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## Use of snow-covered ranges to estimate explosives residues from high-order detonations of army munitions

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### Abstract

Estimation of the amounts of residues resulting from high-order detonation of munitions is complicated by the presence of residues from previous detonations and the inability to easily obtain 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, snow-covered ranges were used to estimate the amount of explosives residues that resulted from detonation of individual mortar rounds and a small antipersonnel land mine. At Fort Drum, NY, 60 mm mortars were fired and at Camp Ethan Allen, VT, 81 mm mortars and a Yugoslavian PMA2 land mine were detonated by EOD (explosives ordnance disposal) personnel after attaching C4 (RDX) and/or 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 mortars the main charge was composition B (60% RDX and 39% TNT); for the land mine, the main charge was TNT with an RDX booster. The major residues produced for the mortars were RDX and nitroglycerine (NG), with lesser amounts of HMX, and TNT. Surface concentrations ranged from as high as 4430  $\mu\text{g}/\text{m}^2$  for RDX to <0.05  $\mu\text{g}/\text{m}^2$  for TNT, both at Camp Ethan Allen. For the land mine, the major residues were TNT and RDX with surface concentrations of 20.8 and 1.8  $\mu\text{g}/\text{m}^2$ , respectively. Published by Elsevier Science B.V.

*Keywords:* Explosives; Detonation; RDX; Firing ranges; Residues

### 1. Introduction

Over the past several years interest in the environmental affects from testing and training activities at the Department of Defense's impact ranges has increased. An ongoing investigation at the Massachusetts

military reservation (MMR) has indicated that the underlying ground water aquifer below this site may be contaminated with low concentrations of RDX [1]. Furthermore, research has demonstrated substantial surface soil contamination with residues of high explosives resulting from the use of LAW rockets at antitank firing ranges [2,3]. Potential sources of contamination at ranges include leakage of explosives from unexploded ordnance in the subsoil, releases from buried ordnance, residues from past disposal

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practices, residues deposited from low-order detonations, or accumulations of residues from the large number of high-order detonations over the years of operation of the impact ranges. Definitive resolution of these candidate sources is highly complex.

The objective of this study was to evaluate the use of snow-covered ranges for determining the explosives-residues produced by detonations of high explosives-containing mortar rounds and a small antipersonnel land mine. Two types of scenarios were tested. The first was the use of a snow cover to estimate the amount of residues that are deposited on a range when an army munition is fired and detonates on impact, or when a land mine is detonated with a blasting cap that is similar in composition to the fuse mechanism. The second was the estimation of the residues that result from the practice of attaching C4 to an item of unexploded ordnance and detonating it in place. Because concentrations were expected to be low, we used large samples and a new gas chromatographic electron capture detector (GC-ECD) method developed recently by Walsh and Ranney [4,5].

### 1.1. Overview of detonations

Two mortar detonation experiments and a land mine detonation were conducted at Camp Ethan Allen Firing Range, Vermont, in March 2000. Three 81 mm mortar rounds and a PMA-2 land mine 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 for the mortars and an M6 blasting cap for the mine. Three 60 mm mortar rounds were fired by US Army personnel in March 2000, and the rounds were allowed to detonate on impact on a snow-covered range at Fort Drum, New York.

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). Propellant increment charges A and B were removed from the round before detonation. A small ignition cartridge containing nitroglycerine was not removed, however, since this charge was present within the tail of the round and could not be easily separated from the assembly. 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 PMA-2 mine was 100 g of TNT with a 13 g booster of RDX.

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, 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.

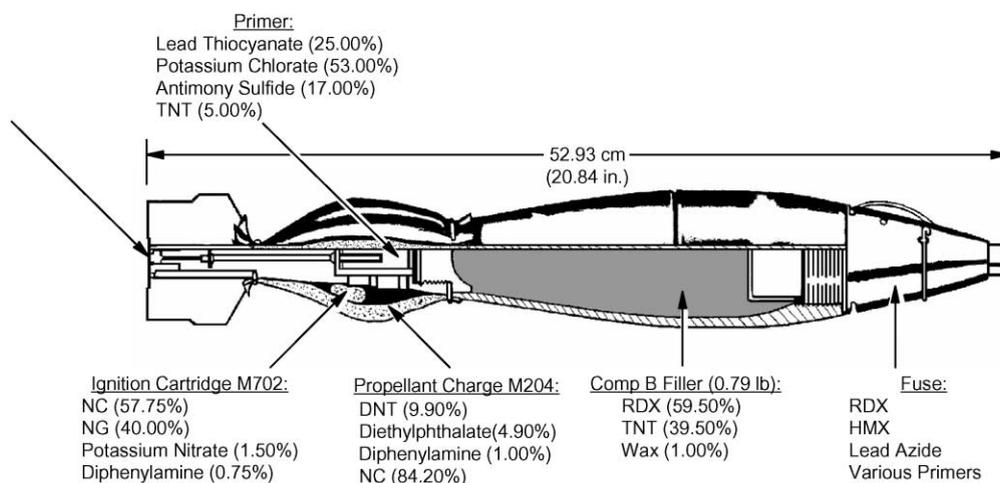


Fig. 1. Diagram of 81 mm mortar rounds detonated with C4 at Camp Ethan Allen firing range.

