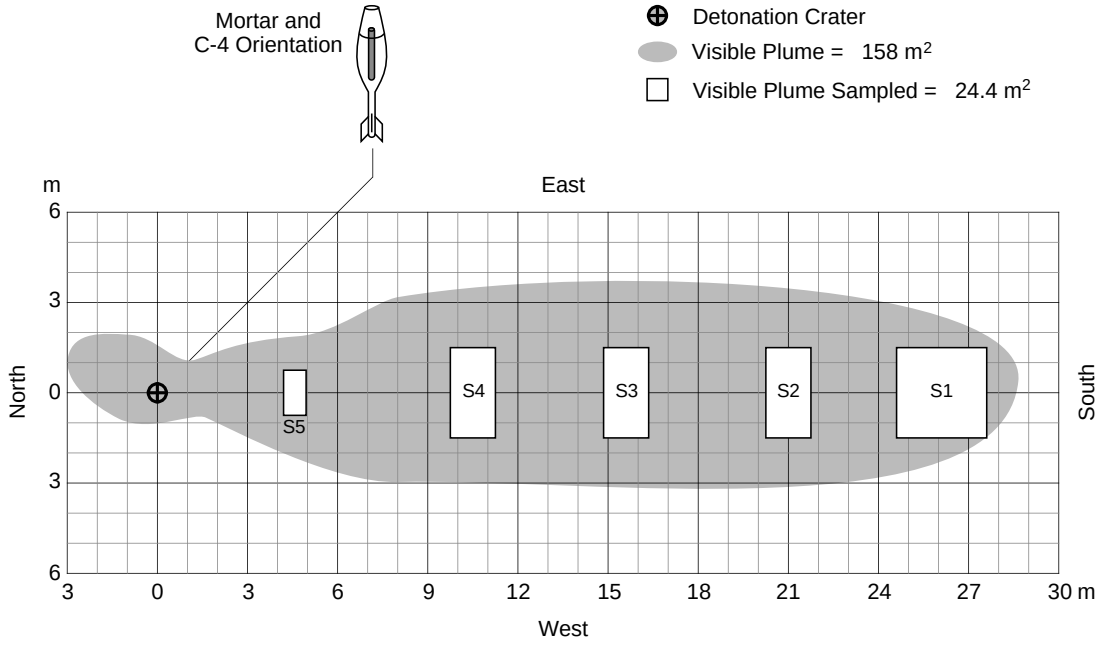
Mortar round detonation and sample collection, Camp Ethan Allen

Three locations were selected at a snow-covered impact range at Camp Ethan Allan. The 81-mm mortar rounds were unpacked and the propellant bags were removed. The first round (M1) was placed on its side on top of a metal plate on the surface of the snow (Fig. 3). The C4 was laid across the top of the round and an M7 blasting cap attached. The mortar round was detonated with a timer by the EOD team at about 1100. The weather was clear, with a light breeze from the southeast.

The detonation produced a cloud of black soot, because of the presence of TNT in the round, that settled on the snow surface and was quite visible, easily delineating the areas where residues were deposited. We collected five surface snow samples that ranged in distance from the crater from 4 to 28 m, and which ranged in area sampled from 1.16 to 9.29 m^2 (Fig. 4a). The five snow samples from this first detonation were collected from 1100 to 1130 and were labeled M1-S1 through M1-S5.

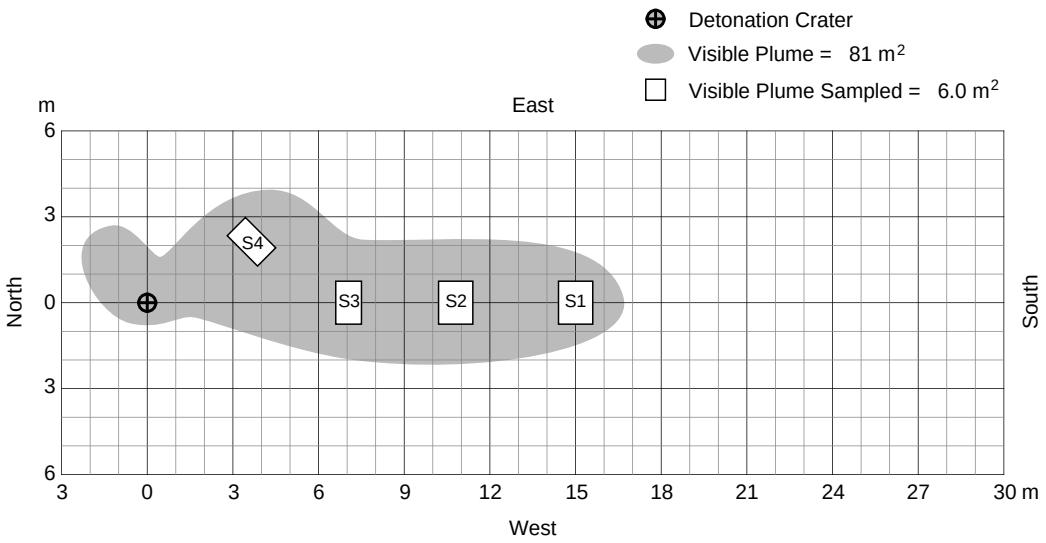
Two more rounds (M2 and M3) were detonated as described above, except that they were placed directly on the snow surface without a metal plate. Sampling was conducted in a similar fashion. Four surface snow samples were collected from each of these areas where surface residues were visible. The approximate areas of deposition from each detonation are shown in Figures 4b and c.

