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Use of Surface Snow Sampling to Estimate the Quantity of Explosives Residues Resulting from Land Mine Detonations

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

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Abstract: A PMA-2 antipersonnel land mine from Yugoslavia was detonated with an M6 blasting cap on a snow-covered range at Camp Ethan Allen Training Site, Jericho, Vermont. The main charge of the PMA-2 was 100 g of TNT with 13 g of RDX as a booster. The surface that was impacted by the detonation (381 m^2) was visually identified by the presence of soot, which was produced by detonation of TNT from the main charge of the PMA-2. A total of 15 surface snow samples (each 2.3 m^2) was collected using an unpainted aluminum snow shovel and analyzed for explosives residues by gas chromatography with an electron capture detector (GC-ECD). These samples accounted for 7.3% of the impacted surface. The major explosives-related chemicals (ERC) detected were TNT and RDX. 2,4-DNT was detected in the detonation crater, apparently because of the presence of propellant from previous range use, and at low concentration in several of the surface snow samples. The surface concentrations of TNT were similar to those resulting from a buried mine. The rate of transformation of TNT is rapid, however, and concentrations would rapidly decline without a continuing source of TNT. Thus the residues resulting from a mine detonation do not seem to pose a serious background problem for the use of chemical sensors to detect the presence of buried land mines. The utility of conducting these types of tests on a snow-covered range was demonstrated.

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PREFACE

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

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NOMENCLATURE

ACN	Acetonitrile
ADNTs	Aminodinitrotoluenes
CEATS	Camp Ethan Allen Training Site
CRREL	Cold Regions Research and Engineering Laboratory
DARPA	Defense Advanced Research Projects Agency
ERC	Explosives-related chemical signatures (TNT, DNT, DNB, ADNTs, TNB)
ERDC	Engineer Research and Development Center
FLW	Fort Leonard Wood
GC-ECD	Gas chromatography-electron capture detection
GC-TID	Gas chromatography-thermionic ionization detection
HMX	1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine
PMA-1A	Plastic-cased Yugoslavian antipersonnel land mine
PMA-2	Plastic-cased Yugoslavian antipersonnel land mine
RDX	1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine
RP-HPLC-UV	Reversed-phase high-performance liquid chromatography ultraviolet detection
Sandia NL	Sandia National Laboratories
SARM	Standard Analytical Reference Materials
TMA-5	Plastic-cased Yugoslavian antitank land mine
TNB	1,3,5-trinitrobenzene
TNT	Trinitrotoluene
URI	University of Rhode Island
1,3-DNB	1,3-dinitrobenzene
2-ADNT	2-amino-4,6-dinitrotoluene
2-ANT	2-amino-4-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,4,6-TNT	2,4,6-trinitrotoluene
3-NA	3-nitroaniline
3,5-DNA	3,5-dinitroaniline
4-ADNT	4-amino-2,6-dinitrotoluene
4-ANT	4-amino-2-nitrotoluene

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INTRODUCTION

Background

The Defense Advanced Research Projects Agency (DARPA) is sponsoring research to determine whether buried land mines can be detected by sensing the evolution of explosives-related chemical signatures (ERC). Analysis of soil collected near buried mines at DARPA's research minefield at Fort Leonard Wood, Missouri, indicates that ERC are detectable in surface soil above buried mines for several types of plastic-cased antipersonnel and antitank mines (Jenkins et al. 2000). For mines containing TNT as a major portion of the main charge, 2,4-dinitrotoluene (2,4-DNT) and two environmental transformation products of TNT (2-amino-4,6-dinitrotoluene [2-ADNT] and 4-amino-2,6-dinitrotoluene [4-ADNT]) were generally present at higher concentrations in the surface soil than TNT itself. Tests with a prototype sensor built by Nomadics Corporation have been very promising, indicating that real-time detection of buried mines using this approach is feasible (la Grone et al. in prep).

An unanswered question, however, is whether residues of ERC from detonations of mines or other types of military ordnance would contaminate the vicinity with ERC to a degree that would compromise the use of chemical sensing for this application. Two preliminary studies were conducted to try to estimate the residues of ERC that result from detonations of explosives containing TNT. Dr. Jimmie Oxley and Dr. James Smith from the Chemistry Department at the University of Rhode Island (URI) detonated blocks of TNT in barrels containing sand and analyzed the sand for residues of ERC. James Phelan and others at Sandia National Laboratories (Sandia NL), Albuquerque, New Mexico, detonated several land mines in an arid environment and collected residues of ERC that were deposited on surface sand.