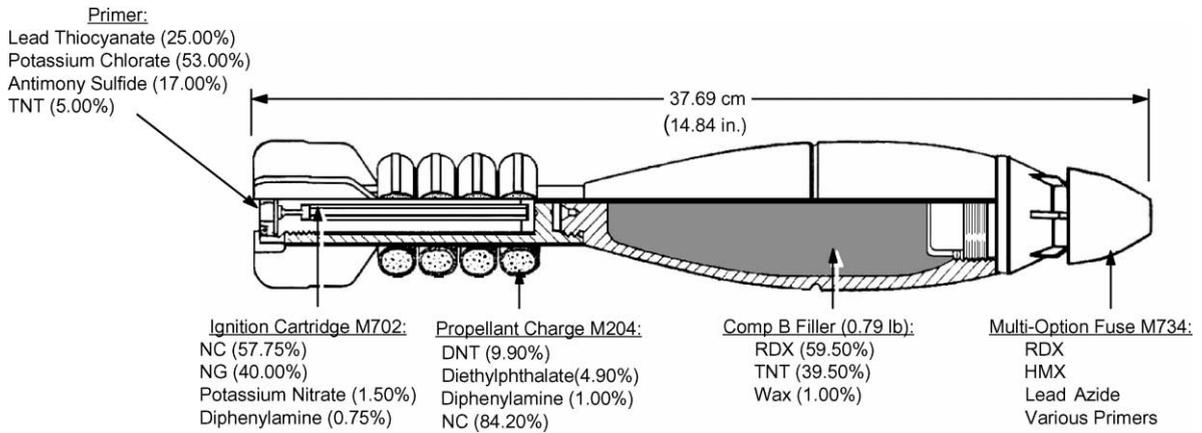


Fig. 2. Diagram of 60 mm mortar rounds fired at Fort Drum firing range.

1.2. Areas of residue deposition

These detonations were characterized by the production of black soot because of the presence of TNT in each main charge. Detonation of explosives with an oxygen-to-carbon ratio less than one produces solid carbon residue (soot) [6]. TNT ( $C_7H_5N_3O_6$ ), which is one such explosive, was present in each main charge. This soot produced a cloud that settled on the snow

surface and was quite visible, easily delineating the areas where residues were deposited.

For the first 81 mm mortar detonation at Camp Ethan Allen, a steel plate was buried in the snow and the mortar detonated above the plate to minimize soil disruption. Five surface snow samples, ranging in distance from the crater from 4 to 28 m, and which ranged in area sampled from 1.16 to 9.29 m<sup>2</sup>, were collected (Fig. 3).

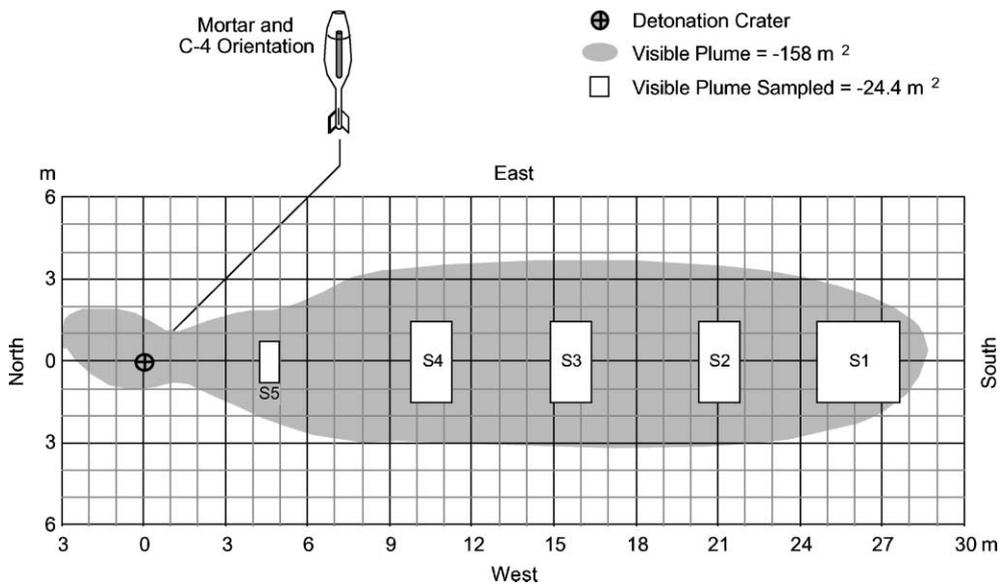


Fig. 3. Residue deposition and surface snow samples collected for first 81 mm mortar round detonation at Camp Ethan Allen.