Surface snow samples were collected using an unpainted aluminum snow shovel. The depth sampled was kept as small as possible to minimize the volume of snowmelt produced. Depths sampled depended on

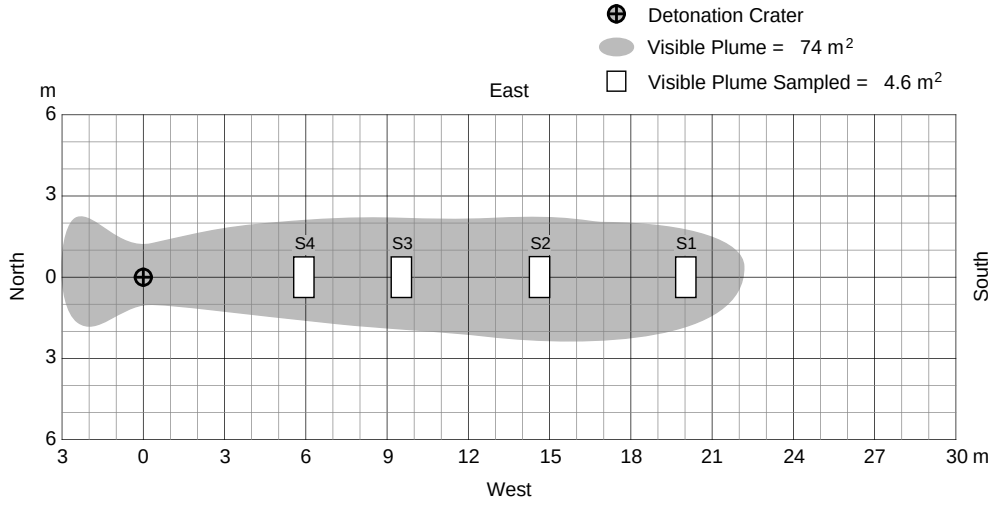


a. First detonation.

Figure 4. Residue deposition and surface snow samples collected for 81-mm mortar round detonations at Camp Ethan Allen.



b. Second detonation.



c. Third detonation.

Figure 4 (cont'd). Residue deposition and surface snow samples collected for 81-mm mortar round detonations at Camp Ethan Allen.

the condition of the snow in the various locations, but averaged about 0.5 cm. The order of collection of samples was from the farthest distance from the crater to the closest to avoid walking on areas that were to be sampled. For collection, snow was shoveled into plastic bags that were sealed with twist ties. The bags were polyethylene that had been specially cleaned by the manufacturer for snow sampling. Snow samples were returned to CRREL the same day that they were collected and were processed the following morning.

Processing of snow samples from Camp Ethan Allen

The plastic bags were left in the laboratory overnight, which melted the snow. Small quantities of ice remained in the bag in the morning, indicating that the samples had remained at 0°C during this period. The snowmelt was black because of the presence of suspended soot particles. Once the last of the snow melted, all of the water in the bags was filtered (Whatman glass microfiber, 47 mm, grade GF/A) to remove the soot. As many as 15 individual filters were required for a given sample, depending on the amount of soot present. Filters were retained and were extracted separately, as described below. A bag blank with reagent grade water was processed in an identical manner to ensure that no interferences were generated by the plastic bags used for collection.

The total volume of snowmelt was measured. To extract the explosives from the water, we placed a 1520-mL aliquot in a 2-L volumetric flask containing 496 g of sodium chloride (Miyares and Jenkins 1991, USEPA 1994). A magnetic stir bar was placed in the flask, and the contents were stirred to dissolve the salt. A 325-mL aliquot of acetonitrile was added, and the flask was stirred vigorously for 30 minutes. The magnetic stirrer was then turned off and the phases were allowed to separate for 30 minutes. The acetonitrile phase on the top, about 25 mL, was removed. Then, we measured the volume using a graduated cylinder and labeled the sample salting out extract (SOE).

To ensure that any explosives residues deposited on the inside of the bags were recovered, the plastic bags were wiped with Whatman filters (two to four per bag) and the filters were placed in a Soxhlet extraction thimble. Then, the Whatman filters that were used on that sample were added to the thimble, which was placed inside a Soxhlet extractor. A 250-mL aliquot of acetonitrile was added to the receiver of the Soxhlet extractor and the heating mantle turned on. The samples were continuously extracted for 22 hours at six cycles per hour. After the solvent cooled, we measured the volume of the solvent and removed an aliquot for analysis. This sample was labeled as SOX.