The URI experiment was configured so that all the ERC that resulted from the detonation were trapped in the barrel, and hence it was possible to obtain representative samples with little uncertainty. On the other hand, the URI study used a block of TNT in an enclosure and hence it could be argued that it was not a good simulation of the detonation of a land mine under less confined conditions. The Sandia NL experiments utilized real PMA-1A and PMA-2 land mines from Yugoslavia and thus the resulting residues should mimic those found in a real minefield. Because their experiment was conducted on sandy soil, though, it was difficult to visually estimate the size of the area impacted, and the percentage of the area that was sampled was quite small by necessity. Thus if the ERC residues were heterogeneously distributed, the small proportion of the area sampled would lead to a large uncertainty in the estimates of percent of explosives remaining after detonation. Early estimates of the percentage of explosive that remains after detonation from these two studies differed by several orders of magnitude.*

Because of the importance of having a good estimate of the residues resulting from detonations, we proposed an experiment very similar to that conducted at Sandia NL except that the experiment would be conducted on a snow-covered surface. The advantage of the snow cover was threefold. First, the snow cover made it possible to visually estimate the surface area

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* Personal communication, J. Oxley, Chemistry Department, University of Rhode Island, Kingston, Rhode Island, April 2000; J. Phelan, Sandia National Laboratories, Albuquerque, New Mexico, April 2000.

impacted with residues. This is because TNT is a soot-producing explosive and the black soot is easily seen on the white snow surface. Second, large surface area samples can be easily taken from the ash-covered areas very simply using a snow shovel. And finally, a fresh snow cover can be clean with respect to residues of ERC. This may not always be the case at ranges where other detonations are commonly conducted. The advantages of conducting this type of test at a snow-covered range were recently demonstrated for estimates of explosives-related residues produced by detonations of mortar rounds (Jenkins et al. in prep.).

Objective

The objective of this work was to evaluate the use of a snow-covered range to assess the identities and concentrations of explosives residues that remain after a land-mine detonation. This information, together with an estimate of the surface area impacted, will permit an estimate of the mean surface concentrations of ERC that result. Coupling these data with estimates of the half-life of the various ERC components in the environment will enable an assessment of the potential interference from detonations of land mines on the ability to detect buried land mines using trace chemical sensing.

Sample collection

On 23 March 2000, we detonated a PMA-2 (EX-150) at Ethan Allen Firing Range in Jericho, Vermont. Although the snow cover on the firing range was mostly gone, we found a shaded location along a tree line that was large enough to conduct the detonation study with the small PMA-2 mine, and on which the snow surface was visibly pristine. A location was selected in the center of the snow-covered area, a small hole was dug in the snow, and a 25-cm × 23-cm × 0.6-cm steel plate was buried in the snow. The surface soil under the snow was thawed and this plate was used in an attempt to minimize the amount of soil thrown by the blast. An M-6 blasting cap was inserted into the fuse well of the PMA-2 mine and the mine was placed on the snow surface, directly above the steel plate. The mine was detonated electronically by the EOD team at about 10:30 a.m. At the time of the detonation, there was a slight breeze from the west that carried the detonation cloud slightly downwind to the east. The main charge in the PMA-2 mine was 100 g of TNT with a 13-g booster of RDX.

Because the mine contained TNT as the main charge, the detonation was characterized by the production of black soot. This soot produced a cloud that settled on the snow surface and was quite visible, easily delineating the areas where residues were deposited. We decided to collect the surface snow samples before we measured the visually impacted surface area so as not to contaminate the snow samples. Snow samples were collected from 10:30 a.m. to 12:00 noon. The steel plate also was recovered and returned to the laboratory for analysis.

Surface snow samples (25 ft^2 [2.3 m^2]) were collected using an unpainted aluminum snow shovel. A sample of snow from the crater was collected with a small stainless-steel hand shovel. The depth sampled for surface snow was kept as small as possible to minimize the volume of snowmelt that would be produced subsequently during sample preparation for ERC analysis. Depths sampled depended on the condition of the snow in the various locations, but averaged about 0.5 cm. For collection, snow was shoveled into specially cleaned polyethylene bags that were sealed with a twist tie. Snow samples were returned to CRREL the same day they were collected and were stored cold until processed the following day.