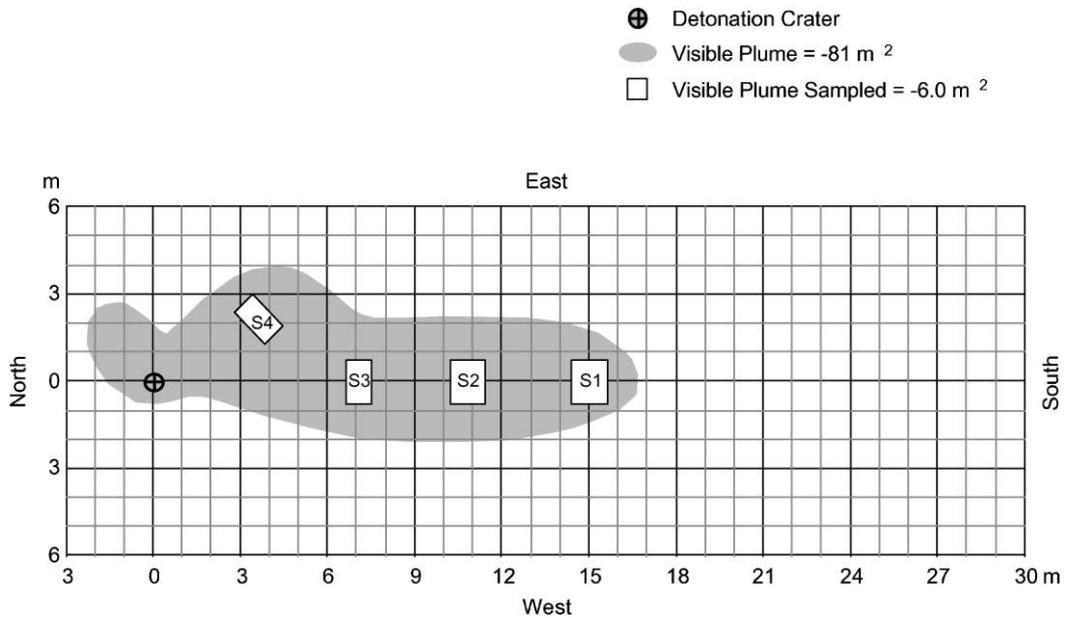


Fig. 4. Residue deposition and surface snow samples collected for second 81 mm mortar round detonation at Camp Ethan Allen.

Two additional detonations of 81 mm mortars were conducted as described above except that the rounds 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 Figs. 4 and 5.

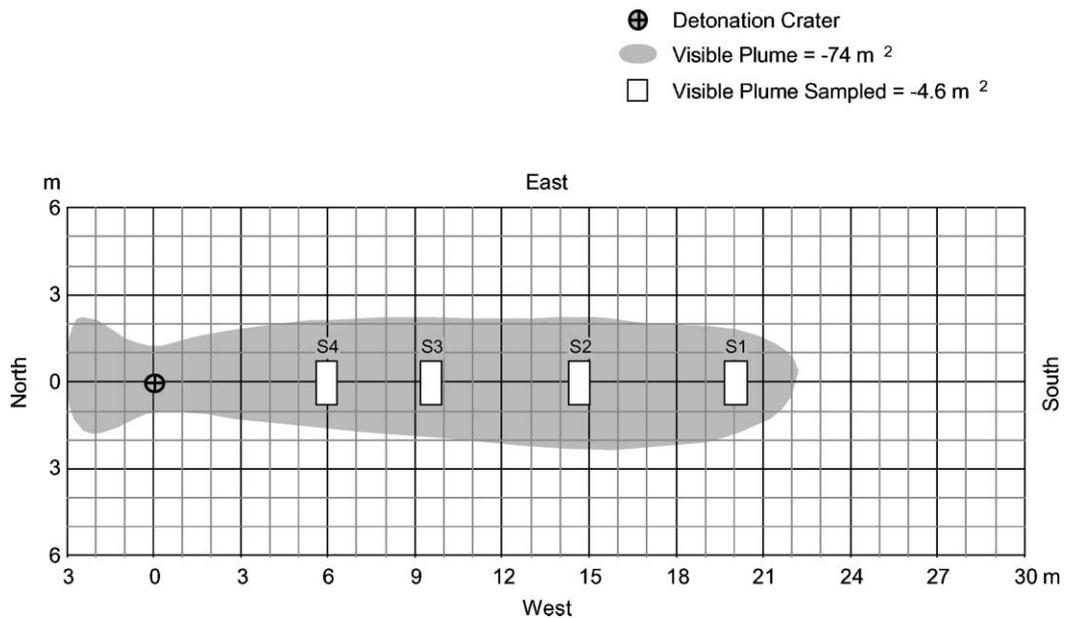


Fig. 5. Residue deposition and surface snow samples collected for third 81 mm mortar round detonation at Camp Ethan Allen.