Mortar round firing and sample collection at Fort Drum

On the morning of the test, we inspected the snow cover on the impact range and selected several areas, which we directed the Army team to target. At about 1000, three 60-mm mortar rounds (Fig. 5) were fired into the range and each detonated on impact. After the three rounds were fired from the mortar tube, the surface snow (1 m^2) just in front of the tube was sampled to determine if residues of the propellant were detectable. A light wind from the northwest coincided with the trajectory of the mortar rounds.

Figure 5. A 60-mm mortar round.

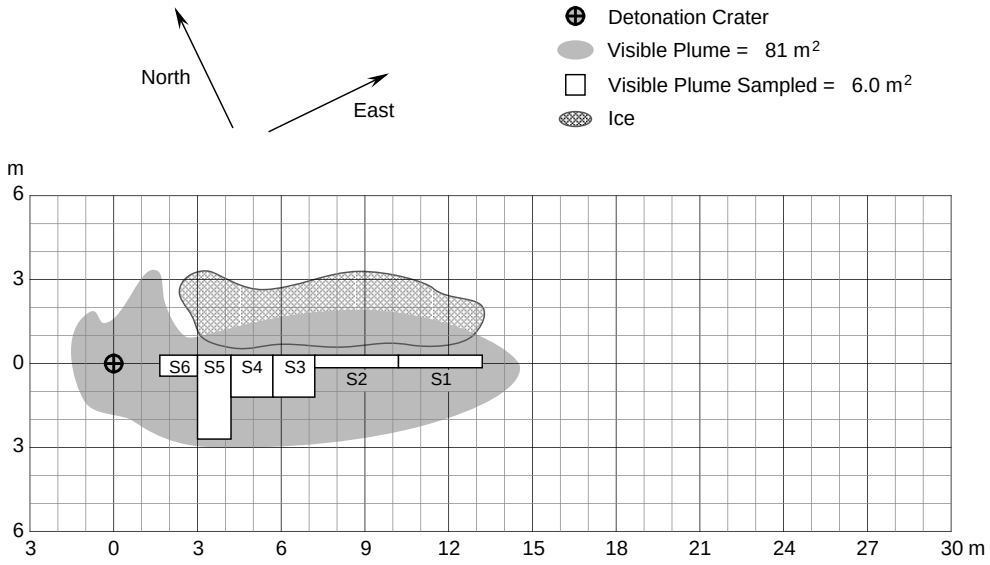
Two of the three mortar rounds landed in areas that were accessible for surface sampling. The third round landed in an inaccessible area of large rocks, so only the first two areas were sampled. The surface of the soil under the snow was thawed at the time of this experiment, and, unfortunately, this resulted in the spraying of some soil particles over the snow surface along with detonation residues.

Area 1 was sampled about 15 minutes after the round was detonated. The trajectory of firing caused the residues to be distributed directionally along the trajectory of firing, away from the impact point (Fig. 6a). Surface snow samples were collected in the visibly contaminated area as described above for Camp Ethan Allen. We collected six surface snow samples in a continuous line from 1 to 14 m from the impact crater. Surface areas sampled varied from 1.16 to 3.72 m^2. The area where soot was visible on the surface was measured after all samples were collected so that residues were not tracked into areas to be sampled. The total debris plume was estimated at 79 m^2 ; the total area sampled was 12 m^2 or about 15%.

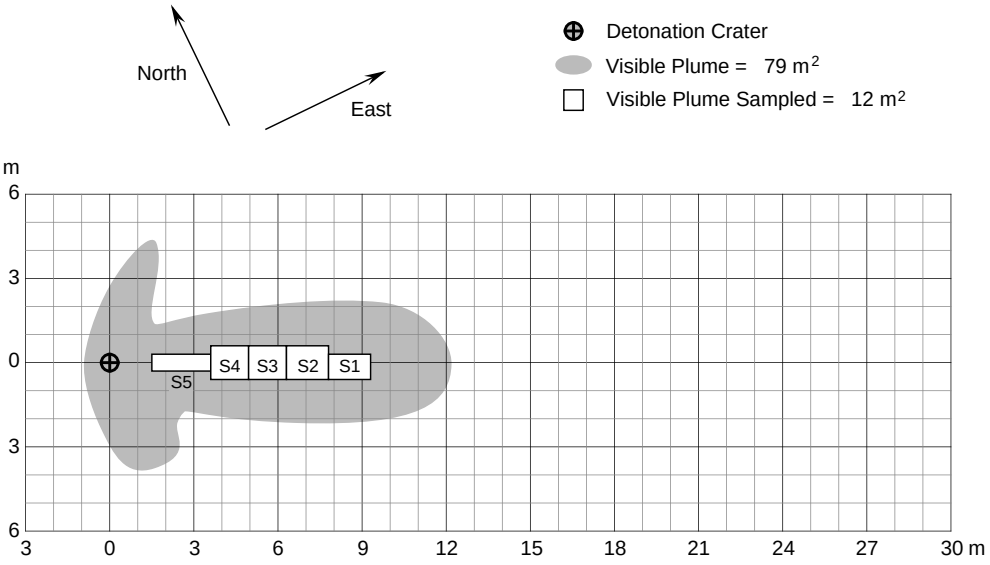
Area 2 was sampled about an hour after detonation. We collected five samples in a continuous line from 1.2 to 9.5 m from the impact crater. The area where residues were visible was estimated at 58 m^2 (Fig. 6b). The total area sampled was 7.3 m^2 or about 13% of the total debris plume. The tail fin from each round was found near the detonation craters. These fins were collected to see if explosives residues were detectable on their surfaces.