A total of 15 snow samples was collected; the locations where samples were collected are shown in Figure 1 relative to the visually impacted surface. Sam-

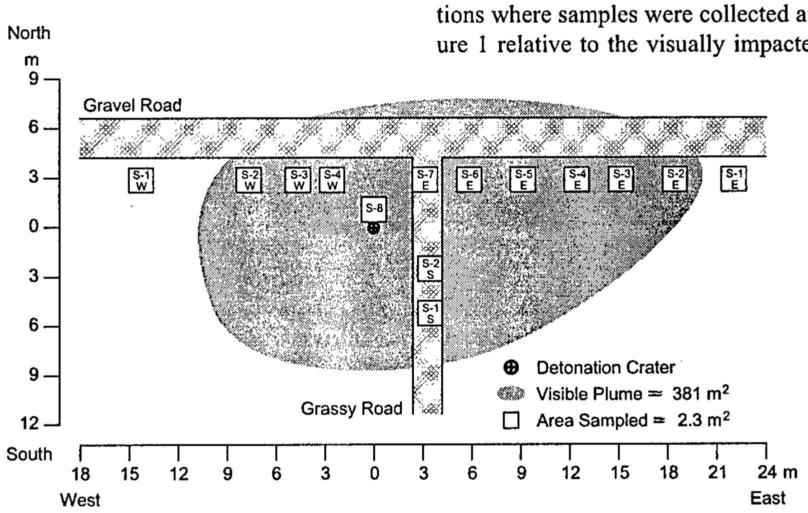

Figure 1. Locations of surface snow samples relative to area of surface deposition.

ples were collected from the crater and from 14 surface areas from immediately to the north of the crater to a distance of 76 ft (23 m) east of the crater, 50 ft (15 m) west of the crater, and 20 ft (6 m) south of the crater. Two samples (S-1E and S-1W) were collected just beyond the area where visual deposition had occurred.

Once sampling was complete, we measured the extent of the surface that was visually contaminated with soot from the detonation. The impacted area is delineated by the shaded area in Figure 1. The total surface area that was visually impacted was estimated at 4100 ft^2 (381 m^2). The total area sampled within the visually impacted zone was 300 ft^2 (28 m^2), which was 7.3% of the impacted area.

Snow-sample processing

The snow in the plastic bags was melted by placing the bags in the laboratory overnight. Small quantities of ice remained in the bags in the morning, indicating that the samples had remained at 0°C during this period. The water was black in color due to the presence of suspended soot particles. Once the last of the snow and ice melted, each of the samples was filtered to remove the soot by passing it through glass fiber filters (Whatman glass microfiber, 47 mm, grade GF/A). Depending on the amount of soot in the sample, it took as many as 14 individual filters for a given sample. These filters were retained and were extracted separately, as described below.

After filtration, each volume of snowmelt was measured and a 1520-mL aliquot was placed in a 2-L volumetric flask containing 496 g of sodium chloride (Miyares and Jenkins 1991, EPA 1994). A magnetic stir bar was added and the flask stirred to dissolve the salt. A 325-mL aliquot of acetonitrile (ACN) 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 ACN phase on the top, about 25 mL, was removed and the volume measured using a graduated cylinder. This first extract was labeled salting-out extract 1 (SOE1). An additional 20 mL of acetonitrile was then added to the volumetric flask and the flask was again stirred vigorously for 30 minutes. The magnetic stirrer was turned off again and the phases allowed to separate. The second ACN extract was then removed, the volume measured (about 20 mL), and it was labeled SOE2.

To ensure that we included any explosives residues that were deposited on the inside of the bags, the sample bags were wiped with a Whatman filter and the filter was placed in a Soxhlet extraction thimble. The filters used to remove soot from that sample were added to the thimble, which was placed inside a Soxhlet extractor. A 250-mL aliquot of ACN was added to the receiver of the Soxhlet extractor and the samples were continuously extracted for 22 hours at a cycle time of six cycles per hour. After cooling, the volume of solvent was measured and an aliquot removed for analysis. This sample was labeled as SOX1.

Analysis of residues on steel plate

The surface of the steel plate was sampled using swiping techniques similar to that developed to estimate the surface concentration of explosives residues on land mines (Leggett et al. 2000). Paper filter disks (1.8 cm^2) were soaked in methanol and placed randomly on the surface of the steel plate. Upon drying, the paper disks were picked up with forceps and placed in an amber vial containing acetone. Two samples of the plate were analyzed. One sample utilized a single filter disk and 0.5 mL of acetone in the amber vial. A second sample used five filter disks and 2.0 mL of acetone in the vial. The acetone extracts of the disks were initially analyzed by gas chromatography-thermionic ionization detection (GC-TID) and quantitative results were obtained by gas chromatography-electron capture detection (GC-ECD) as described below.

GC-ECD determination

All SOE and SOX samples were analyzed by GC-ECD on an HP 6890 gas chromatograph equipped with a microcell Ni^{63} ECD (300°C). We used direct injection (250°C) of 1-µL extracts in a packed port that was equipped with a deactivated Restek Uniliner. Primary analysis was conducted on a 6-m- × 0.32-mm-i.d. 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 min, 10°C/min ramp to 250°C, 3-min hold. The carrier gas was helium at 10 mL/min (linear velocity about 100 cm/sec). The makeup gas was nitrogen (40 mL/min). Further details of the procedure, including conditions for the confirmation column, may be found in SW-846 Method 8095 (Walsh and Ranney 1998, EPA 1999). Retention times for the target signatures are presented in Table 1. Detection limits reported by Walsh and Ranney (1998) for a method that utilized solid phase extraction rather than salting-out extraction are shown in Table 2. All analyte concentrations were within the linear range of the ECD and concentrations reported were taken from the determination on the primary column (RTX-5).