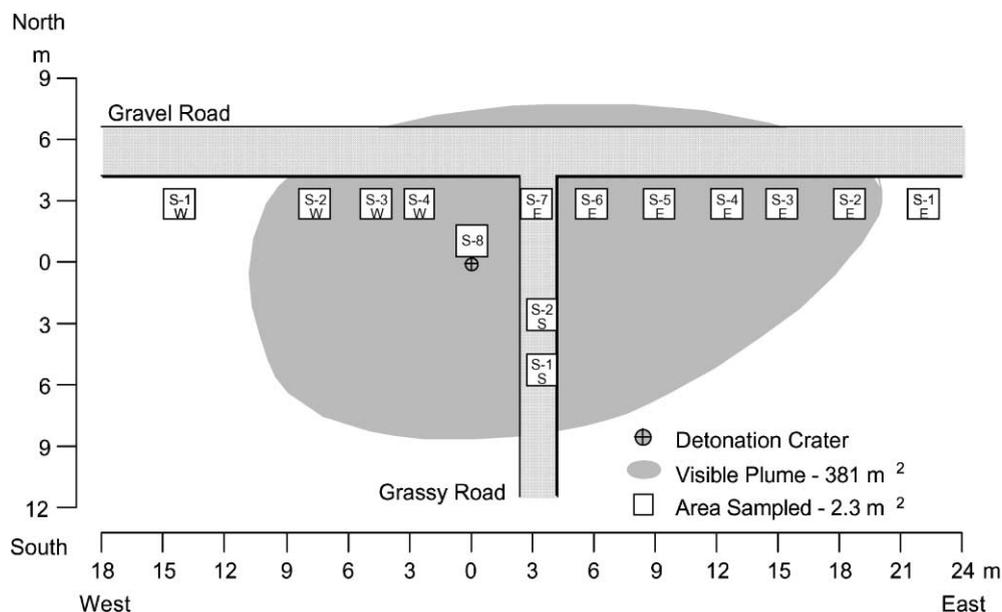


Fig. 6. Residue deposition and surface snow samples collected for PMA-2 land mine detonation at Camp Ethan Allen.

A total of 15 snow samples was collected from the land mine detonation experiment at Camp Ethan Allen as shown in Fig. 6. Samples were collected from the crater and from 14 surface areas from immediately to the north of the crater to a distance of 23 m east of the crater, 15 m west of the crater, and 6 m south of the crater. Two samples were collected just beyond the area where visual deposition had occurred.

Two of the three mortar rounds fired at Fort Drum landed in areas that were accessible for surface sampling. The third round landed in an inaccessible area of large rocks. 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 min 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. 7). A total of six surface snow samples was collected in a continuous line from 1 to 14 m from the impact crater. Surface areas sampled varied from 1.16 to 3.72 m<sup>2</sup>. The area where soot was visible on the surface was measured after all samples were collected

so that residues were not tracked into areas that were sampled. The total impacted area was estimated at 79 m<sup>2</sup>; the total area sampled was 12 m<sup>2</sup> or about 15%.

Area 2 was sampled about an hour after detonation. A total of five samples was collected 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<sup>2</sup> (Fig. 8). The total area sampled for area 2 was 7.3 m<sup>2</sup> or about 13% of the total impacted area.

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 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. Snow samples from craters were collected with a small stainless steel hand shovel. 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 the laboratory the same day they were collected and processed the following morning.

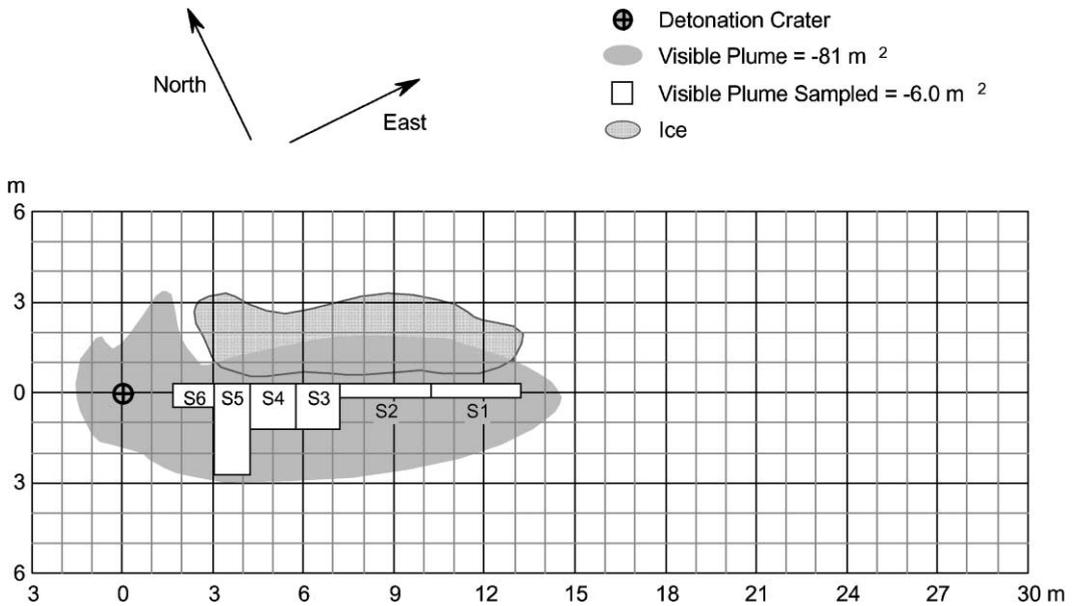


Fig. 7. Residue deposition and surface snow samples collected for first 60 mm mortar round detonation at Fort Drum.

1.3. Processing of snow samples

The snow in the plastic bags was melted by placing the bags in the laboratory overnight. 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 in color due to the presence of suspended soot particles. For all samples