Processing of snow samples from Fort Drum

Snow was melted as described above, but initial attempts to filter the snowmelt were frustrated by the presence of clay-soil particles. Only five of the samples were filtered as described above for samples from Camp Ethan Allen. These five were the firing point sample, a snow blank collected 100 m from the crater, and three surface snow samples from area 1 labeled S-1, S-2, and S-4. It took 40 individual glass fiber filters to process the whole of sample S4, requiring over 6 hours. For this reason the remaining samples from area 1 and all of the samples from area 2 were processed differently. For these samples, the bags were shaken vigorously and a 1520-mL aliquot of the sample containing suspended soot particles was extracted using the salting out procedure described for the Ethan Allen samples. For the five samples that were filtered, 1520-mL aliquots were processed using salting out solvent extraction, and the filters and bag wipes were extracted using the Soxhlet method described for the Ethan Allen sam-



a. First detonation.



b. Second detonation.

Figure 6. Residue deposition and surface snow samples collected for 60-mm mortar round detonations at Fort Drum.

ples. Spiked samples were used to validate the extraction efficiency of this procedure.

GC-ECD determination

All SOE and SOX samples were analyzed by GC-ECD on an HP6890 gas chromatograph equipped with a micro cell Ni^{63} ECD (300°C). We used direct injection (250°C) of 1-µL soil extracts in a packed port that was equipped with a deactivated Restek Uniliner. Primary analysis was conducted on a 6-m × 0. 32-mm ID fused-silica, 1.5-µm film thickness of 5%-(phenyl)–95%-dimethyl polysiloxane RTX-5 column from Restek. The GC oven was temperature programmed as follows: 100°C for 2 minutes, 10°C/min ramp to 250°C, and 3-minute hold. The carrier gas was helium at 10 mL/min (linear velocity about 100 cm/s). The makeup gas was nitrogen (40 mL/min). Selected extracts were reanalyzed on a Restek RTX-225 (50% cyanopropylmethyl–50% phenyl methyl polysiloxane) for analyte confirmation. Further details of the procedure may be found

Table 1. Retention times (minutes) for target analytes on analytical and confirmation columns.

Analyte	RTX-5 1.5 µm	RTX-225 0.1 µm
NB	0.925	0.337
o-NT	1.409	0.416
m-NT	1.740	0.500
p-NT	1.920	0.564
NG	3.761	4.432
1,3-DNB	4.746	3.792
2,6-DNT	4.909	3.460
2,4-DNT	5.736	4.470
TNB	7.542	7.987
2,4,6-TNT	7.690	7.540
RDX	9.335	11.595
4-Am-DNT	9.956	10.582
2-Am-DNT	10.418	11.058
Tetryl	11.322	11.595
HMX	15.629	

RTX-5: oven program 100°C for 2 minutes, to 250°C at 10°/min and held 3 minutes; injector 250°C; detector 280°C.

RTX-225: oven program: 100°C for 2 minutes, to 210°C at 10°/min and held 5 minutes; injector 200°C; detector 210°C.

in SW-846 Method 8095 (USEPA 1999, Walsh and Ranney 1998). Retention times for the target analytes are presented in Table 1.

Because some of the analytes were present at concentrations that saturated the µECD, all samples were also analyzed by RP-HPLC using a 15-cm by 3.9-mm (4-µm) Nova Pak C_8 (Waters Millipore) column eluted with 1.4 mL/min 15:85 isopropanol:water. Absorbance was recorded at 254 nm on a Spectra Physics Spectra 100 variable wavelength UV detector. For further confirmation of analyte identity, some samples were also analyzed on an HPLC equipped with a Waters 996 Photodiode Array detector, a Waters 616 pump, and a Supelco LC-18 column eluted with 1.2 mL/min 60:40 methanol–water.

RESULTS AND DISCUSSION

Analytical results from Camp Ethan Allen experiment—81-mm mortar rounds detonated with C4

Results from the analysis of the snow samples from the first mortar round detonation at Camp Ethan Allen are presented in Table 2a. Four explosives-related analytes were detected: RDX, HMX, NG, and TNT. Surface concentrations of these compounds ranged from

Table 2. Masses of the various explosives identified in residues from the 81-mm mortar rounds detonated with C4 at Camp Ethan Allen, Vermont.

a. Detonation number 1.