GC-TID for acetone extracts of steel plate

The two acetone extracts of the surface of the steel plate were analyzed using GC-TID according to methods developed elsewhere (Hewitt and Jenkins 2000). TNT, RDX, and 2,4-DNT were detected. Analytes were then quantified using the GC-ECD method described above.

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

Analyte	Retention time (min) RTX-5 (1.5 µm)	Retention time (min) 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-ADNT	9.956	10.582
2-ADNT	10.418	11.058
Tetryl	11.322	11.595
HMX	15.629	

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

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

Table 2. Method Detection Limits (µg/L) of nitroaromatics and nitramines in water.*

Analyte	MDL (µg/L)
1,3-DNB	0.004
2,6-DNT	0.003
2,4-DNT	0.009
TNB	0.007
2,4,6-TNT	0.010
RDX	0.004
4-ADNT	0.003
2-ADNT	0.003
Tetryl	0.009

* Determined by GC-ECD using 0.5 L of sample preconcentrated to 5 mL of acetonitrile (Walsh and Ranney 1998).

Table 3. Mass of TNT and RDX residues recovered from the extraction of the filtered water versus that from the soot.

	Mass recovered (µg)			
	TNT		RDX	
Sample	Water*	Soot†	Water*	Soot†
S-1E	0.22	0.00	1.03	0.00
S-2E	2.00	0.62	0.31	0.00
S-3E	16.28	1.15	4.08	0.00
S-4E	7.65	1.20	2.30	0.00
S-5E	28.32	29.73	3.59	0.00
S-6E	1.70	4.54	0.47	0.00
S-7E	0.47	0.29	0.62	0.00
S-8C	0.88	0.00	27.31	0.00
S-1W	0.94	0.23	1.62	0.00
S-2W	0.08	0.00	2.31	0.00
S-3W	0.07	0.00	4.29	0.00
S-4W	0.95	0.52	1.16	0.00
S-1S	13.95	6.58	0.48	0.00
S-2S	47.74	411	3.07	0.00
Crater	0.09	0.79	0.00	0.00

* Mass recovered from the 1520 mL of filtered water multiplied by the ratio of the total snowmelt volume divided by the volume extracted.

† Mass recovered from extraction of soot from the total sample of snowmelt.

RESULTS AND DISCUSSION

Analytical methodology

Analysis of the snow samples collected after a detonation resulting from a TNT-containing munition is complicated by the presence of a large amount of soot. When this snow is melted, the fine soot particles remain in suspension, coloring the water black. The soot must be filtered out prior to extraction of the water using the standard analytical protocol for analysis of explosives in water, SW-846 Method 8330 (EPA 1994). The sorptivity of the soot for the nitroaromatic and nitramine organic chemicals that make up the main charge and booster in the PMA-2 land mine is unknown, hence the soot that was filtered from the water must also be analyzed to account for all the explosives residues that could be present in the surface snow samples.

Extraction of the soot to remove the sorbed explosives could be conducted with an equilibrium-based method such as the soil extraction procedure in SW-846 Method 8330 (EPA 1994). In this method 2 g of soil is equilibrated with 10 mL of ACN overnight in an ultrasonic bath. This procedure works well for soil because the equilibrium partition coefficient is favorable for extraction of the explosive from soil into ACN. The equilibrium partition coefficient between ACN and soot is unknown and may not be favorable for equilibrium extraction. An equilibrium-based extraction procedure therefore may underestimate the amount of explosive sorbed to the soot. Consequently, the continuous-extraction Soxhlet procedure was used. This procedure, while less convenient than the ultrasonic equilibration procedure, has been shown to be equally effective for extraction of explosives from soil (Jenkins and Grant 1987), and it does not rely on a favorable partition coefficient. This is true because the analyte, once extracted, is removed from interaction with the soot each time the Soxhlet device cycles.

We decided to use the Soxhlet procedure, rather than investigate the partition coefficient for the various analytes between soot and ACN. The mass of analytes recovered from extraction of the water and from extraction of the soot is shown in Table 3. The ratio of mass of TNT associated with soot versus that associated in the water ranged from 0 to 8.8. There does not appear to be any relationship between this ratio and the total amount of TNT present, probably because a portion of the TNT present was particulate and only a portion of the total had dissolved. Thus it was important to analyze both the water and soot to estimate the total residues resulting from the detonation of the PMA-2 mine. For RDX, though, it appears that there is less association with soot; RDX was found only in the water analysis.