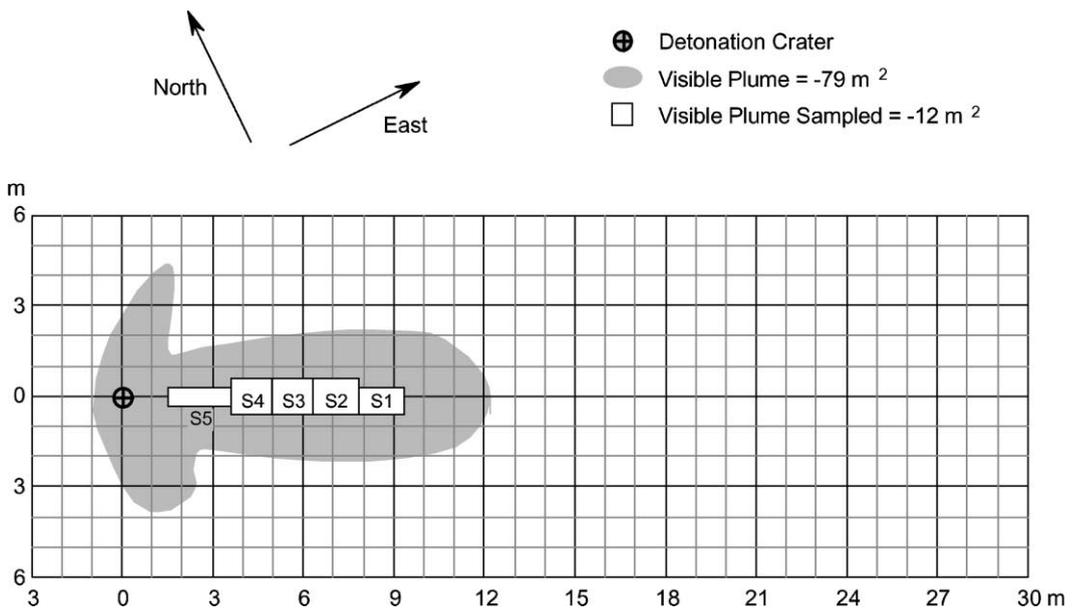


Fig. 8. Residue deposition and surface snow samples collected for second 60 mm mortar round detonation at Fort Drum.

from Camp Ethan Allen and several from Fort Drum, 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 in the sample. 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 from the plastic bags used for collection.

The total volume of snowmelt was measured. To extract the explosives from the water, a 1520 ml aliquot was placed in a 2 l volumetric flask containing 496 g of sodium chloride [7,8]. A magnetic stir bar was added and the flask was stirred to dissolve the salt. A 325 ml aliquot of acetonitrile was added, and the flask was stirred vigorously for 30 min. The magnetic stirrer was then turned off and the phases were allowed to separate for 30 min. The acetonitrile phase on the top, about 25 ml, was removed, the volume was measured using a graduated cylinder, and the sample was labeled “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–four per bag) and the filters were placed in a Soxhlet extraction thimble. The filters that were used to filter the 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 h at a cycle time of 6 cycles/h. After the solvent cooled, the volume of the solvent was measured and an aliquot removed for analysis. This sample was labeled as SOX.

For the snow samples from Fort Drum, snow was melted as described above, but initial attempts to filter the melt 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. Filtration of sample S-4 took 40 individual glass fiber filters to process the entire sample, requiring over 6 h. 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 vigor-

ously 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 of the filtered samples were processed using salting out solvent extraction, and the filters and bag wipes were extracted using the Soxhlet method described for the Ethan Allen samples. Spiked samples were used to validate the extraction efficiency of this procedure.

#### *1.4. Efficiency of residue collection from snow surface*

On 3 May 2000, 2 months after the 81 mm mortars were detonated, we revisited Camp Ethan Allen and collected surface soil samples. Soils were collected at distances from the first mortar detonation corresponding to the snow collection areas and halfway in between these areas (i.e. where the sooty snow was not collected). These soils were extracted and analyzed by Method 8095.

#### *1.5. GC-ECD determination*

All SOE and SOX samples were analyzed by GC-ECD on an HP6890 gas chromatograph equipped with a micro cell Ni<sup>63</sup> ECD (300 °C) [4]. We used direct injection (250 °C) of 1.0 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/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.

Because some of the analytes were present at concentrations that saturated the µECD, samples were also analyzed by reversed-phase high performance liquid chromatography (RP-HPLC) using a 15 cm by 3.9 mm (4 µm) Nova Pak C<sub>8</sub> (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.

## 2. Results and discussion

### 2.1. Results from Camp Ethan Allen experiment, 81 mm mortar detonated with C4

Results from the analysis of the snow samples from the three mortar detonations at Camp Ethan Allen are

presented in Table 1. Four explosives-related analytes were detected: RDX, HMX, NG, and TNT. Surface concentrations of these compounds ranged from 1.0 to 4430  $\mu\text{g}/\text{m}^2$  for RDX, from 0.1 to 597  $\mu\text{g}/\text{m}^2$  for HMX, from 37 to 1530  $\mu\text{g}/\text{m}^2$  for NG, and from  $<d$  to 40  $\mu\text{g}/\text{m}^2$  for TNT. The residues were much higher for detonation number 2 than for either detonation numbers 1 or 3, although all three appeared to be high-order detonations.