	Sample				
	M1-S5	M1-S4	M1-S3	M1-S2	M1-S1
Distance from crater (m)	4.2–5.0	9.9–11.4	15.1–16.6	20.8–22.1	25.3–28.4
Area sampled (m^2)	1.16	4.65	4.65	4.65	9.29
Analytes detected:					
RDX					
Mass-aqueous (µg)	13.7	23.5	18.3	5.9	9.7
Mass-soot (µg)	0.7	0.6	1.6	1.4	0.02
Mass-total (µg)	14.4	24.1	19.9	7.3	9.7
Concentration (µg/m^2)	12.4	5.2	4.3	1.6	1.0
HMX					
Mass-aqueous (µg)	2.0	4.2	2.0	1.6	1.4
Mass-soot (µg)	<d	<d*	<d	<d	<d
Mass-total (µg)	2.0	4.2	2.0	1.6	1.4
Concentration (µg/m^2)	1.8	0.9	0.4	0.3	0.1
NG					
Mass-aqueous (µg)	730	2780	1500	360	1150
Mass-soot (µg)	202	4320	205	195	1.1
Mass-total (µg)	932	7100	1710	555	1150
Concentration (µg/m^2)	802	1530	367	119	124
TNT					
Mass-aqueous (µg)	0.06	<d	<d	0.23	<d
Mass-soot (µg)	<d	<d	<d	<d	<d
Mass-total (µg)	0.06	<d	<d	0.23	<d
Concentration (µg/m^2)	0.05	<d	<d	0.05	<d

* Below detection.

Table 2 (cont'd). Masses of the various explosives identified in residues from the 81-mm mortar rounds detonated with C4 at Camp Ethan Allen, Vermont.

b. Detonation number 2.

	Sample			
	M2-S4	*M2-S3*	*M2-S2*	*M2-S1*
Distance from crater (m)	4.2–5.0	6.9–7.7	10.6–11.4	14.9–15.6
Area sampled (m^2)	1.16	1.16	1.86	1.86
Analytes detected:				
RDX				
Mass-aqueous (µg)	401	3540	1260	722
Mass-soot (µg	27.5	1600	354	187
Mass-total (µg)	428	5140	1610	909
Concentration (µg/m^2)	369	4430	865	489
HMX				
Mass-aqueous (µg)	9.2	79	30	21
Mass-soot (µg)	81	615	283	144
Mass-total (µg)	90	693	313	165
Concentration (µg/m^2)	77	597	168	89
NG				
Mass-aqueous (µg)	35.6	1730	855	312
Mass-soot (µg)	7.8	117	146	22.9
Mass-total (µg)	43	1850	1000	335
Concentration (µg/m^2)	37	1590	539	180
TNT				
Mass-aqueous (µg)	<d*	37.5	1.8	1.1
Mass-soot (µg)	0.3	9.1	0.8	0.5
Mass-total (µg)	0.3	47	2.6	1.6
Concentration (µg/m^2)	0.3	40	1.4	0.9
2,4-DNT				
Mass-total (µg)	21.3	9.3	6.9	11.8
Concentration (µg/m^2)	18.3	8.0	3.7	6.3
2,6-DNT				
Mass-total (µg)	10.1	<d	21.2	26.4
Concentration (µg/m^2)	8.7	<d	11.3	14.1
2A-DNT				
Mass-total (µg)	7.7	<d	<d	<d
Concentration (µg/m^2)	6.6	<d	<d	<d
4A-DNT				
Mass-total (µmg)	5.9	<d	<d	<d
Concentration (µg/m^2)	5.1	<d	<d	<d

* Below detection.

1.0 to 12.4 µg/m^2 for RDX, from 0.1 to 1.8 µg/m^2 for HMX, from 119 to 1530 µg/m^2 for NG, and from below detection to 0.05 µg/m^2 for TNT.

The main charge of the mortar round, together with the C4 used to detonate it, initially contained a total of about 1.1 kg of RDX. RDX was also present in the booster and fuse in this mortar round (Fig. 1). Therefore, it is not surprising that RDX was detected in all of these snow samples. HMX is always present in military-grade RDX, generally at about 10% of the RDX. It was present in the residues at concentrations that ranged from 9 to 19% of the RDX concentration. Although there is about 0.38 kg of TNT in 81-mm mortar rounds, the residues of TNT in these surface samples were always less than 3% of the RDX present. These results are similar to those observed on an antitank firing range, where TNT residue concentrations were two orders of magnitude lower than HMX, even though the explosive used (Octol) was 70:30 HMX:TNT (Jenkins et al. 1997). At the time, the differences in residue concentrations were attributed to differences in rates of dissolution and biotransformation. Apparently, a higher percentage of the TNT is consumed in detonations of Composition B, leaving higher concentrations of RDX and HMX in the post-blast residue.

Before the mortar rounds were detonated, the propellant bags were removed. Therefore, the high concentrations of NG found in the snow samples were surprising. NG has been detected at high concentrations in the paint that coats 81-mm mortar rounds (Phelan et al., in prep.)

Table 2 (cont'd).

c. Detonation number 3.