Table 4. Mass of nitroaromatics and nitramines in each surface snow sample collected after the detonation of a PMA-2 land mine.

Sample	*Mass recovered (µg)*				
	TNT	*RDX*	*2,4-DNT*	*2-ADNT*	*4-ADNT*
S-1E	0.22	1.03	<d	<d	<d
S-2E	2.62	0.31	<d	<d	<d
S-3E	17.43	4.08	<d	<d	<d
S-4E	8.85	2.30	0.75	<d	<d
S-5E	58.05	3.59	4.62	0.68	1.02
S-6E	6.24	0.47	3.16	0.32	0.30
S-7E	0.76	0.62	2.97	<d	<d
S-8C	0.88	27.31	3.53	<d	<d
S-1W	1.17	1.62	<d	<d	<d
S-2W	0.08	2.31	<d	<d	<d
S-3W	0.07	4.29	<d	<d	<d
S-4W	1.47	1.16	0.88	0.30	<d
S-1S	20.53	0.48	1.14	0.22	<d
S-2S	458	3.07	3.07	<d	<d
Total detected (µg)* in surface snow	576	52.6			
Computed† (µg) in surface snow	7890	721			
Crater (µg)	0.88	0.00	48	5.29	3.01
Steel plate (µg)	0.54	0.54	0.41		
% of total recovered**	0.0079%	0.0056%			

* Sum of analytes in all samples, which represents 7.3% of the total surface area impacted by the detonation.

† Total mass of analytes computed by assuming the total detected in the 7.3% sampled is representative of the total surface area impacted by the detonation.

** Total mass of analytes computed relative to amount present in land mine.

Total mass of explosives residues found

The total mass of the various nitroaromatics and nitramines in the residues from each snow sample was obtained by adding the results of SOE1 and SOE2 analyses to obtain the concentration in the water, multiplying the concentration of each analyte in the water sample by the total volume of snowmelt produced, and adding the mass of analyte recovered from the soot. These values are presented in Table 4. Because these samples represent about 7.3% of the total surface area impacted by the detonation, we estimated the total mass of residues residing in the snow by multiplying the total found in the surface snow samples by 100/7.3 (Table 4). To obtain the total residue recovered, the mass of each found in the crater snow sample and that recovered from the steel plate were added (Table 4). The percent of the mass explosive recovered relative to the mass present in the mine prior to detonation was then computed to be 0.0079% for TNT and 0.0056% for RDX. In a previous study, the percent recovery of RDX for three mortar rounds detonated with C4 ranged from 0.00007% to 0.011% while the percent recovery for TNT ranged from 0.000001% to 0.00023% (Jenkins et al. 2000). Similarly, for two mortar rounds that detonated on impact, the RDX recovery was 0.00004% and 0.00009%, while the concentration of TNT in the snow was too low to allow an estimate of recovery (Jenkins et al. 2000).

The percent of TNT remaining after detonation appears to be greater for the PMA-2 mine than for either the composition-B-filled 81-mm or 60-mm mortar rounds. However, only one mine was detonated and the high variability found for the three mortar rounds detonated with C4 might be expected to be present for mine detonations as well. Thus it is impossible to draw a firm conclusion on that score without additional experiments. Likewise, it appears that TNT and RDX are recovered in similar percentages for the mine detonation, whereas RDX was recovered in much higher percentages than TNT for composition-B-containing mortar-round detonations.

Concentrations of nitroaromatics and nitramines in surface snow

Except for the crater snow sample, the concentrations of these analytes in the surface snow samples on a µg/m^2 basis were then obtained by dividing the mass determined from analysis (in µg) by the surface area sampled (2.3 m^2). The major nitroaromatics and nitramines detected in these surface snow samples were 2,4,6-TNT (TNT), RDX, and 2,4-DNT (Table 5). The two monoamino transformation products of TNT (2-

amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene) were also present in a few samples. The two analytes generally present at the highest concentration were TNT and RDX; this is reasonable because these were the two analytes present at the highest concentration in the main charge and booster of the PMA-2 mine, respectively. The distribution of TNT and RDX in the surface snow samples was somewhat different, however (Fig. 2, 3).

The highest TNT concentration, 199 µg/m^2, was found in sample S2S, which was collected about 4 m from the detonation crater. This value is about eight times higher than the second highest value of 25.24 µg/m^2 found for sample S5E, which was located about 10 m downwind of the detonation crater. These two val-

Table 5. Surface snow concentrations of nitroaromatics and nitramines after the detonation of a PMA-2 land mine.