The main charge of the 81 mm mortar, together with the C4 used to detonate it, initially contained a total of about 1.1 kg of RDX. A small amount of 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

Table 1

Surface concentrations of the various explosives in snow from detonations of 81 mm mortars with C4, and a PMA-2 land mine with an M7 blasting cap at Camp Ethan Allen, Vermont

Sample	Distance from crater (m)	Surface area sampled ( $\text{m}^2$ )	Residue ( $\mu\text{g}/\text{m}^2$ )			
			RDX	HMX	TNT	NG
<b>Mortar #1</b>						
M1-S5	4.2–5.0	1.16	12.4	1.8	0.05	802
M1-S4	9.9–11.4	4.65	5.2	0.9	$<d$	1528
M1-S3	15.1–16.6	4.65	4.3	0.4	$<d$	327
M1-S2	20.8–22.1	4.65	1.6	0.3	0.05	119
M1-S1	25.3–28.4	9.29	1.0	0.1	$<d$	124
<b>Mortar #2</b>						
M2-S4	4.2–5.0	1.16	369	77	0.03	37
M2-S3	6.9–7.7	1.16	4425	597	40	1593
M2-S2	10.6–11.4	1.86	865	168	1.4	539
M2-S1	14.9–15.6	1.86	489	89	0.9	180
<b>Mortar #3</b>						
M3-S4	5.4–6.2	1.16	39	9	0.15	649
M3-S3	9.4–10.1	1.16	15	15	0.17	808
M3-S2	14.6–15.3	1.16	31	55	0.19	353
M3-S1	20.0–20.8	1.16	4.8	4.1	0.25	142
<b>PMA-2 land mine</b>						
S-2E		2.30	0.1	$<d$	1.1	$<d$
S-3E		2.30	1.8	$<d$	7.6	$<d$
S-4E		2.30	1.0	$<d$	3.9	$<d$
S-5E		2.30	1.6	$<d$	25.2	$<d$
S-6E		2.30	0.2	$<d$	2.7	$<d$
S-7E		2.30	0.3	$<d$	0.3	$<d$
S-8C		2.30	11.9	$<d$	0.4	$<d$
S-2W		2.30	1.0	$<d$	$<0.1$	$<d$
S-3W		2.30	1.9	$<d$	$<0.1$	$<d$
S-4W		2.30	0.5	$<d$	$<0.1$	$<d$
S-1S		2.30	0.2	$<d$	8.9	$<d$
S-2S		2.30	1.3	$<d$	199	$<d$

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 mortars, the residues of TNT in these surface samples were generally <3% of the RDX present. Either a higher percentage of the TNT is consumed in detonations of composition B than RDX and HMX, or the major source of RDX and HMX in these residues is the C4 that was used to initiate the detonation.

Prior to detonating the 81 mm mortar rounds, the propellant bags were removed. However, NG is also present in the ignition cartridge within the mortar. The concentrations of NG in the snow cover were sufficiently high to saturate the  $\mu$ ECD in some cases, but the NG peaks were always measurable in the HPLC-UV chromatograms at 254 nm, and were sufficiently high in some of the samples to obtain confirmatory spectra using the photodiode array. The NG from the ignition cartridge is apparently less completely consumed in the detonation than TNT and RDX in the main charge, or RDX in the C4, based on the mass of NG found versus the amount of NG present in the round. When a round is fired, however, the NG in the ignition cartridge would be expended during propellant ignition, thus, there would be little NG left to be dispersed when the main charge was detonated. Thus, these NG results are probably not typical of what would be found when an 81 mm mortar was either fired and detonated on impact, or when an undetonated 81 mm mortar discovered on site was detonated by EOD personnel using C4.

## 2.2. Efficiency of residue collection from snow surface

Two months following the 81 mm mortar detonations at Camp Ethan Allen, only two analytes, NG and RDX, were detectable in surface soil samples collected at distances from the first mortar detonation corresponding to the snow collection areas and half-way in between these areas. NG was undetectable in soil samples collected at locations corresponding to four out of the five areas from which sooty snow was collected (Table 1). In contrast, NG was easily detected in four out of five soils taken between the snow collection areas. RDX was only detectable in

soils collected within 0.6 m of the detonation crater. These results show that most of the residue was recovered by collecting the sooty-snow surface and the source of the explosive residues was the mortar round, not previous range activity.

## 2.3. Results from Camp Ethan Allen experiment, PMA-2 land mine detonated with a blasting cap

The mine-related explosives detected in the highest concentrations in the surface snow samples near the PMA-2 land mine detonation were TNT and RDX (Table 1). Low concentrations of the two mono-amino transformation products of TNT (2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene) were also present in a few samples.

The distribution of TNT and RDX in the surface snow samples was somewhat different, though. The highest TNT concentration of  $199 \mu\text{g}/\text{m}^2$  was found in sample S-2S which was collected about 4 m from the detonation crater. This value is about eight times higher than the second highest value of  $25.2 \mu\text{g}/\text{m}^2$  found for sample S-5E which was located about 10 m downwind of the detonation crater. These two values appear to be due to the presence of a small particle of explosive since 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 in the downwind direction 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. 6). The very low concentration of TNT in the crater sample agrees with results from Collins and Calkins [9], who reported that concentrations were below method detection limits for samples taken from craters formed by mortar and howitzer detonations in snow.

The highest RDX concentration of  $11.9 \mu\text{g}/\text{m}^2$  was found in sample S-8C, which was collected about 1 m from the crater (Fig. 6), 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.