	Sample			
	M3-S4	*M3-S3*	*M3-S2*	*M3-S1*
Distance from crater (m)	5.4–6.2	9.4–10.1	14.6–15.3	20.0–20.8
Area sampled (m^2)	1.16	1.16	1.16	1.16
Analytes detected:				
RDX				
Mass-aqueous (μg)	44.0	14.0	10.1	4.5
Mass-soot (μg)	0.8	2.9	26.4	1.1
Mass-total (μg)	45	17	37	5.6
Concentration (μg/m^2)	39	15	31	4.8
HMX				
Mass-aqueous (μg)	2.2	2.1	1.4	0.7
Mass-soot (μg)	7.8	15.6	62.6	4.1
Mass-total (μg)	10	18	64	4.7
Concentration (μg/m^2)	9	15	55	4.1
NG				
Mass-aqueous (μg)	664	915	372	165
Mass-soot (μg)	90	24	38	0.1
Mass-total (μg)	754	939	410	165
Concentration (μg/m^2)	649	808	353	142
TNT				
Mass-aqueous (μg)	<d	<d	<d	<d
Mass-soot (μg)	0.17	0.20	0.22	0.29
Mass-total (μg)	0.17	0.20	0.22	0.29
Concentration (μg/m^2)	0.15	0.17	0.19	0.25

and it can potentially sorb to the aluminum tail fins. NG is also present in the ignition cartridge within the round. NG is frequently found in post-blast propellant residue (Yinon and Zitrin 1993) and it has been detected on demolition ranges (Fine et al. 1984). The concentrations of NG in the snow cover were sufficiently high to saturate the μECD, but the NG peaks were minor in the HPLC-UV chromatograms at 254 nm. The NG concentrations were sufficiently high in some of the samples to obtain confirmatory spectra using the Photodiode Array. NG is apparently less completely consumed in the detonation than TNT and RDX, based on the mass of NG found versus the amount of NG present in the round.

The pattern and degree of contamination from subsequent detonations varied considerably (Tables 2b and c). The residues found in the surface snow collected from the second detonation (Table 2b) were much greater than those observed for the first one. In addition to the four analytes detected for the first detonation (RDX, HMX, NG, and TNT), four additional explosives-related analytes (2,4-DNT, 2,6-DNT, 2-ADNT, and 4-ADNT) were detected in some or all of the samples from the second detonation. Surface concentrations of RDX ranged from 369 to 4430 μg/m^2; this is over 300 times the concentrations found for the first detonation. The concentrations of HMX were also much greater than those found near the first detonation; concentrations ranged from 13 to 20% of the RDX. The concentrations of TNT were also higher by about the same factor as RDX and HMX, but they remained several orders of magnitude lower than RDX. The concentrations of NG were about the same as that found for round detonation 1, which implies that the source of the NG is different from that for RDX, HMX, and TNT. Surface concentrations of RDX, HMX, and TNT for round detonation 3 were intermediate between those found for rounds 1 and 2, while the concentrations found for NG remained similar to that found for rounds 1 and 2 (Table 2c).

The lowest concentrations in these surface snow samples were generally found for samples collected the farthest away from the detonation; however, the opposite was not true for the highest concentrations, which were generally found at some intermediate distance. The surface areas where residues were deposited for these three detonations were estimated from the visual deposition of soot: 158 m^2 for area 1, 81 m^2 for area 2, and 74 m^2 for area 3. The larger area of deposition for the first detonation may be a result of using the steel plate under the round, thereby deflecting a greater percentage of the debris upward and out. The surface areas sampled for these three plumes were 24, 6.0, and 4.7 m^2, respectively. Thus, the percentages of the contaminated surface area that were sampled were 15, 7.4 and 6.3%, respectively.

If the mean surface concentrations that were obtained for each of these three areas are representative of the total surface area in which deposition was

Table 3. Estimates for total residues deposited from detonations of 81-mm rounds with C4 at Camp Ethan Allen, Vermont.

	Detonation		
	1	*2*	*3*
RDX			
Ave. surface conc. (μg/m^2)	4.9	1540	22.5
Total contaminated surface area (m^2)	158	81.3	74.2
Total mass deposited (μg)	774	1.25×10^5	1670
Mass of RDX in 81-mm plus C4 (μg)	1.1×10^9	1.1×10^9	1.1×10^9
Total RDX recovered (%)	0.00007	0.011	0.00015
Estimate of mean soil conc. (μg/kg) resulting from detonation*	0.58	181	2.6
TNT			
Ave. surface conc. (μg/m^2)	0.035	10.7	0.19
Total contaminated surface area (m^2)	158	81.3	74.2
Total mass deposited (μg)	5.53	870	14.1
Mass of TNT in 81-mm (μg)	3.8×10^8	3.8×10^8	3.8×10^8
Total TNT recovered (%)	0.000001	0.00023	0.000004
Estimate of mean soil conc. (μg/kg) resulting from detonation*	0.004	1.3	0.022

* A soil density of 1.7 g/cm^3 and a soil depth of 0.5 cm were used to compute the estimate.

observed, the total mass of residues deposited in each case can be estimated (Table 3). Using this assumption, estimates of the mass of RDX deposited range from 774 to 1.25×10^5 μg (125 mg). Likewise, for TNT, estimates range from 5.5 to 870 μg. In terms of the percentage of initial explosive that was deposited as residues, the estimates range from 0.0007 to 0.011% for RDX, and from 0.000001 to 0.00023% for TNT. If these residues were homogeneously distributed over the surface area where deposition was observed, and contaminated the top 0.5 cm of soil, we estimate resulting soil concentrations of RDX ranging from 0.58 to 181 μg/kg and of TNT ranging from 0.004 to 1.3 μg/kg.