	Mass recovered (µg/m^2)				
Sample	*TNT*	*RDX*	*2,4-DNT*	*2-ADNT*	*4-ADNT*
S-1E	0.10	0.45	<d	<d	<d
S-2E	1.14	0.13	<d	<d	<d
S-3E	7.58	1.77	<d	<d	<d
S-4E	3.85	1.00	0.33	<d	<d
S-5E	25.2	1.56	2.00	0.30	0.44
S-6E	2.71	0.20	1.38	0.14	0.13
S-7E	0.33	0.27	1.29	<d	<d
S-8C	0.38	11.9	1.53	<d	<d
S-1W	0.51	0.70	<d	<d	<d
S-2W	0.03	1.00	<d	<d	<d
S-3W	0.03	1.87	<d	<d	<d
S-4W	0.63	0.50	0.38	0.13	<d
S-1S	8.93	0.21	0.50	0.10	<d
S-2S	199	1.33	1.33	<d	<d

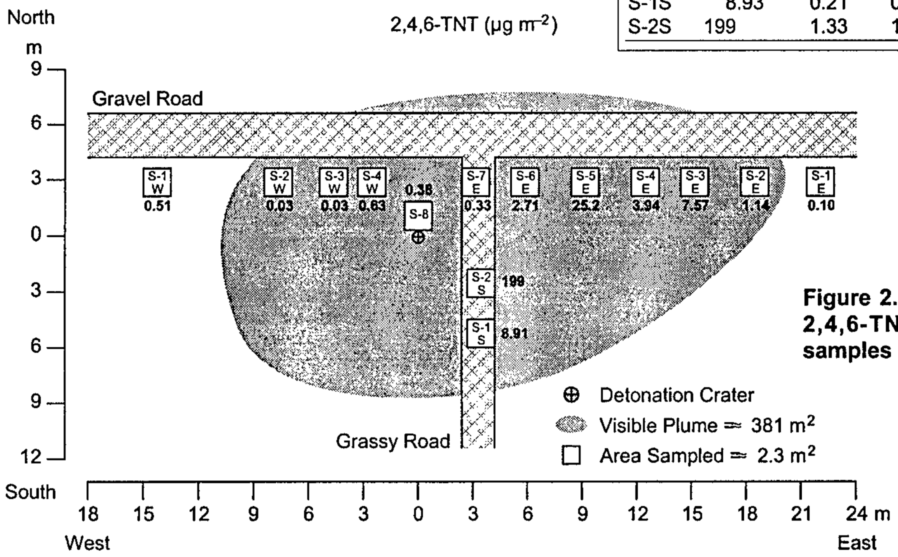

Figure 2. Spatial distribution of 2,4,6-TNT in surface snow samples (µg m^{-2}).

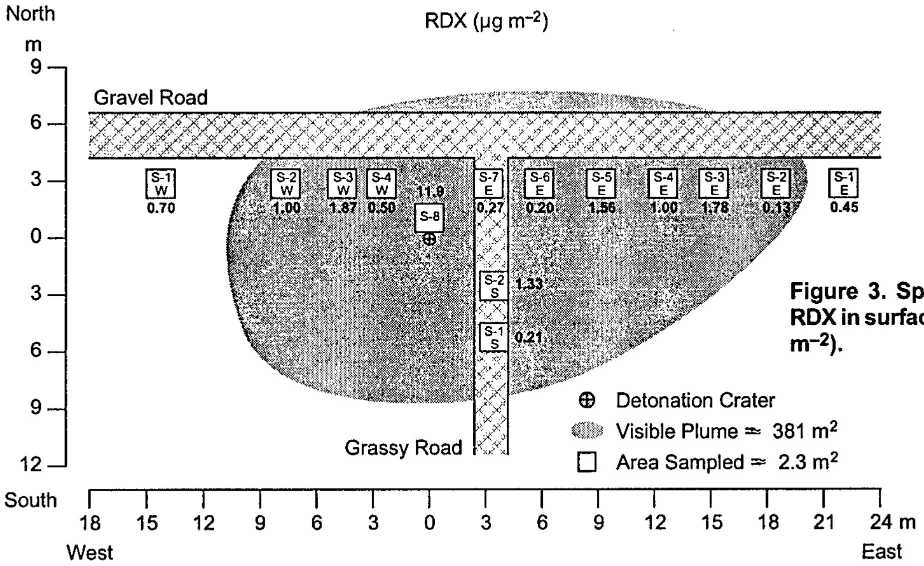

Figure 3. Spatial distribution of RDX in surface snow samples (µg m^{-2}).

ues appear to be due to the presence of a small particle of explosive because they are so much higher than the other surface samples analyzed. Nevertheless, there appears to be a halo of higher concentrations of TNT about 3 m from the crater extending to about 18 m downwind from the detonation. Very low amounts of TNT were found in the crater sample, upwind (west) of the detonation, and outside the area of visible soot deposition (Fig. 2). The very low concentration of TNT in the crater sample agrees with results from Collins and Calkins (1995), who reported that concentrations were below method detection limits for samples taken from a crater formed by a mortar detonation in snow.