Table 2

Surface concentrations of the various explosives identified in snow samples collected near 60 mm mortars detonations at Fort Drum, NY

Sample	Distance from crater (m)	Surface area sampled (m <sup>2</sup> )	Residue (µg/m <sup>2</sup> )			
			RDX	HMX	TNT	NG
Detonation #1						
M1-S1	1.2–3.0	1.39	0.35	< <i>d</i>	< <i>d</i>	< <i>d</i>
M1-S2	3.1–4.3	1.39	0.32	< <i>d</i>	< <i>d</i>	< <i>d</i>
M1-S3	4.3–5.5	2.09	0.33	< <i>d</i>	< <i>d</i>	< <i>d</i>
M1-S4	5.5–7.6	2.09	0.88	< <i>d</i>	< <i>d</i>	< <i>d</i>
M1-S5	7.6–10.7	3.72	6.13	0.86	< <i>d</i>	0.01
M1-S6	10.7–13.7	1.16	0.60	0.35	< <i>d</i>	< <i>d</i>
Detonation #2						
M1-S5	1.2–3.7	1.49	2.10	< <i>d</i>	< <i>d</i>	0.50
M1-S4	3.7–5.2	1.49	1.93	< <i>d</i>	< <i>d</i>	0.10
M1-S3	5.2–6.4	1.49	1.76	< <i>d</i>	< <i>d</i>	0.05
M1-S2	6.4–7.9	1.49	1.70	< <i>d</i>	< <i>d</i>	0.03
M1-S1	7.9–10.7	1.39	12.2	< <i>d</i>	< <i>d</i>	0.06

#### 2.4. Results from Fort Drum, 60 mm mortar detonations

RDX, HMX, and NG were detected in the snow samples from the mortar detonations at Fort Drum. Surface concentrations of these compounds ranged from 0.32 to 12.2 µg/m<sup>2</sup> for RDX, <*d* to 0.86 µg/m<sup>2</sup> for HMX, and <*d* to 0.10 µg/m<sup>2</sup> for NG (Table 2). No TNT was detected above background. Concentrations for the second mortar round were two to four times higher than for the first. Highest concentrations were located approximately 9 m from the point of detonation.

The fired-in 60 mm mortars exhibited less residue overall and no high concentrations, unlike those from the 81 mm mortars detonated by C4. Overall there was less residue, and NG was not found at high concentrations. For these fired rounds, the ignition cartridge would have detonated to ignite the propellant, 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 were found in the rinsate. The significance of NG residues on training ranges will require further investigation.

Similar to the 81 mm mortar detonations, TNT concentrations for the 60 mm detonations at Fort Drum were much lower than RDX even though the filler was composition B (59.5:39.5, RDX:TNT).

Thus, it appears that TNT is more completely consumed during mortar detonations than is RDX.

#### 2.5. Estimation of percent of explosives recovered in residues

The lowest concentrations of residues from these detonations in the surface snow were generally found for samples collected 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 at Camp Ethan Allen were estimated to be 158 m<sup>2</sup> for area 1, 81 m<sup>2</sup> for area 2, and 74 m<sup>2</sup> for area 3. The higher area of deposition for the first detonation may be a result of using the steel plate under the mortar, thereby deflecting a greater percentage of the debris upward and out. The surface areas sampled for these three areas were 24, 6.0, and 4.7 m<sup>2</sup>, respectively. Thus, the percentages of the contaminated surface area that were sampled were 15, 7.4, and 6.3%, respectively.

At Fort Drum, the surface areas of deposition were estimated to be 79.0 and 58.1 m<sup>2</sup> for areas 1 and 2, respectively. The areas sampled were 12.0 and 7.3 m<sup>2</sup>, or 15.2 and 12.6%, respectively, of the area impacted.

If the mean surface concentrations that were obtained for each of these areas are representative

Table 3

Estimates for RDX and TNT deposited from detonations of 81 mm mortars at Camp Ethan Allen, and 60 mm mortars at Fort Drum, NY

	Ethan Allen (81 mm)			Fort Drum (60 mm)	
	1	2	3	1	2
<b>RDX</b>					
Average surface concentration ( $\mu\text{g}/\text{m}^2$ )	4.9	1537	22.5	1.43	3.94
Total contaminated surface area ( $\text{m}^2$ )	158	81.3	74.2	79.0	58.1
Total mass deposited ( $\mu\text{g}$ )	774	$1.25 \times 10^5$	1670	113	229
Mass of RDX (mortar + C4) ( $\mu\text{g}$ )	$1.1 \times 10^9$	$1.1 \times 10^9$	$1.1 \times 10^9$	$2.58 \times 10^8$	$2.58 \times 10^8$
RDX recovered (%)	$7.0 \times 10^{-5}$	$1.1 \times 10^{-2}$	$1.5 \times 10^{-4}$	$4.0 \times 10^{-5}$	$9.0 \times 10^{-5}$
Estimate of mean soil concentration resulting from detonation ( $\mu\text{g}/\text{kg}$ ) <sup>a</sup>	0.58	181	2.6	0.17	0.46
<b>TNT</b>					
Average surface concentration ( $\mu\text{g}/\text{m}^2$ )	0.035	10.7	0.19	<d	<d
Total contaminated surface area ( $\text{m}^2$ )	158	81.3	74.2	<d	<d
Total mass deposited ( $\mu\text{g}$ )	5.53	870	14.1	<d	<d
Mass of TNT in mortar ( $\mu\text{g}$ )	$3.8 \times 10^8$	$3.8 \times 10^8$	$3.8 \times 10^8$	$1.68 \times 10^8$	$1.68 \times 10^8$
TNT recovered (%)	$1.0 \times 10^{-6}$	$2.3 \times 10^{-4}$	$4.0 \times 10^{-6}$	<d	<d
Estimate of mean soil concentration resulting from detonation ( $\mu\text{g}/\text{kg}$ ) <sup>a</sup>	0.004	1.3	0.022	<d	<d