We must acknowledge the uncertainty in the estimates discussed above that stem from our assumption that the mean concentration that we obtained was representative of the total area affected by the blast. For example, we made no attempt to measure the concentration gradient that might result perpendicular to the center line of the deposition, nor did we make sufficient measurements to get an overall analytical uncertainty. This study was preliminary in nature, the emphasis being on demonstrating the technique. Thus, the estimates provided should be considered preliminary, but in the absence of better estimates, they can serve as ballpark estimates until better data are available. We anticipate making improved measurements in future studies.

Analytical results from Fort Drum experiment—60-mm mortar rounds fired

RDX, HMX, and NG were detected in the snow samples from the mortar detonations at Fort Drum (Table 4). Surface concentrations of these compounds for the first mortar round ranged from 0.32 to 6.13 μg/m^2 for RDX, below detection to 0.86 μg/m^2 for HMX, and below detection to 0.01 μg/m^2 for NG. No TNT was detected above background. Concentrations for the second mortar round were two to four times higher than for the first. The highest concentrations were located approximately 9 m from the point of detonation.

The fired-in 60-mm mortars produced less residue overall and no high concentrations, unlike those from the 81-mm mortars detonated by C4, and NG was not found at high concentrations. For the fired rounds, the ignition cartridge would have detonated, but the fins of the rounds remained intact and were deposited near the detonation craters. When one of the mortar fins was rinsed with acetone and the acetone analyzed by GC-μECD, approximately 2 mg of NG was found in the rinsate. The significance of NG residues on training ranges will require further investigation. A review of the gas chromatograms for soil samples that we collected at an antitank firing range at Canadian Force Base Valcartier revealed the presence of NG in these samples as well.

Similar to the 81-mm mortar detonations, TNT concentration estimates at Fort Drum (Table 5) were much lower than RDX, even though the filler was Composition B (59.5:39.5 RDX:TNT). Thus, TNT appears to be more completely consumed during detonations than RDX.

Analysis of the snow sample collected in front of the mortar tubes at Fort Drum revealed the presence of RDX, NG, and TNT. The presence of NG was expected, since it is a common component of propellants, but the presence of TNT and RDX was unexpected. Only one sample was collected. Thus, this result should be viewed as preliminary at this time.

Table 4. Masses of the various explosives identified in residues from 60-mm mortar rounds fired at Fort Drum, New York.

a. Round 1.

	Sample					
	M1-S6	*M1-S5*	*M1-S4*	*M1-S3*	*M1-S2*	*M1-S1*
Distance from crater (m)	10.7–13.7	7.6–10.7	5.5–7.6	4.3–5.5	3.1–4.3	1.2–3.0
Area sampled (m^2)	1.16	3.72	2.09	2.09	1.39	1.39
Analytes detected:						
RDX						
Mass-aqueous (μg)	0.68	22.7	1.84	0.69	0.44	0.49
Mass-soot (μg)	0.02	0.08	*	<d	*	*
Mass-total (μg)	0.70	22.8	1.84	0.69	0.44	0.49
Concentration (μg/m^2)	0.60	6.13	0.88	0.33	0.32	0.35
HMX						
Mass-aqueous (μg)	0.40	3.18	<d	<d	<d	<d
Mass-soot (μg)	<d	<d	*	<d	*	*
Mass-total (μg)	0.40	3.18	<d	<d	<d	<d
Concentration (μg/m^2)	0.35	0.86	<d	<d	<d	<d
NG						
Mass-aqueous (μg)	<d	0.04	<d	<d	<d	<d
Mass-soot (μg)	<d	<d	*	<d	*	*
Mass-total (μg)	<d	0.04	<d	<d	<d	<d
Concentration (μg/m^2)	<d	0.01	<d	<d	<d	<d

* No separate soot sample processed; the soot-containing sample was processed using salting-out solvent extraction.

b. Round 2.

	Sample				
	M2-S1	*M2-S2*	*M2-S3*	*M2-S4*	*M2-S5*
Distance from crater (m)	7.9–9.5	6.4–7.9	5.2–6.4	3.7–5.2	1.2–3.7
Area sampled (m^2)	1.39	1.49	1.49	1.49	1.49
Analytes detected:					
RDX					
Mass-total (μg)	17.0	2.53	2.63	2.87	3.14
Concentration (μg/m^2)	12.2	1.70	1.76	1.93	2.10
NG					
Mass-total (μg)	0.09	0.05	0.07	0.15	0.75
Concentration (μg/m^2)	0.06	0.03	0.05	0.10	0.50

Table 5. Estimates for RDX deposited from detonations of 60-mm mortar rounds at Fort Drum, New York.