The highest RDX concentration, 11.87 μg/m^2, was found in sample S-8C, which was collected about 1 m from the crater (Fig. 3), although the concentration in the sample from the crater itself was quite low. The halo of higher concentration found for TNT was not evident in the surface RDX concentrations, and concentrations upwind were generally as high as those downwind. The reason for the different distribution pattern is unclear, but RDX is present in this mine in the booster and is not present in the main charge.

The distribution of 2,4-DNT in the surface snow samples is presented in Figure 4. The pattern is fairly similar to that for TNT, with a region of highest concentrations from 1 to 10 m from the detonation crater. For 2,4-DNT, however, a relatively high mass (48 μg) was detected in the sample of snow from the detonation crater, and 2,4-DNT was not found in sample S-1S, the sample that had the highest concentration of TNT. The mass of 2,4-DNT recovered from the crater was 50 times the mass of TNT found in this sample. 2,4-DNT is present at only 0.025% in the TNT used in PMA-2 mines, while 2,4,6-TNT was present at 82.4% in this explosive (George et al. 1999). Thus we do not believe the 2,4-DNT found in the crater originated from the explosive in the mine. More likely it was present in the soil below the detonation because of propellant contamination from previous range activities. This experiment was conducted in early spring and the surface soil under the snow cover was thawed. This result reinforces our concern about conducting these types of tests on soil at ranges where other testing and training activities have occurred.

Although tetryl was found in the sample of explosive taken from a PMA-2 land mine by George et al. (1999) at 17.4%, it was not detected in the residues after detonation in this study. Tetryl was probably present as the booster in the mine that was sampled by George et al. and had been replaced with RDX in the specific mine we detonated at CEATS.

The two most commonly encountered environmental transformation products of TNT (2-ADNT and 4-ADNT) were also found in a few surface snow samples (Table 5). It is possible that a portion of these products was formed in the meltwater prior to analysis rather than in the snow since they were found in the samples with the highest TNT concentration. 2-ADNT and 4-ADNT were also found in the crater sample, but their presence in this sample is likely due to previous range activities.

Estimated surface soil concentrations resulting from a land-mine detonation

If no snow was present at the time of a land-mine detonation, the residues produced would be deposited on the surface soil. If we assume a soil depth of 0.5 cm and an average soil density of 1.7 g/cm^3, we can esti-

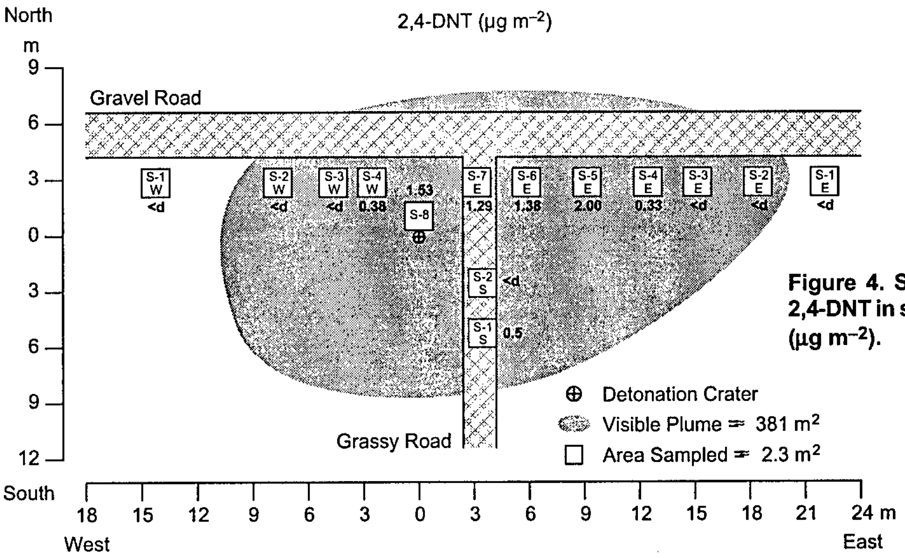

Figure 4. Spatial distribution of 2,4-DNT in surface snow samples (μg m^{-2}).

mate the resulting surface soil concentrations that would result. This was done for TNT, RDX, and 2,4-DNT from the mean and maximum surface snow concentrations obtained (Table 6). For TNT, the mean was 2.4 µg/kg and the maximum was 23 µg/kg. For 2,4-DNT, the mean was 0.08 µg/kg and the maximum was 0.24 µg/kg.