<sup>a</sup> A soil density of  $1.7 \text{ g}/\text{cm}^3$  and a 0.5 cm depth was used to compute the estimate.

of the total surface area in which deposition was observed, the total mass of residues deposited in each case can be estimated. Using this assumption, estimates of the mass of RDX deposited range from 774 to  $1.25 \times 10^5 \mu\text{g}$  (125 mg) for the 81 mm mortars at Camp Ethan Allen, and 113 and 229  $\mu\text{g}$  for the 60 mm mortars at Fort Drum (Table 3). Likewise for TNT, estimates range from 5.5 to 870  $\mu\text{g}$  for 81 mm mortars, but were below our detection threshold at Fort Drum (Table 3). While additional experiments of this kind are underway, the results presented here can serve as interim source estimates for groundwater models and risk assessments.

In terms of the percent of initial explosive that was deposited as residues, the estimates range from  $7.0 \times 10^{-5}$  to  $1.1 \times 10^{-2}\%$  for RDX from 81 mm mortars at Camp Ethan Allen, from  $4.0 \times 10^{-5}$  to  $9.0 \times 10^{-5}\%$  for RDX from 60 mm mortars at Fort Drum, and  $5.3 \times 10^{-3}\%$  from the PMA-2 land mine. 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 0.17 to 181  $\mu\text{g}/\text{kg}$ . TNT was detected only in residues at Camp Ethan Allen. Making the same assumptions, estimates of residue deposition range from 5.5 to

870  $\mu\text{g}$  for the 81 mm mortars, and 7933  $\mu\text{g}$  for the PMA-2 land mine. The resulting soil concentrations for TNT range from 0.004 to 1.3  $\mu\text{g}/\text{kg}$  for the mortars and 23  $\mu\text{g}/\text{kg}$  for the land mine. The reason for the higher average deposition for TNT from the land mine is uncertain, but detonation efficiency may be a function of the total mass of high explosives present. The PMA-2 had only 113 g of high explosive compared with 950 g of composition B and 570 g of C4 for the 81 mm mortar detonations.

We must acknowledge the uncertainty in the estimates discussed above that stem from the assumption that the mean concentration that we obtained was representative of the total area impacted 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 estimate of analytical uncertainty. This study was preliminary in nature, the emphasis being the demonstration of the technique. Thus, the estimates provided should be considered preliminary, but in the absence of better estimates, can serve as ballpark estimates until better data are available. We anticipate making improved measurements in future studies. It is hoped that eventually these estimates will serve as source terms in

models being developed to predict the possibility of groundwater contamination at these ranges, or those aimed at risk assessment.

### 3. Conclusions

The results of this study demonstrate the utility of using snow surfaces to determine the amounts of explosives residues resulting from detonations of military munitions. Ideally, 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 provided a visual pattern of deposition on the white surface. Collection of residues from contaminated snow surfaces was easily accomplished 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 impacted surface area is necessary to ensure that representative samples have been collected.

The results of mortar 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. To minimize the depth of snow that must be sampled, samples should be collected as quickly as possible to ensure that residues do not penetrate deeper into the snowpack.

Because we collected samples from only five mortar detonations and a single land mine detonation 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 initiate the detonation of 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, but consistent with forensic investigations where NG is routinely detected following the discharge of firearms that use NG-propellant [10]. In our study, NG was detected in all cases, even when the ignition cartridge was detonated upon firing. HMX was also observed in residues with approximate surface concentrations about 20% of RDX.

While only three 81 mm mortars using C4, and two 60 mm mortars without C4, were detonated, it appears that higher RDX deposition occurs 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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### References

- [1] J. Clausen, Ogden Environmental, Westford, MA, personal communication.
- [2] T.F. Jenkins, M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, T.A. Ranney, C.L. Grant, 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, 1997.
- [3] T.F. Jenkins, M.E. Walsh, P.G. Thorne, P.H. Miyares, T.A. Ranney, C.L. Grant, J. Esparza, Site Characterization at the

- Inland Firing Range Impact Area at Fort Ord, US Army CRREL Special Report 98-9, 1998.
- [4] M.E. Walsh, T.A. Ranney, Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and GC-ECD: comparison with HPLC, *J. Chromatogr. Sci.* 36 (1998) 406–416.
- [5] Environmental Protection Agency (EPA), Nitroaromatics and Nitramines by GC-ECD, Fourth Update SW846 Method 8095, 1999.
- [6] US Army Materiel Command, Engineering Design Handbook: Principles of Explosive Behavior, AMC Pamphlet No. 706–180, Washington, DC, 1972.
- [7] P.H. Miyares, T.F. Jenkins, Improved Salting- Out Extraction/Preconcentration Method for Determination of Nitroaromatics and Nitramines in Water, US Army CRREL Special Report 91-18, 1991.
- [8] Environmental Protection Agency (EPA), Nitroaromatics and Nitramines by HPLC. Second Update SW846 Method 8330, 1994.
- [9] C.M. Collins, D.J. Calkins, Winter Tests of Artillery Firing into Eagle River Flats, Fort Richardson, Alaska. CRREL Special Report 95–2, 1995.
- [10] J.B.F. Lloyd, Liquid chromatography of firearms propellants traces, *J. Energetic Mater.* 4 (1986) 239–271.