	Detonation	
	1	*2*
Avg. surface conc. (μg/m^2)	1.43	3.94
Total contaminated surface area (m^2)	81	79
Total mass deposited (μg)	116	311
Mass of RDX in 60-mm (μg)	2.58×10^8	2.58×10^8
Total RDX recovered (%)	0.00004	0.0001
Estimate of mean soil conc. (μg/kg)* resulting from detonation	0.17	0.46

* A soil density of 1.7 g/cm^3 and a 0.5-cm depth was used to compute the estimate.

CONCLUSIONS

This study demonstrates the utility of using snow surfaces to determine the amounts of explosives residues left behind after military munitions detonate. The pristine snow surfaces provided a matrix free from residues of previous detonations and free of soil components. The soot produced from the detonation of TNT gave us a visual pattern of deposition on the white surface. We easily collected residues from contaminated snow surfaces using an unpainted aluminum snow shovel. The ability to efficiently collect a thin layer of snow allows sampling of a large percentage of the contaminated surface while minimizing the volume of snowmelt produced. Because the pattern of deposition is quite heterogeneous, collection of a large portion of the affected surface area is necessary to ensure that samples are representative.

The results of mortar round detonations at Camp Ethan Allen demonstrated that very little soil is thrown out if the detonations are conducted where the snow covers a frozen surface. On the other hand, the experiment at Fort Drum showed that if the study was conducted late in the season, when the soil surface has thawed, soil particles were deposited on the snow along with residues of the detonation. This complicated the analytical chemistry and resulted in an increase in the uncertainty associated with determinations. Therefore, we recommend that such tests be conducted during midwinter, when the surface soils are frozen and frost penetration is at its maximum. Because TNT and other residues are susceptible to phototransformation, and the presence of black soot on the surface enhances melting, these studies should be conducted on overcast days and samples should be collected as quickly as possible to ensure that residues do not penetrate deeper into the snow pack, thereby minimizing the depth of snow that must be sampled.

Because we only collected samples from five detonations in this study, the masses of residues that we report should be considered preliminary. In fact, the surface concentrations and estimates of percent residuals differed substantially from test to test, particularly for the C4 initiated detonations at Camp Ethan Allen. Nevertheless, the following generalizations can be made. First, it appears that a higher percentage of TNT is consumed in detonations than RDX when the main charge is Composition B. This appears to be true whether C4 was used to detonate the mortar rounds or not. Thus, residues of RDX are present at much higher surface concentrations than TNT. The presence of NG in range residues was unexpected and appears to be a general phenomenon based on analysis of these samples and samples collected at Canadian Force Base Valcartier, and to a lesser extent, at Fort Ord. HMX was also observed in residues with approximate surface concentrations about 20% of RDX.

While we detonated only three 81-mm mortar rounds using C4, and two 60-mm mortar rounds without C4, it appears that more RDX is deposited when C4 is used. This very preliminary result should be verified by detonations of the same munition with and without C4.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YY)*
August 2000

2. REPORT TYPE
Technical Report

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Evaluating the Use of Snow-Covered Ranges to Estimate the Explosives Residues that Result from Detonation of Army Munitions

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Thomas F, Jenkins, Thomas A. Ranney, Marianne E. Walsh, Paul H. Miyares, Alan D. Hewitt, and Nicholas H. Collins

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDC/CRREL TR-00-15

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

w
Strategic Environmental Research and Development Program

10. SPONSOR / MONITOR'S ACRONYM(S)

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

. Estimating the amounts of residues remaining after munitions detonate is complicated by the presence of residues from previous detonations and the difficulty in easily obtaining adequately sized samples to overcome spatial heterogeneity in residue deposition. This study was conducted to assess the use of snow-covered ranges to provide these types of estimates. Specifically, two snow-covered ranges were used to estimate the amount of explosives residues that result from detonation of individual mortar rounds. At Fort Drum, New York, 60-mm mortar rounds were fired, and at Camp Ethan Allen, Vermont, 81-mm mortar rounds were detonated by EOD personnel using C4 (RDX) and a blasting cap. The locations where residues were deposited were identified by the presence of soot from the detonation of TNT on the surface of the otherwise clean snow. Large surface snow samples were collected with a snow shovel and the melted snow was extracted and analyzed by gas chromatography with an electron capture detector (GC-ECD) and reversed-phase high performance liquid chromatography (RP-HPLC). For both types of rounds, the main charge was Composition B (60% RDX and 39% TNT). The major residues produced were RDX and nitroglycerine (NG), with lesser amounts of HMX and TNT. Surface concentrations ranged from as high as 4430 µg/m^2 for RDX to less than 0.05 µg/m^2 for TNT, both at Camp Ethan Allen.

The major advantages of using snow-covered ranges were: 1) the snow cover provided an uncontaminated surface, unaffected by

15. SUBJECT TERMS

Detonations	Gas chromatography	RDX	TNT
Explosives residues	NG	Snow	Training ranges

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
U	U	U	U	13	

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14. ABSTRACT (cont'd)

previous detonations, 2) the black soot produced from the detonation of TNT delineated the areas where residue had deposited and 3) surface snow provides both a convenient matrix for collection of large surface area samples, essential for characterizing heterogeneously distributed residues, and a matrix free from interferences.

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