Estimates of surface soil concentrations resulting from buried mines have recently been made by Jenkins et al. (2000). For 2,4,6-TNT, the median surface concentration near TMA-5 and PMA-1A mines was 4 µg/kg, a value only slightly higher than the estimated mean concentration resulting from this mine detonation. The estimate for the maximum TNT concentration that would result from a mine detonation was 23 µg/kg, which is considerably higher than the median surface soil concentration near buried mines. The half-life of TNT in the soil, however, is very short (on the order of a few days) and hence the surface concentration of TNT would decline rapidly after the detonation (Miyares and Jenkins in prep). This is not true for the surface soil near a buried mine where the TNT has a continuous source from the mine and therefore the rate of removal due to transformation is counteracted by the continuing flux from the mine.

Table 6. Estimates for surface soil concentrations for TNT, RDX, and 2,4-DNT resulting from detonation of PMA-2 land mine.

	TNT	*RDX*	*2,4-DNT*
Average surface concentration (µg/m^2)	20.8	1.81	0.73
Total contaminated surface area (m^2)	381	381	381
Total mass deposited (µg)	7933	689	277
Estimate of mean surface soil concentration (µg/kg)* resulting from detonation	2.4	0.21	0.08
Estimate of maximum surface soil concentration (µg/kg)† resulting from detonator	23	1.4	0.24

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

† Computed from highest value obtained in surface snow samples.

For 2,4-DNT, the median soil concentrations near TMA-5 and PMA-1A mines were estimated to be 16 and 32 µg/kg, respectively (Jenkins et al. 2000). These values are considerably higher than the estimated mean (0.08 µg/kg), or even the maximum (0.24 µg/kg), resulting from the mine detonation. Thus, if the results here are typical of mine detonations, a mine detonation should not provide a serious background problem for chemical sensors that use 2,4-DNT as the primary signature for buried mines.

CONCLUSIONS

Overall, the results from this experiment demonstrate the utility of conducting these types of tests on a clean snow surface. Residues of TNT and RDX were distributed heterogeneously on the surface snow, emphasizing the need to collect large surface area samples to achieve representativeness. A steel plate was placed under the mine to minimize the amount of soil thrown out by the blast, but this was not completely effective. Some 2,4-DNT contamination of the snow in the crater was apparently caused by propellant from previous range activities. To mitigate this problem, future experiments should be conducted in midwinter when the surface soil under the snow is frozen.

Estimates of the mean initial concentrations of TNT in surface soil resulting from detonation of a land mine were similar in magnitude to those resulting from a buried mine. The half-life of TNT in surface soil is so short, however, that these concentrations would rapidly decline to insignificant levels in only a few days. Because of the large amount of spatial heterogeneity in the distribution, however, there could be a few specific locations where a small particle of TNT would be located that would persist for some time.

The mean surface soil concentration estimates for 2,4-DNT from this mine indicate that residues from detonation are much lower than result from the presence of a buried land mine and hence, if these results are typical of mine detonations, would not result in serious interference for sensors using 2,4-DNT as the primary signature.

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14. ABSTRACT

A PMA-2 antipersonnel land mine from Yugoslavia was detonated with an M6 blasting cap on a snow-covered range at Camp Ethan Allen Training Site, Jericho, Vermont. The main charge of the PMA-2 was 100 g of TNT with 13 g of RDX as a booster. The surface that was impacted by the detonation (381 m^2) was visually identified by the presence of soot, which was produced by detonation of TNT from the main charge of the PMA-2. A total of 15 surface snow samples (each 2.3 m^2) was collected using an unpainted aluminum snow shovel and analyzed for explosives residues by gas chromatography with an electron capture detector (GC-ECD). These samples accounted for 7.3% of the impacted surface. The major explosives-related chemicals (ERC) detected were TNT and RDX. 2,4-DNT was detected in the detonation crater, apparently because of the presence of propellant from previous range use, and at low concentration in several of the surface snow samples. The surface concentrations of TNT were similar to those resulting from a buried mine. The rate of transformation of TNT is rapid, however, and concentrations would rapidly decline without a continuing source of TNT. Thus the residues resulting from a mine detonation do not seem to pose a serious background problem for the use of chemical sensors to detect the presence of buried land mines. The utility of conducting these types of tests on a snow-covered range was demonstrated.

15. SUBJECT TERMS

Composition B	Explosives residues	RDX	Surface sampling
Detonation	Land-mine detection	Snow	TNT

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